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(54) Title: HEAT EXCHANGE METHOD USING FLUORINATED COMPOUNDS HAVING A LOW GWP

(57) Abstract: The present invention relates to a method for exchanging heat with an electronic computing equipment comprising using a heat transfer fluid which: - has a Prandtl number of from 3 to 100 at 40°C and 1atm pressure - comprises one or more chemical compounds having the general formula: Ph(OR_f)_x (I) wherein Ph is an aromatic ring linked to one or more ether groups -OR_f where each -R_f: - is a monovalent fluorinated alkyl group comprising at least one C-F bond, - has a carbon chain, preferably a C₁-C₁₀ carbon chain, which can be linear or can comprise branches and/or cycles, and, optionally, can comprise in chain heteroatoms selected from O, N or S, and wherein, when X>1, the -R_f groups on the same molecule can be equal to or different from each other.



Description

Heat exchange method using fluorinated compounds having a low GWP

Technical Field

[0001] This application claims priority to EP application 18214418.8 filed on 20 December 2018, the whole content of this application being incorporated herein by reference for all purposes.

[0002] The present invention relates to a method for exchanging heat with an object using compositions comprising selected fluorinated compounds having low GWP as heat transfer fluids.

Background Art

[0003] Heat transfer fluids are known in the art to be used in heating and cooling systems; typically, said heat transfer fluids include water, aqueous brines, alcohols, glycols, ammonia, hydrocarbons, ethers and various halogen derivatives of these materials, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HFCs), (per)fluorinated polyethers (PFPEs) and the like.

[0004] Heat transfer fluids are used to transfer heat from one body to another, typically from a heat source to a heat sink so as to effect cooling of the heat source, heating of the heat sink or to remove unwanted heat generated by the heat source. The heat transfer fluid provides a thermal path between the heat source and the heat sink; it may be circulated through a loop system or other flow system to improve heat flow or it can be in direct contact with heat source and heat sink. Simpler systems use simply an airflow, as heat transfer fluid, more complex system use specifically engineered gases or liquids which are heated or refrigerated in a portion of the system and then are delivered in thermal contact with the destination.

[0005] Computing equipment such as computers, servers and the like generate substantial amounts of heat. Massive developments concentrating a large number of computers operating in shared locations such as server farms

are getting more and more common. The industry of server farms, bitcoin mining farms and other supercomputing applications is growing extremely fast. A key factor in determining the building strategy of such installations is a control system which allows exchanging heat with such computing equipment. This system often called "thermal management system" is typically used for cooling the computing equipment during its operation, but it can also be used for heating e.g. when starting up a system in a cold environment. Air is still the most commonly used fluid which however has the drawback to require large air gaps between electronic boards, which causes the installation to have very large footprints. Air cooling also requires massive air conditioning engines and their energy consumption is extremely high and represents a significant portion of the running costs for such installations.

- [0006] Recently, solutions for thermal management of servers based on the use of heat transfer fluids, especially liquid heat transfer fluids are getting a lot interest because they are both energy efficient (use less energy than traditional air conditioning systems) and allow to pack more servers, processors and circuit boards in a smaller space.
- [0007] Other important specialized applications for heat transfer fluids can be found e.g. in the semiconductor industry (TCUs, thermostatic baths, vapor phase soldering) and in the batteries industry especially in the vehicle battery industry for their thermal management systems.
- [0008] A variety of heat transfer fluids exist which are used industrially in various application, however the choice of an appropriate fluid can be critical in some applications. Several of the heat transfer fluids commonly used in the past are no longer viable because of their toxicity (ammonia, ethylene glycol), others have been phased out due to their environmental profile because they are not biodegradable and/or because they are considered to be detrimental to the earth ozone layer and/or to act as greenhouse gases if dispersed in the environment.
- [0009] Fluorinated liquid fluids are very effective heat transfer fluids. Commercial products exist such as Solvay's Galden and 3M's Fluorinert: these are liquid polymers which are dielectric, have a high heat capacity, a low

viscosity and are non-toxic and chemically inert so they do not interact with the materials of the battery nor with its electronics. A drawback associated with these fluorinated fluids used so far is their high GWP value.

- [0010] GWP (Global Warming Potential) is an attribute which can be determined for a given chemical compound which indicates how much heat a given greenhouse gas can entrap in the atmosphere (considering "1" as the reference value for CO₂) and is calculated over a specific interval of time, typically 100 years (GWP₁₀₀).
- [0011] The determination of GWP₁₀₀ is performed by combining experimental data concerning the atmospheric lifetime of the chemical compound and its radiative efficiency with specific computational tool which are standard in the art and are described e.g. in the extensive review published by Hodnebrog et. Al. in Review of Geophysics, 51/2013, p 300-378. Highly stable halogenated molecules such as CF₄ and chloro/fluoro alkanes have a very high GWP₁₀₀ (7350 for CF₄, 4500 for CFC-11).
- [0012] Over the years heat transfer fluids having elevated values of GWP (such as the chloro/fluoro alkanes used in air conditioning systems) have been phased out by the industry and replaced with compounds having a lower GWP₁₀₀ value and there is still a continuous interest in heat transfer fluids having GWP₁₀₀ values which are as low as possible.
- [0013] Hydrofluoroethers, in particular segregated hydrofluoroethers, tend to have relatively low GWP₁₀₀ values while the rest of their properties can be compared to those of the CFCs used in the past, for this reason some hydrofluoroethers have been used industrially and gained popularity as heat transfer fluids and are marketed e.g. by 3M under the trade name "Novec®".
- [0014] Hydrofluoroethers are broadly described as heat transfer media due to their wide temperature range where they are liquid, and due to their low viscosity in a broad range of temperatures which makes them useful for applications as low temperature secondary refrigerants for use in secondary loop refrigeration systems where viscosity should not be too high at operating temperatures.

- [0015] Fluorinated ethers are described for example by 3M in US5713211, by Dupont in US 2007/0187639 and by Solvay Solexis in WO 2007/099055 and WO2010034698.
- [0016] However, while much lower than CFCs, the GWP₁₀₀ of segregated hydrofluoroethers is still in a range from 70 to 500 as shown in US5713211 (table 5):

	GWP ₁₀₀
C ₄ F ₉ -O-CH ₃	330
C ₄ F ₉ -O-C ₂ H ₅	70
c-C ₆ F ₁₁ -O-CH ₃	170

- [0017] Other hydrofluoro-olefins have been commercialized as heat transfer fluids e.g. by Chemours (Opteon™) and Honeywell (Solstice™). These compounds have a very low GWP, around 1, but, differently from the formerly cited compounds, are much more flammable and therefore this limits their field of use.
- [0018] Therefore there is still a need to develop methods for effective heat transfer using heat transfer fluids which have good thermal and dielectric properties, are liquid in a broad range of temperatures, are non flammable, and have very low GWP₁₀₀ (30 and below).

Summary of invention

- [0019] The present invention relates to a method for exchanging heat with an object said method comprising using of a heat transfer fluid wherein said heat transfer fluid:
- has a Prandtl number of from 3 to 100 at 40°C and 1atm (101325 Pa) pressure
 - comprises one or more chemical compounds having the general formula:
- $$\text{Ph}(\text{OR}_f)_x \quad (\text{I})$$
- wherein Ph is an aromatic ring linked to one or more ether groups -OR_f
 where each -R_f :

- is a monovalent fluorinated alkyl group comprising at least one C-F bond,
 - has a carbon chain, preferably a C₁-C₁₀ carbon chain, which can be linear or can comprise branches and/or cycles, and, optionally, can comprise in chain heteroatoms selected from O, N or S,
- and wherein, when X>1, the -R_f groups on the same molecule can be equal to or different from each other.

Description of embodiments

- [0020] For “electronic computing equipment” it is intended any individual or arrays of individual computer boards comprising microprocessors CPUs, GPUs, SSD and DDR Memory, and performing computational work, thus including both large server farms, internet servers, bitcoin mining factories, but also smaller individual computers, internet servers, computer gaming equipment. Both large and small installation may benefit from the heat transfer method of the present invention.
- [0021] The term “semiconductor device” in the present invention include any electronic device which exploits the properties of semiconductor materials. Semiconductor devices are manufactured both as single devices and as integrated circuits which consist of a number (which can go from two to billions) of devices manufactured and interconnected on a single semiconductor substrate or “wafer”. The term “semiconductor devices” includes both the basic building blocks, such as diodes and transistors, to the complex architectures built from these basic blocks which extend to analog, digital and mixed signal circuits, such as processors, memory chips, integrated circuits, circuit boards, photo and solar cells, sensors and the like. The term “semiconductor devices” also includes any intermediate or unfinished product of the semiconductor industry derived from a semiconductor material wafer.
- [0022] The method of the present invention employs heat transfer fluids which are dielectric and non corrosive so that it can also be used in the so called “server immersion cooling”. Such fluids at their working temperature can

be gaseous, liquids or be in a gas/liquid equilibrium (i.e. around the boiling point of the liquid), but are preferably liquid.

- [0023] In immersion cooling electronic computer equipment such as CPUs, GPUs, Memory, and other electronics, including complete servers, are completely immersed in a thermally conductive dielectric liquid or coolant, which temperature is controlled through the use of a circulation system which pumps the liquid through pipes and to a heat exchangers or to a radiator type coolers to reject the heat from the coolant.
- [0024] Server immersion cooling is becoming a popular solution for server cooling solution, as it allows to drastically reduce energy usage through the elimination of the expensive air conditioning infrastructure. These systems are replaced with efficient low speed liquid circulation pumps and simpler heat exchanger and/or radiator systems.
- [0025] The temperatures used in liquid immersion cooling are determined by the highest temperature at which the devices being immersed can reliably operate. For servers this temperature range is typically between 15 to 65 °C, however in some cases this range is extended up to 75°C.
- [0026] Current commercial applications for immersion cooling range from data center oriented solutions for commodity server cooling, server clusters, HPC applications and Bitcoin Mining and mainstream cloud-based and web hosting architectures. Liquid immersion cooling is also used in the thermal management of computing equipment related to LEDs, Lasers, X-Ray machines, and Magnetic Resonance Imaging devices.
- [0027] The method of the present invention is particularly suitable for open bath immersion cooling which uses single phase dielectric liquid. The compounds of the invention exist as liquids in a broad range of temperatures and are therefore suitable for open bath systems where the heat exchange composition remains liquid in all phases of operation. Typically the heat transfer fluid is pumped to an external heat exchanger where it is cooled (or heated in case of need) and recirculated into the bath. A more or less sophisticated control system may be present controlling the instant temperature of the fluid and the temperature of the servers optimizing the fluid temperature in each moment. Also the low

vapour pressure of the compounds (typically below 0.2 torr / $3 \cdot 10^{-4}$ atm at 20°C) allows to minimize evaporation and loss of the compounds.

- [0028] The method of the invention can also be used in non immersion cooling system where the heat exchange fluid is circulated in a closed system and brought in thermal contact with the processors through plates of thermally conductive materials, such as the server cooling solutions produced by Ebullient under the name of “module loops”. The use of a dielectric fluid is anyway beneficial because the risk of leakages is always present and conductive liquids may have destructive effects on the electronics.
- [0029] Beyond electronic computing equipment, the method of the invention can be also adapted to any heat exchange method e.g. for heating or cooling compartments (e.g. food stuffs compartments) including those on board of aircrafts, vehicles or boats, for heating or cooling industrial production equipment, for heating or cooling batteries during their operations, for forming thermostatic baths.
- [0030] The method of the invention can find application for example in the semiconductor industry where temperature control during manufacturing of semiconductor devices is of great importance. Temperature control units (TCUs) are used all along the production line for the fabrication of semiconductor devices, and use heat transfer fluids to remove unwanted heat during steps like wafer etching and deposition processes, ion implantation and lithographic processes. The heat transfer fluid is typically circulated through the wafer mounts and each process tool which require temperature control has its own individual TCU.
- [0031] Some tools of particular importance which include TCUs are silicone wafer etchers, steppers and ashers. Etching is performed using reactive plasma at temperatures ranging from 70°C to 150°C and the temperature of the wafer must be controlled precisely during the plasma treatment. Following the plasma treatment the etched parts are normally immersed in a solvent which removes the etched parts. This second step does not normally require temperature control as it is performed at mild or ambient temperature. When referring to an “etcher” in the present application, it is

intended the equipment wherein the plasma treatment at high temperature is performed and which therefore requires a TCU.

- [0032] Steppers are used in the photolithography of wafers to form the reticules which are then used to expose the photosensitive mask. This process is carried out at temperatures between 40°C and 80°C, however temperature control is extremely important as the wafer need to be maintained at a precise fixed temperature (+/- 0.2°C) along the process to ensure good results.
- [0033] Ashing is a process where the photosensitive mask is removed from the wafer and which is performed at temperatures from 40°C to 150°C. The system uses plasma and also here temperature control is particularly important.
- [0034] Another relevant process is plasma enhanced chemical vapour deposition (PECVD) wherein films of silicon oxide, silicon carbide and/or silicone nitride are grown on a wafer within a chamber. Also in this case, while the temperature at which this step is performed can be selected in the range between 50°C and 150°C, during the deposition process the wafer must be kept uniformly at the selected temperature.
- [0035] In a semiconductor device production facility typically each Etcher, Asher, Stepper and plasma enhanced chemical vapour deposition (PECVD) chamber have their own TCU wherein a heat transfer fluid is recirculated.
- [0036] Another process steps where heat transfer fluids are used in the manufacturing of semiconductor devices is vapour phase reflow (VPR) soldering. This is the most common method used to connect surface mount devices, multi chip modules and hybrid components to circuit boards. In this method the soldering material is applied in paste form and then the semiconductor device e.g. an unfinished circuit board is placed in a closed chamber with heat transfer fluid at its boiling point in equilibrium with its vapour phase. The fluid in vapour phase transfers heat to the soldering paste which then melts and stabilize the contacts. In this case the fluid is in direct contact with the circuit board so that it must be dielectric and non corrosive. For this application is also important that the

boiling point of the heat transfer fluid is sufficient to melt the soldering paste.

- [0037] Another system which is a key part of the production process of many semiconductor devices is thermal shock testing. In thermal shock testing a semiconductor device is tested at two very different temperature. Different standards exist, but in general the test consists in submitting the semiconductor device to high and low temperatures and then testing the physical and electronic properties of the device. Typically the semiconductor device to be tested is directly immersed alternatively in a hot bath (which can be at a temperature of from 60°C to 250 °C) and a cold bath (which can be typically at a temperature of from -10°C and -100°C). The transfer time between the two bath must be minimized, generally below 10 seconds. Also in this test the fluid making up the baths go in direct contact with the device and therefore must be dielectric and non corrosive. In addition, to avoid contamination of the baths, it is highly preferable that the same fluid is used both in the cold and in the hot bath. Therefore heat transfer fluids which exist as liquid in a broad range of temperatures are preferred.
- [0038] Heat transfer fluids for use in the manufacturing of semiconductor devices are typically liquids which are dielectric, non corrosive, and exist in the liquid state in a broad range of temperatures with relatively low viscosity which makes them easily pumpable.
- [0039] Another area wherein the method of the present invention can find application is the thermal management of batteries, in particular rechargeable batteries such as vehicle batteries for cars, trams, trains and the like. All types of batteries perform optimally in a very narrow range of temperatures while there are of application and the heat generated by the battery itself makes it difficult to maintain the operating temperature within a preferred range. Therefore batteries often feature a thermal management system. Particularly for high power batteries thermal management systems based on fluids, liquids in particular, are being used and the method of the invention offers an improved thermal management at a lowered GWP₁₀₀.

- [0040] As mentioned in the introduction, heat transfer fluids used in these fields include fluorocompounds. In particular hydrofluoroethers have found application in these fields due to their chemical inertness, dielectricity, wide range of T in which they are liquid and pumpable (typically having a viscosity between 1 and 50 cps at the temperatures of use), low flammability and relatively low GWP.
- [0041] Commercially available hydrofluoroethers for use in these fields are e.g. those from the Novec™ series of 3M which combine all these properties with a relatively low GWP₁₀₀ of from about 70 to 300.
- [0042] Still, GWP is a critical property nowadays also due to the regulatory environment so that there is always a demand to develop new heat exchange fluids which have even lower GWP than then currently commercialized hydrofluoroethers.
- [0043] The present invention in fact relates to a method for exchanging heat with an object such as e.g. electronic computing equipment, batteries such as rechargeable vehicle batteries, or semiconductor devices, said method comprising using a heat transfer fluid which has a Prandtl number of from 3 to 100 at 40°C and 1atm pressure and comprises one or more chemical compounds having the general formula:
- $$\text{Ph}(\text{OR}_f)_x \quad (\text{I})$$
- wherein Ph is an aromatic ring linked to one or more ether groups -OR_f where each -R_f is a monovalent fluorinated alkyl group comprising at least one C-F bond, and has a carbon chain which can be linear or can comprise branches and/or cycles, and, optionally, can comprise in chain heteroatoms selected from O, N or S, and wherein, when X>1, the -R_f groups on the same molecule can be equal to or different from each other.
- [0044] The applicant has surprisingly found that the heat transfer fluid employed in the method of the invention is non-flammable, provides efficient heat transfer, can be used across a wide temperature range and has equal or improved dielectric properties with respect to other hydrofluoroethers commercialized as heat transfer fluids. Surprisingly heat transfer fluids used in the invention have an extremely low GWP₁₀₀, in general lower than

10 and for some materials even lower than 2, as it will be shown below in the experimental section. This is a particularly unexpected result and in fact previous reviews such as Hodnebrog et. al. cited above did not investigate or propose fluorinated aromatic ether compounds as low GWP compounds.

[0045] Therefore, using these selected chemical compounds in accordance to the general formula (I) heat transfer fluids can be formulated which have a GWP₁₀₀ value of less than 30, preferably less than 10, even more preferably less than 5. The heat transfer fluids according to the invention also have low toxicity, exist in liquid state in a broad range from about -100°C to about 200°C showing good heat transfer properties and relatively low viscosity across the whole range. Also, the fluids of the invention have good electrical compatibility, i.e. they are non corrosive, have high dielectric strength, high volume resistivity and low solvency for polar material. The electrical properties of the fluids of the invention are such that they can be used in immersion cooling system for electronics in direct contact with the circuits as well as in indirect contact applications using loops and/or conductive plates.

[0046] Another important factor to consider is that heat transfer systems, while varying greatly in design and in the way the heat transfer fluid is distributed, in general require a heat transfer fluid which must exchange heat with and object (e.g. the electronic computer equipment) and which is then pumped and recirculated to a heat exchanger, external to the system which controls the temperature of the heat transfer fluid. Numerous parameters influence the capacity of a fluid to exchange heat. It has been found that using heat transfer fluids which have a Prandtl number between 3 and 100 at 40°C and 1atm (101325 Pa) pressure allow to obtain optimum performance and energy efficiency of the system. Preferably heat transfer fluids to be employed in the method of the invention have a Prandtl number from 20-90, more preferably 30-80 and an even more preferably 40-70 at 40°C and 1atm pressure.

[0047] The Prandtl number (Pr) is a dimensionless number defined as:

$$\text{Pr} = \frac{c_p \mu}{k}$$

where:

c_p = specific heat J/kg*K

μ = dynamic viscosity N*s/m²

k = Thermal conductivity W/mK

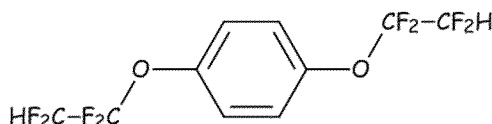
- [0048] The Prandtl number indicates for a given fluid in given temperature (T) and pressure (P) conditions what is the predominant phenomenon among heat conduction and heat convection. A Prandtl number lower than 1 indicates that conduction is more significant than convection while a Prandtl number higher than 1 indicates that convection is more significant than conduction. The Prandtl number is commonly found in the property tables of heat transfer fluids provided by the fluid manufacturers.
- [0049] It has also been found that maintaining the temperature of the heat transfer fluid between 15°C and 60°C, preferably between 20°C and 50°C, more preferably between 30°C and 45°C improves the energy efficiency of the system.
- [0050] Preferably, compounds according to the general formula (I) for the present invention have a value of x selected from 1, 2, 3 or 4, more preferably x is selected from 2 and 3, even more preferably $x=2$. Each R_f has preferably a C₁-C₁₀, more preferably a C₂-C₆ carbon chain which can be linear or comprise branches and/or cycles. The carbon chain may optionally include in chain heteroatoms selected from O, N or S, in case in chain heteroatoms are present it is preferred that the heteroatom is O.
- [0051] As mentioned above each R_f group must comprise at least one C-F bond. Preferably each R_f group also comprises at least one C-H bond. More preferably each R_f is a fluorinated alkyl group with one single C-H bond, even more preferably wherein said single C-H bond is on the carbon atom in position 2 of the carbon chain.
- [0052] Of the six C atoms of the Ph ring, x are bonded to -OR_f groups and (6- x) can be bonded to any type of substituents, preferably they are bonded to H atoms or to F atoms, more preferably H atoms.
- [0053] Compounds according to the formula (I) for use in the method of the invention can be easily prepared by reacting mono or polyhydric phenols

with fluorinated olefins, preferably fully fluorinated olefins. The Ph-OH group adds to the double C=C bond and the H atom adds on the C atom in position 2. The resulting compound is a thus hydrofluoroether. This hydrofluoroether can be further fluorinated to a perfluoroether, but preferably is used as a hydrofluoroether, as already mentioned above.

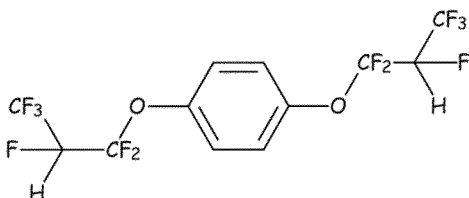
[0054] Preferred mono and polyhydric phenols for use herein are phenol, hydroquinone, resorcinol and catechol. Preferred fluorinated olefins for use herein are tetrafluoroethylene, hexafluoropropylene and perfluorovinylethers such as perfluoromethylvinylether, perfluoroethylvinylether and perfluoropropylvinylether.

[0055] Most preferred compounds among those encompassed by the general formula mentioned above are:

1,4-bis(1,1,2,2-tetrafluoroethoxy)benzene of formula :



1,4-bis(2-trifluoromethyl-1,1,2-trifluoroethoxy)benzene of formula :



and their corresponding ortho and meta isomers

1,3-bis(1,1,2,2-tetrafluoroethoxy)benzene

1,3-bis(2-trifluoromethyl-1,1,2-trifluoroethoxy)benzene

1,2-bis(1,1,2,2-tetrafluoroethoxy)benzene

1,2-bis(2-trifluoromethyl-1,1,2-trifluoroethoxy)benzene ,

and the corresponding derivatives of perfluoromethylvinylether with catechol, resorcinol and hydroquinone:

1,2-bis(2-trifluoromethoxy-1,1,2-trifluoroethoxy)benzene

1,3-bis(2-trifluoromethoxy-1,1,2-trifluoroethoxy)benzene

1,4-bis(2-trifluoromethoxy-1,1,2-trifluoroethoxy)benzene

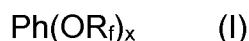
- [0056] The heat transfer fluids for use in the method of invention preferably comprise more than 5% of one or more compounds according to formula (I) above, more preferably more than 50%, even more preferably more than 90%. In one embodiment the heat transfer fluid is entirely made of one or more compounds according to the general formula above.
- [0057] In some embodiments the heat transfer fluid of the invention comprises a blend of chemical compounds according to formula (I). A blend may be beneficial in providing a fluid which is liquid in a larger temperature range. A preferred blend is a blend comprising at least two different isomers having the same substituents in different positions of the aromatic ring.
- [0058] In all embodiments it is preferred that the heat exchange fluid is essentially free of CFCs and fluoroalkanes such as 1,1,1,2-tetrafluoroethane, 1,1-difluoromethane, 1,1,1,2,2-pentafluoroethane. These materials have a high GWP₁₀₀ and even in minor amount contribute to the GWP₁₀₀ of the heat exchange fluid more than its main components according to formula (I).
- For “essentially free” it is intended that the heat exchange fluid in the present invention comprises less than 5%, preferably less than 1%, more preferably less than 0.1% of a given component (all percentages are expressed as weight percent of the total of the heat exchange fluid).
- [0059] The method of the invention can be applied to any heating and/or cooling system which uses an heat transfer fluid and in particular to all those exemplified in the description. Particularly for the temperature control of electronic computing equipment, both in immersion cooling of such equipment, where the electronic circuit boards are directly immersed in the liquid, to distributed systems where the fluids are distributed to cooling elements capable of exchanging heat with boards such as plates of thermally conductive materials such as metals and metallic alloys.
- [0060] Other applications are in the thermal management of batteries, particularly rechargeable batteries, e.g. for vehicles such as cars, trams, trains.

[0061] Further applications are found in the semiconductor industry where the object of the heat exchange is a semiconductor device, such as in temperature control units (TCUs) for etchers, ashers, steppers and pecvd chambers, in thermostatic baths for thermal shock testing and in vapor phase soldering.

[0062] In another aspect the present invention also encompasses an apparatus comprising an electronic computing equipment and a heat transfer fluid wherein said heat transfer fluid

- has a Prandtl number of from 3 to 100 at 40°C and 1 atm (101325 Pa) pressure

- comprises one or more chemical compounds having the general formula:



wherein Ph is an aromatic ring linked to one or more ether groups -OR_f

where each -R_f :

- is a monovalent fluorinated alkyl group comprising at least one C-F bond,
 - has a carbon chain, preferably a C₁-C₁₀ carbon chain, which can be linear or can comprise branches and/or cycles, and, optionally, can comprise in chain heteroatoms selected from O, N or S,
- and wherein, when X>1, the -R_f groups on the same molecule can be equal to or different from each other.

[0063] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

[0064] The invention will be now described in more detail with reference to the following examples whose purpose is merely illustrative and not limitative of the scope of the invention.

[0065] **Raw materials used**

Hydroquinone, KOH, acetonitrile were all sourced from Sigma Aldrich

Tetrafluoroethylene was sourced from Solvay. Novec™ 7000, 7100 and 7200 are commercially available hydrofluoroethers from 3M

Standards:

Measurement of electrical properties were performed according to the following standards:

Volume resistivity – ASTM D5682-08[2012]

Dielectric strength – ASTM D877 / D877M - 13

Dielectric constant - ASTM D924-15

[0066] Examples**Synthesis of 1,4-Bis(1,1,2,2-tetrafluoroethoxy)benzene (HFE 1,4):**

In a 600mL steel autoclave were loaded 60,0g of hydroquinone, with 16g of KOH and 360mL of acetonitrile. The autoclave was purged four times with nitrogen and drawn to moderate vacuum (0.2bar).

The mixture was stirred vigorously for 30 minutes at 70°C, then tetrafluoroethylene was introduced gradually up to 10bar in 6 hours.

The reactor was left stirring for a total of 20h, then it was cooled and tetrafluoroethylene pressure was released. Its content was then purged four times with nitrogen. Consumption of tetrafluoroethylene was 110g. 468g of mixture were unloaded from reactor. This mixture was diluted in a separator funnel with 1,5L water and neutralized with hydrochloric acid. The organic layer at the bottom was washed two times with 0,5L of water and then finally separated from the top water layer, dried over MgSO₄, filtered and distilled at 94°C at a reduced pressure of 15mbar.

150g of pure 1,4-bis(1,1,2,2-tetrafluoroethoxy)benzene were obtained.

[0067] The GWP₁₀₀ for HFE1,4 has been determined at the University of Oslo according to established procedures, by measuring the integrated absorption cross section of infrared spectra over the region 3500-500 cm⁻¹, the kinetic of reaction with OH radicals, and calculating the consequent atmospheric lifetime and radiative forcing efficiency. As a result of these measurements a GWP₁₀₀ of 1.8 has been obtained.

HFE1,4 data relevant to GWP₁₀₀:

Integrated absorption cross section at 3500-500cm⁻¹:

53.6 cm² molecule⁻¹ cm⁻¹

Radiative forcing efficiency (calc)= 0.165 W m⁻²

OH radicals kinetic $k_{\text{HFE1,4+OH}} = 2 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 298K

Atmospheric lifetime of HFE1,4 = 2 months

GWP₁₀₀=1.8

[0068] Electric and thermal properties of HFE1,4 in comparison with other commercially available hydrofluoroethers:

	GWP ₁₀₀	Volume resistivity (ohm cm-1)	Dielectric strength (kV)	Dielectric constant
NOVEC 7200	70	1,00E+08	30	7,3
NOVEC 7000	530	1,00E+08	40	7,4
HFE1,4	1,8	2,00E+9	45	6,2

[0069] Other physical properties of compounds according to the invention:

1,4-Bis(1,1,2,2-tetrafluoroethoxy)benzene (HFE 1,4)

1,3-Bis(1,1,2,2-tetrafluoroethoxy)benzene (HFE 1,3)

1,2-Bis(1,1,2,2-tetrafluoroethoxy)benzene (HFE 1,2)

	HFE1,4	HFE1,3	HFE1,2
Dielectric constant @1kHz	6.2	7.84	
Dielectric strength kV	45		
Volume resistivity Ohm*cm	2E+09	1E+10	
heat capacity cal/g°C,	0.34		
viscosity (25°C) cSt,	3.56	2.75	2.86
density (25°C) g/cm3,	1.5	1.5	1.5
heat of vaporization kcal/kg	34		
surface tension mN/m	28		
pour point °C	-10	-93	-87

Boiling point °C	202	192	206
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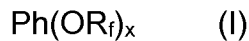
[0070] The results show how the compounds of the invention have overall equal or improved properties when compared with existing commercial materials used for similar purposes and have lower GWP. Heat transfer fluids comprising these compounds can be used in all the mentioned applications involving heat exchange with an electronic computing equipment, batteries or semiconductor devices.

Claims

Claim 1

A method for exchanging heat with an object said method comprising using a heat transfer fluid wherein said heat transfer fluid:

- has a Prandtl number of from 3 to 100 at 40°C and 1atm (101325 Pa) pressure
- comprises one or more chemical compounds having the general formula:



wherein Ph is an aromatic ring linked to one or more ether groups -OR_f

where each -R_f :

- is a monovalent fluorinated alkyl group comprising at least one C-F bond,
- has a carbon chain, preferably a C₁-C₁₀ carbon chain, which can be linear or can comprise branches and/or cycles, and, optionally, can comprise in chain heteroatoms selected from O, N or S,

and wherein, when X>1, the -R_f groups on the same molecule can be equal to or different from each other.

Claim 2

A method according to claim 1 wherein said object is an electronic computing equipment

Claim 3

A method according to claim 1 wherein said electronic computing equipment is one or more servers.

Claim 4

A method according to claim 1 wherein said object is a battery, preferably a rechargeable battery, more preferably a rechargeable vehicle battery.

Claim 5

A method according to claim 1 wherein said object is a semiconductor device.

Claim 6

A method according to claim 2 or 3 wherein said electronic computing equipment comprises one or more electronic circuit boards, said method comprising the step of contacting directly said electronic circuit boards with said heat transfer fluid.

Claim 7

A method according to any preceding claim wherein, in said chemical compounds having general formula (I), x is preferably selected from 1, 2, 3 and 4, preferably from 2 and 3, even more preferably x is 2.

Claim 8

A method according to any preceding claim wherein, in said chemical compounds having general formula (I), multiple R_f groups on the same molecule are equal to each other.

Claim 9

A method according to any preceding claim wherein, in said chemical compounds having general formula (I), each R_f group comprises at least one C-H bond.

Claim 10

A method according to any preceding claim wherein, in said chemical compounds having general formula (I), each R_f group has exactly one C-H bond.

Claim 11

A method according to claim 10 wherein, in said chemical compounds having general formula (I), each R_f group has exactly one C-H bond on the carbon atom in position 2.

Claim 12

A method according to any preceding claim wherein said one or more chemical compounds of general formula (I) make up at least 5% by weight of said heat

transfer fluid, preferably more than 50% by weight, more preferably more than 90% by weight.

Claim 13

A method according to any preceding claim wherein said one or more chemical compounds are selected from

1,4-bis(1,1,2,2-tetrafluoroethoxy)benzene
1,4-bis(2-trifluoromethyl-1,1,2-trifluoroethoxy)benzene
1,3-bis(1,1,2,2-tetrafluoroethoxy)benzene
1,3-bis(2-trifluoromethyl-1,1,2-trifluoroethoxy)benzene
1,2-bis(1,1,2,2-tetrafluoroethoxy)benzene
1,2-bis(2-trifluoromethyl-1,1,2-trifluoroethoxy)benzene
1,2-bis(2-trifluoromethoxy-1,1,2-trifluoroethoxy)benzene
1,3-bis(2-trifluoromethoxy-1,1,2-trifluoroethoxy)benzene
1,4-bis(2-trifluoromethoxy-1,1,2-trifluoroethoxy)benzene
and mixtures thereof.

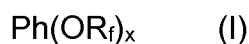
Claim 14

A method according to any preceding claim wherein said heat transfer fluid has a GWP_{100} determined according to the method reported in Hodnebrog et. Al. in Review of Gephysics, 51/2013, p 300-378, of less than 30, preferably less than 10, more preferably less than 5.

Claim 15

An apparatus comprising an electronic computing equipment and a heat transfer fluid wherein said heat transfer fluid

- has a Prandtl number of from 3 to 100 at 40°C and 1 atm (101325 Pa) pressure
- comprises one or more chemical compounds having the general formula:



wherein Ph is an aromatic ring linked to one or more ether groups -OR_f

where each -R_f :

- is a monovalent fluorinated alkyl group comprising at least one C-F bond,

- has a carbon chain, preferably a C₁-C₁₀ carbon chain, which can be linear or can comprise branches and/or cycles, and, optionally, can comprise in chain heteroatoms selected from O, N or S,
and wherein, when X>1, the -R_f groups on the same molecule can be equal to or different from each other.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/086361

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K5/10 H01L21/67
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)
C09K H01L

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/331325 A1 (DEFRANCO JOHN ANDREW [US] ET AL) 19 November 2015 (2015-11-19) paragraphs [0020] - [0023], [0066] -----	1-15
A	US 7 055 579 B2 (3M INNOVATIVE PROPERTIES CO [US]) 6 June 2006 (2006-06-06) claims 1,12-18 -----	1-15
A	US 3 265 741 A (ARTHUR SHEPPARD WILLIAM) 9 August 1966 (1966-08-09) column 1, line 40 - column 2, line 49 -----	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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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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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/086361

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