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(73) Assignee: **Arkerna France**, Colombes (FR)**Publication Classification**(21) Appl. No.: **13/122,606**(51) **Int. Cl.**
C09K 5/04 (2006.01)(52) **U.S. Cl.** **252/67**(22) PCT Filed: **Sep. 24, 2009**(57) **ABSTRACT**(86) PCT No.: **PCT/FR2009/051814**§ 371 (c)(1),
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The present invention relates to compositions which are based on tetrafluoropropene and more particularly relates to compositions comprising 60% to 90% by weight of 2,3,3,3-tetrafluoropropene and 10% to 40% by weight of at least one compound selected from difluoroethane and difluoromethane, which can be used as a heat transfer fluid.

HEAT TRANSFER FLUID

[0001] The present invention relates to compositions comprising hydrofluoroolefins and to their uses as heat transfer fluids, blowing agents, solvents and aerosols.

[0002] The problems posed by substances which deplete the atmospheric ozone layer (ODP: ozone depletion potential) were tackled at Montreal, where a protocol was signed which imposes a reduction on the production and use of chlorofluorocarbons (CFCs). This protocol has been the subject of amendments, which have imposed the abandonment of CFCs and have extended the regulations to other products, among them hydrochlorofluorocarbons (HCFCs).

[0003] The refrigeration industry and the air conditioning industry have invested much in the replacement of these refrigerant fluids, and a product of this investment has been the commercialization of hydrofluorocarbons (HFCs).

[0004] (Hydro)chlorofluorocarbons which are used as expandants or solvents have also been replaced by HFCs.

[0005] In the automotive industry, the air-conditioning systems of vehicles which are sold in many countries have switched from a chlorofluorocarbon (CFC-12) refrigerant fluid to that of a hydrofluorocarbon (1,1,1,2-tetrafluoroethane: HFC-134a), which is less harmful to the ozone layer. However, in view of the objectives set by the Kyoto Protocol, HFC-134a (GWP=1300) is considered to have a high warming potential. The contribution to the greenhouse effect of a fluid is quantified by a criterion, the GWP (global warming potential), which indexes the warming potential by taking a reference value of 1 for carbon dioxide.

[0006] Carbon dioxide, being non-toxic, non-flammable and having a very low GWP, has been proposed as a refrigerant fluid for air-conditioning systems, as a replacement for HFC-134a. However, the use of carbon dioxide presents a number of disadvantages, associated in particular with the very high pressure of its use as a refrigerant fluid in existing apparatus and technologies.

[0007] Moreover, the mixture R-404A, composed of 44% by weight of pentafluoroethane, 52% by weight of trifluoroethane and 4% by weight of HFC-134a, is widely used as a refrigerant fluid in superstores (supermarket) and in refrigerated transport. This mixture, however, has a GWP of 3900. The mixture R-407C, composed of 52% by weight of HFC-134a, 25% by weight of pentafluoroethane and 23% by weight of difluoromethane, is used as a heat transfer fluid in air conditioning and in heat pumps. This mixture, however, has a GWP of 1800.

[0008] Document JP 4110388 describes the use of hydrofluoropropenes of formula $C_3H_mF_n$, where m and n represent an integer between 1 and 5 inclusive and $m+n=6$, as heat transfer fluids, especially tetrafluoropropene and trifluoropropene. Document WO 2004/037913 discloses the use of compositions comprising at least one fluoroalkene having three or four carbon atoms, more particularly pentafluoropropene and tetrafluoropropene, preferably having a GWP of not more than 150, as heat transfer fluids.

[0009] Document WO 2005/105947 teaches the addition to tetrafluoropropene, preferably 1,3,3,3-tetrafluoropropene, of a co-blowing agent such as difluoro-methane, pentafluoroethane, tetrafluoroethane, difluoroethane, heptafluoro-propane, hexafluoropropane, pentafluoropropane, pentafluorobutane, water or carbon dioxide.

[0010] Document WO 2006/094303 discloses an azeotropic composition containing 7.4% by weight of 2,3,3,3-tetrafluoropropene (1234yf) and 92.6% by weight of difluoromethane (HFC-32). This document likewise discloses an azeotropic composition containing 91% by weight of 2,3,3,3-tetrafluoropropene and 9% by weight of difluoroethane (HFC-152a).

[0011] The applicant has now developed compositions which contain hydrofluoropropenes, which can be used as a heat transfer fluid, which do not have the aforementioned drawbacks and which combine a zero ODP with a GWP lower than that of existing heat transfer fluids such as R-404A or R-407C or R22 (chlorodifluoromethane).

[0012] The compositions according to the present invention are characterized in that they comprise 60% to 90% by weight of 2,3,3,3-tetrafluoropropene and 10% to 40% by weight of at least one compound selected from difluoroethane and difluoromethane.

[0013] According to a first embodiment of the invention the compositions comprise 60% to 79% by weight of 2,3,3,3-tetrafluoropropene and 21% to 40% by weight of a compound selected from difluoroethane and difluoromethane.

[0014] The compositions according to this first embodiment preferably comprise 60% to 70% by weight of 2,3,3,3-tetrafluoropropene and 30% to 40% by weight of a compound selected from difluoroethane and difluoromethane.

[0015] Advantageously the compositions according to this first embodiment comprise 60% to 65% by weight of 2,3,3,3-tetrafluoropropene and 35% to 40% by weight of a compound selected from difluoroethane and difluoromethane.

[0016] The compositions which are particularly preferred according to this first embodiment comprise 2,3,3,3-tetrafluoropropene and difluoromethane.

[0017] Advantageously these compositions contain essentially 2,3,3,3-tetrafluoropropene and difluoromethane.

[0018] According to a second embodiment of the invention the compositions comprise 60% to 90% by weight of 2,3,3,3-tetrafluoropropene and 10% to 40% by weight of a mixture composed of dichloromethane and difluoroethane.

[0019] The compositions which are preferred according to this second embodiment comprise 60% to 80% by weight of 2,3,3,3-tetrafluoropropene and 20% to 40% by weight of a mixture composed of difluoromethane and difluoroethane.

[0020] The compositions which are advantageously preferred according to this second embodiment comprise 60% to 75% by weight of 2,3,3,3-tetrafluoropropene and 25% to 40% by weight of a mixture composed of difluoromethane and difluoroethane.

[0021] Particularly preferred compositions comprise 60% to 80% by weight of 2,3,3,3-tetrafluoropropene and 5% to 35% by weight of difluoromethane and 5% to 35% by weight of difluoroethane.

[0022] The compositions which are of interest are those comprising or containing essentially 60% to 80% by weight of 2,3,3,3-tetrafluoropropene and 10% to 30% by weight of difluoromethane and 10% to 30% by weight of difluoroethane.

[0023] The compositions according to the invention may comprise a stabilizer for 2,3,3,3-tetrafluoropropene. The stabilizer represents not more than 5% by weight, relative to the total composition.

[0024] Stabilizers include more particularly nitromethane, ascorbic acid, terephthalic acid, azoles such as tolutriazole or benzotriazole, phenolic compounds such as tocopherol, hyd-

roquinone, tert-butylhydroquinone, 2,6-di-tert-butyl-4-methylphenol, epoxides (alkyl, optionally fluorinated or perfluorinated, or alkenyl or aromatic) such as n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether and butylphenyl glycidyl ether, phosphites, phosphates, phosphonates, thiols and lactones.

[0025] The compositions according to the present invention may comprise lubricants such as mineral oil, alkylbenzene, polyalkylene glycol and polyvinyl ether.

[0026] The compositions according to the present invention are suitable for replacing R-404A in refrigeration and/or R-407C in air conditioning and heat pumps in existing systems. They may also be suitable for replacing R-404A in refrigeration systems with a cascaded compression regime in which at least one stage is operated with the compositions according to the present invention. Examples of compositions which are of particular interest for the replacement of R-404A in existing systems include those comprising or containing essentially 60% by weight of 2,3,3,3-tetrafluoropropene and 40% by weight of difluoromethane; 70% by weight of 2,3,3,3-tetrafluoropropene and 30% by weight of difluoromethane; and 60% by weight of 2,3,3,3-tetrafluoropropene, 30% by weight of difluoromethane and 10% by weight of difluoroethane.

[0027] Examples of compositions which are of particular interest for the replacement of R-404A in systems operating with a cascaded compression regime include those comprising or containing essentially 60% by weight of 2,3,3,3-tetrafluoropropene and 40% by weight of difluoroethane; 70% by weight of 2,3,3,3-tetrafluoropropene and 30% by weight of difluoroethane; and 75% by weight of 2,3,3,3-tetrafluoropropene, 20% by weight of difluoromethane and 5% by weight of difluoroethane.

[0028] The compositions according to the present invention may also be used as a replacement for R-407C, for example in heat pumps.

[0029] Examples of compositions which are of particular interest for the replacement of R-407C in existing systems include those comprising or containing essentially 60% by weight of 2,3,3,3-tetrafluoropropene and 40% by weight of difluoromethane; 70% by weight of 2,3,3,3-tetrafluoropropene and 30% by weight of difluoromethane; 60% by weight of 2,3,3,3-tetrafluoropropene, 30% by weight of difluoromethane and 10% by weight of difluoroethane; and 70% by weight of 2,3,3,3-tetrafluoropropene, 25% by weight of difluoromethane and 5% by weight of difluoroethane.

[0030] The compositions according to the present invention can be used, furthermore, as blowing agents, aerosols and solvents.

EXPERIMENTAL SECTION

[0031] The performance data of the compositions according to the invention under the operating conditions of refrigeration are given in Table 1. The values of the constituents (1234yf, 32 and 152a) for each composition are given as percentages by weight.

[0032] For R404A, the nominal operating pressure is 18 bar, the volumetric capacity is 1500 kJ/m³ and the COP is 1.8 under the following operating conditions.

Evaporation temperature: -20° C.

Condensation temperature: 40° C.

Compressor inlet temperature: -5° C.

Super cooled liquid temperature: 33° C.

Isentropic yield of the compressor: 70%

BP: pressure at the evaporator

HP: pressure at the condenser

Ratio: compression ratio

T comp outlet: temperature at the compressor outlet

COP: coefficient of performance—defined, for the purposes of refrigeration, as being the useful cooling power supplied by the system, as a proportion of the power provided or consumed by the system.

CAP: volumetric capacity (kJ/m³)

% CAP or COP is the ratio of the value of the CAP or COP of the mixture in relation to the same value for R404A.

TABLE 1

Compositions	BP (bar)	HP (bar)	Ratio (p/p)	T comp. outlet	% COP	% CAP
R404A	3	18	6.10	77	100	100
1234yf 32 152a						
60 40 0	2.7	21	7.57	111	96	102
70 30 0	2.4	19	8.02	104	94	89
75 25 0	2.2	18	8.19	101	94	83
1234yf 32 152a						
60 20 20	2.0	16	8.01	100	98	76
60 30 10	2.3	18	7.94	106	96	88
70 25 5	2.2	18	8.10	101	95	83
70 20 10	2.0	16	8.07	98	96	77
75 20 5	2.0	16	8.16	97	95	77
75 15 10	1.9	15	8.01	93	97	72
85 10 5	1.8	14	7.92	86	99	67
1234yf 32 152a						
60 0 40	1.5	10	6.60	79	114	59
70 0 30	1.5	10	6.53	76	113	59

[0033] The performance data of the compositions according to the present invention under the operating conditions of a heat pump and air conditioning are given in Table 2. The values of the constituents (1234yf, 32 and 152a) for each composition are given as percentages by weight.

[0034] For R407c, the nominal operating pressure is 34 bar, the volumetric capacity is 1461 kJ/m³ and the COP is 2.1 under the following operating conditions:

Evaporation temperature: -5° C.

Condensation temperature: 70° C.

Compressor inlet temperature: 5° C.

Supercooled liquid temperature: 65° C.

Isentropic yield of the compressor: 70% BR pressure at the evaporator

HP: pressure at the condenser

Ratio: compression ratio

T comp outlet: temperature at the compressor outlet

COP: coefficient of performance—defined, for the purposes of a heat pump, as being the useful heating power supplied by the system, as a proportion of the power provided or consumed by the system.

CAP: volumetric capacity (kJ/m³)

% CAP or COP is the ratio of the value of the CAP or COP of the mixture in relation to the same value for the R-407C.

TABLE 2

Compositions	BP (bar)	HP (bar)	Ratio (p/p)	T comp. outlet	% COP	% CAP
R407C	3.9	34.4		127	100	100
1234yf 32 152a						
60 40 0	4.8	39.7	8.30	133	91.9	112
70 30 0	4.2	36.5	8.69	126	92.4	99
75 25 0	3.9	34.6	8.85	122	93.2	93

TABLE 2-continued

Compositions			BP (bar)	HP (bar)	Ratio (p/p)	T comp. outlet	% COP	% CAP
1234yf	32	152a						
60	20	20	3.5	30.1	8.64	121	101.5	89
60	30	10	4.1	35.0	8.60	128	97.1	101
70	25	5	3.9	33.9	8.74	123	95.5	94
70	20	10	3.6	31.2	8.70	119	98.3	88
75	20	5	3.6	31.8	8.79	118	96.4	88
75	15	10	3.3	28.9	8.64	113	99.3	82
85	10	5	3.1	26.7	8.58	107	99.3	75
1234yf	32	152a						
60	0	40	2.6	18.9	7.27	98	113.7	67
70	0	30	2.7	19.1	7.19	95	111.3	66

1. Composition comprising 60% to 90% by weight of 2,3,3,3-tetrafluoropropene and 10% to 40% by weight of at least one compound selected from difluoroethane and difluoromethane.

2. Composition according to claim 1, characterized in that it comprises 60% to 79% by weight of 2,3,3,3-tetrafluoropropene and 21% to 40% by weight of a compound selected from the group consisting of difluoroethane and difluoromethane.

3. Composition according to either of claim 1, characterized in that it comprises 60% to 70% by weight of 2,3,3,3-tetrafluoropropene and 30% to 40% by weight of a compound selected from the group consisting of difluoroethane and difluoromethane.

4. Composition according to claim 1, characterized in that it comprises 60% to 80% by weight of 2,3,3,3-tetrafluoropropene and 20% to 40% by weight of a mixture composed of difluoromethane and difluoroethane.

5. Composition according to claim 1, characterized in that it comprises 60% to 80% by weight of 2,3,3,3-tetrafluoropropene and 5% to 35% by weight of difluoromethane and 5% to 35% by weight of difluoroethane.

6. Composition according to claim 1, characterized in that it comprises 60% to 80% by weight of 2,3,3,3-tetrafluoropropene and 10% to 30% by weight of difluoromethane and 10% to 30% by weight of difluoroethane.

7. Heat transfer fluid according to claim 1.

8. Composition according to claim 1, characterized in that it is used as a replacement for R-404A in refrigeration and/or as a replacement for R-407C in heat pumps or air conditioning.

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