



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2148854 C 2003/03/18

(11)(21) **2 148 854**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(22) **Date de dépôt/Filing Date:** 1991/06/17

(41) **Mise à la disp. pub./Open to Public Insp.:** 1992/01/27

(45) **Date de délivrance/Issue Date:** 2003/03/18

(30) **Priorités/Priorities:** 1990/07/26 (07/558,346) US;
1991/04/05 (07/681,565) US

(51) **Cl.Int.⁶/Int.Cl.⁶** C09K 5/04

(72) **Inventeurs/Inventors:**
BIVENS, DONALD BERNARD, US;
SHIFLETT, MARK BRANDON, US;
YOKOZEKI, AKIMICHI, US

(73) **Propriétaire/Owner:**
E.I. DU PONT DE NEMOURS AND COMPANY, US

(74) **Agent:** DIMOCK STRATTON CLARIZIO LLP

(54) **Titre : MELANGES QUASI-AZEOTROPES POUR UTILISATION COMME REFRIGERANTS**

(54) **Title: NEAR-AZEOTROPIC BLENDS FOR USE AS REFRIGERANTS**

(57) **Abrégé/Abstract:**

Near-Azeotropic blends of: pentafluoroethane and 1,1,1-trifluoroethane with one or more of chlorodifluoromethane, 1,2,2,2-tetrafluoroethane, 1,1,2,2-tetrafluoroethane, 1-chloro-1,1,2,2-tetrafluoroethane, 1-chloro-1,2,2,2-tetrafluoroethane, 1,1,1,2,3,3,3-heptafluoropropane, 1,1,1,2,2,3,3-heptafluoropropane, and perfluorocyclopropane; chlorodifluoromethane and pentafluoroethane with one or more of ethane, butane, isobutane, dimethyl ether, propylene, and difluoromethane; chlorodifluoromethane with 1,1,1-trifluoroethane and 1,2,2,2-tetrafluoroethane, propane and pentafluoroethane, or 1,1,1-trifluoroethane and octafluoropropane; and pentafluoroethane with fluoroethane and 1,2,2,2-tetrafluoroethane, alone with their use as refrigerants.



ABSTRACTTITLENEAR-AZEOTROPIC BLENDS FOR USE AS REFRIGERANTS

5 Near-Azeotropic blends of: pentafluoroethane
and 1,1,1-trifluoroethane with one or more of
chlorodifluoromethane, 1,2,2,2-tetrafluoroethane,
1,1,2,2-tetrafluoroethane, 1-chloro-1,1,2,2-
tetrafluoroethane, 1-chloro-1,2,2,2-tetrafluoroethane,
10 1,1,1,2,3,3,3-heptafluoropropane, 1,1,1,2,2,3,3-
heptafluoropropane, and perfluorocyclopropane;
chlorodifluoromethane and pentafluoroethane with one or
more of ethane, butane, isobutane, dimethyl ether,
propylene, and difluoromethane; chlorodifluoromethane with
15 1,1,1-trifluoroethane and 1,2,2,2-tetrafluoroethane,
propane and pentafluoroethane, or 1,1,1-trifluoroethane
and octafluoropropane; and pentafluoroethane with
fluoroethane and 1,2,2,2-tetrafluoroethane, alone with
their use as refrigerants.

TITLE

NEAR-AZEOTROPIC BLENDS FOR USE AS REFRIGERANTS

5

10

BACKGROUND OF THE INVENTION

The present invention relates to ternary and higher blends of fluorinated hydrocarbons and more specifically to near-azeotrope constant-boiling blends and expands upon refrigerant compositions for cooling and heating applications, as heretofore described in U.S. Patent No. 4,810,403. Such blends are useful as refrigerants, heat transfer media, gaseous dielectrics, expansion agents, aerosol propellants and power cycle working fluids. Concern over the ozone depletion potential of certain halocarbons has resulted in a search for alternative compounds having lower ozone depletion potentials. A present day commercial binary azeotrope refrigerant widely used in supermarket refrigerators consists of 48.8 wt% chlorodifluoromethane (HCFC-22) and 51.2 wt% chloropentafluoroethane (CFC-115) and is generally referred to as Refrigerant-502. Due to the presence of chlorine in CFC-115, CClF_2CF_3 , is expected to be subject to reduced usage because of its high ozone depletion potential. Additionally chlorine containing medium to low temperature refrigerants which may be subject to reduced usage could be replaced with all HFC containing blends described within.

In refrigeration applications, refrigerant is often lost through leaks during operation, such as

through shaft seals, hose connections, solder joints, and broken lines. In addition, refrigerant may be released to the atmosphere during maintenance procedures performed on refrigeration equipment.

5 Most commercial refrigerants which are now used are pure fluids or azeotropes, many of these refrigerants have ozone depletion potentials when released to the atmosphere. Some nonazeotropic blends of refrigerants may also be used but they have the
10 disadvantage of changing composition when a portion of the refrigerant charge is leaked or discharged to the atmosphere. Should these blends contain a flammable component, they could also become flammable due to the change of composition which occurs during the leakage
15 of vapor from refrigeration equipment. Refrigeration equipment operation could also be adversely affected due to this change in composition and vapor pressure which results from fractionation.

 What is needed, therefore, are substitute
20 refrigerants which maintain important refrigerant properties of vapor pressure and nonflammability over a wide range of compositions, while also having reduced ozone depletion potential.

25 SUMMARY OF THE INVENTION

 According to the present invention, near-azeotrope constant-boiling blends have been discovered comprising effective amounts of pentafluoroethane (HFC-125) and 1,1,1-trifluoroethane
30 (HFC-143a) with one or more of the compounds set forth in Table I:

TABLE I

<u>Chemical Name</u>	<u>Generally Accepted Nomenclature</u>
chlorodifluoromethane	HCFC-22
1,1,1,2-tetrafluoroethane	HFC-134a
1,1,2,2-tetrafluoroethane	HFC-134
1-chloro-1,1,2,2-tetrafluoroethane	HFC-124a
1-chloro-1,2,2,2-tetrafluoroethane	HFC-124
1,1,1,2,3,3,3-heptafluoropropane	HFC-227ea
1,1,1,2,2,3,3-heptafluoropropane	HFC-227ca
perfluorocyclopropane	FC-C216

The near-azeotrope constant-boiling compositions are blends of HFC-125 and HFC-143a with any one of HCFC-22, HFC-134a, HFC-134, HFC-124a, HFC-124, HFC-227ea, HFC-227ca, and FC-C216 or mixtures thereof as set forth below. The compositions are chosen such that the blends have vapor pressures substantially equal to the vapor pressure of Refrigerant-502 and other medium to low temperature refrigerants, over a temperature range as encountered in their use as refrigerants such as -50 to 100 degrees Celcius. The compositions have ozone depletion potentials (ODP) and global warming potentials (GWP) of 0 to 0.02 and 0.5 to 1.0 respectively which are substantially lower than the Refrigerant-502 value of 0.25 ODP and 5.1 GWP.

Additional, near-azeotrope constant-boiling blends have been discovered comprising effective amounts of chlorodifluoromethane (HFC-22) and/or pentafluoroethane (HFC-125) with one or more of the compounds set forth in Tables I and II:

TABLE II

<u>Chemical Name</u>	<u>Generally Accepted Nomenclature</u>
propane	HC-290
5 octafluoropropane	FC-218
fluoroethane	HFC-161

10 The near-azeotrope constant-boiling compositions are blends of HCFC-22 with propane and HFC-125, HCFC-22 with HFC-143a and HFC-134a, or HCFC-22 with HFC-143a and FC-218. Also, a near-azeotrope constant-boiling composition is a blend of HFC-125 with HFC-161 and HFC-134a. The compositions are chosen such that the blends have

15 vapor pressures substantially equal to the vapor pressure of Refrigerant-502 and other medium to low temperature refrigerants, over a temperature range as encountered in their use as refrigerants such as -50 to 100 degrees Celcius. The compositions have ozone

20 depletion potentials (ODP) lower than Refrigerant-502, however, blends formulated with octafluoropropane may have global warming potentials lower, or equal to Refrigerant-502 depending on the composition of octafluoropropane.

25 The near-azeotropic blends may also be used to produce heat by condensing the composition in the vicinity of the body to be heated and thereafter evaporating the condensate.

30 The use of near-azeotropic blends minimizes the problem of component fractionation and handling in system operations.

35 Finally, the near-azeotropic blends can be formulated to offer the same advantage as Refrigerant-502 and other medium to low temperature refrigerants as being nonflammable at room temperature and atmospheric pressure.

DETAILED DESCRIPTION OF THE INVENTION

By refrigeration is meant the utilization of physical change in a substance to produce a cooling or heating effect. The physical change can be, for
5 example, a change from the solid state to the liquid state or a change from the liquid state to the vapor state or the reverse order.

By refrigerant is meant the substance which undergoes physical change in refrigeration.

10 By ozone depletion potential is meant the ratio of the calculated ozone depletion in the stratosphere resulting from the emission of a compound compared to the ozone depletion potential resulting from the same rate of emission of CFC-11 which is set
15 at 1.0. A method of calculating ozone depletion potential is described in "The Relative Efficiency of a Number of Halocarbons for Destroying Stratospheric Ozone", by D. J. Wuebbles, Lawrence Livermore Laboratory report UCID-18924, January, 1981, and
20 "Chlorocarbon Emission Scenarios: Potential Impact on Stratospheric Ozone", by D. J. Wuebbles, Journal Geophysics Research, 88, 1433-1443, 1983.

By nonflammable is meant a gas mixture in air which will not burn when subjected to a spark
25 igniter as described in "Limits of Flammability of Gases and Vapours", Bulletin 503, H.F. Coward et al., Washington, U.S. Bureau of Mines, 1952.

By "vapor pressures substantially equal to the vapor pressure of Refrigerant-502 and other medium
30 to low temperature refrigerants" is meant a vapor pressure which is plus or minus twenty-five percent of the vapor pressure of Refrigerant-502 and other medium to low temperature refrigerants at the same temperature within the range of -50 to 100 degrees
35 Celsius.

By substantially lower ozone depletion potential than the ozone depletion of Refrigerant-502 is meant an ozone depletion potential at least fifty percent less than the ozone depletion potential of Refrigerant-502, i.e. less than 0.125.

By substantially lower global warming potential than the global warming potential of Refrigerant-502 is meant a global warming potential at least fifty percent less than the global warming potential of Refrigerant-502, i.e., less than 2.55.

As mentioned above, when a refrigerant blend contains a flammable component, the possibility of either the discharged vapor or the remaining refrigerant upon leakage becoming flammable constitutes a highly undesirable safety hazard. The present compositions can be so formulated that the lowest boiling and highest boiling components are nonflammable so that even when the intermediate boiling component is flammable, not only is the original composition nonflammable, but additionally, neither the leaking vapor nor the remaining refrigerant becomes flammable.

The present invention provides near-azeotropic blends which have vapor pressures near that of Refrigerant-502 and other medium to low temperature refrigerants and surprisingly even after an 80 percent evaporation loss by weight. A vapor pressure/temperature relation similar to that of Refrigerant-502 and other medium to low temperature refrigerants is particularly desirable since much existing refrigeration equipment which has been designed to use Refrigerant-502 and other medium to low temperature refrigerants can also use the refrigerants of the present invention with little or no modification.

The preferred halocarbon components in the blends are listed in the Table III:

TABLE III

5	Refrigerant	Chemical Formula	Boiling		
			Pt (°C)	DP	GWP
	R-502	$\text{CHClF}_2 \text{ CClF}_2\text{CF}_3$	-50.0	.25	5.1
	HFC-125	CHF_2CF_3	48.5	.0	.65
	HFC-143a	CF_3CH_3	-47.6	.0	.76
10	HCFC-22	CHClF_2	-40.8	.05	.37
	HFC-134a	$\text{CF}_3\text{CH}_2\text{F}$	-26.5	.0	.29
	HFC-134	CHF_2CHF_2	-19.7	.0	.30
	HFC-124a	$\text{CHF}_2\text{CClF}_2$	-10.2	.02	.10
	HFC-124	CHClFCF_3	-12.0	.02	.10
15	HFC-227ea	$\text{CF}_3\text{CHF}_2\text{CF}_3$	-18.0	.0	*
	HFC-227ca	$\text{CF}_3\text{CF}_2\text{CHF}_2$	-17.0	.0	*
	HFC-161	CH_3CFH_2	-37.1	.0	*
	FC-C216	$\text{CF}_2\text{CF}_2\text{CF}_2$ (cyclic)	-31.5	.0	*
	FC-218	$\text{CF}_3\text{CF}_2\text{CF}_3$	-36.5	.0	*
20	HC-290	$\text{CH}_3\text{CH}_2\text{CH}_3$	-42.1	.0	*

The blends of the instant invention comprise HCFC-22 and/or HFC-125 with one or more of the others from Table III.

25 The near-azeotropic blends of the instant invention can be prepared by any convenient method including mixing or combining the desired component amounts. A preferred method is to weigh the desired component amounts and thereafter combine them in an appropriate container.

30 The near-azeotropic blends of the present invention have the following compositions:

- 35 to 65, preferably 50 to 60, and most preferably 55.0 weight percent HFC-125; 30 to 60, preferably 35 to 45, and most preferably 40.0

- weight percent HFC-143a; and 3 to 15, preferably 3 to 10, and most preferably 5.0 weight percent HFC-134a.
- 5 - 35 to 65, preferably 50 to 60, and most preferably 55.0 weight percent HFC-125; 30 to 60, preferably 35 to 45, and most preferably 40.0 weight percent HFC-143a; and 3 to 15, preferably 3 to 10, and most preferably 5.0 weight percent HFC-134.
 - 10 - 35 to 65, preferably 50 to 60, and most preferably 55.0 weight percent HFC-125; 30 to 60, preferably 35 to 45, and most preferably 40.0 weight percent HFC-143a; and 3 to 15, preferably 3 to 10, and most preferably 5.0 weight percent HFC-124a.
 - 15 - 35 to 65, preferably 50 to 60, and most preferably 55.0 weight percent HFC-125; 30 to 60, preferably 35 to 45, and most preferably 40.0 weight percent HFC-143a; and 3 to 15, preferably 3 to 10, and most preferably 5.0 weight percent HFC-124.
 - 20 - 35 to 65, preferably 50 to 60, and most preferably 55.0 weight percent HFC-125; 30 to 60, preferably 35 to 45, and most preferably 40.0 weight percent HFC-143a; and 3 to 15, preferably 3 to 10, and most preferably 5.0 weight percent HFC-227ea.
 - 25 - 35 to 65, preferably 50 to 60, and most preferably 55.0 weight percent HFC-125; 30 to 60, preferably 35 to 45, and most preferably 40.0 weight percent HFC-143a; and 3 to 15, preferably 3 to 10, and most preferably 5.0 weight percent HFC-227ca.
 - 30 - 35 to 65, preferably 50 to 60, and most preferably 55.0 weight percent HFC-125; 30 to 60, preferably 35 to 45, and most preferably 40.0 weight percent HFC-143a; and 3 to 15, preferably 3 to 10, and most preferably 5.0 weight percent HFC-227ca.
 - 35 - 35 to 65, preferably 50 to 60, and most preferably 55.0 weight percent HFC-125; 30 to 60,

- preferably 35 to 45, and most preferably 40.0 weight percent HFC-143a; and 3 to 15, preferably 3 to 10, and most preferably 5.0 weight percent FC-C216.
- 5 - 5 to 30, preferably 15 to 25, and most preferably 20.0 weight percent HFC-125; 30 to 60, preferably 30 to 40, and most preferably 35.0 weight percent HFC-143a; and 30 to 55, preferably 40 to 50, and most preferably 45.0 weight percent HCFC-22.
- 10 - 30 to 55, preferably 40 to 50, and most preferably 45.0 weight percent HCFC-22; 30 to 60, preferably 45 to 55, and most preferably 50.0 weight percent HFC-143a; and 3 to 15, preferably 3 to 10, and most preferably 5.0 weight percent HFC-134a.
- 15 - 1 to 98.9, preferably 30 to 85, and most preferably 45 to 65 weight percent HCFC-22; 0.1 to 15, preferably 1 to 10, and most preferably 2 to 5 weight percent propane; and 1 to 98.9, preferably 14 to 69, and most preferably 33 to 53 weight percent HFC-125.
- 20 - 60 to 90, preferably 75 to 85, and most preferably 80.0 weight percent HFC-125; 5 to 20, preferably 10 to 15, and most preferably 15.0 weight percent HFC-161; and 3 to 15, preferably 3 to 10, and most preferably 5.0 weight percent HFC-134a.
- 25 - 30 to 50, preferably 35 to 45, and most preferably 37.0 weight percent HCFC-22; 20 to 60, preferably 25 to 40, and most preferably 28.0 weight percent HFC-143a; and 10 to 45, preferably 30 to 40, and most preferably 35.0 weight percent FC-218.
- 30

35 There are other ternary and higher blends having these desirable characteristics that could be formulated by those skilled in the art from the

halocarbons defined and exemplified herein. For example, other blends that may be formulated for the purposes of this invention are:

5

TABLE IVLiquid Weight Percentage

<u>Blend Components</u>		<u>Acceptable</u>	<u>Preferred</u>	Most <u>Preferred</u>
10	HFC-125/HFC-143a/	35-65/30-60/	45-55/35-45/	50/40/5/5
	HFC-134/HFC-134a	3-15/3-15	3-10/3-10	
	HFC-125/HFC-143a/	35-65/30-60/	35-50/30-40/	40/35/5/20
	HFC-134a/HCFC-22	3-15/30-55	3-10/15-25	
15	HFC-125/HFC-143a/	35-65/30-60	45-55/30-40/	50/35/10/5
	HFC-134a/HFC-124a	3-20/3-15	5-15/3-10	

15

In addition, more than one halocarbon can be selected from each of the temperature ranges. The objective of this description is not to identify every possible blend composition, but to illustrate our discovery of the unexpected properties that the ternary (or higher) blends can take on, depending on the components, and the chosen compositions.

20

The refrigerant of the instant invention can be prepared by a simple mixing process as is well known to those skilled in the art.

25

Specific examples of the present invention will now be set forth. Unless otherwise stated, all percentages are by weight. It is to be understood that these examples are merely illustrative and are in no way to be interpreted as limiting the scope of this invention.

30

EXAMPLE 1

Impact of Vapor Leakage on Vapor Pressure at 24°C.

TABLE V

5	Refrigerant/ Composition	Vapor Pressures		
		0% Evaporated	80% Evaporated	%Change
		psia (KPa)	psia (KPa)	
	R-502	171.1 (1180)	171.1 (1180)	0.0
	HFC-125/HFC-143a/	176.2 (1215)	165.2 (1139)	6.2
10	HFC-134a (55/40/5)			
	HFC-125/HFC-143a/	176.3 (1216)	164.3 (1133)	6.8
	HFC-134 (55/40/5)			
	HFC-125/HFC-143a/	179.0 (1234)	173.4 (1196)	3.1
	HFC-124a (55/40/5)			
15	HFC-125/HFC-143a/	178.2 (1229)	169.1 (1166)	5.1
	HFC-124 (55/40/5)			
	HFC-125/HFC-143a/	179.1 (1235)	171.5 (1182)	4.2
	HFC-227ea (55/40/5)			
	HFC-125/HFC-143a/	179.5 (1238)	174.8 (1205)	2.6
20	FC-C216 (55/40/5)			
	HFC-125/HFC-143a/	170.3 (1174)	160.1 (1104)	6.0 *
	HCFC-22 (20/35/45)			
	HCFC-22/HFC-143a/	160.8 (1109)	156.8 (1081)	4.0
	HFC-134a (45/50/5)			
25	HCFC-22/Propane/	206.3 (1422)	187.4 (1292)	9.2
	HFC-125 (45/10/45)			
	HFC-125/HFC-161/	194.1 (1338)	181.7 (1253)	12.4
	HFC-134a (80/15/5)			
	HCFC-22/HFC-143a/	174.7 (1205)	160.0 (1103)	8.4
30	FC-218 (37/28/35)			

* 87% evaporated

Example 1 demonstrates that all of the
 35 near-azeotropic blends of the present invention
 exhibit very low vapor pressure changes after 80 or

2148854

WO 92/01762

-12-

more percent by weight of the charge was leaked away. This vapor pressure versus leak performance behavior closely approximates that of a Refrigerant-502 alone. The vapor pressure performance indicates that the
5 near-azeotropic blends would maintain their vapor pressure characteristics, even if 80 weight percent of the refrigerant were to be lost.

HFC-227ca is very similar to HFC-227ea and can be substituted therefore in similar proportions.
10

15

20

25

30

35

EXAMPLE 2TABLE VIRefrigerant Performance

5	Refrigerant	Compressor	Exit		
		Capacity	COP	Pressure	Temp
	Composition	Btu/min (kW)*		psia (KPa)	F(°C)
	R-502	80.1(1407)1.89		282(1944)	239(115)
	HFC-125	82.2(1462)1.69		327(2255)	223(106)
	HFC-125/HFC-143a/	82.7(1453)1.82		307(2117)	227(108)
10	HFC-134a (55/40/5)				.8 (.4)
	HFC-125/HFC-143a/	82.6(1451)1.83		307(2117)	229(109)
	HFC-134a (55/40/5)				1.1 (.6)
	HFC-125/HFC-143a/	80.5(1414)1.82		304(2096)	229(109)
	HFC-124 (55/40/5)				2.0(1.0)
15	HFC-125/HFC-143a/	81.4(1430)1.81		307(2117)	226(108)
	HFC-227ea (55/40/5)				1.4 (.7)
	HFC-125/HFC-143a/	85.6(1504)1.93		291(2006)	255(124)
	HCFC-22 (20/35/45)				.7 (.4)
	HCFC-22/HFC-143a/	81.1(1425)1.96		277(1910)	256(123)
20	HFC-134a (45/50/5)				.6 (.3)
	HCFC-22/Propane/	80.1(1407)1.88		290(1999)	253(123)
	HFC-125 (45/10/45)				1.6 (.9)
	HFC-125/HFC-161/	74.5(1309)1.81		294(2027)	239(115)
	HFC-134a (80/15/5)				1.5 (.8)
25	HCFC-22/HFC-143a/	79.4(1395)1.90		282(1944)	232(111)
	FC-218 (35/40/25)				.1 (.1)

Conditions test were run under:

Condenser Temp 115°F (46°C)
 Evaporator Temp -30°F (-34°C)

30 Suction superheated to Temp 95°F (35°C)
 Heat Exchanger used in refrigeration cycle

Compressor Efficiency assumed 1.0

* based on a compressor displacement of 3.5 ft³/min
 (0.099 m³/min)

35 ** represents condensing temperature differential
 across condenser

Example 2 data suggest that the near-azeotropic blends compare quite favorably with the commercial Refrigerant-502 refrigeration performance. Also, pentafluoroethane (HFC-125), the
5 refrigerant recognized by the refrigeration industry as a plausible substitute for Refrigerant-502 has a 10-15 percent decrease in energy efficiency. Energy efficiency is measured by coefficient of performance (COP). Therefore, the present blends of
10 chlorodifluoromethane (HCFC-22) and/or pentafluoroethane (HFC-125) with one or more additional components exhibit a substantial improvement in energy efficiency. All the blends have better energy efficiencies than pentafluoroethane
15 (HFC-125) alone and some better than Refrigerant-502.

HCFC-124a is very similar to HCFC-124 and can be substituted therefore in similar proportions, HFC-227ca is very similar to HFC-227ea and can be substituted therefore in similar proportions, and
20 FC-C216 can be substituted as a third component giving similar refrigeration performance.

EXAMPLE 3 - COMPARATIVE EXAMPLE

A blend was prepared consisting of liquid
25 concentrations of 57.9% pentafluoroethane (HFC-125) and 42.1% 1,1,1-trifluoroethane (HFC-143a). The vapor pressure of the blend was 185.5 psia (1279 KPa) at 24 deg Celcius. After 84.6% of the initial blend charge was lost via a vapor leak, the liquid composition had
30 changed to 53.2% HFC-125 and 46.8% HFC-143a. The vapor composition of HFC-143a was 39.1% initially and increased to 44.3%. The vapor pressure decreased to 172.5 psia (1189 KPa). The conclusion of this test was the HFC-143a composition would continue to
35 increase during the remainder of the leak and this blend will become flammable; therefore, a third

component is necessary when blending HFC-125 and HFC-143a to prevent the blend from becoming flammable.

EXAMPLE 4 - COMPARATIVE EXAMPLE

5 A blend was prepared consisting of liquid
concentrations of 55.8% pentafluoroethane (HFC-125),
38.4% 1,1,1-trifluoroethane (HFC-143a), and 5.8%
1,2,2,2-tetrafluoroethane (HFC-134a). The ozone
10 depletion potential of the blend is 0 and the global
warming potential was calculated to be 0.68. Compared
with Refrigerant-502 the blend has no ozone depletion
potential and a 87% reduction in global warming
potential. The vapor pressure was within 5% of the
15 vapor pressure of Refrigerant-502 over the temperature
range of -50 - 100 deg Celcius. At 24 deg Celcius,
the blend had a vapor pressure of 176.2 psia (1215
KPa) compared with a vapor pressure of 171.1 psia
(1180 KPa) for Refrigerant-502.

20 To illustrate the surprisingly small changes
in vapor pressure with compositional changes that
occur during vapor leaks, vapor was allowed to leak
from a suitable container holding the liquid blend and
equilibrium vapor. After 96% of the initial blend
25 charge had been lost via the vapor leak, the liquid
compositions had changed to 45.9% HFC-125, 37.3%
HFC-143a, and 16.8% HFC-134a. The vapor pressure
after an 80% leak had decreased to 165.2 (1139 KPa) at
24 deg Celcius, being within 3.5% of the
Refrigerant-502 vapor pressure.

30 To illustrate the nonflammability of the
blend, liquid and vapor samples were analyzed at the
beginning and end of the leak test as well as vapor
samples taken at blend charge weight losses of 5 to
95% in increments of 5%. The highest HFC-143a
35 concentration was 39.2% in the vapor at 69.6% weight
loss. At this point, the total vapor content was

53.8% HFC-125, 39.2% HFC-143a, and 7.0% HFC-134a. The lower flammability limit at this point of HFC-125 and HFC-143a is above 39.2% at room temperature, therefore, with only 39.2% HFC-143a the blend is nonflammable at room temperature and atmospheric pressure.

EXAMPLE 5 - COMPARATIVE EXAMPLE

Another blend was prepared consisting of liquid compositions of 53.7% pentafluoroethane (HFC-125), 41.0% 1,1,1-trifluoroethane (HFC-143a), and 5.3% 1,1,2,2-tetrafluoroethane (HFC-134). The ozone depletion potential of the blend is 0 and the global warming potential was calculated to be 0.68. Compare with Refrigerant-502 the blend has no ozone depletion potential and a 87% reduction in global warming potential. The vapor pressure of the blend was 176.3 psia (1216 KPa) at 24 deg Celcius compared with 171.1 psia (1180 KPa) for Refrigerant-502. After 97.7% of the initial blend charge was lost via a vapor leak, the liquid compositions had changed to 43.3% HFC-125, 39.0% HFC-143a, and 17.7% HFC-134. The vapor pressure after 80% leak had decreased to 164.3 psia (1133 KPa) at 24 deg Celcius, being within 6.4% of the Refrigerant-502 vapor pressure. The highest HFC-143a concentration was 42.7% in the vapor at 85% weight loss. At this point, the total vapor content was 51.0% HFC-125, 42.7% HFC-143a, and 6.3% HFC-134. Again, experimentally, the maximum nonflammable concentration of HFC-143a in HFC-125 at any air concentration is above 42.7% at room temperature; therefore, with only 42.7% HFC-143a, the blend is nonflammable at room temperature and atmospheric pressure.

EXAMPLE 6 - COMPARATIVE EXAMPLE

Another blend was prepared consisting of liquid compositions of 20.7% pentafluoroethane (HFC-125), 35.7% 1,1,1-trifluoroethane (HFC-143a), and 43.6% chlorodifluoromethane (HCFC-22). The ozone depletion potential was calculated to be 0.02 and the global warming potential 0.56. A 92% and 89% reduction in ozone depletion and global warming potentials, respectively. The vapor pressure of the blend was 170.3 psia (1174 KPa) at 24 deg Celcius compared with 171.1 psia (1180 KPa) for Refrigerant-502. After 87 % of the initial blend charge was lost via a vapor leak, the liquid composition had changed to 8.6% HFC-125, 30.3% HFC-143a, and 61.1% HCFC-22. The vapor pressure had decreased to 160.1 psia (1104 KPa) at 24 deg Celcius being within 6.5% of the Refrigerant-502 vapor pressure. The highest HFC-143a concentration was 36.9% in the vapor at 46.4% weight loss, again being a nonflammable blend at room temperature and atmospheric pressure.

EXAMPLE 7 - COMPARATIVE EXAMPLE

A blend was prepared consisting of liquid concentrations of 37.2% chlorodifluoromethane (HCFC-22), 28.1% 1,1,1-trifluoroethane (HFC-143a), and 34.7% octafluoropropane (FC-218). The ozone depletion of the blend is 0.02 and the global warming potential is dependent on the concentration of FC-218. Compared with Refrigerant-502 the blend has lower ozone depletion potential and may be formulated to have lower or equal global warming potential to Refrigerant-502. At 24 deg Celcius, the blend had a vapor pressure of 174.7 psia (1205 KPa) compared with the vapor pressure of 171.1 psia (1180 KPa) for Refrigerant-502.

To illustrate the surprisingly small changes in vapor pressure with compositional changes that occur during vapor leaks, vapor was allowed to leak from a suitable container holding the liquid blend and equilibrium vapor. After 95.6% of the initial blend charge had been lost via the vapor leak, the liquid compositions had changed to 50.3% HCFC-22, 30.3% HFC-143a, and 19.4% FC-218. The vapor pressure after an 80% leak had decreased to 168.4 psia (1161 KPa) at 24 deg Celcius, being within 2% of the Refrigerant-502 vapor pressure. Due to the increase in HFC-143a liquid composition the vapor was allowed to continue leaking. Initial liquid compositions were again measured at 50.7% HCFC-22, 30.9% HFC-143a, and 18.4% FC-218. After 94.5% of the blend charge at the above liquid compositions had been lost after further evaporation via a vapor leak, the liquid compositions had changed to 74.0% HCFC-22, 25.4% HFC-143a, and 0.6% FC-218. Again, the vapor pressure after an 80% leak had decreased to 160.0 psia (110 3 KPa) at 24 deg Celsius, being within 6.5% of the Refrigerant-502 vapor pressure.

To illustrate the nonflammability of the blend, liquid and vapor samples were analyzed at the beginning and end of both leak tests as well as vapor samples taken at blend charge weight losses of 5 to 95% in increments of 5%. The highest HFC-143a concentration was 33.4% in the vapor at 78.8% weight loss during the continued leak test. At this point, the total vapor content was 56.4% HCFC-22, 33.4% HFC-143a, and 10.2% FC-218. Experimentally, the maximum nonflammable concentration of HFC-143a in HFC-125 at any air concentration is above 33.4% HFC-143a at room temperature, therefore, with only 33.4% HFC-143a, the blend is nonflammable at room temperature and atmospheric pressure.

EXAMPLE 8 - COMPARATIVE EXAMPLE

A commercial icemaker was used to evaluate the performance of the near-azeotrope blends with Refrigerant-502. High and low side pressure were measured as well as inlet and exit temperature around the condenser, evaporator, and compressor. The energy consumption was measured and the quality and quantity of ice produced. For similar operating conditions the blends of HCFC-22/HFC-143a/HFC-125, HFC-125/HFC-143a/HFC-134a, and HFC-125/Propane/HCFC-22 performed essentially the same as Refrigerant-502.

EXAMPLE 9 - COMPARATIVE EXAMPLE

A study shows that a mixture of HCFC-22, propane, and HFC-125 at the following composition is constant boiling. Allowing 50 weight percent of the mixture to leak out as vapor at room temperature the vapor pressure changes less than 10 percent. (IQ) is initial liquid composition, (FQ) is final liquid composition, (1-5) is vapor compositions, (VP) is vapor pressure, (DP) is change in vapor pressure from original mixture, and (leakage) represents the weight % leakage.

TABLE VII

<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
		<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
IQ	0	90.0	8.0	2.0	164.3	---
1	10	84.6	11.8	3.5	163.3	0.6
2	20	85.7	11.1	3.2	162.3	1.2
3	30	86.8	10.4	2.8	161.3	1.8
4	40	88.1	9.5	2.4	160.1	2.6
5	50	89.4	8.6	2.0	159.0	3.2
FQ	50	93.7	5.3	1.0	159.0	3.2

TABLE VIII

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
5	IQ	0	70.0	28.0	2.0	178.8	---
	1	10	60.7	35.9	3.4	177.5	0.7
	2	20	62.1	34.8	3.0	176.2	1.5
	3	30	63.7	33.6	2.8	174.8	2.2
	4	40	65.5	32.1	2.4	173.1	3.2
	5	50	67.6	30.3	2.1	171.4	4.1
10	FQ	50	77.2	21.8	1.1	171.4	4.1

TABLE IX

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
15	IQ	0	50.0	48.0	2.0	191.3	---
	1	10	41.9	54.8	3.3	190.2	0.6
	2	20	42.9	54.1	3.0	189.0	1.2
	3	30	44.0	53.2	2.7	187.8	1.8
	4	40	45.4	52.2	2.4	186.3	2.6
	5	50	47.1	50.9	2.1	184.6	3.5
20	FQ	50	56.6	42.3	1.1	184.6	3.5

TABLE X

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
25	IQ	0	30.0	68.0	2.0	201.8	---
	1	10	25.5	71.1	3.4	200.9	0.4
	2	20	26.0	70.9	3.1	199.9	0.9
	3	30	26.6	70.6	2.8	198.9	1.4
	4	40	27.4	70.2	2.4	197.7	2.0
	5	50	28.2	69.7	2.1	196.5	2.6
30	FQ	50	33.6	65.3	1.1	196.5	2.6

-21-

TABLE XI

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
	IQ	0	10.0	88.0	2.0	209.8	---
5	1	10	9.1	87.2	3.7	208.8	0.5
	2	20	9.3	87.5	3.3	207.7	1.0
	3	30	9.4	87.7	2.9	206.7	1.5
	4	40	9.6	88.0	2.4	205.4	2.1
	5	50	9.8	88.2	2.0	204.2	2.7
10	FQ	50	10.6	88.4	0.9	204.2	2.7

TABLE XII

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
15	IQ	0	80.0	5.0	15.0	180.2	---
	1	10	74.0	7.7	18.3	179.7	0.3
	2	20	74.8	7.2	18.0	179.1	0.6
	3	30	75.8	6.6	17.6	178.5	0.9
	4	40	76.9	6.0	17.2	177.7	1.4
20	5	50	78.1	5.3	16.6	176.8	1.9
	FQ	50	84.5	3.2	12.3	176.8	1.9

TABLE XIII

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
25	IQ	0	60.0	25.0	15.0	196.9	---
	1	10	50.1	33.1	16.7	195.9	0.5
	2	20	51.5	31.9	16.6	194.9	1.0
	3	30	53.0	30.5	16.5	193.8	1.6
30	4	40	54.8	28.9	16.3	192.4	2.3
	5	50	56.9	27.0	16.1	190.8	3.1
	FQ	50	67.7	18.8	13.4	190.8	3.1

2148854

WO 92/01762

-22-

TABLE XIV

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
	IQ	0	40.0	45.0	15.0	211.7	---
5	1	10	31.6	52.4	16.0	211.0	0.3
	2	20	32.5	51.5	16.0	210.2	0.7
	3	30	33.6	50.5	15.9	209.2	1.2
	4	40	35.0	49.2	15.8	208.1	1.7
	5	50	36.6	47.8	15.6	206.7	2.4
10	FQ	50	47.0	39.0	14.1	206.7	2.4

TABLE XV

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
15	IQ	0	20.0	65.0	15.0	224.9	---
	1	10	15.6	68.4	16.0	224.6	0.1
	2	20	16.1	68.0	15.9	224.2	0.3
	3	30	16.6	67.6	15.8	223.7	0.5
	4	40	17.2	67.1	15.7	223.1	0.8
20	5	50	18.0	66.5	15.5	222.4	1.1
	FQ	50	23.6	62.2	14.1	222.4	1.1

TABLE XVI

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
25	IQ	0	1.0	97.0	2.0	212.1	---
	1	10	1.0	95.2	3.8	210.9	0.6
	2	20	1.0	95.6	3.4	209.6	1.2
	3	30	1.0	96.1	2.9	208.3	1.8
30	4	40	1.0	96.5	2.5	206.9	2.5
	5	50	1.0	97.0	2.0	205.4	3.2
	FQ	50	1.0	98.1	0.9	205.4	3.2

2148854

WO 92/01762

-23-

TABLE XVII

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
	IQ	0	97.0	1.0	2.0	158.7	---
5	1	10	94.8	1.6	3.6	158.0	0.4
	2	20	95.3	1.4	3.3	157.4	0.8
	3	30	95.8	1.3	2.9	156.7	1.3
	4	40	96.4	1.2	2.4	155.9	1.8
	5	50	96.9	1.1	2.0	155.2	2.2
10	FQ	50	98.4	0.6	1.0	155.2	2.2

TABLE XVIII

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
15	IQ	0	98.9	1.0	0.1	152.5	---
	1	10	98.2	1.6	0.2	152.4	0.1
	2	20	98.4	1.5	0.1	152.3	0.1
	3	30	98.5	1.3	0.1	152.2	0.2
	4	40	98.7	1.2	0.1	152.1	0.3
20	5	50	98.9	1.0	0.1	152.0	0.3
	FQ	50	99.3	0.6	0.1	152.0	0.3

TABLE XIX

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
25	IQ	0	49.95	49.95	0.1	184.5	---
	1	10	42.7	57.1	0.2	184.0	0.3
	2	20	43.5	56.3	0.2	183.4	0.6
	3	30	44.5	55.3	0.2	182.7	1.0
30	4	40	45.7	54.1	0.2	181.9	1.4
	5	50	47.2	52.7	0.1	181.0	1.9
	FQ	50	56.0	43.9	0.1	181.0	1.9

TABLE XX

	<u>SAMPLE</u>	<u>LEAKAGE</u>	<u>COMPOSITION (Weight %)</u>			<u>VP</u> <u>(psia)</u>	<u>DP</u> <u>(%)</u>
			<u>HCFC-22</u>	<u>HFC-125</u>	<u>Propane</u>		
	IQ	0	1.0	98.9	0.1	199.9	---
5	1	10	1.0	98.8	0.2	199.8	0.1
	2	20	1.0	98.8	0.2	199.7	0.1
	3	30	1.0	98.9	0.1	199.6	0.2
	4	40	1.0	98.9	0.1	199.5	0.2
	5	50	1.0	98.9	0.1	199.4	0.3
10	FQ	50	1.0	98.9	0.1	199.4	0.3

EXAMPLE 10

Additional fluorocarbons, ethers, and hydrocarbons can be added to HCFC-22 and HFC-125 comprising effective amounts of ethane, butane, isobutane, dimethyl ether (DME), propylene, and difluoromethane (HFC-32) to make mixtures which are constant-boiling and could be useful as replacements for Refrigerant-502 and other medium-to-low-temperature refrigerants. This Example is not intended to identify all compositions of these constant-boiling mixtures, but rather to show that these mixtures are constant boiling.

A study shows that mixtures of HCFC-22 and HFC-125 with the following additional compounds in varying amounts in Table XXI form constant-boiling mixtures.

Impact of Vapor Leakage on Vapor Pressure at 25°C

TABLE XXI

		Vapor Pressures		
5	Refrigerant/ Composition	0% Evaporated	50% Evaporated	%Change
		psia	psia	
	HCFC-22/HFC-125/ Ethane (49/49/2)	206.7	187.7	9.2
	HCFC-22/HFC-125/ Butane (49/49/2)	181.8	177.1	2.6
10	HCFC-22/HFC-125/ Isobutane (49/49/2)	183.4	179.5	2.1
	HCFC-22/HFC-125/ DME (49/49/2)	178.2	170.0	4.6
15	HCFC-22/HFC-125/ Propylene (49/49/2)	186.1	182.1	2.1
	HCFC-22/HFC-125/ HFC-32 (40/40/20)	216.6	210.0	3.0
20	Additional components from Table I, II, or III could be added to form quaternary and greater mixtures. For example, a mixture of HCFC-22/HFC-125/HFC-32/HFC-134a and/or HFC-134 could be formed.			

25

30

35

- 26 -

1. A near-azeotropic composition consisting essentially of pentafluoroethane and/or
5 chlorodifluoromethane selected from the group consisting of 35 to 65 percent by weight pentafluoroethane, 30 to 60 percent by weight 1,1,1-trifluoroethane, and 3 to 15 percent by weight 1-chloro-1,1,2,2-tetrafluoroethane; 35 to 65 percent by
10 weight pentafluoroethane, 30 to 60 percent by weight 1,1,1-trifluoroethane, and 3 to 15 percent by weight 1-chloro-1,1,1,2-tetrafluoroethane; 35 to 65 percent by weight pentafluoroethane, 30 to 60 percent by weight 1,1,1-trifluoroethane, and 3 to 15 percent by
15 weight 1,1,1,2,3,3,3-heptafluoropropane; 35 to 65 percent by weight pentafluoroethane, 30 to 60 percent by weight 1,1,1-trifluoroethane, and 3 to 15 percent by weight 1,1,1,2,2,3,3-heptafluoropropane; 35 to 65 percent by weight pentafluoroethane, 30 to 60 percent
20 by weight 1,1,1-trifluoroethane, and 3 to 15 percent by weight hexafluorocyclopropane; 5 to 8.6 percent by weight pentafluoroethane, 30 to 60 percent by weight 1,1,1-trifluoroethane, and 40 to 50 percent by weight chlorodifluoromethane; 30 to 55 percent by weight
25 chlorodifluoromethane, 30 to 60 percent by weight 1,1,1-trifluoroethane, and 3 to 15 percent 1,1,1,2-tetrafluoroethane;

- 27 -

- 60 to 90 percent by weight
- 5 pentafluoroethane, 5 to 20 percent by weight
fluoroethane, and 3 to 15 percent by weight 1,1,1,2-
tetrafluoroethane; 30 to 50 percent by weight
chlorodifluoromethane, 20 to 60 percent by weight
1,1,1-trifluoroethane, and 10 to 45 percent by weight
- 10 octafluoropropane; 35 to 65 percent by weight
pentafluoroethane, 30 to 60 percent by weight 1,1,1-
trifluoroethane, 3 to 15 percent by weight 1,1,1,2-
tetrafluoroethane, and 30 to 55 percent by weight
chlorodifluoromethane; 35 to 65 percent by weight
- 15 pentafluoroethane, 30 to 60 percent by weight 1,1,1-
trifluoroethane, 3 to 20 percent by weight 1,1,1,2-
tetrafluoroethane, and 3 to 15 percent by weight 1-
chloro-1,1,2,2-tetrafluoroethane;
- 35 to 65 percent by weight chlorodifluoromethane,
- 20 34 to 64 percent by weight pentafluoroethane and
1 to 15 percent by weight dimethyl ether; 15 to
85 percent by weight

25

30

- 28 -

chlorodifluoromethane, 10 to 80 percent by weight pentafluoroethane and 5
5 to 45 percent by weight difluoromethane;
provided that in all cases the composition comprises components whose
weight percentages total 100.

2. A process for producing refrigeration which comprises evaporating
10 a composition as claimed in claim 1 in the vicinity of a body to be cooled.

3. Use of a composition as claimed in claim 1 as a replacement for
refrigeration R502 wherein R502 consists of about 48.8 weight percent
chlorodifluoromethane (HCFC-22) and about 51.2 weight percent
15 chloropentafluoroethane (CFC-115).