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(54) **Title:** COMPOSITIONS

(57) **Abstract:** A composition comprising: (i) 1,1-difluoroethene (vinylidene fluoride, R-1132a); (ii) carbon dioxide (CO_2, R-744); (iii) pentafluoroethane (R-125); and (iv) one or more of trifluoromethane (R-23) and hexafluoroethane (R-116).

Compositions

The invention relates to compositions, preferably to heat transfer compositions, and in particular to ultra-low temperature heat transfer compositions which may be suitable as replacements for existing refrigerants such as R-23, R-13B1, R-508A or R-508B.

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.

“Blast freezer” equipment is used for rapid freezing of food or pharmaceutical products by contact of the product to be frozen inside a closed compartment with recirculating low-temperature air.

Conventional blast freezing for food uses a single stage refrigeration system, to generate rapid cooling down to temperatures between about -18 and about -30°C. A typical refrigerant used for this would be R-404A (by weight 44% pentafluoroethane (R-125), 52% 1,1,1-trifluoroethane (R-143a) and 4% 1,1,1,2-tetrafluoroethane (R-134a)).

It has been found that using a lower cooling temperature can allow sea transport of high value seafood (e.g. sea urchin, swordfish, tuna) over long distances. Several shipping companies offer refrigerated transport container systems (‘reefers’) capable of maintaining temperatures of about -60 °C. In these cascade systems a low temperature refrigeration loop using trifluoromethane (R-23) cools the container air to -60 °C then rejects its heat to a second higher temperature refrigeration loop (using R-134a or R-404A). The high temperature stage rejects the heat to ambient air. These systems work well but the GWP of R-23 is very high at 14,800. It would therefore be desirable to have a low-flammability or non-flammable fluid of lower GWP capable of replacing R-23 in this application.

The pharmaceutical industry also uses blast freezing at low temperatures to freeze and preserve active ingredients and other biologically derived materials, as discussed in the reference monograph "*Freeze-Drying/Lyophilization of Pharmaceutical and Biological Products, Third Edition*" edited by Louis Rey published by CRC Press, 19 Apr 2016, incorporated by reference herein. Specific examples include, but are not limited to, insulin, vaccines and tissue samples. Traditional refrigerants used in these systems include bromotrifluoromethane (R-13B1), R-23, R-508A (39% R-23, 61% R-116) and R-508B (46% R-23, 56% R-116), where the operating temperatures range from about -60 °C to about -90 °C.

There are several refrigerant and application characteristics that need to be considered in developing feasible alternatives for R-23 (and other low-temperature refrigerants used in cascade systems), including:

- Low flammability
- Suitable operating temperature
- An operating pressure similar to that of R-23
- Performance as a refrigerant (e.g. cooling capacity and energy efficiency)
- Minimal temperature glide of refrigerant
- Low Global Warming Potential (GWP)

The design of a suitable refrigerant therefore involves making multiple informed selections of composition and component to reach a feasible alternative.

One way of assessing non-flammability is to apply the flammability analysis methodology stipulated by ASHRAE Standard 34:2016, which prescribes a range of leakage scenarios that should be applied to refrigerant blends to identify the potentially flammable worst-case compositions.

If the fluid is to be used as a retrofit or conversion fluid in existing equipment, or as a "drop-in" to new equipment (e.g. using an essentially unchanged R-23 system design), then non-flammability is highly desired, as the existing design will have been based on the use of non-flammable fluid. In particular, for larger systems and marine transport (reefer) applications, non-flammability in all circumstances (including leakage) is highly preferred.

It is also advantageous to have acceptably low toxicity as a characteristic of the fluid.

The volumetric capacity (a measure of the cooling power achievable by a given size of compressor) and energy efficiency are important considerations for any composition with heat transfer properties. This is especially so in cascade operation as any inefficiency in the low temperature stage also increases power consumption of the compressor in the top stage of the cascade.

R-170 (ethane) has very low GWP, acceptable refrigeration performance and low toxicity but its high flammability limits its application. For instance, safety regulations can restrict the maximum charge quantity of refrigerant in appliances.

R-744 (carbon dioxide) is non-flammable but cannot be used alone in the bottom stage of low temperature cascade systems because the operating temperatures are below the triple point of R-744, which is -56.7°C. This means that solid carbon dioxide (dry-ice) could form in low pressure sections of the system, leading to blockages, poor control and inefficient operation.

R-1132a (1,1-difluoroethene, also known as vinylidene fluoride) also has low GWP and acceptable toxicity. The flammability of R-1132a is reduced compared to ethane but it is still in ASHRAE flammability class 2 (“moderately flammable”). The thermodynamic energy efficiency of pure R-1132a is close to that of R-508 and better than that of R-23 but its refrigeration capacity is reduced compared to R-508 and R-23.

Thus, there is a need to provide alternative refrigerants having improved properties such as low GWP, yet possessing acceptable refrigeration performance, flammability characteristics and toxicology. 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.

The subject invention addresses the above and other deficiencies by the provision of a composition comprising: 1,1-difluoroethene (vinylidene fluoride, R-1132a); carbon dioxide (CO_2, R-744); pentafluoroethane (R-125); and one or more of trifluoromethane (R-23) and hexafluoroethane (R-116).

The invention also provides the use of the compositions of the invention as refrigerants, preferably low temperature refrigerants suitable for use in blast freezing equipment. The temperatures reached by using the compositions of the invention as refrigerants may be -60 °C or below, such as -70 °C or below, preferably -80 °C or below, or even -90 °C or below.

Surprisingly, it has been found that the compositions of the invention exhibit a combination of suitable flammability properties, a similar operating pressure to R-23, comparable or superior refrigeration performance to R-23, desirable temperature glide and low GWP.

The compositions of the invention may comprise from about 1 to about 90% by weight R-1132a, such as from about 1 to about 80% by weight, from about 1 to about 70% by weight or from about 1 to about 60% by weight. Preferably, the compositions comprise from about 1 to about 50% by weight R-1132a, such as from about 5 to about 45% by weight, from about 10 to about 45% by weight, from about 15 to about 40% by weight. Advantageously, the compositions may comprise from about 20 to about 40% by weight R-1132a, preferably from about 25 to about 35% by weight R-1132a.

The compositions of the invention may comprise from about 1 to about 90% by weight carbon dioxide, such as from about 1 to about 80% by weight, from about 5 to about 70% by weight or from about 10 to about 60% by weight. Preferably, the compositions comprise from about 25 to about 60% by weight carbon dioxide, such as from about 30 to about 55% by weight, or even more preferably, from about 35 to about 50% by weight.

The compositions of the invention are surprisingly able to operate below -56.7 °C (the triple point of carbon dioxide) without the formation of dry ice in the system.

The compositions of the invention may comprise from about 1 to about 90% by weight R-125, such as from about 1 to about 80% by weight, from about 1 to about 70% by weight or from about 1 to about 60% by weight. Preferably, the compositions comprise from about 1 to about 50% by weight, such as from about 5 to about 45% by weight, from about 5 to about 30% by weight, or even from about 10 to about 25% by weight.

The compositions of the invention may comprise from about 1 to about 90% by weight of the fourth component, such as from about 1 to about 80% by weight, from about 1 to about 70% by weight or from about 1 to about 60% by weight. Preferably, the compositions of the invention can comprise from about 1 to about 50% by weight of the fourth component.

In an embodiment, the fourth component comprises or is R-23. Thus, a preferred composition of the invention comprises R-1132a, CO_2, R-125 and R-23.

In a preferred embodiment, there is provided a composition comprising from about 20 to about 40% by weight R-1132a, from about 30 to about 60% by weight carbon dioxide, from about 1 to about 20% by weight R-23 and from about 1 to about 35 % by weight R-125.

Advantageously, there is provided a composition comprising from about 25 to about 35% by weight R-1132a, from about 35 to about 50% by weight carbon dioxide, from about 5 to about 15% by weight R-23 and from about 5 to about 30% by weight R-125.

In a preferred embodiment, there is provided a composition comprising from about 25 to about 30% by weight R-1132a, from about 35 to about 50% by weight carbon dioxide, from about 10 to about 25% by weight R-125 and from about 5 to about 20% by weight R-23.

In an alternative embodiment, the fourth component comprises or is R-116. Thus, a preferred composition of the invention comprises R-1132a, CO_2, R-125 and R-116.

In a preferred embodiment, there is provided a composition comprising from about 30 to about 60% by weight carbon dioxide, from about 10 to about 40% by weight R-1132a, from about 5 to about 30% by weight R-125 and from about 1 to about 20% by weight R-116.

A preferred composition of the invention comprises from about 35 to about 55% by weight carbon dioxide, from about 15 to about 35% by weight R-1132a, from about 10 to about 30% by weight R-125 and from about 1 to about 15% by weight R-116.

Advantageously, there is provided a composition comprising from about 25 to about 35% by weight R-1132a (e.g. about 30%), from about 40 to about 50% by weight carbon dioxide (e.g. about 45%), from about 15 to about 25% by weight R-125 (e.g. about 20%) and from about 1 to about 15% by weight R-116 (e.g. about 5%).

Preferably, the R-1132a is present in an amount of less than 50% by mol. The ASHRAE fractionation analysis referred to above requires an assessment of liquid and vapour compositions during vapour leakage from a cylinder and should be conducted for two levels of refrigerant charge (15% and 90% of maximum fill) and over a range of temperatures from -40 °C to +60 °C. A composition comprising less than 50% by mol. of R-1132a, preferably less than 30% by mol., will result in a weakly flammable or, preferably, a non-flammable composition under fractionation analysis.

The ASHRAE fractionation analysis is conservative in nature. The blends of the invention, like R-23, typically will have critical temperatures close to ambient temperature. This means that if the system is not operational, and warms to ambient temperature, then it is possible that the blend could be above its critical temperature. In this case, it will exist as a homogenous supercritical fluid. Leakage would therefore be of the bulk composition, not of a fractionated vapour. Therefore, if the bulk fluid is non-flammable the composition could be used for various applications without a significant risk of generating a flammable atmosphere.

In an embodiment, the compositions may consist essentially of the stated components.

By the term “consist essentially of”, we mean that the compositions of the invention contain substantially no other components, particularly no further (hydro)(fluoro)compounds (e.g. (hydro)(fluoro)alkanes or (hydro)(fluoro)alkenes) known to be used in heat transfer compositions. The term “consist of” is included within the meaning of “consist essentially of”.

In an embodiment, the compositions of the invention are substantially free of any component that has heat transfer properties (other than the components specified). For instance, the compositions of the invention may be substantially free of any other hydrofluorocarbon compound.

By “substantially no” and “substantially free of”, we include the meaning that the compositions of the invention contain 0.5% by weight or less of the stated component, preferably 0.1% or less, based on the total weight of the composition.

The compositions of the invention may be azeotropic or near azeotropic, preferably azeotropic.

By azeotropic composition, we include the meaning of a composition which at vapour-liquid equilibrium has the same composition in both phases, and whose boiling point is lower than that of the pure components. All the azeotropic compositions of the invention have been found to exhibit a positive deviation from ideality. By near-azeotropic composition we include the meaning of liquid compositions whose vapour pressure is above that of the pure component with the lower boiling point when measured at equivalent temperature, but whose equilibrium vapour composition may differ from the liquid composition.

All of the chemicals herein described are commercially available. For example, the fluorochemicals may be obtained from Apollo Scientific (UK) and carbon dioxide may be obtained from liquefied gas suppliers such as Linde AG.

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

By the term “about”, as used in connection with numerical values of amounts of components in % by weight, we include the meaning of ± 0.5 % by weight, for example ± 0.2 % by weight or ± 0.1 % by weight.

For the avoidance of doubt, it is to be understood that the stated upper and lower values for ranges of amounts of components in the compositions of the invention described herein may be interchanged in any way, provided that the resulting ranges fall within the broadest scope of the invention.

The compositions of the invention have zero ozone depletion potential.

The GWP is desired to be as low as possible whilst respecting the other constraints on flammability, performance and operational temperature range

The compositions have a GWP of less than 7400, such as less than 5000, less than 4000 or preferably less than 3700. The compositions advantageously have a GWP of less than 3000, less than 2500, less than 2000, less than 1500 or even less than 1000.

Typically, the compositions of the subject invention are of reduced flammability hazard when compared to R-1132a.

Flammability may be determined in accordance with ASHRAE Standard 34:2016 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 embodiments, the compositions have one or more of (a) a higher lower flammable limit; (b) a higher ignition energy (sometimes referred to as auto ignition energy or pyrolysis); or (c) a lower flame velocity compared to R-1132a alone. Preferably, the compositions of the invention are less flammable compared to R-1132a in one or more of the following respects: lower flammable limit at 23°C; lower flammable limit at 60°C; breadth of flammable range at 23°C or 60°C; auto-ignition temperature (thermal decomposition temperature); minimum ignition energy in dry air or flame speed. The flammable limits being determined according to the methods specified in ASHRAE Standard 34:2016 and the auto-ignition temperature being determined in a 500ml glass flask by the method of ASTM E659-78.

In a preferred embodiment, the compositions of the invention are non-flammable. For example, the compositions of the invention are non-flammable at a test temperature of 60°C using the ASHRAE methodology. Advantageously, the mixtures of vapour that exist in equilibrium with the compositions of the invention at any temperature between about –40°C and 60°C are also non-flammable.

In some applications it may not be necessary for the formulation to be classed as non-flammable by the ASHRAE 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.

In one embodiment, the compositions of the invention have a flammability classifiable as 1 or 2L according to the ASHRAE classification method, indicating non-flammability (class 1) or a weakly flammable fluid with flame speed lower than 10 cm/s (class 2L).

Temperature glide can be managed within a system and glides of less than about 10 K are acceptable with only minor effects on performance. Glides of greater than about 10 K can cause some degradation in expected performance unless heat exchangers are designed to accommodate the glide effect.

A composition of the invention preferably have a temperature glide in an evaporator or condenser of less than about 10 K, even more preferably less than about 7 K, such as less than about 5 K (e.g. less than 3 K). “Temperature glide” is the term given to the change in temperature experienced during evaporation or condensation of a non-azeotropic refrigerant mixture.

The critical temperature of a heat transfer composition should be higher than the maximum expected condenser temperature. This is because the cycle efficiency typically drops as critical temperature is approached. As this happens, the latent heat of the refrigerant is reduced and so more of the heat rejection in the condenser takes place by cooling gaseous refrigerant; this requires more area per unit heat transferred. The critical temperature of R-508B is about 11 °C and the critical temperature of R-23 is about 26 °C.

In one aspect, the compositions of the invention have a critical temperature of greater than about 0 ºC, preferably greater than about 10 ºC, more preferably greater than about 25°C.

The compositions of the invention typically have a volumetric refrigeration capacity that is at least 85% of that of R-23 at comparable cycle conditions. Preferably, the compositions of the invention have a volumetric refrigeration capacity that is at least 90% of that of R-23, for example from about 95% to about 120% (e.g. about 96% to about 115%) of that of R-23.

The compositions of the invention, in use as refrigerants, typically are capable of reaching temperatures of -60 °C or lower, preferably -70 °C or lower, for example -80 °C or lower whilst maintaining the evaporation pressure above atmospheric pressure.

In one embodiment, the cycle efficiency (Coefficient of Performance, COP) of the compositions of the invention is at least 95% and/or within about 5% of the existing refrigerant fluid it is replacing (e.g. R-23).

Conveniently, the compressor discharge temperature of the compositions of the invention is within about 15 K of the existing refrigerant fluid it is replacing, preferably about 10 K or even about 5 K.

The compositions of the invention are typically suitable for use in existing designs of equipment, for example, low temperature refrigeration equipment and are compatible with all classes of lubricant currently used with established HFC refrigerants. They may be optionally stabilised or compatibilised 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. PAGs and POEs (particularly the latter) are currently preferred lubricants for the compositions of the invention.

Advantageously, the lubricant further comprises a stabiliser. The lubricant may preferably further comprise pentane (e.g. n-pentane or iso-pentane). The pentane may be present in an amount of from about 1 to about 10% by weight, such as from about 2 to about 6% by weight of the refrigerant charge (e.g. a composition containing the pentane, lubricant and heat transfer composition).

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

Conveniently, the composition of the invention may be combined with a flame retardant.

Advantageously, the 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.

In one embodiment, the invention provides a heat transfer device comprising a composition of the invention.

Preferably, the heat transfer device is a refrigeration device.

Conveniently, the heat transfer device is an ultra-low temperature refrigeration system, such as a blast freezer.

Advantageously, the heat transfer device contains a cascade system.

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 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 substance 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 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, more preferably still the device is an ultra-low temperature refrigeration system, such as a blast freezer. Preferably, the refrigeration system cools a compartment to less than about -55 °C, preferably less than about -60 °C, more preferably to less than about -85 °C, or even less than -90 °C.

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.

The compositions of the invention may also be prepared simply by mixing the R-1132a, carbon dioxide, R-125 and the fourth component (and further 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).

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-23 is avoided then an emission credit of 1x14800 = 14800 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, gaseous dielectrics, flame suppression, solvents (e.g. carriers for flavourings and fragrances), cleaners, topical anaesthetics, and expansion applications. Preferably, the field is ultra-low temperature refrigeration.

Examples of suitable products include heat transfer devices, solvents and mechanical power generation devices. In a preferred embodiment, the product is a heat transfer device, such as a refrigeration device or an ultra-low temperature refrigeration system.

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 ULT refrigerants such as R-508A, R-508B, R-23 and R-13B1.

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

Compositions of R-1132a, R-744, R-125 and R-23

The performance of quaternary compositions of the invention were modelled and the results are provided in the following Tables. The tables list the GWP, condenser and evaporator glide, capacity and COP relative to R-23, the difference in discharge temperature and condenser pressure, The Tables provide the contents as weight percentages, unless otherwise specified.

The cycle conditions used in the modelling are as Table 1.

Table 1

Cycle conditions for modelling		
Reference fluid for cycle calculation is R-23		
Condensing temperature	°C	-20
Evaporating temperature	°C	-70
Suction gas temperature	°C	-50
Isentropic efficiency		0.65
Subcooling	K	5
Evaporator superheat	K	5
Cooling duty	kW	1
Clearance ratio		0.03
Suction line diameter for PD calculation	mm	22
Cycle calculation results		R-23 reference
Pressure ratio		7.20
Volumetric efficiency		89.3%
Condenser glide	K	0.0
Evaporator glide	K	0.0
Evaporator inlet temperature	°C	-70.0
Condenser exit temperature	°C	-25.0

Condenser pressure	bar	13.95
Evaporator pressure	bar	1.94
Refrigeration effect	kJ/kg	174.1
Coefficient of Performance		1.90
Discharge temperature	°C	86.4
Mass flow rate	kg/hr	20.7
Volumetric flow rate	m3/hr	2.72
Volumetric capacity	kJ/m3	1322
Suction line pressure drop	kPa/m	8.75
Suction line density	kg/m3	7.59
Condenser inlet density	kg/m3	58.94
Capacity relative to R-23		100.0%
COP relative to R-23		100.0%
Discharge temperature difference	K	0.0
Condenser pressure difference	bar	0.00
Pressure ratio relative to that of R-23		100.0%

The thermodynamic model used for the mixture calculations uses a cubic equation of state to model the vapour phase, with a Gibbs free energy correlation (the Wilson equation) to model the liquid phase and temperature correlations of the component vapour pressures. The binary interaction parameters for the fluids were correlated to measured phase equilibrium data where available.

Many compositions have been identified that have volumetric capacity significantly higher than that of R-23 and may be better suited to a new system design to take advantage of the fluid properties.

Table 2

R744		60	60	55	55	50	50	50	50
R1132a		30	25	30	25	40	35	35	30
R-23		5	10	10	10	5	10	5	15
R125		5	5	5	10	5	5	10	5
Global Warming Potential (AR4 basis)		916	1656	1656	1831	916	1656	1091	2396
Cycle calculation results									
Condenser glide	K	2.5	2.4	2.6	4.3	2.9	2.7	4.7	2.6
Evaporator glide	K	2.8	2.8	2.8	4.8	2.9	2.8	5.1	2.7
Capacity relative to R-23		126.4%	124.6%	123.2%	115.9%	122.8%	121.5%	115.6%	120.2%
COP relative to R-23		97.2%	96.1%	96.5%	96.4%	98.0%	97.0%	97.8%	96.0%
Discharge temperature difference	K	18.1	21.1	17.0	18.1	10.5	13.1	11.5	15.8
Condenser pressure difference	bar	3.78	3.85	3.59	2.86	3.20	3.30	2.48	3.39

R744		50	50	50	50	45	45	45	45	45	45	45	45	45	45
R1132a		30	25	25	25	40	35	35	35	30	30	30	30	25	25
R-23		10	15	10	5	10	15	10	5	15	10	7	5	15	10
R125		10	10	15	20	5	5	10	15	10	15	18	20	15	20
Global Warming Potential (AR4 basis)		1831	2571	2006	1441	1656	2396	1831	1266	2571	2006	1667	1441	2746	2181
Cycle calculation results															
Condenser glide	K	4.5	4.3	6.1	7.8	2.9	2.7	4.6	6.5	4.4	6.3	7.3	8.0	6.0	7.8
Evaporator glide	K	4.8	4.6	6.5	8.4	2.8	2.7	4.8	6.9	4.6	6.6	7.7	8.4	6.2	8.0
Capacity relative to R-23		114.4%	113.1%	108.0%	103.4%	119.7%	118.6%	112.7%	107.4%	111.6%	106.4%	103.6%	101.8%	105.4%	100.7%
COP relative to R-23		96.9%	95.9%	96.9%	98.1%	97.4%	96.5%	97.4%	98.4%	96.5%	97.4%	98.1%	98.6%	96.5%	97.6%
Discharge temperature difference	K	14.1	16.7	14.6	12.3	9.3	11.8	10.1	8.2	12.6	10.6	9.3	8.4	13.1	10.9
Condenser pressure difference	bar	2.58	2.66	1.91	1.18	2.98	3.08	2.28	1.51	2.37	1.61	1.17	0.89	1.70	0.98

45	43	43	43	43	43	43	40	40	40	40	40	40	40
25	35	30	30	30	27	25	35	35	35	30	30	30	25
5	7	10	7	5	8	10	15	10	5	20	15	10	15
25	15	17	20	22	22	22	10	15	20	10	15	20	20
1616	1562	2076	1737	1511	1955	2251	2571	2006	1441	3311	2746	2181	2921
9.4	6.4	6.9	8.0	8.6	8.5	8.4	4.6	6.4	8.1	4.4	6.2	7.9	7.7
9.7	6.8	7.2	8.3	9.0	8.7	8.6	4.6	6.6	8.5	4.4	6.3	8.1	7.7
96.6%	106.3%	103.5%	100.7%	99.0%	98.4%	98.0%	110.0%	104.7%	99.9%	109.1%	103.9%	99.1%	98.2%
98.9%	98.2%	97.7%	98.4%	98.9%	98.3%	97.9%	97.0%	98.0%	99.1%	96.2%	97.1%	98.2%	97.3%
8.3	7.6	9.2	7.8	6.8	8.3	9.3	8.6	6.7	4.6	10.9	9.0	6.9	9.2
0.29	1.43	1.23	0.80	0.52	0.58	0.62	2.05	1.29	0.57	2.13	1.39	0.67	0.76

40	35	35	35	35	35	35	35	35	35	35	35	35
25	50	45	40	35	45	40	35	30	40	35	30	25
10	5	5	5	5	10	10	10	10	15	15	15	15
25	10	15	20	25	10	15	20	25	10	15	20	25
2356	1091	1266	1441	1616	1831	2006	2181	2356	2571	2746	2921	3096
9.3	5.0	6.6	8.1	9.5	4.8	6.4	7.9	9.3	4.7	6.3	7.7	9.1
9.3	5.1	6.9	8.5	9.8	4.9	6.6	8.1	9.4	4.6	6.3	7.7	8.9
93.9%	109.2%	103.3%	97.9%	92.9%	108.7%	102.8%	97.3%	92.3%	108.2%	102.2%	96.7%	91.5%
98.5%	99.2%	99.3%	99.6%	100.0%	98.4%	98.5%	98.8%	99.1%	97.6%	97.8%	98.0%	98.3%
6.8	0.5	0.8	0.8	0.6	2.6	2.9	3.0	2.8	4.7	5.0	5.1	5.0
0.08	1.45	0.83	0.23	-0.35	1.59	0.95	0.34	-0.25	1.70	1.05	0.44	-0.16

Compositions of R-1132a, R-744, R-125 and R-116

The performance of quaternary compositions of the invention were modelled and the results are provided in the following Tables. The tables list the GWP, condenser and evaporator glide, capacity and COP relative to R-23, the difference in discharge temperature and condenser pressure, the maximum VDF in vapour and liquid, the molar percentage of R-1132a. The Tables show the contents as weight percentages, unless otherwise specified.

The conditions used are as set out in Table 1.

Table 3

R744		60	50	50	50	50	50	50	50	50	50	45	45	45	43	45	45	45	45	43	43	43
R1132a		30	40	35	30	30	25	25	20	20	20	40	35	35	35	35	30	30	30	25	25	25
R116		5	5	10	15	10	15	10	20	15	10	10	15	10	7	5	15	10	5	20	18	16
R125		5	5	5	5	10	10	15	10	15	20	5	5	10	15	15	10	15	20	12	14	16
Global Warming Potential (AR4 basis)		786	786	1396	2006	1571	2181	1746	2791	2356	1921	1396	2006	1571	1380	1136	2181	1746	1311	2861	2687	2513
Cycle calculation results																						
Condenser glide	K	2.9	3.2	3.3	3.3	5.2	5.3	7.1	5.3	7.2	8.8	3.4	3.5	5.4	7.1	7.0	5.5	7.2	8.6	6.3	7.1	7.8
Evaporator glide	K	3.3	3.4	3.7	4.0	6.2	6.6	8.3	6.9	8.7	10.0	3.8	4.0	6.2	8.0	7.8	6.6	8.3	9.5	7.8	8.6	9.2
Capacity relative to R-23		130.8%	126.7%	129.3%	131.9%	121.5%	123.9%	114.8%	126.1%	117.0%	108.9%	126.8%	129.4%	119.3%	110.5%	110.5%	121.5%	112.7%	104.9%	119.8%	116.4%	113.1%
COP relative to R-23		98.7%	99.4%	99.7%	99.9%	99.5%	99.7%	99.6%	99.9%	99.9%	99.9%	100.0%	100.3%	99.9%	100.0%	99.7%	100.2%	100.1%	100.0%	100.6%	100.6%	100.7%
Discharge temperature difference	K	12.9	5.6	3.3	1.0	4.4	2.1	4.9	-0.2	2.6	5.1	-0.2	-2.5	0.8	1.2	3.5	-1.5	1.2	3.7	-5.0	-3.9	-2.9
Condenser pressure difference	bar	4.05	3.42	3.77	4.13	3.03	3.37	2.34	3.71	2.66	1.69	3.40	3.75	2.68	1.68	1.70	3.01	2.00	1.07	2.89	2.48	2.09

43	43	43	40	40	40	40	40	40	35	35	35	35	35
25	25	25	35	35	35	30	30	30	50	45	40	35	45
14	12	10	15	10	5	20	15	10	5	5	5	5	10
18	20	22	10	15	20	10	15	20	10	15	20	25	10
2339	2165	1991	2181	1746	1311	2791	2356	1921	961	1136	1311	1486	1571
8.4	9.0	9.6	5.6	7.3	8.7	5.6	7.4	9.0	5.4	7.1	8.7	10.2	5.6
9.8	10.3	10.7	6.6	8.3	9.5	6.9	8.7	10.1	5.8	7.7	9.4	10.9	6.2
110.0%	106.9%	104.0%	119.0%	110.4%	102.8%	121.1%	112.5%	104.8%	111.7%	105.8%	100.4%	95.5%	113.9%
100.7%	100.8%	100.8%	100.6%	100.5%	100.5%	100.8%	100.8%	100.9%	100.3%	100.5%	100.9%	101.4%	100.7%
-2.0	-1.1	-0.2	-5.0	-2.3	0.0	-7.3	-4.6	-2.3	-3.8	-3.5	-3.6	-3.9	-6.1
1.71	1.33	0.97	2.61	1.64	0.73	2.93	1.93	1.01	1.60	0.97	0.36	-0.22	1.89

35	35	35	35	35	35	35
40	35	30	40	35	30	25
10	10	10	15	15	15	15
15	20	25	10	15	20	25
1746	1921	2096	2181	2356	2531	2706
7.3	9.0	10.6	5.7	7.5	9.2	10.9
8.2	10.0	11.6	6.5	8.7	10.5	12.2
107.8%	102.3%	97.4%	116.1%	109.8%	104.2%	99.1%
100.9%	101.4%	102.0%	101.0%	101.3%	101.8%	102.4%
-5.8	-5.9	-6.2	-8.4	-8.1	-8.3	-8.6
1.24	0.63	0.04	2.19	1.52	0.89	0.28

In summary, the compositions of the invention exhibit an unexpected combination of advantageous properties such as (i) low- or non-flammability, (ii) low GWP compared to existing ultra-low temperature refrigerants (e.g. R-23) and (iii) comparable or improved refrigeration performance at suitable operating temperatures and pressures compared to existing ultra-low temperature refrigerants (e.g. R-23) in terms of, for example, low glide and/or cooling capacity and/or energy efficiency.

Preferences and options for a given aspect, feature or parameter of the invention should, unless the context indicates otherwise, be regarded as having been disclosed in combination with any and all preferences and options for all other aspects, features and parameters of the invention.

The invention is defined by the following claims.

Claims

1. A composition comprising:
   - (i) 1,1-difluoroethene (vinylidene fluoride, R-1132a);
   - (ii) carbon dioxide (CO_2, R-744);
   - (iii) pentafluoroethane (R-125); and
   - (iv) one or more of trifluoromethane (R-23) and hexafluoroethane (R-116).

2. A composition according to claim 1 comprising from about 1 to about 90% by weight R-1132a.

3. A composition according to claim 2 comprising from about 1 to about 50% by weight R-1132a.

4. A composition according to any of the preceding claims comprising from about 1 to about 90% by weight carbon dioxide.

5. A composition according to claim 4 comprising from about 5 to about 70% by weight carbon dioxide.

6. A composition according to any of the preceding claims comprising from about 1 to about 90% by weight R-125.

7. A composition according to claim 6 comprising from about 1 to about 50% by weight R-125.

8. A composition according to any of the preceding claims comprising from about 1 to about 90% by weight of the fourth component.

9. A composition according to claim 8 comprising from about 1 to about 50% by weight of the fourth component (iv).

10. A composition according to any of the preceding claims comprising from about 20 to about 40% by weight R-1132a, from about 30 to about 60% by weight carbon dioxide, from about 1 to about 20% by weight R-23 and from about 1 to about 35% by weight R-125.

11. A composition according to claim 10 comprising from about 25 to about 35% by weight R-1132a, from about 35 to about 50% by weight carbon dioxide, from about 5 to about 15% by weight R-23 and from about 5 to about 30% by weight R-125.

12. A composition according to any of claims 1 to 9 comprising from about 25 to about 30% by weight R-1132a, from about 35 to about 50% by weight carbon dioxide, from about 10 to about 25% by weight R-125 and from about 5 to about 20% by weight R-23.

13. A composition according to any of claims 1 to 9 comprising from about 30 to about 60% by weight carbon dioxide, from about 10 to about 40% by weight R-1132a, from about 5 to about 30% by weight R-125 and from about 1 to about 20% by weight R-116.

14. A composition according to any of the preceding claims, wherein the R-1132a is present in an amount of less than 50% by mol.

15. A composition according to claim 14, wherein R-1132a is present in an amount of less than 30% by mol.

16. A composition according to any of the preceding claims consisting essentially of the stated components.

17. A composition according to any of the preceding claims which is azeotropic or near azeotropic.

18. A composition according to any of the preceding claims, wherein the composition is less flammable than R-1132a alone.

19. A composition according to claim 18 wherein the composition has:
a. a higher flammable limit;
b. a higher ignition energy; and/or
c. a lower flame velocity
compared to R-1132a alone.

20. A composition according to any of the preceding claims which is non-flammable.

21. A composition according to any of the preceding claims which has a temperature glide in an evaporator or a condenser of less than about 10 K, preferably less than about 7 K.

22. A composition according to any of the preceding claims which has a critical temperature of greater than about 0 ºC, preferably greater than about 10 ºC.

23. A composition according to any of the preceding claims whose volumetric refrigeration capacity is at least 90%, preferably at least 95%, of that of R-23 at comparable cycle conditions.

24. A composition according to any of the preceding claims whose cycle efficiency (Coefficient of Performance, COP) is at least 95% and/or within about 5% than the existing refrigerant fluid it is replacing.

25. A composition according to any of the preceding claims whose compressor discharge temperature is within 15 K of that of R-23 at comparable cycle conditions.

26. A composition comprising a lubricant and a composition according to any of the preceding claims.

27. A composition according to claim 26, 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, preferably wherein the lubricant is selected from PAGs or POEs.

28. A composition according to claim 27, wherein the composition further comprises pentane.

29. A composition comprising a stabiliser and a composition according to any of the preceding claims.

30. A composition according to claim 29, wherein the stabiliser is selected from diene-based compounds, phosphates, phenol compounds and epoxides, and mixtures thereof.

31. A composition comprising a flame retardant and a composition according to any of the preceding claims.

32. A composition according to claim 31, wherein the 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.

33. A heat transfer device containing a composition as defined in any one of claims 1 to 32.

34. A heat transfer device according to claim 33 wherein the heat transfer device is a refrigeration device.

35. A heat transfer device according to claim 33 or 34 wherein the heat transfer device comprises an ultra-low temperature refrigeration system, such as a blast freezer.

36. A heat transfer device according to any of claims 33 to 35 wherein the heat transfer device comprises a cascade system.

37. A method for cooling an article which comprises condensing a composition defined in any of claims 1 to 32 and thereafter evaporating the composition in the vicinity of the article to be cooled.

38. A method for heating an article which comprises condensing a composition as defined in any one of claims 1 to 32 in the vicinity of the article to be heated and thereafter evaporating the composition.

39. 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 32, and separating the substance from the solvent.

40. A method of cleaning an article comprising contacting the article with a solvent comprising a composition as defined in any of claims 1 to 32.

41. A method of extracting a material from an aqueous solution or from a particulate solid matrix comprising contacting the aqueous solution or the particulate solid matrix with a solvent comprising a composition as defined in any of claims 1 to 32, and separating the material from the solvent.

42. A method of retrofitting a heat transfer device comprising the step of removing an existing heat transfer composition, and introducing a composition as defined in any one of claims 1 to 32.

43. A method of claim 42 wherein the heat transfer device is a refrigeration device, preferably an ultra-low temperature refrigeration system.

44. A method of claim 43 wherein the refrigeration system cools a compartment to less than about -60 °C, preferably less than about -70 °C.

45. 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 32.

46. 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 32, wherein the composition as defined in any one of claims 1 to 32 has a lower GWP than the existing compound or composition; and (ii) obtaining greenhouse gas emission credit for said replacing step.

47. A method of claim 46 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 attained by use of the existing compound or composition.

48. A method of claim 45 carried out on a product from the fields of air-conditioning, refrigeration, heat transfer, gaseous dielectrics, flame suppression, solvents, cleaners, topical anesthetics, and expansion applications.

49. A method according to claim 45 or 48 wherein the product is selected from a heat transfer device or a solvent, preferably a heat transfer device.

50. A method according to claim 49 wherein the product is a heat transfer device, preferably an ultra-low temperature refrigeration system.

51. A method according to any of claims 45 to 50 wherein the existing compound or composition is a heat transfer composition, preferably wherein the heat transfer composition is a refrigerant selected from R-508A, R-508B, R-23 and R-13B1.

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2018/051344

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K5/04 C11D7/50
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 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 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	GB 2 516 694 A (MEXICHEM AMANCO HOLDING SA [MX]) 4 February 2015 (2015-02-04) page 4, lines 24-35; claims 6-9,26,37-52,55-63 page 6, lines 20-31 -----	1-9, 13-52
X	WO 2016/120645 A1 (MEXICHEM FLUOR SA DE CV) 4 August 2016 (2016-08-04) page 8, lines 4-14; claims 1-22,32-41,43-47,50-59 -----	1-52
A	US 2013/153817 A1 (SINGH RAJIV RATNA [US] ET AL) 20 June 2013 (2013-06-20) paragraphs [0001] - [0005], [0023] -----	1-52

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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

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

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 8 August 2018	Date of mailing of the international search report 16/08/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Martinez Marcos, V

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2018/051344

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

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

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

2. ☒ Claims Nos.: 46, 47(partially)
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:
see FURTHER INFORMATION sheet PCT/ISA/210

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.2

Claims Nos.: 46, 47(partially)

Present claims 46-47 (completely) relate to a subject-matter which is excluded from patentability since they are directed towards a business method (Rule 39.1(iii) PCT). Therefore a complete meaningful search for the whole of the subject-matter could not be carried out, Art. 17(2) (b) PCT.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2018/051344

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		GB 2516694 A	04-02-2015
		GB 2535383 A	17-08-2016
		JP 6196735 B2	13-09-2017
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