(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 388 495 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
26.08.2020 Bulletin 2020/35

(51) Int Cl.:
C09K 5/04 *(2006.01)* ***C10M 171/00*** *(2006.01)*
B60H 1/00 *(2006.01)*

(21) Application number: **18164734.8**

(22) Date of filing: **03.03.2006**

(54) COMPOSITIONS COMPRISING A FLUOROOLEFIN

ZUSAMMENSETZUNGEN MIT EINEM FLUOROLEFIN

COMPOSITIONS COMPORTANT UNE FLUOROLÉFINE

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR

(30) Priority: **04.03.2005 US 658543 P**
23.08.2005 US 710439 P
01.11.2005 US 732769 P

(43) Date of publication of application:
17.10.2018 Bulletin 2018/42

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:
08014611.1 / 1 985 680
06737345.6 / 1 853 679

(73) Proprietor: **The Chemours Company FC, LLC**
Wilmington DE 19801 (US)

(72) Inventors:
- **Rao, Velliyur Nott Mallikarjuna deceased (US)**
- **Minor, Barbara Haviland Elkton, MD Maryland 21921 (US)**

(74) Representative: **Dannenberger, Oliver Andre et al**
Abitz & Partner
Patentanwälte mbB
Arabellastrasse 17
81925 München (DE)

(56) References cited:
US-A1- 2004 127 383 US-A1- 2004 256 594

- **YIN J M ET AL: "TEWI COMPARISON OF R744 AND R134A SYSTEMS FOR MOBILE AIR CONDITIONING", SAE WORLD CONGRESS, XX, XX, 1 March 1999 (1999-03-01), pages 1-06, XP001169087,**
- **HIRATA T ET AL: "IMPROVEMENT OF MOBILE AIR CONDITIONING SYSTEM FROM POINT OF GLOBAL WARMING PROBLEMS", IIR - GUSTAV LORENTZEN CONFERENCE ON NATURAL WORKING FLUIDS.PROCEEDINGS, XX, XX, 2 June 1998 (1998-06-02), pages 314-323, XP001169058,**
- **DATABASE WPI Week 199221 Thomson Scientific, London, GB; AN 1992-172539 XP002343594, & JP 4 110388 A (DAIKIN KOGYO KK) 10 April 1992 (1992-04-10)**

EP 3 388 495 B1

Description

CROSS REFERENCE(S) TO RELATED APPLICATION(S)

[0001] This application claims the priority benefit of U.S. Provisional Application 60/658,543, filed March 4, 2005, and U.S. Provisional Application 60/710,439, filed August 23, 2005, and U.S. Provisional Application 60/732,769, filed November 1, 2005.

BACKGROUND OF THE INVENTION

1. Field of the Invention.

[0002] The present invention relates to a mobile air-conditioning apparatus containing a composition comprising HFC-1234yf and at least one compound selected from HFC-1234ze (trans), HFC-1234ze (cis), HFC-1243zf, HFC-32, and CO_2.

2. Description of Related Art.

[0003] The refrigeration industry has been working for the past few decades to find replacement refrigerants for the ozone depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) being phased out as a result of the Montreal Protocol. The solution for most refrigerant producers has been the commercialization of hydrofluorocarbon (HFC) refrigerants. The new HFC refrigerants, HFC-134a being the most widely used at this time, have zero ozone depletion potential and thus are not affected by the current regulatory phase out as a result of the Montreal Protocol.

[0004] Further environmental regulations may ultimately cause global phase out of certain HFC refrigerants. Currently, the automobile industry is facing regulations relating to global warming potential for refrigerants used in mobile air-conditioning. Therefore, there is a great current need to identify new refrigerants with reduced global warming potential for the mobile air-conditioning market. Should the regulations be more broadly applied in the future, an even greater need will be felt for refrigerants that can be used in all areas of the refrigeration and air-conditioning industry.

[0005] Currently proposed replacement refrigerants for HFC-134a include HFC-152a, pure hydrocarbons such as butane or propane, or "natural" refrigerants such as CO_2. Many of these suggested replacements are toxic, flammable, and/or have low energy efficiency. Therefore, new alternative refrigerants are being sought.

[0006] J. M. Yin et al. in "TEWI Comparison of R744 and R134a Systems for Mobile Air Conditioning" SAE World Congress, March 1, 1999, describe mobile air conditioning systems using carbon dioxide (R744) and 1,1,1,2 tetrafluoroethane (R134a) refrigerants.

[0007] The object of the present invention is to provide a mobile air-conditioning apparatus containing refrigerant compositions and heat transfer fluid compositions that provide unique characteristics to meet the demands of low or zero ozone depletion potential and lower global warming potential as compared to current refrigerants.

BRIEF SUMMARY OF THE INVENTION

[0008] The present invention relates to a mobile air-conditioning apparatus containing a composition comprising HFC-1234yf and at least one compound selected from HFC-1234ze (trans), HFC-1234ze (cis), HFC-1243zf, HFC-32, and CO_2.

[0009] The present invention further relates to an apparatus as defined in claims 2 to 8.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The present invention relates to a mobile air-conditioning apparatus containing a composition comprising HFC-1234yf and at least one compound selected from HFC-1234ze (trans), HFC-1234ze (cis), HFC-1243zf, HFC-32, and CO_2.

[0011] Fluoroolefin compounds and other compounds are listed in Table 1.

TABLE 1

Compound	Chemical name	Chemical formula
HFC-1225ye	1,2,3,3,3-pentafluoropropene	$CF_3CF=CHF$
HFC-1234ze	1,3,3,3-tetrafluoropropene	$CF_3CH=CHF$
HFC-1234yf	2,3,3,3-tetrafluoropropene	$CF_3CF=CH_2$
HFC-1234ye	1,2,3,3-tetrafluoropropene	$CHF_2CF=CHF$

(continued)

Compound	Chemical name	Chemical formula
HFC-1243zf	3,3,3-trifluoropropene	$CF_3CH=CH_2$
HFC-32	difluoromethane	CH_2F_2
HFC-125	pentafluoroethane	CF_3CHF_2
HFC-134	1,1,2,2-tetrafluoroethane	CHF_2CHF_2
HFC-134a	1,1,1,2-tetrafluoroethane	CH_2FCF_3
HFC-143a	1,1,1-trifluoroethane	CH_3CF_3
HFC-152a	1,1-difluoroethane	CHF_2CH_3
HFC-161	fluoroethane	CH_3CH_2F
HFC-227ea	1,1,1,2,3,3,3-heptafluoropropane	CF_3CHFCF_3
HFC-236ea	1,1,1,2,3,3-hexafluoropropane	$CF_3CHFCHF_2$
HFC-236fa	1,1,1,3,3,3-hexafluoroethane	$CF_3CH_2CF_3$
HFC-245fa	1,1,1,3,3-pentafluoropropane	$CF_3CH_2CHF_2$
HFC-365mfc	1,1,1,3,3-pentafluorobutane	$CF_3CH_2CH_2CHF_2$
	propane	$CH_3CH_2CH_3$
	n-butane	$CH_3CH_2CH_2CH_3$
i-butane	isobutane	$CH_3CH(CH_3)CH_3$
	2-methylbutane	$CH_3CH(CH_3)CH_2CH_3$
	n-pentane	$CH_3CH_2CH_2CH_2CH_3$
	cyclopentane	cyclo-(CH2)5-
DME	dimethylether	CH_3OCH_3
CO_2	carbon dioxide	CO_2
CF_3SCF_3	bis(trifluoromethyl)sulfide	CF_3SCF_3
	iodotrifluoromethane	CF_3I

[0012] The individual components listed in Table 1 may be prepared by methods known in the art.

[0013] The fluoroolefin compounds HFC-1225ye, HFC-1234ze, and HFC-1234ye may exist as different configurational isomers or stereoisomers. The present invention is intended to include all single configurational isomers, single stereoisomers or any combination or mixture thereof. For instance, 1,3,3,3-tetra-fluoropropene (HFC-1234ze) is meant to represent the cis-isomer, trans-isomer, or any combination or mixture of both isomers in any ratio. Another example is HFC-1225ye, by which is represented the cis-isomer, trans-isomer, or any combination or mixture of both isomers in any ratio.

[0014] The compositions used in the apparatus of the present invention include the following:

HFC-1234ze, HFC-1234yf, and optionally at least one compound selected from the group consisting of HFC-1243zf, HFC-32 and CO_2;

HFC-1234yf and at least one compound selected from the group consisting of HFC-1243zf, HFC-32, and CO_2.

[0015] The compositions used in the apparatus of the present invention may be generally useful when the fluoroolefin is present at about 1 weight percent to about 99 weight percent, preferably about 20 weight percent to about 99 weight percent, more preferably about 40 weight percent to about 99 weight percent and still more preferably 50 weight percent to about 99 weight percent.

[0016] The apparatus of present invention preferably contains compositions as listed in Table 2.

TABLE 2

Components	Concentration ranges (wt%)		
	Preferred	More preferred	Most preferred
HFC-1234yf/HFC-32	1-99/99-1	40-99/60-1	95/5
HFC-1225ye/HFC-1234yf/HFC-32	1-98/1-98/0.1-98	10-90/10-90/0.1-50	25/73/2, 75/23/2, and 49/49/2
HFC-32/HFC-125/HFC-1234yf	0.1-98/0.1-98/0.1-98	5-70/5-70/5-70	40/50/10, 23/25/52, 15/45/40, and 10/60/30
HFC-1234yf/HFC-32/HFC-143a	1-50/1-98/1-98	15-50/20-80/5-60	
HFC-1234yf/HFC-32/isobutane	1-40/59-98/1-30	10-40/59-90/1-10	
HFC-1225ye/HFC-1234yf/HFC-32/HFC-125	1-97/1-97/1-97/1-97/1-97	1-80/1-70/5-70/5-70	
HFC-1225ye/HFC-1234yf/HFC-32/HFC-134a	1-97/1-97/1-97/1-97/1-97	5-70/5-70/5-80/5-70	
HFC-1225ye/HFC-1234yf/HFC-32/HFC-125/CF_3I	1-96/1-96/1-96/1-96/1-96	1-70/1-60/1-70/1-60/1-60	
HFC-1234yf/HFC-32/CF_3I	1-98/1-98/1-98	10-80/1-70/1-80	
HFC-1234yf/HFC-32/HFC-134a/CF_3I	1-97/1-97/1-97/1-97	5-70/5-80/1-70/5-70	
HFC-1234yf/HFC-32/HFC-125	1-98/1-98/1-98	10-80/5-80/10-80	
HFC-1234yf/HFC-32/HFC-125/CF_3I	1-97/1-97/1-97/1-97	10-80/5-70/10-80/5-80	

[0017] The most preferred compositions used in the apparatus of the present invention listed in Table 2 are generally expected to maintain the desired properties and functionality when the components are present in the concentrations as listed +/- 2 weight percent.

[0018] The compositions used in the apparatus of the present invention may be azeotropic or near-azeotropic compositions. By azeotropic composition is meant a constant-boiling mixture of two or more substances that behave as a single substance. One way to characterize an azeotropic composition is that the vapor produced by partial evaporation or distillation of the liquid has the same composition as the liquid from which it is evaporated or distilled, i.e., the mixture distills/refluxes without compositional change. Constant-boiling compositions are characterized as azeotropic because they exhibit either a maximum or minimum boiling point, as compared with that of the non-azeotropic mixture of the same compounds. An azeotropic composition will not fractionate within a refrigeration or air conditioning system during operation, which may reduce efficiency of the system. Additionally, an azeotropic composition will not fractionate upon leakage from a refrigeration or air conditioning system. In the situation where one component of a mixture is flammable, fractionation during leakage could lead to a flammable composition either within the system or outside of the system.

[0019] A near-azeotropic composition (also commonly referred to as an "azeotrope-like composition") is a substantially constant boiling liquid admixture of two or more substances that behaves essentially as a single substance. One way to characterize a near-azeotropic composition is that the vapor produced by partial evaporation or distillation of the liquid has substantially the same composition as the liquid from which it was evaporated or distilled, that is, the admixture distills/refluxes without substantial composition change. Another way to characterize a near-azeotropic composition is that the bubble point vapor pressure and the dew point vapor pressure of the composition at a particular temperature are substantially the same. Herein, a composition is near-azeotropic if, after 50 weight percent of the composition is removed, such as by evaporation or boiling off, the difference in vapor pressure between the original composition and the composition remaining after 50 weight percent of the original composition has been removed is less than about 10 percent.

[0020] An azeotropic composition for use in the apparatus of the present invention at a specified temperature is shown in Table 3.

TABLE 3

Component A	Component B	Wt% A	Wt% B	Psia	kPa	T(C)
HFC-1234yf	HFC-32	7.4	92.6	49.2	339	-25

[0021] Additionally, ternary azeotropic compositions may be used as listed in Table 4.

TABLE 4

Component A	Component B	Component C	Wt% A	Wt% B	Wt% C	Pres (psi)	Pres (kPa)	Temp (°C)
HFC-1234yf	HFC-32	HFC-143A	3.9	74.3	21.8	50.02	345	-25
HFC-1234yf	HFC-32	isobutane	1.1	92.1	6.8	50.05	345	-25

[0022] A near-azeotropic composition for use in the apparatus of the present invention at a specified temperature is listed in Table 5.

TABLE 5

Component A	Component B	(wt% A/wt% B)	T(C)
HFC-1234yf	HFC-32	1-57/99-43	-25

[0023] Ternary and higher order near-azeotrope compositions comprising fluoroolefin have also been identified as listed in Table 6.

TABLE 6

Components	Near-azeotrope range (weight percent)	Temp (°C)
HFC-32/HFC-125/HFC-1234yf	1-98/1-98/1-55	25
HFC-1234yf/HFC-32/HFC-143a	1-50/1-98/1-98	-25
HFC-1234yf/HFC-32/isobutane	1-40/59-98/1-30	-25

[0024] Certain of the compositions used in the apparatus of the present invention are non-azeotropic compositions. Those compositions used in the apparatus of the present invention falling within the preferred ranges of Table 2, but outside of the near-azeotropic ranges of Table 5 and Table 6 may be considered to be non-azeotropic.

[0025] A non-azeotropic composition may have certain advantages over azetropic or near azeotropic mixtures. A non-azeotropic composition is a mixture of two or more substances that behaves as a mixture rather than a single substance. One way to characterize a non-azeotropic composition is that the vapor produced by partial evaporation or distillation of the liquid has a substantially different composition as the liquid from which it was evaporated or distilled, that is, the admixture distills/refluxes with substantial composition change. Another way to characterize a non-azeotropic composition is that the bubble point vapor pressure and the dew point vapor pressure of the composition at a particular temperature are substantially different. Herein, a composition is non-azeotropic if, after 50 weight percent of the composition is removed, such as by evaporation or boiling off, the difference in vapor pressure between the original composition and the composition remaining after 50 weight percent of the original composition has been removed is greater than about 10 percent.

[0026] The compositions used in the apparatus of the present invention may be prepared by any convenient method to combine the desired amounts of the individual components. A preferred method is to weigh the desired component amounts and thereafter combine the components in an appropriate vessel. Agitation may be used, if desired.

[0027] An alternative means for making compositions used in the apparatus of the present invention may be a method for making a refrigerant blend composition, wherein said refrigerant blend composition comprises a composition as disclosed herein, said method comprising (i) reclaiming a volume of one or more components of a refrigerant composition from at least one refrigerant container, (ii) removing impurities sufficiently to enable reuse of said one or more of the reclaimed components, (iii) and optionally, combining all or part of said reclaimed volume of components with at least one additional refrigerant composition or component.

[0028] A refrigerant container may be any container in which is stored a refrigerant blend composition that has been used in a refrigeration apparatus, air-conditioning apparatus or heat pump apparatus. Said refrigerant container may be the refrigeration apparatus, air-conditioning apparatus or heat pump apparatus in which the refrigerant blend was used. Additionally, the refrigerant container may be a storage container for collecting reclaimed refrigerant blend components, including but not limited to pressurized gas cylinders.

[0029] Residual refrigerant means any amount of refrigerant blend or refrigerant blend component that may be moved out of the refrigerant container by any method known for transferring refrigerant blends or refrigerant blend components.

[0030] Impurities may be any component that is in the refrigerant blend or refrigerant blend component due to its use in a refrigeration apparatus, air-conditioning apparatus or heat pump apparatus. Such impurities include but are not limited to refrigeration lubricants, being those described earlier herein, particulates including but not limited to metal, metal salt or elastomer particles, that may have come out of the refrigeration apparatus, air-conditioning apparatus or heat pump apparatus, and any other contaminants that may adversely effect the performance of the refrigerant blend composition.

[0031] Such impurities may be removed sufficiently to allow reuse of the refrigerant blend or refrigerant blend component without adversely effecting the performance or equipment within which the refrigerant blend or refrigerant blend component will be used.

[0032] It may be necessary to provide additional refrigerant blend or refrigerant blend component to the residual refrigerant blend or refrigerant blend component in order to produce a composition that meets the specifications required for a given product. For instance, if a refrigerant blend has 3 components in a particular weight percentage range, it may be necessary to add one or more of the components in a given amount in order to restore the composition to within the specification limits.

[0033] Compositions used in the apparatus of the present invention have zero or low ozone depletion potential and low global warming potential (GWP). Additionally, the compositions used in the apparatus of the present invention will have global warming potentials that are less than many hydrofluorocarbon refrigerants currently in use. One aspect of the present invention is to provide a refrigerant with a global warming potential of less than 1000, less than 500, less than 150, less than 100, or less than 50. Another aspect of the present invention is to reduce the net GWP of refrigerant mixtures by adding fluoroolefins to said mixtures.

[0034] The compositions used in the apparatus of the present invention may be useful as low global warming potential (GWP) replacements for currently used refrigerants, including but not limited to R134a (or HFC-134a, 1,1,1,2-tetrafluoroethane), R22 (or HCFC-22, chlorodifluoromethane), R123 (or HFC-123, 2,2-dichloro-1,1,1-trifluoroethane), R11 (CFC-11, fluorotrichloromethane), R12 (CFC-12, dichlorodifluoromethane), R245fa (or HFC-245fa, 1,1,1,3,3-pentafluoropropane), R114 (or CFC-114, 1,2-dichloro-1,1,2,2-tetrafluoroethane), R236fa (or HFC-236fa, 1,1,1,3,3,3-hexafluoropropane), R124 (or HCFC-124, 2-chloro-1,1,1,2-tetrafluoroethane), R407C (ASHRAE designation for a blend of 52 weight percent R134a, 25 weight percent R125 (pentafluoroethane), and 23 weight percent R32 (difluoromethane)), R410A (ASHRAE designation for a blend of 50 weight percent R125 and 50 weight percent R32), R417A, (ASHRAE designation for a blend of 46.6 weight percent R125, 50.0 weight percent R134a, and 3.4 weight percent n-butane), R422A (ASHRAE designation for a blend of 85.1 weight percent R125, 11.5 weight percent R134a, and 3.4 weight percent isobutane), R404A, (ASHRAE designation for a blend of 44 weight percent R125, 52 weight percent R143a (1,1,1-trifluoroethane), and 4.0 weight percent R134a) and R507A (ASHRAE designation for a blend of 50 weight percent R125 and 50 weight percent R143a). Additionally, the compositions used in the apparatus of the present invention may be useful as replacements for R12 (CFC-12, dichlorodifluoromethane) or R502 (ASHRAE designation for a blend of 51.2 weight percent CFC-115 (chloropentafluoroethane) and 48.8 weight percent HCFC-22).

[0035] Often replacement refrigerants are most useful if capable of being used in the original refrigeration equipment designed for a different refrigerant. The compositions used in the apparatus of the present invention may be useful as replacements for the above-mentioned refrigerants in original equipment. Additionally, the compositions used in the apparatus of the present invention may be useful as replacements for the above mentioned refrigerants in equipment designed to use the above-mentioned refrigerants.

[0036] The compositions used in the apparatus of the present invention may further comprise a lubricant.

[0037] Lubricants comprise refrigeration lubricants, i.e. those lubricants suitable for use with refrigeration, air-conditioning, or heat pump apparatus. Among these lubricants are those conventionally used in compression refrigeration apparatus utilizing chlorofluorocarbon refrigerants. Such lubricants and their properties are discussed in the 1990 ASHRAE Handbook, Refrigeration Systems and Applications, chapter 8, titled "Lubricants in Refrigeration Systems", pages 8.1 through 8.21. Lubricants may comprise those commonly known as "mineral oils" in the field of compression refrigeration lubrication. Mineral oils comprise paraffins (i.e. straight-chain and branched-carbon-chain, saturated hydrocarbons), naphthenes (i.e. cyclic paraffins) and aromatics (i.e. unsaturated, cyclic hydrocarbons containing one or more rings characterized by alternating double bonds). Lubricants further comprise those commonly known as "synthetic oils" in the field of compression refrigeration lubrication. Synthetic oils comprise alkylaryls (i.e. linear and branched alkyl alkylbenzenes), synthetic paraffins and napthenes, and poly(alphaolefins). Representative conventional lubricants are the commercially available BVM 100 N (paraffinic mineral oil sold by BVA Oils), Suniso® 3GS and Suniso® 5GS (naphthenic mineral oil sold by Crompton Co.), Sontex® 372LT (naphthenic mineral oil sold by Pennzoil), Calumet® RO-30 (naphthenic mineral oil sold by Calumet Lubricants), Zerol® 75, Zerol® 150 and Zerol® 500 (linear alkylbenzenes sold by Shrieve Chemicals) and HAB 22 (branched alkylbenzene sold by Nippon Oil).

[0038] Lubricants further comprise those that have been designed for use with hydrofluorocarbon refrigerants and are miscible with refrigerants under compression refrigeration, air-conditioning, or heat pump apparatus' operating conditions. Such lubricants and their properties are discussed in "Synthetic Lubricants and High-Performance Fluids", R. L. Shubkin, editor, Marcel Dekker, 1993. Such lubricants include, but are not limited to, polyol esters (POEs) such as Castrol® 100 (Castrol, United Kingdom), polyalkylene glycols (PAGs) such as RL-488A from Dow (Dow Chemical, Midland, Michigan), and polyvinyl ethers (PVEs). These lubricants are readily available from various commercial sources.

[0039] Lubricants are selected by considering a given compressor's requirements and the environment to which the lubricant will be exposed. Lubricants preferably have a kinematic viscosity of at least about 5 cs (centistokes) at 40°C.

[0040] Commonly used refrigeration system additives may optionally be added, as desired, to compositions used in the apparatus of the present invention in order to enhance lubricity and system stability. These additives are generally known within the field of refrigeration compressor lubrication, and include anti wear agents, extreme pressure lubricants, corrosion and oxidation inhibitors, metal surface deactivators, free radical scavengers, foaming and antifoam control agents, leak detectants and the like. In general, these additives are present only in small amounts relative to the overall lubricant composition. They are typically used at concentrations of from less than about 0.1 % to as much as about 3 % of each additive. These additives are selected on the basis of the individual system requirements. Some typical examples of such additives may include, but are not limited to, lubrication enhancing additives, such as alkyl or aryl esters of phosphoric acid and of thiophosphates. Additionally, the metal dialkyl dithiophosphates (e.g. zinc dialkyl dithiophosphate or ZDDP, Lubrizol 1375) and other members of this family of chemicals may be used in compositions used in the apparatus of the present invention. Other antiwear additives include natural product oils and assymetrical polyhydroxyl lubrication additives such as Synergol TMS (International Lubricants). Similarly, stabilizers such as anti oxidants, free radical scavengers, and water scavengers may be employed. Compounds in this category can include, but are not limited to, butylated hydroxy toluene (BHT) and epoxides.

[0041] The compositions used in the apparatus of the present invention may further comprise about 0.01 weight percent to about 5 weight percent of an additive such as, for example, a stabilizer, free radical scavenger and/or antioxidant. Such additives include but are not limited to, nitromethane, hindered phenols, hydroxylamines, thiols, phosphites, or lactones. Single additives or combinations may be used.

[0042] The compositions used in the apparatus of the present invention may further comprise about 0.01 weight percent to about 5 weight percent of a water scavenger (drying compound). Such water scavengers may comprise ortho esters such as trimethyl-, triethyl-, or tripropylortho formate.

[0043] The compositions used in the apparatus of the present invention may further comprise a tracer selected from the group consisting of hydrofluorocarbons (HFCs), deuterated hydrocarbons, deuterated hydrofluorocarbons, perfluorocarbons, fluoroethers, brominated compounds, iodated compounds, alcohols, aldehydes, ketones, nitrous oxide (N_2O) and combinations thereof. The tracer compounds are added to the compositions in previously determined quantities to allow detection of any dilution, contamination or other alteration of the composition, as described in U. S. Patent application serial no. 11/062044, filed February 18, 2005.

[0044] Typical tracer compounds for use in the present compositions are listed in Table 7.

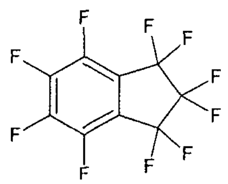
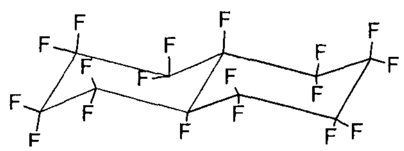
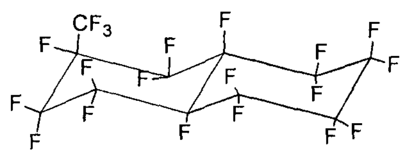
TABLE 7

Compound	Structure
Deuterated hydrocarbons and hydrofluorocarbons	
Ethane-d6	CD_3CD_3
Propane-d8	$CD_3CD_2CD_3$
HFC-32-d2	CD_2F_2
HFC-134a-d2	CD_2FCF_3
HFC-143a-d3	CD_3CF_3
HFC-125-d	CDF_2CF_3
HFC-227ea-d	CF_3CDFCF_3
HFC-227ca-d	$CF_3CF_2CDF_2$
HFC-134-d2	CDF_2CDF_2

(continued)

Compound	Structure
Deuterated hydrocarbons and hydrofluorocarbons	
HFC-236fa-d2	$CF_3CD_2CF_3$
HFC-245cb-d3	$CF_3CF_2CD_3$
HFC-263fb-d2*	$CF_3CD_2CH_3$
HFC-263fb-d3	$CF_2CH_2CD_3$
Fluoroethers	
HFOC-125E	CHF_2OCF_3
HFOC-134aE	CH_2FOCF_3
HFOC-143aE	CH_3OCF_3
HFOC-227eaE	$CF_3OCHFCF_3$
HFOC-236faE	$CF_3OCH_2CF_3$
HFOC-245faEβγ or HFOC-245faEαβ	$CHF_2OCH_2CF_3$ (or $CHF_2CH_2OCF_3$)
HFOC-245cbEβγ or HFOC-245cbαβ	$CH_3OCF_2CF_3$ (or $CH_3CF_2OCF_3$)
HFE-42-11mcc (or Freon® E1)	$CF_3CF_2CF_2OCHFCF_3$
Freon® E2	$CF_3CF_2CF_2OCF(CF_3)CF_2OCHFCF_3$
Hydrofluorocarbons	
HFC-23	CHF_3
HFC-161	CH_3CH_2F
HFC-152a	CH_3CHF_2
HFC-134	CHF_2CHF_2
HFC-227ea	CF_3CHFCF_3
HFC-227ca	$CHF_2CF_2CF_3$
HFC-236cb	$CH_2FCF_2CF_3$
HFC-236ea	$CF_3CHFCHF_2$
HFC-236fa	$CF_3CH_2CF_3$
HFC-245cb	$CF_3CF_2CH_3$
HFC-245fa	$CHF_2CH_2CF_3$
HFC-254cb	$CHF_2CF_2CH_3$
HFC-254eb	CF_3CHFCH_3
HFC-263fb	$CF_3CH_2CH_3$
HFC-272ca	$CH_3CF_2CH_3$
HFC-281ea	CH_3CHFCH_3
HFC-281fa	$CH_2FCH_2CH_3$
HFC-329p	$CHF_2CF_2CF_2CF_3$
HFC-329mmz	$(CH_3)\ _2CHCF_3$
HFC-338mf	$CF_3CH_2CF_2CF_3$
HFC-338pcc	$CHF_2CF_2CF_2CHF_2$

(continued)

Hydrofluorocarbons	
HFC-347s	$CH_3CF_2CF_2CF_3$
HFC-43-10mee	$CF_3CHFCHFCF_2CF_3$
Perfluorocarbons	
PFC-116	CF_3CF_3
PFC-C216	Cyclo($-CF_2CF_2CF_2-$)
PFC-218	$CF_3CF_2CF_3$
PFC-C318	Cyclo($-CF_2CF_2CF_2CF_2-$)
PFC-31-10mc	$CF_3CF_2CF_2CF_3$
PFC-31-10my	$(CF_3)_2CFCF_3$
PFC-C51-12mycm	Cyclo($-CF(CF_3)CF_2CF(CF_3)CF_2-$)
PFC-C51-12mym, trans	Cyclo($-CF_2CF(CF_3)CF(CF_3CF_2-$)
PFC-C51-12mym, cis	Cyclo($-CF_2CF(CF_3)CF(CF_3)CF_2-$)
Perfluoromethylcyclo-pentane	Cyclo($-CF_2CF_2(CF_3)CF_2CF_2CF_2-$)
Perfluoromethylcyclo-hexane	Cyclo($-CF_2CF_2(CF_3)CF_2CF_2CF_2CF_2-$)
Perfluorodimethylcyclo-hexane (ortho, meta, or para)	Cyclo($-CF_2CF_2(CF_3)CF_2CF_2(CF_3)CF_2-$)
Perfluoroethylcyclohexane	Cyclo($-CF_2CF_2(CF_2CF_3)CF_2CF_2CF_2CF_2-$)
Perfluoroindan	C_9F_{10} (see structure below)
	
Perfluorotrimethylcyclo-hexane (all possible isomers)	Cyclo($-CF_2(CF_3)CF_2(CF_3)CF_2CF_2(CF_3)CF_2-$)
Perfluoroisopropylcyclo-hexane	Cyclo($-CF_2CF_2(CF_2(CF_3)_2)CF_2CF_2CF_2CF_2-$)
Perfluorodecalin (cis or trans, trans shown)	$C_{10}F_{18}$ (see structure below) 
Perfluoromethyldecalin (cis or trans and all additional possible isomers)	$C_{11}F_{20}$ (see structure below) 
Brominated compounds	
Bromomethane	CH_3Br
Bromofluoromethane	CH_2FBr
Bromodifluoromethane	CHF_2Br

(continued)

Brominated compounds	
Dibromofluoromethane	$CHFBr_2$
Tribromomethane	$CHBr_3$
Bromoethane	CH_3CH_2Br
Bromoethene	CH_2=CHBr
1,2-dibromoethane	CH_2BrCH_2Br
1 -bromo-1,2-difluoroethene	CFBr=CHF
Iodated compounds	
Iodotrifluoromethane	CF_3I
Difluoroiodomethane	CHF_2I
Fluoroiodomethane	CH_2FI
1,1,2-trifluoro-1-iodoethane	CF_2ICH_2F
1,1,2,2-tetrafluoro-1-iodoethane	CF_2ICHF_2
1,1,2,2-tetrafluoro-1,2-diiodoethane	CF_2ICF_2I
Iodopentafluorobenzene	C_6F_5I
Alcohols	
Ethanol	CH_3CH_2OH
n-propanol	$CH_3CH_2CH_2OH$
Isopropanol	$CH_3CH(OH)CH_3$
Aldehydes and Ketones	
Acetone (2-propanone)	$CH_3C(O)CH_3$
n-propanal	CH_3CH_2CHO
n-butanal	$CH_3CH_2CH_2CHO$
Methyl ethyl ketone (2-butanone)	$CH_3C(O)CH_2CH_3$
Other	
Nitrous oxide	N_2O

[0045] The compounds listed in Table 7 are available commercially (from chemical supply houses) or may be prepared by processes known in the art.

[0046] Single tracer compounds may be used in combination with a refrigeration/heating fluid in the compositions used in the apparatus of the present invention or multiple tracer compounds may be combined in any proportion to serve as a tracer blend. The tracer blend may contain multiple tracer compounds from the same class of compounds or multiple tracer compounds from different classes of compounds. For example, a tracer blend may contain 2 or more deuterated hydrofluorocarbons, or one deuterated hydrofluorocarbon in combination with one or more perfluorocarbons.

[0047] Additionally, some of the compounds in Table 7 exist as multiple isomers, structural or optical. Single isomers or multiple isomers of the same compound may be used in any proportion to prepare the tracer compound. Further, single or multiple isomers of a given compound may be combined in any proportion with any number of other compounds to serve as a tracer blend.

[0048] The tracer compound or tracer blend may be present in the compositions at a total concentration of about 50 parts per million by weight (ppm) to about 1000 ppm. Preferably, the tracer compound or tracer blend is present at a total concentration of about 50 ppm to about 500 ppm and most preferably, the tracer compound or tracer blend is present at a total concentration of about 100 ppm to about 300 ppm.

[0049] The compositions used in the apparatus of the present invention may further comprise a compatibilizer selected from the group consisting of polyoxyalkylene glycol ethers, amides, nitriles, ketones, chlorocarbons, esters, lactones, aryl ethers, fluoroethers and 1,1,1-trifluoroalkanes. The compatibilizer is used to improve solubility of hydrofluorocarbon refrigerants in conventional refrigeration lubricants. Refrigeration lubricants are needed to lubricate the compressor of a refrigeration, air-conditioning or heat pump apparatus. The lubricant must move throughout the apparatus with the refrigerant in particular it must return from the non-compressor zones to the compressor to continue to function as lubricant and avoid compressor failure.

[0050] Hydrofluorocarbon refrigerants are generally not compatible with convention refrigeration lubricants such as mineral oils, alkylbenzenes, synthetic paraffins, synthetic napthenes and poly(alpha)olefins. Many replacement lubricants have been proposed, however, the polyalkylene glycols, polyol esters and polyvinyl ethers, suggested for use with hydrofluorocarbon refrigerants are expensive and absorb water readily. Water in a refrigeration, air-conditioning system or heat pump can lead to corrosion and the formation of particles that may plug the capillary tubes and other small orifices in the system, ultimately causing system failure. Additionally, in existing equipment, time-consuming and costly flushing procedures are required to change to a new lubricant. Therefore, it is desirable to continue to use the original lubricant if possible.

[0051] The compatibilizers used in the apparatus of the present invention improve solubility of the hydrofluorocarbon refrigerants in conventional refrigeration lubricants and thus improve oil return to the compressor.

[0052] Polyoxyalkylene glycol ether compatibilizers are represented by the formula $R^1[(OR^2)_xOR^3]_y$, wherein: x is an integer from 1-3; y is an integer from 1-4; R^1 is selected from hydrogen and aliphatic hydrocarbon radicals having 1 to 6 carbon atoms and y bonding sites; R^2 is selected from aliphatic hydrocarbylene radicals having from 2 to 4 carbon atoms; R^3 is selected from hydrogen and aliphatic and alicyclic hydrocarbon radicals having from 1 to 6 carbon atoms; at least one of R^1 and R^3 is said hydrocarbon radical; and wherein said polyoxyalkylene glycol ethers have a molecular weight of from about 100 to about 300 atomic mass units. As used herein, bonding sites mean radical sites available to form covalent bonds with other radicals. Hydrocarbylene radicals mean divalent hydrocarbon radicals. Preferred polyoxyalkylene glycol ether compatibilizers are represented by $R^1[(OR^2)_xOR^3]_y$: x is preferably 1-2; y is preferably 1; R^1 and R^3 are preferably independently selected from hydrogen and aliphatic hydrocarbon radicals having 1 to 4 carbon atoms; R^2 is preferably selected from aliphatic hydrocarbylene radicals having from 2 or 3 carbon atoms, most preferably 3 carbon atoms; the polyoxyalkylene glycol ether molecular weight is preferably from about 100 to about 250 atomic mass units, most preferably from about 125 to about 250 atomic mass units. The R^1 and R^3 hydrocarbon radicals having 1 to 6 carbon atoms may be linear, branched or cyclic. Representative R^1 and R^3 hydrocarbon radicals include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, *tert*-butyl, pentyl, isopentyl, neopentyl, *tert*-pentyl, cyclopentyl, and cyclohexyl. Where free hydroxyl radicals on the present polyoxyalkylene glycol ether compatibilizers may be incompatible with certain compression refrigeration apparatus materials of construction (e.g. Mylar®), R^1 and R^3 are preferably aliphatic hydrocarbon radicals having 1 to 4 carbon atoms, most preferably 1 carbon atom. The R^2 aliphatic hydrocarbylene radicals having from 2 to 4 carbon atoms form repeating oxyalkylene radicals - $(OR^2)_x$ - that include oxyethylene radicals, oxypropylene radicals, and oxybutylene radicals. The oxyalkylene radical comprising R^2 in one polyoxyalkylene glycol ether compatibilizer molecule may be the same, or one molecule may contain different R^2 oxyalkylene groups. The present polyoxyalkylene glycol ether compatibilizers preferably comprise at least one oxypropylene radical. Where R^1 is an aliphatic or alicyclic hydrocarbon radical having 1 to 6 carbon atoms and y bonding sites, the radical may be linear, branched or cyclic. Representative R^1 aliphatic hydrocarbon radicals having two bonding sites include, for example, an ethylene radical, a propylene radical, a butylene radical, a pentylene radical, a hexylene radical, a cyclopentylene radical and a cyclohexylene radical. Representative R^1 aliphatic hydrocarbon radicals having three or four bonding sites include residues derived from polyalcohols, such as trimethylolpropane, glycerin, pentaerythritol, 1,2,3-trihydroxycyclohexane and 1,3,5-trihydroxycyclohexane, by removing their hydroxyl radicals.

[0053] Representative polyoxyalkylene glycol ether compatibilizers include but are not limited to: $CH_3OCH_2CH(CH_3)O(H \text{ or } CH_3)$ (propylene glycol methyl (or dimethyl) ether), $CH_3O[CH_2CH(CH_3)O]_2(H \text{ or } CH_3)$ (dipropylene glycol methyl (or dimethyl) ether), $CH_3O[CH_2CH(CH_3)O]_3(H \text{ or } CH_3)$ (tripropylene glycol methyl (or dimethyl) ether), $C_2H_5OCH_2CH(CH_3)O(H \text{ or } C_2H_5)$ (propylene glycol ethyl (or diethyl) ether), $C_2H_5O[CH_2CH(CH_3)O]_2(H \text{ or } C_2H_5)$ (dipropylene glycol ethyl (or diethyl) ether), $C_2H_5O[CH_2CH(CH_3)O]_3(H \text{ or } C_2H_5)$ (tripropylene glycol ethyl (or diethyl) ether), $C_3H_7OCH_2CH(CH_3)O(H \text{ or } C_3H_7)$ (propylene glycol n-propyl (or din-propyl) ether), $C_3H_7O[CH_2CH(CH_3)O]_2(H \text{ or } C_3H_7)$ (dipropylene glycol n-propyl (or di-n-propyl) ether), $C_3H_7O[CH_2CH(CH_3)O]_3(H \text{ or } C_3H_7)$ (tripropylene glycol n-propyl (or di-n-propyl) ether), $C_4H_9OCH_2CH(CH_3)OH$ (propylene glycol n-butyl ether), $C_4H_9O[CH_2CH(CH_3)O]_2(H \text{ or } C_4H_9)$ (dipropylene glycol n-butyl (or di-n-butyl) ether), $C_4H_9O[CH_2CH(CH_3)O]_3(H \text{ or } C_4H_9)$ (tripropylene glycol n-butyl (or di-n-butyl) ether), $(CH_3)_3COCH_2CH(CH_3)OH$ (propylene glycol t-butyl ether), $(CH_3)_3CO[CH_2CH(CH_3)O]_2(H \text{ or } (CH_3)_3)$ (dipropylene glycol t-butyl (or di-t-butyl) ether), $(CH_3)_3CO[CH_2CH(CH_3)O]_3(H \text{ or } (CH_3)_3)$ (tripropylene glycol t-butyl (or di-t-butyl) ether), $C_5H_{11}OCH_2CH(CH_3)OH$ (propylene glycol n-pentyl ether), $C_4H_9OCH_2CH(C_2H_5)OH$ (butylene glycol n-butyl ether), $C_4H_9O[CH_2CH(C_2H_5)O]_2H$ (dibutylene glycol n-butyl ether), trimethylolpropane tri-n-butyl ether $(C_2H_5C(CH_2O(CH_2)_3CH_3)_3)$ and trimethylolpropane di-n-butyl ether $(C_2H_5C(CH_2OC(CH_2)_3CH_3)_2CH_2OH)$.

[0054] Amide compatibilizers comprise those represented by the formulae $R^1C(O)NR^2R^3$ and cyclo-$[R^4C(O)N(R^5)]$, wherein R^1, R^2, R^3 and R^5 are independently selected from aliphatic and alicyclic hydrocarbon radicals having from 1 to 12 carbon atoms; R^4 is selected from aliphatic hydrocarbylene radicals having from 3 to 12 carbon atoms; and wherein said amides have a molecular weight of from about 100 to about 300 atomic mass units. The molecular weight of said amides is preferably from about 160 to about 250 atomic mass units. R^1, R^2, R^3 and R^5 may optionally include substituted hydrocarbon radicals, that is, radicals containing non-hydrocarbon substituents selected from halogens (e.g., fluorine, chlorine) and alkoxides (e.g. methoxy). R^1, R^2, R^3 and R^5 may optionally include heteroatom-substituted hydrocarbon radicals, that is, radicals, which contain the atoms nitrogen (aza-), oxygen (oxa-) or sulfur (thia-) in a radical chain otherwise composed of carbon atoms. In general, no more than three non-hydrocarbon substituents and heteroatoms, and preferably no more than one, will be present for each 10 carbon atoms in R^{1-3}, and the presence of any such non-hydrocarbon substituents and heteroatoms must be considered in applying the aforementioned molecular weight limitations. Preferred amide compatibilizers consist of carbon, hydrogen, nitrogen and oxygen. Representative R^1, R^2, R^3 and R^5 aliphatic and alicyclic hydrocarbon radicals include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, *tert*-butyl, pentyl, isopentyl, neopentyl, *tert*-pentyl, cyclopentyl, cyclohexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl and their configurational isomers. Preferred amide compatibilizers are those wherein R^4 in the aforementioned formula cyclo-[$R^4C(O)N(R^5)$-] may be represented by the hydrocarbylene radical $(CR^6R^7)_n$, in other words, the formula: cyclo-[$(CR^6R^7)_nC(O)N(R^5)$-] wherein: the previously-stated values for molecular weight apply; n is an integer from 3 to 5; R^5 is a saturated hydrocarbon radical containing 1 to 12 carbon atoms; R^6 and R^7 are independently selected (for each n) by the rules previously offered defining R^{1-3}. In the lactams represented by the formula: cyclo-[$(CR^6R^7)_nC(O)N(R^5)$-], all R^6 and R^7 are preferably hydrogen, or contain a single saturated hydrocarbon radical among the n methylene units, and R^5 is a saturated hydrocarbon radical containing 3 to 12 carbon atoms. For example, 1-(saturated hydrocarbon radical)-5-methylpyrrolidin-2-ones.

[0055] Representative amide compatibilizers include but are not limited to: 1-octylpyrrolidin-2-one, 1-decylpyrrolidin-2-one, 1-octyl-5-methylpyrrolidin-2-one, 1-butylcaprolactam, 1-cyclohexylpyrrolidin-2-one, 1-butyl-5-methylpiperid-2-one, 1-pentyl-5-methylpiperid-2-one, 1-hexylcaprolactam, 1-hexyl-5-methylpyrrolidin-2-one, 5-methyl-1-pentylpiperid-2-one, 1,3-dimethylpiperid-2-one, 1-methylcaprolactam, 1-butyl-pyrrolidin-2-one, 1,5-dimethylpiperid-2-one, 1-decyl-5-methylpyrrolidin-2-one, 1-dodecylpyrrolid-2-one, N,N-dibutylformamide and N,N-diisopropylacetamide.

[0056] Ketone compatibilizers comprise ketones represented by the formula $R^1C(O)R^2$, wherein R^1 and R^2 are independently selected from aliphatic, alicyclic and aryl hydrocarbon radicals having from 1 to 12 carbon atoms, and wherein said ketones have a molecular weight of from about 70 to about 300 atomic mass units. R^1 and R^2 in said ketones are preferably independently selected from aliphatic and alicyclic hydrocarbon radicals having 1 to 9 carbon atoms. The molecular weight of said ketones is preferably from about 100 to 200 atomic mass units. R^1 and R^2 may together form a hydrocarbylene radical connected and forming a five, six, or seven-membered ring cyclic ketone, for example, cyclopentanone, cyclohexanone, and cycloheptanone. R^1 and R^2 may optionally include substituted hydrocarbon radicals, that is, radicals containing non-hydrocarbon substituents selected from halogens (e.g., fluorine, chlorine) and alkoxides (e.g. methoxy). R^1 and R^2 may optionally include heteroatom-substituted hydrocarbon radicals, that is, radicals, which contain the atoms nitrogen (aza-), oxygen (keto-, oxa-) or sulfur (thia-) in a radical chain otherwise composed of carbon atoms. In general, no more than three non-hydrocarbon substituents and heteroatoms, and preferably no more than one, will be present for each 10 carbon atoms in R^1 and R^2, and the presence of any such non-hydrocarbon substituents and heteroatoms must be considered in applying the aforementioned molecular weight limitations. Representative R^1 and R^2 aliphatic, alicyclic and aryl hydrocarbon radicals in the general formula $R^1C(O)R^2$ include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, *tert*-butyl, pentyl, isopentyl, neopentyl, *tert*-pentyl, cyclopentyl, cyclohexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl and their configurational isomers, as well as phenyl, benzyl, cumenyl, mesityl, tolyl, xylyl and phenethyl.

[0057] Representative ketone compatibilizers include but are not limited to: 2-butanone, 2-pentanone, acetophenone, butyrophenone, hexanophenone, cyclohexanone, cycloheptanone, 2-heptanone, 3-heptanone, 5-methyl-2-hexanone, 2-octanone, 3-octanone, diisobutyl ketone, 4-ethylcyclohexanone, 2-nonanone, 5-nonanone, 2-decanone, 4-decanone, 2-decalone, 2-tridecanone, dihexyl ketone and dicyclohexyl ketone.

[0058] Nitrile compatibilizers comprise nitriles represented by the formula R^1CN, wherein R^1 is selected from aliphatic, alicyclic or aryl hydrocarbon radicals having from 5 to 12 carbon atoms, and wherein said nitriles have a molecular weight of from about 90 to about 200 atomic mass units. R^1 in said nitrile compatibilizers is preferably selected from aliphatic and alicyclic hydrocarbon radicals having 8 to 10 carbon atoms. The molecular weight of said nitrile compatibilizers is preferably from about 120 to about 140 atomic mass units. R^1 may optionally include substituted hydrocarbon radicals, that is, radicals containing non-hydrocarbon substituents selected from halogens (e.g., fluorine, chlorine) and alkoxides (e.g. methoxy). R^1 may optionally include heteroatom-substituted hydrocarbon radicals, that is, radicals, which contain the atoms nitrogen (aza-), oxygen (keto-, oxa-) or sulfur (thia-) in a radical chain otherwise composed of carbon atoms. In general, no more than three non-hydrocarbon substituents and heteroatoms, and preferably no more than one, will be present for each 10 carbon atoms in R^1, and the presence of any such non-hydrocarbon substituents and heteroatoms must be considered in applying the aforementioned molecular weight limitations. Representative R^1 aliphatic, alicyclic and aryl hydrocarbon radicals in the general formula R^1CN include pentyl, isopentyl, neopentyl, *tert-pentyl,* cyclopentyl, cyclohexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl and their configurational isomers, as well as phenyl, benzyl, cumenyl, mesityl, tolyl, xylyl and phenethyl.

[0059] Representative nitrile compatibilizers include but are not limited to: 1-cyanopentane, 2,2-dimethyl-4-cyanopentane, 1-cyanohexane, 1-cyanoheptane, 1-cyanooctane, 2-cyanooctane, 1-cyanononane, 1-cyanodecane, 2-cyanodecane, 1-cyanoundecane and 1-cyanododecane.

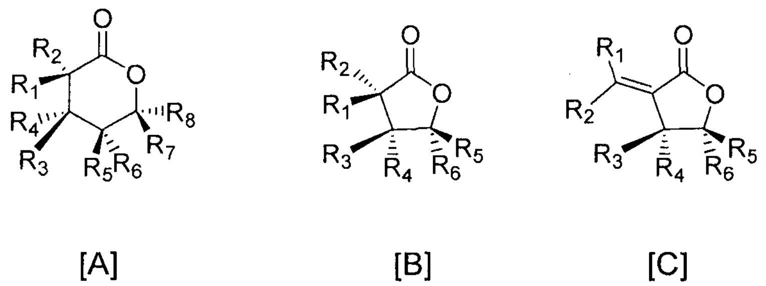
[0060] Chlorocarbon compatibilizers comprise chlorocarbons represented by the formula RCl_x, wherein; x is selected from the integers 1 or 2; R is selected from aliphatic and alicyclic hydrocarbon radicals having 1 to 12 carbon atoms; and wherein said chlorocarbons have a molecular weight of from about 100 to about 200 atomic mass units. The molecular weight of said chlorocarbon compatibilizers is preferably from about 120 to 150 atomic mass units. Representative R aliphatic and alicyclic hydrocarbon radicals in the general formula RCl_x include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, *tert*-butyl, pentyl, isopentyl, neopentyl, *tert*-pentyl, cyclopentyl, cyclohexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl and their configurational isomers.

[0061] Representative chlorocarbon compatibilizers include but are not limited to: 3-(chloromethyl)pentane, 3-chloro-3-methylpentane, 1-chlorohexane, 1,6-dichlorohexane, 1-chloroheptane, 1-chlorooctane, 1-chlorononane, 1-chlorodecane, and 1,1,1-trichlorodecane.

[0062] Ester compatibilizers comprise esters represented by the general formula $R^1CO_2R^2$, wherein R^1 and R^2 are independently selected from linear and cyclic, saturated and unsaturated, alkyl and aryl radicals. Preferred esters consist essentially of the elements C, H and O, have a molecular weight of from about 80 to about 550 atomic mass units.

[0063] Representative esters include but are not limited to: $(CH_3)_2CHCH_2OOC(CH_2)_{2\text{-}4}OCOCH_2CH(CH_3)_2$ (diisobutyl dibasic ester), ethyl hexanoate, ethyl heptanoate, n-butyl propionate, n-propyl propionate, ethyl benzoate, di-n-propyl phthalate, benzoic acid ethoxyethyl ester, dipropyl carbonate, "Exxate 700" (a commercial C_7 alkyl acetate), "Exxate 800" (a commercial C_8 alkyl acetate), dibutyl phthalate, and tert-butyl acetate.

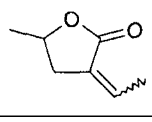
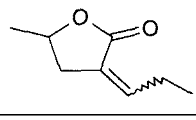
[0064] Lactone compatibilizers comprise lactones represented by structures [A], [B], and [C]:



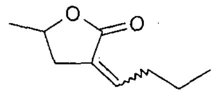
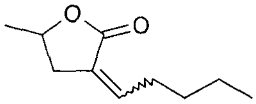
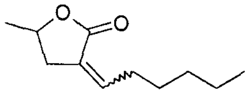
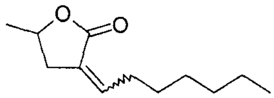
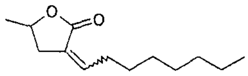
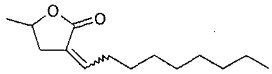
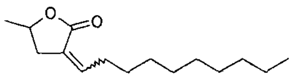
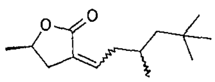
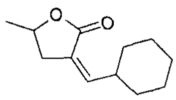
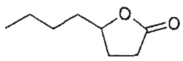
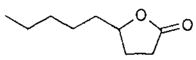
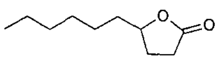
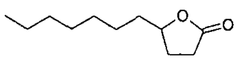
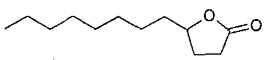
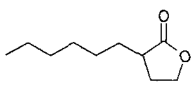
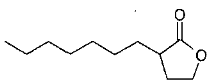
These lactones contain the functional group $-CO_2-$ in a ring of six (A), or preferably five atoms (B), wherein for structures [A] and [B], R_1 through R_8 are independently selected from hydrogen or linear, branched, cyclic, bicyclic, saturated and unsaturated hydrocarbyl radicals. Each R_1 though R_8 may be connected forming a ring with another R_1 through R_8. The lactone may have an exocyclic alkylidene group as in structure [C], wherein R_1 through R_6 are independently selected from hydrogen or linear, branched, cyclic, bicyclic, saturated and unsaturated hydrocarbyl radicals. Each R_1 though R_6 may be connected forming a ring with another R_1 through R_6. The lactone compatibilizers have a molecular weight range of from about 80 to about 300 atomic mass units, preferred from about 80 to about 200 atomic mass units.

[0065] Representative lactone compatibilizers include but are not limited to the compounds listed in Table 8.

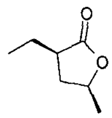
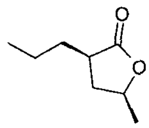
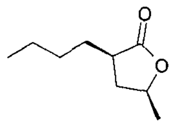
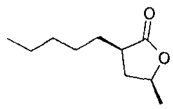
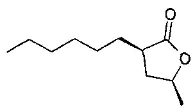
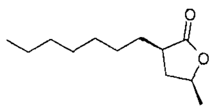
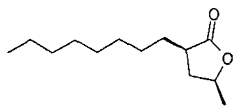
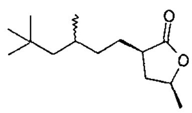
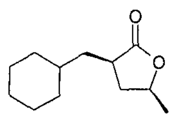
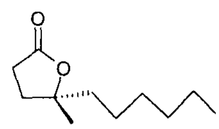
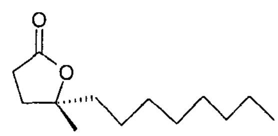
TABLE 8

Additive	Molecular Structure	Molecular Formula	Molecular Weight (amu)
(E,Z)-3-ethylidene-5-methyl-dihydro-furan-2-one		$C_7H_{10}O_2$	126
(E,Z)-3-propylidene-5-methyl-dihydro-furan-2-one		$C_8H_{12}O_2$	140

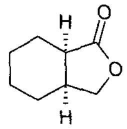
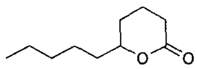
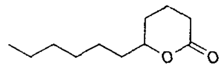
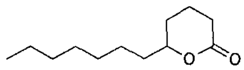
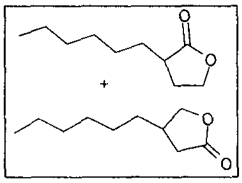
(continued)

Additive	Molecular Structure	Molecular Formula	Molecular Weight (amu)
(E,Z)-3-butylidene-5-methyl-dihydro-furan-2-one		$C_9H_{14}O_2$	154
(E,Z)-3-pentylidene-5-methyl-dihydro-furan-2-one		$C_{10}H_{16}O_2$	168
(E,Z)-3-Hexylidene-5-methyl-dihydro-furan-2-one		$C_{11}H_{18}O_2$	182
(E,Z)-3-Heptylidene-5-methyl-dihydro-furan-2-one		$C_{12}H_{20}O_2$	196
(E,Z)-3-octylidene-5-methyl-dihydro-furan-2-one		$C_{13}H_{22}O_2$	210
(E,Z)-3-nonylidene-5-methyl-dihydro-furan-2-one		$C_{14}H_{24}O_2$	224
(E,Z)-3-decylidene-5-methyl-dihydro-furan-2-one		$C_{15}H_{26}O_2$	238
(E,Z)-3-(3,5,5-trimethylhexylidene)-5-methyl-d ihydrofuran-2-one		$C_{14}H_{24}O_2$	224
(E,Z)-3-cyclohexylmethylidene-5-methyl-dihydrofuran-2-one		$C_{12}H_{18}O_2$	194
gamma-octalactone		$C_8H_{14}O_2$	142
gamma-nonalactone		$C_9H_{16}O_2$	156
gamma-decalactone		$C_{10}H_{18}O_2$	170
gamma-undecalactone		$C_{11}H_{20}O_2$	184
gamma-dodecalactone		$C_{12}H_{22}O_2$	198
3-hexyldihydro-furan-2-one		$C_{10}H_{18}O_2$	170
3-heptyldihydro-furan-2-one		$C_{11}H_{20}O_2$	184

(continued)

Additive	Molecular Structure	Molecular Formula	Molecular Weight (amu)
cis-3-ethyl-5-methyl-dihydro-furan-2-one		$C_7H_{12}O_2$	128
cis-(3-propyl-5-methyl)-dihydro-furan-2-one		$C_8H_{14}O_2$	142
cis-(3-butyl-5-methyl)-dihydro-furan-2-one		$C_9H_{16}O_2$	156
cis-(3-pentyl-5-methyl)-dihydro-furan-2-one		$C_{10}H_{18}O_2$	170
cis-3-hexyl-5-methyl-dihydro-furan-2-one		$C_{11}H_{20}O_2$	184
cis-3-heptyl-5-methyl-dihydro-furan-2-one		$C_{12}H_{22}O_2$	198
cis-3-octyl-5-methyl-dihydro-furan-2-one		$C_{13}H_{24}O_2$	212
cis-3-(3,5,5-trimethylhexyl)-5-methyl-dihydro-furan-2-one		$C_{14}H_{26}O_2$	226
cis-3-cyclohexylmethyl-5-methyl-dihydro-furan-2-one		$C_{12}H_{20}O_2$	196
5-methyl-5-hexyl-dihydro-furan-2-one		$C_{11}\ H_{20}O_2$	184
5-methyl-5-octyl-dihydro-furan-2-one		$C_{13}H_{24}O_2$	212

(continued)

Additive	Molecular Structure	Molecular Formula	Molecular Weight (amu)
Hexahydro-isobenzofuran-1-one		$C_8H_{12}O_2$	140
delta-decalactone		$C_{10}H_{18}O_2$	170
delta-undecalactone		$C_{11}H_{20}O_2$	184
delta-dodecalactone		$C_{12}H_{22}O_2$	198
mixture of 4-hexyl-dihydrofuran-2-one and 3-hexyl-dihyd ro-fu ran-2-one		$C_{10}H_{18}O_2$	170

[0066] Lactone compatibilizers generally have a kinematic viscosity of less than about 7 centistokes at 40°C. For instance, gamma-undecalactone has kinematic viscosity of 5.4 centistokes and cis-(3-hexyl-5-methyl)dihydrofuran-2-one has viscosity of 4.5 centistokes both at 40°C. Lactone compatibilizers may be available commercially or prepared by methods as described in U. S. patent application 10/910,495 filed August 3, 2004.

[0067] Aryl ether compatibilizers further comprise aryl ethers represented by the formula R^1OR^2, wherein: R^1 is selected from aryl hydrocarbon radicals having from 6 to 12 carbon atoms; R^2 is selected from aliphatic hydrocarbon radicals having from 1 to 4 carbon atoms; and wherein said aryl ethers have a molecular weight of from about 100 to about 150 atomic mass units. Representative R^1 aryl radicals in the general formula R^1OR^2 include phenyl, biphenyl, cumenyl, mesityl, tolyl, xylyl, naphthyl and pyridyl. Representative R^2 aliphatic hydrocarbon radicals in the general formula R^1OR^2 include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl and *tert*-butyl. Representative aromatic ether compatibilizers include but are not limited to: methyl phenyl ether (anisole), 1,3-dimethyoxybenzene, ethyl phenyl ether and butyl phenyl ether.

[0068] Fluoroether compatibilizers comprise those represented by the general formula $R^1OCF_2CF_2H$, wherein R^1 is selected from aliphatic, alicyclic, and aromatic hydrocarbon radicals having from about 5 to about 15 carbon atoms, preferably primary, linear, saturated, alkyl radicals. Representative fluoroether compatibilizers include but are not limited to: $C_8H_{17}OCF_2CF_2H$ and $C_6H_{13}OCF_2CF_2H$. It should be noted that if the refrigerant is a fluoroether, then the compatibilizer may not be the same fluoroether.

[0069] Fluoroether compatibilizers may further comprise ethers derived from fluoroolefins and polyols. The fluoroolefins may be of the type CF_2=CXY, wherein X is hydrogen, chlorine or fluorine, and Y is chlorine, fluorine, CF_3 or ORf, wherein R_f is CF_3, C_2F_5, or C_3F_7. Representative fluoroolefins are tetrafluoroethylene, chlorotrifluoroethylene, hexafluoropropylene, and perfluoromethylvinyl ether. The polyols may be linear or branched. Linear polyols may be of the type $HOCH_2(CHOH)_x(CRR')_yCH_2OH$, wherein R and R' are hydrogen, or CH_3, or C_2H_5 and wherein x is an integer from 0-4, and y is an integer from 0-4. Branched polyols may be of the type $C(OH)_t(R)_u(CH_2OH)_v[(CH_2)_mCH_2OH]_w$, wherein R may be hydrogen, CH_3 or C_2H_5, m may be an integer from 0 to 3, t and u may be 0 or 1, v and w are integers from 0 to 4, and also wherein t + u + v + w = 4. Representative polyols are trimethylol propane, pentaerythritol, butanediol, and ethylene glycol.

[0070] 1,1,1-Trifluoroalkane compatibilizers comprise 1,1,1-trifluoroalkanes represented by the general formula CF_3R^1, wherein R^1 is selected from aliphatic and alicyclic hydrocarbon radicals having from about 5 to about 15 carbon atoms, preferably primary, linear, saturated, alkyl radicals. Representative 1,1,1-trifluoroalkane compatibilizers include but are not limited to: 1,1,1-trifluorohexane and 1,1,1-trifluorododecane.

[0071] By effective amount of compatibilizer is meant that amount of compatibilizer that leads to efficient solubilizing of the lubricant in the composition and thus provides adequate oil return to optimize operation of the refrigeration, air-conditioning or heat pump apparatus.

[0072] The compositions used in the apparatus of the present invention will typically contain from about 0.1 to about 40 weight percent, preferably from about 0.2 to about 20 weight percent, and most preferably from about 0.3 to about 10 weight percent compatibilizer in the compositions.

[0073] The compositions used in the apparatus of the present invention may further comprise an ultra-violet (UV) dye and optionally a solubilizing agent. The UV dye is a useful component for detecting leaks of the composition by permitting one to observe the fluorescence of the dye in the composition at a leak point or in the vicinity of refrigeration, air-conditioning, or heat pump apparatus. One may observe the fluoroscence of the dye under an ultra-violet light. Solubilizing agents may be needed due to poor solubility of such UV dyes in some compositions.

[0074] By "ultra-violet" dye is meant a UV fluorescent composition that absorbs light in the ultra-violet or "near" ultra-violet region of the electromagnetic spectrum. The fluorescence produced by the UV fluorescent dye under illumination by a UV light that emits radiation with wavelength anywhere from 10 nanometer to 750 nanometer may be detected. Therefore, if a composition containing such a UV fluorescent dye is leaking from a given point in a refrigeration, air-conditioning, or heat pump apparatus, the fluorescence can be detected at the leak point. Such UV fluorescent dyes include but are not limited to naphthalimides, perylenes, coumarins, anthracenes, phenanthracenes, xanthenes, thioxanthenes, naphthoxanthenes, fluoresceins, and derivatives or combinations thereof.

[0075] Solubilizing agents comprise at least one compound selected from the group consisting of hydrocarbons, hydrocarbon ethers, polyoxyalkylene glycol ethers, amides, nitriles, ketones, chlorocarbons, esters, lactones, aryl ethers, fluoroethers and 1,1,1-trifluoroalkanes. The polyoxyalkylene glycol ethers, amides, nitriles, ketones, chlorocarbons, esters, lactones, aryl ethers, fluoroethers and 1,1,1-trifluoroalkanes solubilizing agents have been defined previously herein as being compatibilizers for use with conventional refrigeration lubricants.

[0076] Hydrocarbon solubilizing agents comprise hydrocarbons including straight chained, branched chain or cyclic alkanes or alkenes containing 5 or fewer carbon atoms and only hydrogen with no other functional groups. Representative hydrocarbon solubilizing agents comprise propane, propylene, cyclopropane, n-butane, isobutane, 2-methylbutane and n-pentane. It should be noted that if the composition contains a hydrocarbon, then the solubilizing agent may not be the same hydrocarbon.

[0077] Hydrocarbon ether solubilizing agents comprise ethers containing only carbon, hydrogen and oxygen, such as dimethyl ether (DME).

[0078] Solubilizing agents may be present as a single compound, or may be present as a mixture of more than one solubilizing agent. Mixtures of solubilizing agents may contain two solubilizing agents from the same class of compounds, say two lactones, or two solubilizing agents from two different classes, such as a lactone and a polyoxyalkylene glycol ether.

[0079] In the present compositions comprising refrigerant and UV fluorescent dye, or comprising heat transfer fluid and UV fluorescent dye, from about 0.001 weight percent to about 1.0 weight percent of the composition is UV dye, preferably from about 0.005 weight percent to about 0.5 weight percent, and most preferably from 0.01 weight percent to about 0.25 weight percent.

[0080] Solubilizing agents such as ketones may have an objectionable odor, which can be masked by addition of an odor masking agent or fragrance. Typical examples of odor masking agents or fragrances may include Evergreen, Fresh Lemon, Cherry, Cinnamon, Peppermint, Floral or Orange Peel all commercially available, as well as d-limonene and pinene. Such odor masking agents may be used at concentrations of from about 0.001% to as much as about 15% by weight based on the combined weight of odor masking agent and solubilizing agent.

[0081] Solubility of these UV fluorescent dyes in the compositions used in the apparatus of the present invention may be poor. Therefore, methods for introducing these dyes into the refrigeration, air-conditioning, or heat pump apparatus have been awkward, costly and time consuming. US patent no. RE 36,951 describes a method, which utilizes a dye powder, solid pellet or slurry of dye that may be inserted into a component of the refrigeration, air-conditioning, or heat pump apparatus. As refrigerant and lubricant are circulated through the apparatus, the dye is dissolved or dispersed and carried throughout the apparatus. Numerous other methods for introducing dye into a refrigeration or air conditioning apparatus are described in the literature.

[0082] Ideally, the UV fluorescent dye could be dissolved in the refrigerant itself thereby not requiring any specialized method for introduction to the refrigeration, air conditioning apparatus, or heat pump. Described herein are compositions including UV fluorescent dye, which may be introduced into the system as a solution in the refrigerant. The compositions will allow the storage and transport of dye-containing compositions even at low temperatures while maintaining the dye in solution.

[0083] In the present compositions comprising refrigerant, UV fluorescent dye and solubilizing agent, or comprising heat transfer fluid and UV fluorescent dye and solubilizing agent, from about 1 to about 50 weight percent, preferably from about 2 to about 25 weight percent, and most preferably from about 5 to about 15 weight percent of the combined composition is solubilizing agent. In the compositions used in the apparatus of the present invention the UV fluorescent dye is present in a concentration from about 0.001 weight percent to about 1.0 weight percent, preferably from 0.005 weight percent to about 0.5 weight percent, and most preferably from 0.01 weight percent to about 0.25 weight percent.

[0084] Further described herein is a method of using the compositions further comprising ultraviolet fluorescent dye, and optionally, solubilizing agent, in refrigeration, air-conditioning, or heat pump apparatus. The method comprises introducing the composition into the refrigeration, air-conditioning, or heat pump apparatus. This may be done by dissolving the UV fluorescent dye in the composition in the presence of a solubilizing agent and introducing the combination into the apparatus. Alternatively, this may be done by combining solubilizing agent and UV fluorescent dye and introducing said combination into refrigeration or air-conditioning apparatus containing refrigerant and/or heat transfer fluid. The resulting composition may be used in the refrigeration, air-conditioning, or heat pump apparatus.

[0085] Further described herein is a method of using the compositions comprising ultraviolet fluorescent dye to detect leaks. The presence of the dye in the compositions allows for detection of leaking refrigerant in a refrigeration, air-conditioning, or heat pump apparatus. Leak detection helps to address, resolve or prevent inefficient operation of the apparatus or system or equipment failure. Leak detection also helps one contain chemicals used in the operation of the apparatus.

[0086] The method comprises providing the composition comprising refrigerant, ultra-violet fluorescent dye, as described herein, and optionally, a solubilizing agent as described herein, to refrigeration, air-conditioning, or heat pump apparatus and employing a suitable means for detecting the UV fluorescent dye-containing refrigerant. Suitable means for detecting the dye include, but are not limited to, ultra-violet lamps, often referred to as a "black light" or "blue light". Such ultra-violet lamps are commercially available from numerous sources specifically designed for this purpose. Once the ultra-violet fluorescent dye containing composition has been introduced to the refrigeration, air-conditioning, or heat pump apparatus and has been allowed to circulate throughout the system, a leak can be found by shining said ultra-violet lamp on the apparatus and observing the fluorescence of the dye in the vicinity of any leak point.

[0087] Further described herein is a method for replacing a high GWP refrigerant in a refrigeration, air-conditioning, or heat pump apparatus, wherein said high GWP refrigerant is selected from the group consisting of R134a, R22, R245fa, R114, R236fa, R124, R410A, R407C, R417A, R422A, R507A, and R404A, said method comprising providing a composition as defined above to said refrigeration, air-conditioning, or heat pump apparatus that uses, used or is designed to use said high GWP refrigerant.

[0088] Vapor-compression refrigeration, air-conditioning, or heat pump systems include an evaporator, a compressor, a condenser, and an expansion device. A vapor-compression cycle re-uses refrigerant in multiple steps producing a cooling effect in one step and a heating effect in a different step. The cycle can be described simply as follows. Liquid refrigerant enters an evaporator through an expansion device, and the liquid refrigerant boils in the evaporator at a low temperature to form a gas and produce cooling. The low-pressure gas enters a compressor where the gas is compressed to raise its pressure and temperature. The higher-pressure (compressed) gaseous refrigerant then enters the condenser in which the refrigerant condenses and discharges its heat to the environment. The refrigerant returns to the expansion device through which the liquid expands from the higher-pressure level in the condenser to the low-pressure level in the evaporator, thus repeating the cycle.

[0089] As used herein, mobile refrigeration apparatus or mobile air-conditioning apparatus refers to any refrigeration or air-conditioning apparatus incorporated into a transportation unit for the road, rail, sea or air. In addition, apparatus, which are meant to provide refrigeration or air-conditioning for a system independent of any moving carrier, known as "intermodal" systems, are included in the present invention. Such intermodal systems include "containers" (combined sea/land transport) as well as "swap bodies" (combined road and rail transport). The present invention is particularly useful for road transport refrigerating or air-conditioning apparatus, such as automobile air-conditioning apparatus or refrigerated road transport equipment.

[0090] Further described herein is a process for producing cooling comprising evaporating the compositions as defined above in the vicinity of a body to be cooled, and thereafter condensing said compositions.

[0091] Further described herein is a process for producing heat comprising condensing the compositions as defined above in the vicinity of a body to be heated, and thereafter evaporating said compositions.

[0092] Further described herein is a refrigeration, air-conditioning, or heat pump apparatus containing a composition as defined above.

[0093] The present invention relates to a mobile air-conditioning apparatus containing a composition as defined above.

[0094] Further described herein is a method for early detection of a refrigerant leak in a refrigeration, air-conditioning or heat pump apparatus said method comprising using a non-azeotropic composition in said apparatus, and monitoring for a reduction in cooling performance. The non-azeotropic compositions will fractionate upon leakage from a refrigeration, air-conditioning or heat pump apparatus and the lower boiling (higher vapor pressure) component will leak out of the apparatus first. When this occurs, if the lower boiling component in that composition provides the majority of the refrigeration capacity, there will be a marked reduction in the capacity and thus performance of the apparatus. In an automobile air-conditioning system, as an example, the passengers in the automobile will detect a reduction in the cooling capability of the system. This reduction in cooling capability can be interpreted to mean that refrigerant is being leaked and that the system requires repair.

[0095] Further described herein is a method of using the compositions as defined above as a heat transfer fluid composition, said process comprising transporting said composition from a heat source to a heat sink.

[0096] Heat transfer fluids are utilized to transfer, move or remove heat from one space, location, object or body to a different space, location, object or body by radiation, conduction, or convection. A heat transfer fluid may function as a secondary coolant by providing means of transfer for cooling (or heating) from a remote refrigeration (or heating) system. In some systems, the heat transfer fluid may remain in a constant state throughout the transfer process (i.e., not evaporate or condense). Alternatively, evaporative cooling processes may utilize heat transfer fluids as well.

[0097] A heat source may be defined as any space, location, object or body from which it is desirable to transfer, move or remove heat. Examples of heat sources may be spaces (open or enclosed) requiring refrigeration or cooling, such as refrigerator or freezer cases in a supermarket, building spaces requiring air-conditioning, or the passenger compartment of an automobile requiring air-conditioning. A heat sink may be defined as any space, location, object or body capable of absorbing heat. A vapor compression refrigeration system is one example of such a heat sink.

EXAMPLES

EXAMPLE 1

Impact of vapor leakage

[0098] A vessel is charged with an initial composition at a temperature of either -25 °C or if specified, at 25 °C, and the initial vapor pressure of the composition is measured. The composition is allowed to leak from the vessel, while the temperature is held constant, until 50 weight percent of the initial composition is removed, at which time the vapor pressure of the composition remaining in the vessel is measured. Results are shown in Table 9.

TABLE 9

Composition wt%	Initial P (Psia)	Initial P (kPa)	After 50% Leak (Psia)	After 50% Leak (kPa)	Delta P (%)
HFC-1234yf/HFC-32					
7.4/92.6	49.2	339	49.2	339	0.0%
1/99	49.2	339	49.2	339	0.0%
20/80	49.0	338	48.8	337	0.3%
40/60	47.5	327	47.0	324	1.0%
57/43	44.9	309	40.5	280	9.6%
58/42	44.6	308	40.1	276	10.2%
HFC-1234yf/trans-HFC-1234ze					
1/99	11.3	78	11.3	78	0.4%
10/90	12.2	84	11.8	81	3.3%
20/80	13.1	90	12.5	86	4.6%
40/60	14.6	101	14.0	96	4.3%
60/40	15.8	109	15.4	106	2.7%
80/20	16.9	117	16.7	115	1.1%
90/10	17.4	120	17.3	119	0.5%
99/1	17.8	123	17.8	123	0.1%
HFC-1234yf/HFC-1243zf					
1/99	13.1	90	13.0	90	0.2%
10/90	13.7	94	13.5	93	1.6%
20/80	14.3	99	14.0	97	2.4%
40/60	15.5	107	15.1	104	2.2%
60/40	16.4	113	16.2	112	1.4%
80/20	17.2	119	17.1	118	0.5%
90/10	17.5	121	17.5	121	0.2%
99/1	17.8	123	17.8	123	0.0%

(continued)

HFC-1234yf/HFC-1243zf					
HFC-32/HFC-125/HFC-1234yf (25 °C)					
40/50/10	240.6	1659	239.3	1650	0.5%
23/25/52	212.6	1466	192.9	1330	9.3%
15/45/40	213.2	1470	201.3	1388	5.6%
10/60/30	213.0	1469	206.0	1420	3.3%

[0099] The difference in vapor pressure between the original composition and the composition remaining after 50 weight percent is removed is less then about 10 percent for compositions used in the apparatus of the present invention. This indicates that the compositions used in the apparatus of the present invention would be azeotropic or near-azeotropic.

EXAMPLE 2

Refrigeration Performance Data

[0100] Table 10 shows the performance of various refrigerant compositions used in the apparatus of the present invention as compared to HFC-134a. In Table 10, Evap Pres is evaporator pressure, Cond Pres is condenser pressure, Comp Disch T is compressor discharge temperature, COP is energy efficiency, and CAP is capacity. The data are based on the following conditions.

Evaporator temperature	40.0°F (4.4°C)
Condenser temperature	130.0°F (54.4°C)
Subcool temperature	10.0°F (5.5°C)
Return gas temperature	60.0°F (15.6°C)
Compressor efficiency is	100%

Note that the superheat is included in cooling capacity calculations.

TABLE 10

Composition (wt%)	Evap Pres (Psia)	Evap Pres (kPa)	Cond Pres (Psia)	Cond Pres (kPa)	Comp Disch T (F)	Comp Disch T (C)	Cap (Btu/min)	Cap (kW)	COP
HFC-134a	50.3	346	214	1476	156	68.9	213	373	4.41
HFC-1234yf/HFC-32 (95/5)	58.6	404	230	1586	149	65.0	228	4.00	4.36
HFC-1225ye/HFC-1234yf/HFC-32 (25/73/2)	53.0	365	212	1464	146	63.3	210	3.68	4.37
HFC-1225ye/HFC-1234yf/HFC-32 (75/23/2)	45.3	312	190	1312	148	64.4	189	3.31	4.43
HFC-1225ye/HFC-1234yf/HFC-32 (49/49/2)	49.5	341	202.5	1396	146.9	63.8	201	3.52	4.4

[0101] Several compositions have even higher energy efficiency (COP) than HFC-134a while maintaining lower discharge pressures and temperatures. Capacity for the present compositions is also similar to R134a indicating these could be replacement refrigerants for R134a in refrigeration and air-conditioning, and in mobile air-conditioning applications in particular.

EXAMPLE 3

Refrigeration Performance Data

[0102] Table 11 shows the performance of various refrigerant compositions of the present invention as compared to R404A and R422A. In Table 11, Evap Pres is evaporator pressure, Cond Pres is condenser pressure, Comp Disch T is compressor discharge temperature, EER is energy efficiency, and CAP is capacity. The data are based on the following conditions.

Evaporator temperature	-17.8°C
Condenser temperature	46.1°C
Subcool temperature	5.5°C
Return gas temperature	15.6°C
Compressor efficiency is	70%

Note that the superheat is included in cooling capacity calculations.

TABLE 11

Existing Refrigerant Product		Evap Press (kPa))	Cond P Press (kPa)	Compr Disch T (C)	CAP (kJ/m3)	EER
R22		267	1774	144	1697	4.99
R404A		330	2103	101.1	1769	4.64
R507A		342	2151	100.3	1801	4.61
R422A		324	2124	95.0	1699	4.54
Candidate Replacement	wt%					
HFC-32/CF_3I/HFC-1234yf	5/50/45	199	1377	107	1254	5.11
HFC-32/CF_3I/HFC-1234yf	5/30/65	197	1382	103	1241	5.11
HFC-32/CF_3I/HFC-1234yf	10/25/65	220	1542	107	1374	5.04
HFC-32/CF_3I/HFC-1234yf	20/10/70	255	1786	114	1577	4.95
HFC-32/CF_3I/HFC-1234yf	30/10/60	295	2020	123	1795	4.88
HFC-32/CF_3I/HFC-1234yf	30/20/50	305	2057	125	1843	4.85
HFC-32/CF_3I/HFC-1234yf	30/30/40	314	2091	128	1887	4.85
HFC-32/CF_3I/HFC-1234yf	20/40/40	275	1861	121	1679	4.92
HFC-32/CF_3I/HFC-1234yf	10/40/50	225	1558	111	1404	5.04
HFC-32/CF_3I/HFC-1234yf	50/20/30	378	2447	143	2238	4.73
HFC-32/CF_3I/HFC-1234yf	40/30/30	354	2305	137	2099	4.76
HFC-32/CF_3I/HFC-1234yf	40/40/20	360	2336	142	2136	4.74
HFC-32/CF_3I/HFC-1234yf	35/35/30	338	2217	135	2015	4.78
HFC-32/CF_3I/HFC-1234yf	35/30/35	334	2202	133	1996	4.80
HFC-32/CF_3I/HFC-1234yf	50/25/25	384	2468	145	2267	4.72
HFC-32/CF_3I/HFC-1225ye/HFC-1234yf	40/20/20/20	331	2246	136	1999	4.76
HFC-32/CF_3I/HFC-1225ye/HFC-1234yf	30/20/25/25	290	2029	127	1782	4.83
HFC-32/CF_3I/HFC-1225ye/HFC-1234yf	30/10/30/30	279	1987	125	1728	4.83
HFC-32/HFC-125/HFC-1234yf/HFC-1225ye	25/25/25/25	297	2089	118	1772	4.76
HFC-32/HFC-125/HFC-1234yf/H FC-1225ye	20/30/25/25	286	2025	113	1702	4.64
HFC-32/HFC-125/HFC-1234yf/HFC-1225ye	20/30/30/20	290	2033	113	1717	4.76
HFC-32/HFC-125/HFC-1234yf/HFC-1225ye	20/30/40/10	297	2048	112	1746	4.78

(continued)

Candidate Replacement	wt%					
HFC-32/HFC-125/HFC-1234yf/HFC-1225ye	30/30/20/20	328	2251	122	1925	4.71
HFC-32/HFC-125/HFC-1234yf/HFC-1225ye	30/30/1/39	312	2217	123	1858	4.68
HFC-32/HFC-125/HFC-1234yf/HFC-1225ye	30/30/39/1	342	2275	120	1979	4.73
HFC-32/HFC-125/HFC-1234yf/HFC-1225ye	30/30/10/30	320	2235	123	1891	4.68
HFC-32/HFC-125/HFC-1234yf/HFC-1225ye	35/30/5/30	337	2330	127	1986	4.66
HFC-32/HFC-125/HFC-1234yf/HFC-1225ye	20/15/10/55	240	1818	115	1513	4.85
HFC-32/HFC-125/HFC-1234yf/HFC-1225ye	30/15/10/45	284	2066	124	1743	4.76
HFC-32/HFC-125/HFC-1234yf/HFC-1225ye	40/30/15/15	341	2364	132	2022	4.66
HFC-32/HFC-125/CF_3I/HFC-1234yf/HFC-1225ye	30/25/5/35/5	335	2240	121	1954	4.76
HFC-32/HFC-125/CF_3I/HFC-1234yf	30/25/5/40	338	2245	121	1966	4.76
HFC-32/HFC-125/HFC-1234yf	25/50/25	365	2376	115	2040	4.66
HFC-32/HFC-125/HFC-1234yf	30/30/40	343	2276	120	1982	4.73
HFC-32/HFC-125/HFC-1234yf	20/30/50	303	2059	112	1770	4.78
HFC-32/HFC-125/CF_3I/HFC-1234yf	25/25/10/40	323	2154	118	1884	4.78

[0103] Several compositions have energy efficiency (COP) comparable to R404A and R422A. Capacity for the present compositions is also similar to R404A, R507A, and R422A indicating these could be replacement refrigerants for in refrigeration and air-conditioning.

EXAMPLE 4

Refrigeration Performance Data

[0104] Table 12 shows the performance of various refrigerant compositions used in the apparatus of the present invention as compared to HCFC-22, R410A, R407C, and R417A. In Table 12, Evap Pres is evaporator pressure, Cond Pres is condenser pressure, Comp Disch T is compressor discharge temperature, EER is energy efficiency, and CAP is capacity. The data are based on the following conditions.

Evaporator temperature	4.4°C
Condenser temperature	54.4°C
Subcool temperature	5.5°C
Return gas temperature	15.6°C
Compressor efficiency is	100%

Note that the superheat is included in cooling capacity calculations.

TABLE 12

Existing Refrigerant Product	Evap Press (kPa))	Cond Press (kPa)	Compr Disch T (C)	CAP (kJ/m3)	EER
R22	573	2149	88.6	3494	14.73
R410A	911	3343	89.1	4787	13.07

(continued)

R407C		567	2309	80.0	3397	14.06
R417A		494	1979	67.8	2768	13.78
Candidate Replacement	wt%					
HFC-32/HFC-125/HFC-1234yf	40/50/10	868	3185	84.4	4496	13.06
HFC-32/HFC-125/HFC-1234yf	23/25/52	656	2517	76.7	3587	13.62
HFC-32/HFC-125/HFC-1234yf	15/45/40	669	2537	73.3	3494	13.28
HFC-32/HFC-125/HFC-1234yf	10/60/30	689	2586	71.3	3447	12.96

[0105] Compositions have energy efficiency (EER) comparable to R22, R407C, R417A, and R410A while maintaining low discharge temperatures. Capacity for the present compositions is also similar to R22, R407C and R417A indicating these could be replacement refrigerants for in refrigeration and air-conditioning.

EXAMPLE 5

Refrigeration Performance Data

[0106] Table 13 shows the performance of various refrigerant compositions used in the apparatus of the present invention as compared to HCFC-22 and R410A. In Table 12, Evap Pres is evaporator pressure, Cond Pres is condenser pressure, Comp Disch T is compressor discharge temperature, EER is energy efficiency, and CAP is capacity. The data are based on the following conditions.

Evaporator temperature	4°C
Condenser temperature	43°C
Subcool temperature	6°C
Return gas temperature	18°C
Compressor efficiency is	70%

Note that the superheat is included in cooling capacity calculations.

TABLE 13

Composition (wt%)	Evap Press (kPa)	Cond Press (kPa)	Compr Disch Temp (C)	CAP (kJ/m3)	EER
R22	565	1648	90.9	3808	9.97
R410A	900	2571	88.1	5488	9.27
HFC-32/HFC-134a/HFC-1225ye/HFC-1234yf (30/8/52/10)	561	1752	81.9	3841	9.73
HFC-32/HFC-134a/HFC-1225ye/HFC-1234yf (35/6/52/7)	597	1852	84.3	4051	9.66

Compositions have energy efficiency (EER) comparable to R22 and R410A while maintaining reasonable discharge temperatures. Capacity for the present compositions is also similar to R22 indicating these could be replacement refrigerants for in refrigeration and air-conditioning.

Claims

1. A mobile air-conditioning apparatus containing a composition comprising HFC-1234yf and at least one compound selected from HFC-1234ze (trans), HFC-1234ze (cis), HFC-1243zf, HFC-32, and CO_2.

2. The apparatus of claim 1, wherein the composition comprises HFC-1234yf and at least one compound selected from HFC-1234ze (trans) and CO_2.

3. The apparatus of claim 1 or 2, wherein the composition consists of HFC-1234yf, HFC-1234ze (trans) and CO_2.

4. The apparatus of claim 1, wherein the composition comprises HFC-1234yf and at least one compound selected from HFC-1234ze (trans), HFC-1234ze (cis) and HFC-1243zf.

5. The apparatus of claim 1, wherein the composition comprises HFC-1234yf and at least one compound selected from HFC-1234ze (trans) and HFC-32.

6. The apparatus of claim 1, wherein the composition comprises HFC-1234yf and at least one compound selected from HFC-32 and CO_2.

7. The apparatus of claim 6, wherein the composition consists of HFC-1234yf and HFC-32.

8. The apparatus of claim 7, wherein the composition consists of 40 to 99 weight percent HFC-1234yf and 1 to 60 weight percent HFC-32, preferably of 40 to 95 weight percent of HFC-1234yf and 5 to 60 weight percent of HFC-32.

Patentansprüche

1. Mobile Klimaanlagenvorrichtung enthaltend eine Zusammensetzung umfassend HFC-1234yf und mindestens eine Verbindung ausgewählt aus HFC-1234ze (trans), HFC-1234ze (cis), HFC-1234zf, HFC-32 und CO_2.

2. Vorrichtung nach Anspruch 1, wobei die Zusammensetzung HFC-1234yf und mindestens eine Verbindung ausgewählt aus HFC-1234ze (trans) und CO_2 umfasst.

3. Vorrichtung nach Anspruch 1 oder 2, wobei die Zusammensetzung aus HFC-1234yf, HFC-1234ze (trans) und CO_2 besteht.

4. Vorrichtung nach Anspruch 1, wobei die Zusammensetzung HFC-1234yf und mindestens eine Verbindung ausgewählt aus HFC-1234ze (trans), HFC-1234ze (cis) und HFC-1234zf umfasst.

5. Vorrichtung nach Anspruch 1, wobei die Zusammensetzung HFC-1234yf und mindestens eine Verbindung ausgewählt aus HFC-1234ze (trans) und HFC-32 umfasst.

6. Vorrichtung nach Anspruch 1, wobei die Zusammensetzung HFC-1234yf und mindestens eine Verbindung ausgewählt aus HFC-32 und CO_2 umfasst.

7. Vorrichtung nach Anspruch 6, wobei die Zusammensetzung aus HFC-1234yf und HFC-32 besteht.

8. Vorrichtung nach Anspruch 7, wobei die Zusammensetzung aus 40 bis 99 Gewichtsprozent HFC-1234yf und 1 bis 60 Gewichtsprozent HFC-32, vorzugsweise 40 bis 95 Gewichtsprozent HFC-1234yf und 5 bis 60 Gewichtsprozent HFC-32 besteht.

Revendications

1. Appareil de conditionnement d'air mobile contenant une composition comprenant du HFC-1234yf et au moins un composé choisi parmi le HFC-1234ze (trans), le HFC-1234ze (cis), le HFC-1243zf, HFC-32 et le CO_2.

2. Appareil selon la revendication 1, dans lequel la composition comprend du HFC-1234yf et au moins un composé choisi parmi le HFC-1234ze (trans) et le CO_2.

3. Appareil selon la revendication 1 ou 2, dans lequel la composition est constituée de HFC-1234yf, de HFC-1234ze (trans) et de CO_2.

4. Appareil selon la revendication 1, dans lequel la composition comprend du HFC-1234yf et au moins un composé choisi parmi le HFC-1234ze (trans), le HFC-1234ze (cis) et le HFC-1243zf.

5. Appareil selon la revendication 1, dans lequel la composition comprend du HFC-1234yf et au moins un composé choisi parmi le HFC-1234ze (trans) et le HFC-32.

6. Appareil selon la revendication 1, dans lequel la composition comprend du HFC-1234yf et au moins un composé choisi parmi le HFC-32 et le CO_2.

7. Appareil selon la revendication 6, dans lequel la composition est constituée de HFC-1234yf et de HFC-32.

8. Appareil selon la revendication 7, dans lequel la composition est constituée de 40 à 99 pour cent en poids de HFC-1234yf et 1 à 60 pour cent en poids de HFC-32, de préférence de 40 à 95 pour cent en poids de HFC-1234yf et 5 à 60 pour cent en poids de HFC-32.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 65854305 **[0001]**
- US 71043905 **[0001]**
- US 73276905 **[0001]**
- US 06204405 **[0043]**
- US 91049504 **[0066]**
- US RE36951 E **[0081]**

Non-patent literature cited in the description

- **J. M. YIN et al.** TEWI Comparison of R744 and R134a Systems for Mobile Air Conditioning. *SAE World Congress,* 01 March 1999 **[0006]**
- Lubricants in Refrigeration Systems. Refrigeration Systems and Applications. 8.1-8.21 **[0037]**
- Synthetic Lubricants and High-Performance Fluids. Marcel Dekker, 1993 **[0038]**