(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 June 2010 (10.06.2010)

PCT

(10) International Publication Number
WO 2010/064011 A1

(51) International Patent Classification:
C09K 5/04 (2006.01) *C08J 9/14* (2006.01)
C09K 3/30 (2006.01) *C11D 7/50* (2006.01)

(21) International Application Number:
PCT/GB2009/002809

(22) International Filing Date:
2 December 2009 (02.12.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0821924.8 2 December 2008 (02.12.2008) GB
0902144.5 10 February 2009 (10.02.2009) GB
0906549.1 16 April 2009 (16.04.2009) GB

(71) Applicant *(for all designated States except US)*: **INEOS FLUOR HOLDINGS LIMITED** [GB/GB]; PO Box 13, The Heath, Runcorn, Cheshire WA7 4QF (GB).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **LOW, Robert, Elliott** [GB/GB]; Ineos Fluor Holdings Limited, PO Box 13, The Heath, Runcorn, Cheshire WA7 4QF (GB).

(74) Agent: **PUGH, Robert**; Potter Clarkson LLP, Park View House, 58 The Ropewalk, Nottingham NG1 5DD (GB).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2010/064011 A1

(54) **Title**: HEAT TRANSFER COMPOSITIONS

(57) **Abstract**: The invention provides a heat transfer composition comprising R-1243zf, R-32 (difluoromethane) and R-161 (fluoroethane).

HEAT TRANSFER COMPOSITIONS

The invention relates to heat transfer compositions, and in particular to heat transfer compositions which may be suitable as replacements for existing refrigerants such as R-134a, R-152a, R-1234yf, R-22, R-410A, R-407A, R-407B, R-407C, R507 and R-404a.

The listing or discussion of a prior-published document or any background in the specification should not necessarily be taken as an acknowledgement that a document or background is part of the state of the art or is common general knowledge.

Mechanical refrigeration systems and related heat transfer devices such as heat pumps and air-conditioning systems are well known. In such systems, a refrigerant liquid evaporates at low pressure taking heat from the surrounding zone. The resulting vapour is then compressed and passed to a condenser where it condenses and gives off heat to a second zone, the condensate being returned through an expansion valve to the evaporator, so completing the cycle. Mechanical energy required for compressing the vapour and pumping the liquid is provided by, for example, an electric motor or an internal combustion engine.

In addition to having a suitable boiling point and a high latent heat of vaporisation, the properties preferred in a refrigerant include low toxicity, non-flammability, non-corrosivity, high stability and freedom from objectionable odour. Other desirable properties are ready compressibility at pressures below 25 bars, low discharge temperature on compression, high refrigeration capacity, high efficiency (high coefficient of performance) and an evaporator pressure in excess of 1 bar at the desired evaporation temperature.

Dichlorodifluoromethane (refrigerant R-12) possesses a suitable combination of properties and was for many years the most widely used refrigerant. Due to international concern that fully and partially halogenated chlorofluorocarbons were damaging the earth's protective ozone layer, there was general agreement that their manufacture and use should be severely restricted and eventually phased out completely. The use of dichlorodifluoromethane was phased out in the 1990's.

Chlorodifluoromethane (R-22) was introduced as a replacement for R-12 because of its lower ozone depletion potential. Following concerns that R-22 is a potent greenhouse gas, its use is also being phased out.

Whilst heat transfer devices of the type to which the present invention relates are essentially closed systems, loss of refrigerant to the atmosphere can occur due to leakage during operation of the equipment or during maintenance procedures. It is important, therefore, to replace fully and partially halogenated chlorofluorocarbon refrigerants by materials having zero ozone depletion potentials.

In addition to the possibility of ozone depletion, it has been suggested that significant concentrations of halocarbon refrigerants in the atmosphere might contribute to global warming (the so-called greenhouse effect). It is desirable, therefore, to use refrigerants which have relatively short atmospheric lifetimes as a result of their ability to react with other atmospheric constituents such as hydroxyl radicals or as a result of ready degradation through photolytic processes.

R-410A and R-407 (including R-407A, R-407B and R-407C) have been introduced as a replacement refrigerant for R-22. However, R-22, R-410A and R-407 all have a high global warming potential (GWP, also known as greenhouse warming potential).

1,1,1,2-tetrafluoroethane (refrigerant R-134a) was introduced as a replacement refrigerant for R-12. However, despite having a low ozone depletion potential, R-134a has a GWP of 1300. It would be desirable to find replacements for R-134a that have a lower GWP.

R-152a (1,1-difluoroethane) has been identified as an alternative to R-134a. It is somewhat more efficient than R-134a and has a greenhouse warming potential of 120. However the flammability of R-152a is judged too high, for example to permit its safe use in mobile air conditioning systems. In particular it is believed that its lower flammable limit in air is too low, its flame speeds are too high, and its ignition energy is too low.

Thus there is a need to provide alternative refrigerants having improved properties, such as low flammability. Fluorocarbon combustion chemistry is complex and unpredictable. It is not always the case that mixing a non flammable fluorocarbon with a flammable fluorocarbon reduces the flammability of the fluid. For example, the inventors have found that if non flammable R-134a is mixed with flammable R-152a, the lower flammable limit of the mixture can be reduced relative to that of pure R-152a (i.e. the mixture can be more flammable than pure R-152a). The situation is rendered more complex and less predictable if ternary or quaternary compositions are considered.

There is also a need to provide alternative refrigerants that may be used in existing devices such as refrigeration devices with little or no modification.

R-1234yf (2,3,3,3-tetrafluoropropene) has been identified as a candidate alternative refrigerant to replace R-134a in certain applications, notably the mobile air conditioning or heat pumping applications. Its GWP is about 4. R-1234yf is flammable but its flammability characteristics are generally regarded as acceptable for some applications including mobile air conditioning or heat pumping. In particular its lower flammable limit, ignition energy and flame speed are all significantly lower than that of R-152a.

The environmental impact of operating an air conditioning or refrigeration system, in terms of the emissions of greenhouse gases, should be considered with reference not only to the so-called "direct" GWP of the refrigerant, but also with reference to the so-called "indirect" emissions, meaning those emissions of carbon dioxide resulting from consumption of electricity or fuel to operate the system. Several metrics of this total GWP impact have been developed, including those known as Total Equivalent Warming Impact (TEWI) analysis, or Life-Cycle Carbon Production (LCCP) analysis. Both of these measures include estimation of the effect of refrigerant GWP and energy efficiency on overall warming impact.

The energy efficiency and refrigeration capacity of R-1234yf have been found to be significantly lower than those of R-134a and in addition the fluid has been found to exhibit increased pressure drop in system pipework and heat exchangers. A consequence of this is that to use R-1234yf and achieve energy efficiency and cooling performance equivalent to R-134a, increased complexity of equipment and increased size of pipework is required, leading to an increase in indirect emissions associated with equipment. Furthermore, the production of R-1234yf is thought to be more complex and less efficient in its use of raw materials (fluorinated and chlorinated) than R-134a. So the adoption of R-1234yf to replace R-134a will consume more raw materials and result in more indirect emissions of greenhouse gases than does R-134a.

R-1243zf is a low flammability refrigerant, and has a relatively low GWP. R-1243zf (also known as HFC1243zf) is 3,3,3-trifluoropropene ($CF_3CH=CH_2$). Its boiling point, critical temperature, and other properties make it a potential alternative to higher GWP refrigerants such as R-134a, R-410A and R-407. However, the properties of R-1243zf are such that it is not ideal as a direct replacement for existing refrigerants such as R-134a, R-410A and R-407. In particular, its capacity is too low, by which is meant that a refrigerator or air conditioning system having a fixed compressor displacement and designed for existing refrigerants will deliver less cooling when charged with R-1243zf and controlled to the same operating temperatures. This deficiency is in addition to its flammability, which also impacts on its suitability as a substitute for existing refrigerants when used alone.

Some existing technologies designed for R-134a may not be able to accept even the reduced flammability of some heat transfer compositions (any composition having a GWP of less than 150 is believed to be flammable to some extent).

The inventors have used the ASHRAE Standard 34 methodology at 60°C in a 12 litre flask to determine the limiting non flammable composition of binary mixtures of R-1243zf with R-134a and R-1234yf with R-134a. It was found that a 48%/52% (weight basis) R-134a/R-1234yf mixture would be non flammable and that a 79%/21% (weight basis) R-134a/R-1243zf mixture would be non flammable. The R-1234yf mixture has a lower GWP (625) than the equivalent non flammable R-1243zf mixture and also will exhibit slightly higher volumetric capacity. However its pressure drop characteristics and cycle energy efficiency will be worse than the R-1243zf blend. It is desirable to attempt to ameliorate these effects.

A principal object of the present invention is therefore to provide a heat transfer composition which is usable in its own right or suitable as a replacement for existing refrigeration usages which should have a reduced GWP, yet have a capacity and energy efficiency (which may be conveniently expressed as the "Coefficient of Performance") ideally within 20% of the values, for example of those attained using existing refrigerants (e.g. R-134a, R-152a, R-1234yf, R-22, R-410A, R-407A, R-407B, R-407C, R507 and R-404a), and preferably within 10% or less (e.g. about 5%) of these values. It is known in the art that differences of this order between fluids are usually resolvable by redesign of equipment and system operational features without entailing significant cost differences. The composition should also ideally have reduced toxicity and acceptable flammability.

The subject invention addresses the above deficiencies by the provision of a heat transfer composition comprising R-1243zf, R-32 (difluoromethane) and R-161 (fluoroethane). These are referred to herein as a composition of the invention.

Typically, the compositions of the invention contain from about 50 to about 99 % (e.g. from about 70 to about 98 %) by weight of R-1243zf, from about 0.5 to about 25 % (e.g.

from about 1 to about 15 %) by weight of R-161, and from about 0.5 to about 25 % (e.g. from about 1 to about 15 %) by weight of R-32, based on the total weight of the composition. Preferably, the above compositions are ternary blends of R-1243zf, R-32 and R-161.

Compositions of the invention comprising R-1243zf, R-32 and R-161 may additionally contain R-1234yf, R-134a, or a mixture thereof.

All of the chemicals herein described are commercially available. For example, the fluorochemicals may be obtained from Apollo Scientific (UK).

This specification describes many embodiments falling within the scope of the compositions of the invention defined above. For example, some of the compositions of the invention are suitable alternatives to existing refrigerants such as R-22, R-410A, R-407A, R-407B, R-407C, R507 and R-404a (used, for instance, in low and medium temperature refrigeration). Some of the compositions of the invention are suitable replacements for refrigerants such as R-134a, R-1234yf and R-152a (used, for instance, in air conditioning). Preferred combinations of compounds in the compositions of the invention, together with preferred amounts for those compounds, are described in detail, as well as advantageous properties of the compositions of the invention and their proposed utility. It is to be understood that such features of the invention as described herein may be combined in any way, as appropriate, as would be understood by the person of ordinary skill in the art.

The use of relatively low levels of R-134a in the compositions of the invention (e.g. in addition to a composition comprising R-1243zf, R-32, and R-161) can allow further reduction of GWP while achieving reduced flammability in both liquid and vapour phases of the refrigerant.

Typically, R-134a may be present in the compositions of the invention in an amount of from about 1 to about 15 % by weight (e.g. 2 to 10 % by weight), based on the total weight of the composition. For example, a preferred composition of the invention contains from about 20 to about 70 % of R-1243zf, from about 10 to about 40 % of R-32, from about 10 to about 40 % by weight of R-161 and from about 5 to about 15 % of R-134a by weight, based on the total weight of the composition.

The amount of R-161 preferably is limited such that the overall flammability of either liquid or vapour phases of the refrigerant composition is lower than R-1243zf alone. Typically, the R-161 is present in the compositions of the invention in an amount of from about 1 to about 25 or 30 % by weight, for example from about 2 to about 15%, based on the total weight of the composition.

A preferred composition of the invention that is suitable replacements for refrigerants such as R-134a, R-1234yf and R-152a is a blend of R-1243zf, R-32, R-161 and R-1234yf.

Blends of R-1243zf, R-32, R-161 and R-1234yf typically contain from about 15 to about 80 % (e.g. about 20 to about 70 %) of R-1243zf, from about 15 to about 80 % (e.g. about 20 to about 70 %) of R-1234yf, from about 1 to about 25 % (e.g. from about 2 to about 15 %) of R-32 and from about 1 to about 25 % (e.g. from about 2 to about 15 %) of R-161, by weight, based on the total weight of the composition.

In addition to R-1243zf, R-32, R-161 (and optionally R-134a and/or R-1234yf), the compositions of the invention may also contain pentafluoroethane (R-125), carbon dioxide (R-744), or a mixture thereof.

Any R-125 is typically present in an amount of from about 5 to about 40% by weight, such as from about 10 to about 30% by weight, based on the total weight of the composition.

Any R-744 is typically present in an amount of from about 1 to about 15% by weight, such as from about 2 to about 10% by weight, based on the total weight of the composition.

The compositions of the invention have zero ozone depletion potential.

Surprisingly, it has been found that the compositions of the invention can deliver acceptable properties for use in air conditioning and low and medium temperature refrigeration systems as alternatives to existing refrigerants such as R-22, R-410A, R-407A, R-407B, R-407C, R507 and R-404a, while reducing GWP and without resulting in high flammability hazard.

Unless otherwise stated, as used herein "low temperature refrigeration" means refrigeration having an evaporation temperature of from about -40 to about -80 °C. "Medium temperature refrigeration" means refrigeration having an evaporation temperature of from about -15 to about -40 °C.

Unless otherwise stated, IPCC (Intergovernmental Panel on Climate Change) TAR (Third Assessment Report) values of GWP have been used herein. The GWP of R-1243zf has been taken as 4 in line with known atmospheric reaction rate data and by analogy with R-1234yf and R-1225ye (1,2,3,3,3-pentafluoroprop-1-ene).

The GWP of selected existing refrigerant mixtures on this basis is as follows:

R-407A	1990
R-407B	2695
R-407C	1653
R-404A	3784
R507	3850

In an embodiment, the compositions of the invention have a GWP less than R-22, R-410A, R-407A, R-407B, R-407C, R507 or R-404a. Conveniently, the GWP of the compositions of the invention is less than about 3500, 3000, 2500 or 2000. For instance, the GWP may be less than 2500, 2400, 2300, 2200, 2100, 2000, 1900, 1800, 1700, 1600 or 1500.

Preferably, the compositions of the invention (e.g. those that are suitable refrigerant replacements for R-134a, R-1234yf or R-152a) have a GWP that is less than 1300, preferably less than 1000, more preferably less than 500, 400, 300 or 200, especially less than 150 or 100, even less than 50 in some cases.

Advantageously, the compositions are of reduced flammability hazard when compared to the individual flammable components of the compositions (e.g. R-1243zf). In one aspect, the compositions have one or more of (a) a higher lower flammable limit; (b) a higher ignition energy; or (c) a lower flame velocity compared to R-1243zf alone. In a preferred embodiment, the compositions of the invention are non-flammable (or inflammable).

Flammability may be determined in accordance with ASHRAE Standard 34 incorporating the ASTM Standard E-681 with test methodology as per Addendum 34p dated 2004, the entire content of which is incorporated herein by reference.

In some applications it may not be necessary for the formulation to be classed as non-flammable by the ASHRAE 34 methodology; it is possible to develop fluids whose flammability limits will be sufficiently reduced in air to render them safe for use in the application, for example if it is physically not possible to make a flammable mixture by leaking the refrigeration equipment charge into the surrounds. We have found that the effect of adding further refrigerants to flammable refrigerant R-1243zf is to modify the flammability in mixtures with air in this manner.

Temperature glide, which can be thought of as the difference between bubble point and dew point temperatures of a zeotropic (non-azeotropic) mixture at constant pressure, is a characteristic of a refrigerant; if it is desired to replace a fluid with a mixture then it is often preferable to have similar or reduced glide in the alternative fluid. In an embodiment, the compositions of the invention are zeotropic.

Conveniently, the temperature glide (in the evaporator) of the compositions of the invention is less than about 15K, for example less than about 10K or 5K.

Advantageously, the volumetric refrigeration capacity of the compositions of the invention is within about 15% of the existing refrigerant fluid it is replacing, preferably within about 10% or even about 5%.

In one embodiment, the cycle efficiency (Coefficient of Performance) of the compositions of the invention is within about 10% of the existing refrigerant fluid it is replacing, preferably within about 5% or even better than the existing refrigerant fluid it is replacing.

Conveniently, the compressor discharge temperature of the compositions of the invention is within about 15K of the existing refrigerant fluid it is replacing, preferably about 10K or even about 5K (e.g. in the case of R-407B/R-404A/R-507).

As used herein, all % amounts mentioned in compositions herein, including in the claims, are by weight based on the total weight of the compositions, unless otherwise stated.

Compositions according to the invention conveniently comprise substantially no (e.g. 0.5% or less, preferably 0.1% or less) R-1225 (pentafluoropropene), conveniently substantially no R-1225ye (1,2,3,3,3-pentafluoropropene) or R-1225zc (1,1,3,3,3-pentafluoropropene), which compounds may have associated toxicity issues.

In one aspect, the compositions of the invention do not contain any R-1234yf.

The compositions of the invention preferably have energy efficiency at least 95% (preferably at least 98%) of R-134a under equivalent conditions, while having reduced or equivalent pressure drop characteristic and cooling capacity at 95% or higher of R-134a values. The compositions also advantageously have better energy efficiency and pressure drop characteristics than R-1234yf alone.

The heat transfer compositions of the invention are suitable for use in existing designs of equipment, and are compatible with all classes of lubricant currently used with established HFC refrigerants. They may be optionally stabilized or compatibilized with mineral oils by the use of appropriate additives.

Preferably, when used in heat transfer equipment, the composition of the invention is combined with a lubricant.

Conveniently, the lubricant is selected from the group consisting of mineral oil, silicone oil, polyalkyl benzenes (PABs), polyol esters (POEs), polyalkylene glycols (PAGs), polyalkylene glycol esters (PAG esters), polyvinyl ethers (PVEs), poly (alpha-olefins) and combinations thereof.

Advantageously, the lubricant further comprises a stabiliser.

Preferably, the stabiliser is selected from the group consisting of diene-based compounds, phosphates, phenol compounds and epoxides, and mixtures thereof.

Conveniently, the refrigerant composition further comprises an additional flame retardant.

Advantageously, the additional flame retardant is selected from the group consisting of tri-(2-chloroethyl)-phosphate, (chloropropyl) phosphate, tri-(2,3-dibromopropyl)-phosphate, tri-(1,3-dichloropropyl)-phosphate, diammonium phosphate, various halogenated aromatic compounds, antimony oxide, aluminium trihydrate, polyvinyl chloride, a fluorinated iodocarbon, a fluorinated bromocarbon, trifluoro iodomethane, perfluoroalkyl amines, bromo-fluoroalkyl amines and mixtures thereof.

Preferably, the heat transfer composition is a refrigerant composition.

Preferably, the heat transfer device is a refrigeration device.

Conveniently, the heat transfer device is selected from group consisting of automotive air conditioning systems, residential air conditioning systems, commercial air conditioning systems, residential refrigerator systems, residential freezer systems, commercial refrigerator systems, commercial freezer systems, chiller air conditioning systems, chiller refrigeration systems, and commercial or residential heat pump systems. Preferably, the heat transfer device is a refrigeration device or an air-conditioning system.

Advantageously, the heat transfer device contains a centrifugal-type compressor.

The invention also provides the use of a composition of the invention in a heat transfer device as herein described.

According to a further aspect of the invention, there is provided a blowing agent comprising a composition of the invention.

According to another aspect of the invention, there is provided a foamable composition comprising one or more components capable of forming foam and a composition of the invention.

Preferably, the one or more components capable of forming foam are selected from polyurethanes, thermoplastic polymers and resins, such as polystyrene, and epoxy resins.

According to a further aspect of the invention, there is provided a foam obtainable from the foamable composition of the invention.

Preferably the foam comprises a composition of the invention.

According to another aspect of the invention, there is provided a sprayable composition comprising a material to be sprayed and a propellant comprising a composition of the invention.

According to a further aspect of the invention, there is provided a method for cooling an article which comprises condensing a composition of the invention and thereafter evaporating said composition in the vicinity of the article to be cooled.

According to another aspect of the invention, there is provided a method for heating an article which comprises condensing a composition of the invention in the vicinity of the article to be heated and thereafter evaporating said composition.

According to a further aspect of the invention, there is provided a method for extracting a substance from biomass comprising contacting the biomass with a solvent comprising a composition of the invention, and separating the material from the solvent.

According to another aspect of the invention, there is provided a method of cleaning an article comprising contacting the article with a solvent comprising a composition of the invention.

According to a further aspect of the invention, there is provided a method for extracting a material from an aqueous solution comprising contacting the aqueous solution with a solvent comprising a composition of the invention, and separating the material from the solvent.

According to another aspect of the invention, there is provided a method for extracting a material from a particulate solid matrix comprising contacting the particulate solid matrix with a solvent comprising a composition of the invention, and separating the material from the solvent.

According to a further aspect of the invention, there is provided a mechanical power generation device containing a composition of the invention.

Preferably, the mechanical power generation device is adapted to use a Rankine Cycle or modification thereof to generate work from heat.

According to another aspect of the invention, there is provided a method of retrofitting a heat transfer device comprising the step of removing an existing heat transfer fluid, and introducing a composition of the invention. Preferably, the heat transfer device is a refrigeration device or (a static) air conditioning system. Advantageously, the method further comprises the step of obtaining an allocation of greenhouse gas (e.g. carbon dioxide) emission credit.

In accordance with the retrofitting method described above, an existing heat transfer fluid can be fully removed from the heat transfer device before introducing a composition of the invention. An existing heat transfer fluid can also be partially removed from a heat transfer device, followed by introducing a composition of the invention.

In another embodiment wherein the existing heat transfer fluid is R-134a, and the composition of the invention contains a third component comprising R134a, R-1243zf, R-32, R-161, any optional R-1234yf and/or R-125 and/or R-744, (and optional components such as a lubricant, a stabiliser or an additional flame retardant) can be added to the R-134a in the heat transfer device, thereby forming the compositions of the invention, and the heat transfer device of the invention, *in situ*. Some of the existing R-134a may be removed from the heat transfer device prior to adding the R-1243zf, R-32, R-161 etc, to facilitate providing the components of the compositions of the invention in the desired proportions.

Thus, the invention provides a method for preparing a composition and/or heat transfer device of the invention comprising introducing R-1243zf, R-32, R-161, any optional R-1234yf and/or R-125 and/or R-744, and optional components such as a lubricant, a stabiliser or an additional flame retardant, into a heat transfer device containing an existing heat transfer fluid which is R-134a. Optionally, at least some of the R-134a is removed from the heat transfer device before introducing the R-1243zf, R-32, R-161 etc.

Of course, the compositions of the invention may also be prepared simply by mixing the R-1243zf, R-32, R-161, any optional R-1234yf and/or R-125 and/or R-744 (and optional components such as a lubricant, a stabiliser or an additional flame retardant) in the desired proportions. The compositions can then be added to a heat transfer device (or used in any other way as defined herein) that does not contain R-134a or any other existing heat transfer fluid, such as a device from which R-134a or any other existing heat transfer fluid have been removed.

In a further aspect of the invention, there is provided a method for reducing the environmental impact arising from operation of a product comprising an existing compound or composition, the method comprising replacing at least partially the existing compound or composition with a composition of the invention. Preferably, this method comprises the step of obtaining an allocation of greenhouse gas emission credit.

By environmental impact we include the generation and emission of greenhouse warming gases through operation of the product.

As mentioned above, this environmental impact can be considered as including not only those emissions of compounds or compositions having a significant environmental impact from leakage or other losses, but also including the emission of carbon dioxide arising from the energy consumed by the device over its working life. Such environmental impact may be quantified by the measure known as Total Equivalent Warming Impact (TEWI). This measure has been used in quantification of the environmental impact of certain stationary refrigeration and air conditioning equipment, including for example supermarket refrigeration systems (see, for example, http://en.wikipedia.org/wiki/Total_equivalent_warming_impact).

The environmental impact may further be considered as including the emissions of greenhouse gases arising from the synthesis and manufacture of the compounds or compositions. In this case the manufacturing emissions are added to the energy consumption and direct loss effects to yield the measure known as Life-Cycle Carbon Production (LCCP, see for example http://www.sae.org/events/aars/presentations/2007papasavva.pdf). The use of LCCP is common in assessing environmental impact of automotive air conditioning systems.

Emission credit(s) are awarded for reducing pollutant emissions that contribute to global warming and may, for example, be banked, traded or sold. They are conventionally expressed in the equivalent amount of carbon dioxide. Thus if the emission of 1 kg of R-407A is avoided then an emission credit of 1x1990 = 1990 kg CO_2 equivalent may be awarded.

In another embodiment of the invention, there is provided a method for generating greenhouse gas emission credit(s) comprising (i) replacing an existing compound or composition with a composition of the invention, wherein the composition of the invention has a lower GWP than the existing compound or composition; and (ii) obtaining greenhouse gas emission credit for said replacing step.

In a preferred embodiment, the use of the composition of the invention results in the equipment having a lower Total Equivalent Warming Impact, and/or a lower Life-Cycle Carbon Production than that which would be attained by use of the existing compound or composition.

These methods may be carried out on any suitable product, for example in the fields of air-conditioning, refrigeration (e.g. low and medium temperature refrigeration), heat transfer, blowing agents, aerosols or sprayable propellants, gaseous dielectrics, cryosurgery, veterinary procedures, dental procedures, fire extinguishing, flame suppression, solvents (e.g. carriers for flavorings and fragrances), cleaners, air horns, pellet guns, topical anesthetics, and expansion applications. Preferably, the field is air-conditioning or refrigeration.

Examples of suitable products include a heat transfer devices, blowing agents, foamable compositions, sprayable compositions, solvents and mechanical power generation devices. In a preferred embodiment, the product is a heat transfer device, such as a refrigeration device or an air-conditioning unit.

The existing compound or composition has an environmental impact as measured by GWP and/or TEWI and/or LCCP that is higher than the composition of the invention which replaces it. The existing compound or composition may comprise a fluorocarbon compound, such as a perfluoro-, hydrofluoro-, chlorofluoro- or hydrochlorofluoro-carbon compound or it may comprise a fluorinated olefin

Preferably, the existing compound or composition is a heat transfer compound or composition such as a refrigerant. Examples of refrigerants that may be replaced include R-134a, R-152a, R-1234yf, R-410A, R-407A, R-407B, R-407C, R507, R-22 and R-404A.

Any amount of the existing compound or composition may be replaced so as to reduce the environmental impact. This may depend on the environmental impact of the existing compound or composition being replaced and the environmental impact of the replacement composition of the invention. Preferably, the existing compound or composition in the product is fully replaced by the composition of the invention.

The invention is illustrated by the following non-limiting Examples.

Examples

Mixture E shown in Table 1 is an example of a composition of the invention that can be used as an alternative to R-22, R-407A, R-407B, R-407C, R-404A or R507.

Table 1: example refrigerant mixtures with composition given in % w/w (mass basis)

	Mixture A	Mixture B	Mixture C	Mixture D	Mixture E
R-32	20	12	10	22	10
CO_2	0	0	0	0	5
R-134a	0	0	0	10	20
R-125	36	57	62	24	20
R-161	0	0	0	0	10
R-1243zf	44	31	28	44	35
GWP	**1336**	**2005**	**2164**	**1069**	**998**

We have determined the flammability behaviour of mixtures of R-125 and R-1243zf, and of mixtures of R-125 and R-32, using an ASTM E681 12 litre flask test. For mixtures of R-32 and R-125, mixtures containing at least 25% v/v R-125 are non flammable. The lower flammable limit in air of mixtures of R-125 in R-1243zf varies as follows:

R-125 content (%v/v)	Lower flammable limit
0%	4.1%
25%	6%
30%	7%%
40%	8.5%
50%	10%
54%	non flammable

Mixtures of R-32/R-125/R-1243zf can therefore be generated having significantly reduced flammability compared to that of R-1243zf alone. This is demonstrated in Table 2 below, which shows the liquid and vapour equilibrium compositions of mixtures A-E. The composition of vapour is that predicted by the REFPROP property model (see below) to exist in equilibrium with the liquid at 20 °C. The liquid compositions are the "as-charged" compositions of the blends re-expressed on a molar basis. All the mixtures A-E are predicted to have reduced flammability compared to R-1243zf alone.

Table 2: Liquid and vapour equilibrium compositions as % v/v (mole basis) at 20°C

	Mixture A		**Mixture C**	
	Vapour composition	Liquid composition	Vapour composition	Liquid composition
R-32	46.74%	33.65%	26.92%	19.22%
CO_2	0.00%	0.00%	0.00%	0.00%
R-134a	0.00%	0.00%	0.00%	0.00%
R-125	29.30%	26.25%	56.08%	51.64%
R-161	0.00%	0.00%	0.00%	0.00%
R-1243zf	23.96%	40.10%	17.01%	29.14%

	Mixture B		**Mixture D**	
	Vapour composition	Liquid composition	Vapour composition	Liquid composition
R-32	31.32%	22.43%	50.79%	35.87%
CO_2	0.00%	0.00%	0.00%	0.00%
R-134a	0.00%	0.00%	5.42%	8.31%
R-125	50.30%	46.18%	19.72%	16.96%
R-161	0.00%	0.00%	0.00%	0.00%
R-1243zf	18.38%	31.39%	24.07%	38.86%

	Mixture E	
	Vapour composition	Liquid composition
R-32	21.29%	15.49%
CO_2	26.10%	9.16%
R-134a	9.58%	15.80%
R-125	13.85%	13.43%
R-161	13.59%	16.77%
R-1243zf	15.59%	29.36%

The theoretical refrigeration performance of Mixtures A-E was calculated using a vapour compression cycle model using the REFPROP thermodynamic property engine and compared to existing refrigerants. These calculations were performed following the standard approach as used in (for example) the INEOS Fluor "KleaCalc" software (and also may be performed using other available models for predicting the performance of refrigeration and air conditioning systems known to the skilled person in the art), using the following commercial low temperature refrigeration conditions:

Mean evaporating temperature	–25°C
Mean condensing temperature	40°C
Evaporator superheat	8K

Condenser subcooling	5K
Compressor isentropic efficiency	66%
Compressor suction temperature	0°C

The results are summarised in Table 3. The refrigeration performance of R507 would be expected to be almost identical to R-404A.

It is clear from these results that Mixture A is a good match to the performance of R-407A and R-407C. Mixture B and Mixture C are good matches to the performance of R-407B and are also close to the performance of R-404A. In particular the use of Mixture B or Mixture C would offer improved energy efficiency and reduced GWP as compared to either of R-407B, R-404A or R507.

Table 3: Low temperature refrigeration cycle simulation

Thermodynamic properties calculated using REFPROP 8.0 with REFPROP mixing rules used to estimate missing interaction parameters

Simulated performance of refrigerant mixtures in commercial refrigeration conditions

Cycle parameter	Units	R-407A	R-407B	R-407C	R-404A	Mixture A	Mixture B	Mixture C	Mixture D	Mixture E
COP		1.69	1.60	1.72	1.56	1.68	1.64	1.63	1.70	1.71
Volumetric capacity	kJ/m3	1230	1255	1179	1229	1154	1158	1156	1119	1172
Refrigeration effect	kJ/kg	142.85	111.73	155.98	107.87	144.13	122.94	117.70	153.28	165.25
Pressure ratio		8.41	7.95	8.63	7.30	8.24	8.05	7.99	8.42	8.64
Compressor discharge temperature	°C	110.6	97.3	115.6	91.6	106.5	98.3	96.2	109.9	112.7
Evaporator inlet pressure	bar	2.07	2.35	1.91	2.50	1.98	2.09	2.12	1.86	1.91
Condenser inlet pressure	bar	17.41	18.70	16.45	18.22	16.32	16.85	16.97	15.70	16.53
Evaporator inlet temperature	°C	-27.0	-26.3	-27.2	-25.2	-27.3	-26.9	-26.8	-27.3	-28.0
Evaporator dewpoint	°C	-23.0	-23.7	-22.8	-24.8	-22.7	-23.1	-23.2	-22.7	-22.0
Evaporator exit gas temperature	°C	-15.0	-15.7	-14.8	-16.8	-14.7	-15.1	-15.2	-14.7	-14.0
Evaporator glide (out-in)	K	4.1	2.6	4.4	0.4	4.7	3.9	3.6	4.6	6.0
Estimated suction line pressure drop	Pa/m	9272	10922	9051	11448	9810	11014	11404	9665	8721
actual suction line pressure drop	kPa	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Compressor suction pressure	bar	2.07	2.35	1.91	2.50	1.98	2.09	2.12	1.86	1.91
Compressor discharge pressure	bar	17.41	18.70	16.45	18.22	16.32	16.85	16.97	15.70	16.53
Condenser dew point	°C	42.2	41.3	42.5	40.2	43.2	42.6	42.4	43.2	45.4
Condenser bubble point	°C	37.8	38.7	37.5	39.8	36.8	37.4	37.6	36.8	34.6
Condenser exit liquid temperature	°C	32.8	33.7	32.5	34.8	31.8	32.4	32.6	31.8	29.6
Condenser glide (in-out)	K	4.4	2.6	5.0	0.3	6.3	5.1	4.8	6.4	10.9

Further R-1243zf-based compositions of the invention are set out below in table 4. These compositions all have GWPs of less than 100. They are considered to be suitable replacements for the existing refrigerant R-134a. They are additionally considered to be suitable alternatives to the refrigerant R-1234yf.

Table 4: Compositions of blends expressed as weight%

	R-32	R-161	R-1243zf	R-1234yf	R-134a	GWP
Blend A	5	0	95	0	0	31
Blend B	5	5	90	0	0	32
Blend C	5	10	85	0	0	32
Blend D	10	5	85	0	0	59
Blend E	10	10	80	0	0	59
Blend H	5	5	70	20	0	32
Blend J	5	5	45	45	0	32
Blend K	5	5	20	70	0	32
Blend L	0	15	80	0	5	70
Blend M	0	15	40	40	5	70

These blends are thought to exhibit improved refrigeration performance (capacity and/or energy efficiency) relative to the pure materials R-1243zf or R-1234yf while retaining flammability characteristics that are reduced compared to pure R-161 or pure R-1243zf.

The theoretical refrigeration performance of Blends A-E and H-M was calculated using a vapour compression cycle model using the REFPROP thermodynamic property engine and compared to existing refrigerants. These calculations were performed following the standard approach as used in (for example) the INEOS Fluor "KleaCalc" software (and also may be performed using other available models for predicting the performance of refrigeration and air conditioning systems known to the skilled person in the art), using the following conditions:

Mean evaporating temperature	5°C
Mean condensing temperature	50°C
Evaporator superheat	10K
Condenser subcooling	6K
Compressor isentropic efficiency	67%
Compressor suction temperature	15°C

The results are summarised in Table 5.

Table 5:

Results	R-134a	R-1234yf	Blend A	Blend B	Blend C	Blend D	Blend E	Blend H	Blend J	Blend K	Blend L	Blend M
COP	3.41	3.30	3.40	3.41	3.42	3.41	3.41	3.39	3.36	3.35	3.43	3.39
Volumetric capacity (kJ/m^3)	2414	2256	2334	2439	2537	2692	2788	2510	2566	2576	2397	2517
Refrigeration effect (kJ/kg)	148.24	115.44	156.28	163.61	170.91	169.31	176.44	154.44	144.40	136.76	171.36	155.37
Pressure ratio	3.77	3.47	3.62	3.60	3.57	3.60	3.58	3.54	3.48	3.46	3.53	3.46
Compressor discharge temperature (°C)	76.66	65.84	74.23	75.58	76.86	78.19	79.36	74.26	72.76	71.51	75.44	73.37
Evaporator inlet pressure (bara)	3.50	3.71	3.53	3.68	3.83	4.05	4.20	3.88	4.07	4.14	3.65	3.96
Condenser inlet pressure (bara)	13.18	12.85	12.76	13.25	13.69	14.59	15.03	13.74	14.18	14.33	12.86	13.71
Evaporator inlet temperature (°C)	5.00	5.00	3.98	3.84	3.75	3.09	3.04	4.01	4.33	4.52	4.55	4.78
Evaporator dewpoint (°C)	5.00	5.00	6.02	6.16	6.25	6.91	6.96	5.99	5.67	5.48	5.45	5.22
Evaporator exit gas temperature (°C)	15.00	15.00	16.02	16.16	16.25	16.91	16.96	15.99	15.67	15.48	15.45	15.22
Evaporator glide (out-in) (K)	0.0	0.0	2.0	2.3	2.5	3.8	3.9	2.0	1.3	1.0	0.9	0.4
Specific suction line pressure drop (kPa)	411	531	409	378	352	334	313	384	395	410	372	381
actual suction line pressure drop	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Compressor suction pressure (bara)	3.50	3.71	3.53	3.68	3.83	4.05	4.20	3.88	4.07	4.14	3.65	3.96
Compressor discharge pressure (bara)	13.18	12.85	12.76	13.25	13.69	14.59	15.03	13.74	14.18	14.33	12.86	13.71
Condenser dew point (°C	50.00	50.00	51.91	52.00	52.03	52.97	52.93	51.58	51.08	50.79	50.58	50.27
Condenser bubble point (°C)	50.00	50.00	48.09	48.00	47.97	47.03	47.07	48.42	48.91	49.21	49.42	49.73
Condenser exit liquid temperature (°C)	44.00	44.00	42.09	42.00	41.97	41.03	41.07	42.42	42.91	43.21	43.42	43.73
Condenser glide (in-out) (K)	0.00	0.00	3.82	4.00	4.06	5.94	5.87	3.16	2.17	1.59	1.15	0.54

All of mixtures A-M in Table 5 exhibit improved energy efficiency and volumetric capacity relative to R-1234yf.

Furthermore they exhibit equal or lower specific suction line pressure drop as compared to either R-134a or R-1234yf. The suction line is the pipe connecting the air conditioning system evaporator to the compressor. The specific pressure drop shown is calculated assuming a common suction line diameter (16.2mm was used in this case) and cooling duty (6.7 kW was used in this case) for each fluid. The energy efficiency of real air conditioning systems – in particular automotive air conditioners – is affected by the pressure drop in the suction line with higher pressure drops leading to reduced efficiencies. The mixtures of the invention can thus be expected to display more favourable pressure drops as compared to R-1234yf.

The mixtures of the invention also exhibit equal or reduced compressor discharge temperatures compared to R-134a.

The invention is defined by the following claims.

CLAIMS

1. A heat transfer composition comprising R-1243zf, R-32 (difluoromethane) and R-161 (fluoroethane).

2. A composition according to claim 1 comprising from about 50 to about 99 % by weight of R-1243zf, from about 0.5 to about 25 % by weight of R-161, and from about 0.5 to about 25 % by weight of R-32, based on the total weight of the composition.

3. A composition according to claim 2 comprising from about 70 to about 98 % by weight of R-1243zf, from about 1 to about 15 % by weight of R-161, and from about 1 to about 15 % by weight of R-32, based on the total weight of the composition.

4. A composition according to any of the preceding claims, further comprising R-1234yf, R-134a, or a mixture thereof.

5. A composition according to claim 4, wherein the composition is a blend of R-1243zf, R-32, R-161 and R-1234yf.

6. A composition according to claim 5 comprising from about 15 to about 80 % of R-1243zf, from about 15 to about 80 % of R-1234yf, from about 1 to about 25 % of R-32, and from about 1 to about 25 % of R-161, by weight, based on the total weight of the composition.

7. A composition according to claim 6 comprising from about 20 to about 70 % of R-1243zf, from about 20 to about 70 % of R-1234yf, from about 2 to about 15 % of R-32, and from about 2 to about 15 % of R-161, by weight, based on the total weight of the composition.

8. A composition according to any of the preceding claims, further comprising pentafluoroethane (R-125), carbon dioxide (R-744), or a mixture thereof.

9. A composition according to any of the preceding claims, wherein the composition has a GWP of less than 3500, preferably less than 2000.

10. A composition according to claim 9, wherein the composition has a GWP of less than 1000, preferably less than 150.

11. A composition according to any of the preceding claims, wherein the temperature glide is less than about 15k, preferably less than about 10k.

12. A composition according to any of the preceding claims, wherein the composition has a volumetric refrigeration capacity within about 15%, preferably within about 10% of the existing refrigerant that it is intended to replace.

13. A composition according to any of the preceding claims, wherein the composition is less flammable than R-1243zf alone.

14. A composition according to claim 13 wherein the composition has:

(a) a higher flammable limit;

(b) a higher ignition energy; and/or

(c) a lower flame velocity

compared to R-1243zf alone.

15. A composition according to claim 13 or 14 which is inflammable.

16. A composition according to any of the preceding claims, wherein the composition has a cycle efficiency within about 10% of the existing refrigerant that it is intended to replace.

17. A composition according to any of the preceding claims, wherein the composition has a compressor discharge temperature within about 15k, preferably within about 10k, of the existing refrigerant that it is intended to replace.

18. A composition according to any of the preceding claims further comprising a lubricant.

19. A composition according to claim 18, wherein the lubricant is selected from mineral oil, silicone oil, polyalkyl benzenes (PABs), polyol esters (POEs), polyalkylene glycols (PAGs), polyalkylene glycol esters (PAG esters), polyvinyl ethers (PVEs), poly (alpha-olefins) and combinations thereof.

20. A composition according to any of the preceding claims further comprising a stabiliser.

21. A composition according to claim 20, wherein the stabiliser is selected from diene-based compounds, phosphates, phenol compounds and epoxides, and mixtures thereof.

22. A composition according to any of the preceding claims further comprising an additional flame retardant.

23. A composition according to claim 22, wherein the additional flame retardant is selected from the group consisting of tri-(2-chloroethyl)-phosphate, (chloropropyl) phosphate, tri-(2,3-dibromopropyl)-phosphate, tri-(1,3-dichloropropyl)-phosphate, diammonium phosphate, various halogenated aromatic compounds, antimony oxide, aluminium trihydrate, polyvinyl chloride, a fluorinated iodocarbon, a fluorinated bromocarbon, trifluoro iodomethane, perfluoroalkyl amines, bromo-fluoroalkyl amines and mixtures thereof.

24. A composition according to any of the preceding claims which is a refrigerant composition.

25. A heat transfer device containing a composition as defined in any one of claims 1 to 24.

26. Use of a composition defined in any of claims 1 to 24 in a heat transfer device.

27. A heat transfer device according to claim 25 or 26 which is a refrigeration device.

28. A heat transfer device according to claim 27 which is selected from group consisting of automotive air conditioning systems, residential air conditioning systems, commercial air conditioning systems, residential refrigerator systems, residential freezer systems, commercial refrigerator systems, commercial freezer systems, chiller air conditioning systems, chiller refrigeration systems, and commercial or residential heat pump systems.

29. A heat transfer device according to claim 27 or 28 which contains a compressor.

30. A blowing agent comprising a composition as defined in any of claims 1 to 24.

31. A foamable composition comprising one or more components capable of forming foam and a composition as defined in any of claims 1 to 24, wherein the one or more components capable of forming foam are selected from polyurethanes, thermoplastic polymers and resins, such as polystyrene, and epoxy resins, and mixtures thereof.

32. A foam obtainable from the foamable composition of claim 31.

33. A foam according to claim 32 comprising a composition as defined in any one of claims 1 to 24.

34. A sprayable composition comprising material to be sprayed and a propellant comprising a composition as defined in any of claims 1 to 24.

35. A method for cooling an article which comprises condensing a composition defined in any of claims 1 to 24 and thereafter evaporating the composition in the vicinity of the article to be cooled.

36. A method for heating an article which comprises condensing a composition as defined in any one of claims 1 to 24 in the vicinity of the article to be heated and thereafter evaporating the composition.

37. A method for extracting a substance from biomass comprising contacting biomass with a solvent comprising a composition as defined in any of claims 1 to 24, and separating the substance from the solvent.

38. A method of cleaning an article comprising contacting the article with a solvent comprising a composition as defined in any of Claims 1 to 24.

39. A method of extracting a material from an aqueous solution comprising contacting the aqueous solution with a solvent comprising a composition as defined in any of claims 1 to 24, and separating the material from the solvent.

40. A method for extracting a material from a particulate solid matrix comprising contacting the particulate solid matrix with a solvent comprising a composition as defined in any of claims 1 to 24, and separating the material from the solvent.

41. A mechanical power generation device containing a composition as defined in any of claims 1 to 24.

42. A mechanical power generating device according to claim 41 which is adapted to use a Rankine Cycle or modification thereof to generate work from heat.

43. A method of retrofitting a heat transfer device comprising the step of removing an existing heat transfer fluid, and introducing a composition as defined in any one of claims 1 to 24.

44. A method of claim 43 wherein the heat transfer device is a refrigeration device.

45. A method according to claim 44 wherein the heat transfer device is an air conditioning system.

46. A method for reducing the environmental impact arising from the operation of a product comprising an existing compound or composition, the method comprising replacing at least partially the existing compound or composition with a composition as defined in any one of claims 1 to 24.

47. A method for preparing a composition as defined in any of claims 1 to 24, and/or a heat transfer device as defined in any of claims 25 or 27 to 29, which composition or heat transfer device contains R-134a, the method comprising introducing R-1243zf, R-32, R-161, any optional R-1234yf and/or R-125 and/or R-744, and optionally a lubricant, a stabiliser and/or an additional flame retardant, into a heat transfer device containing an existing heat transfer fluid which is R-134a.

48. A method according to claim 47 comprising the step of removing at least some of the existing R-134a from the heat transfer device before introducing the R-1243zf, R-32, R-161, any optional R-1234yf and/or R-125 and/or R-744, and optionally the lubricant, the stabiliser and/or the additional flame retardant.

49. A method for generating greenhouse gas emission credit comprising (i) replacing an existing compound or composition with a composition as defined in any one of claims 1 to 24, wherein the composition as defined in any one of claims 1 to 24 has a lower GWP than the existing compound or composition; and (ii) obtaining greenhouse gas emission credit for said replacing step.

50. A method of claim 49 wherein the use of the composition of the invention results in a lower Total Equivalent Warming Impact, and/or a lower Life-Cycle Carbon Production than is be attained by use of the existing compound or composition.

51. A method of claim 49 or 50 carried out on a product from the fields of air-conditioning, refrigeration, heat transfer, blowing agents, aerosols or sprayable propellants, gaseous dielectrics, cryosurgery, veterinary procedures, dental procedures, fire extinguishing, flame suppression, solvents, cleaners, air horns, pellet guns, topical anesthetics, and expansion applications.

52. A method according to claim 48 or 51 wherein the product is selected from a heat transfer device, a blowing agent, a foamable composition, a sprayable composition, a solvent or a mechanical power generation device.

53. A method according to claim 52 wherein the product is a heat transfer device.

54. A method according to any one of claims 48 to 53 wherein the existing compound or composition is a heat transfer composition.

55. A method according to claim 54 wherein the heat transfer composition is a refrigerant selected from R-22, R-410A, R-407A, R-407B, R-407C, R507 and R-404a.

56. A method according to claim 54 wherein the heat transfer composition is a refrigerant selected from R-134a, R-1234yf and R-152a.

57. Any novel heat transfer composition substantially as hereinbefore described, optionally with reference to the examples.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2009/002809

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K5/04 C09K3/30 C08J9/14 C11D7/50

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 C08J C11D

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 practical, 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.
Y	US 2007/108403 A1 (SIEVERT ALLEN C [US] ET AL) 17 May 2007 (2007-05-17) claim 5; table 14	1-57
Y	US 2006/243944 A1 (MINOR BARBARA H [US] ET AL) 2 November 2006 (2006-11-02) claims 5,25	1-57

☐ 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 document 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	Date of mailing of the international search report
23 March 2010	29/03/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Fax: (+31–70) 340–3016	Puetz, Christine

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2009/002809

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. [X] Claims Nos.: 49-56(all partially)
because they relate to subject matter not required to be searched by this Authority, namely:

see FURTHER INFORMATION sheet PCT/ISA/210

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:

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 an 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.:

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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.1

Claims Nos.: 49-56(all partially)

Rule 39 (iii) schemes, rules or methods for doing business
The search for the claims 49-51 and 52-56 (all in part) has been restricted to the technical subject-matter of these claims, namely the use of a composition comprising R-1243zf, R-161 and R-32 in place of an existing compound or composition, wherein the former has a lower GWP than the latter in the fields listed in claim 51.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2009/002809

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007108403 A1	17-05-2007	NONE	
US 2006243944 A1	02-11-2006	BR PI0607994 A2	03-11-2009
		EP 1853679 A2	14-11-2007
		EP 1985680 A2	29-10-2008
		EP 1985681 A2	29-10-2008
		JP 2008531836 T	14-08-2008