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EXAMPLE 4

The performances of two R125/R134a/pentane compositions were evaluated using standard refrigeration cycle analysis techniques in order to assess their suitability as extenders for R22 in hermetic or semi-hermetic systems. The operating conditions selected for the analyses are typical of those conditions found in air conditioning systems. Since the blends were zeotropes the midpoints of their temperature glides in the evaporator and condenser were chosen to define the temperature limits of the cycle and were also used to generate the performance of R22 for comparison.

The pentane was present at 4% by weight based on the total weight of the R125/R134a blend. To simplify the calculation this small amount of pentane was omitted.

The following R22 extender compositions were subjected to cycle analysis:

1. A composition comprising 64% R125: 36% R134a.
2. A composition comprising 44% R125: 56% R134a.

To establish the effects on unit performance resulting from successive dilutions of R22 by the above extenders the cycle was analysed for refrigerant compositions containing mass fractions of R22 from 1.0 down to 0.0. The results are summarised in Tables 4a and 4b. Key parameters are plotted in Chart 1 with the calculated points connected by smooth curves.

The following cycle conditions were used in the analysis:

COOLING DUTY	10 kW
EVAPORATOR	
Midpoint fluid evaporation temperature	7.0 °C
Superheating	5.0 °C
Suction line pressure drop (in saturated temperature)	1.5 °C

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CONDENSER

Midpoint fluid condensing temperature	45.0 °C
Subcooling	5.0 °C
Exhaust line pressure drop (in saturated temperature)	1.5 °C

LIQUID LINE

Electric motor efficiency	0.85
Compressor isentropic efficiency	0.7
Compressor volumetric efficiency	0.82

PARASITIC POWER

Indoor fan	0.3 kW
Outdoor fan	0.4 kW
Controls	0.1 kW

All compositions have lower exhaust temperatures than R22 and are therefore superior on this account.

Composition 1 provides a cooling capacity greater than 90% of that of R22 over the whole of the dilution range. Blends containing more than 45% R22 have capacities equal to or better than that of R22. The COP (system) is within 2% of that of R22 over the whole of the dilution range. This composition therefore meets the requirements of this invention.

Composition 2 provides a cooling capacity greater than that 90% of R22 for blends containing down to 20% of R22. Its COP (system) is essentially the same as that of R22 over the whole of the dilution range. This composition therefore meets the requirements of this invention for blends containing down to 20% R22.

EXAMPLE 5

An R32/R134a/pentane composition was evaluated using standard refrigeration cycle analysis techniques to assess its suitability as an extender for R22 in hermetic or

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semi-hermetic systems. The operating conditions selected for the analysis are typical of those conditions found in air conditioning systems. Since the blend was a zeotrope the midpoints of its temperature glides in the evaporator and condenser were chosen to define the temperature limits of the cycle. The same temperatures were also used to generate performance data for R22.

The pentane was present at 4% by weight based on the total weight of the R32/R134a blend. To simplify the calculation this small amount of pentane was omitted.

The following R22 extender composition was subjected to cycle analysis:
A composition comprising 44% R125 by weight, 56% by weight R134a.

To establish the effect on unit performance resulting from successive dilutions of R22 by topping up with the above extender the cycle was analysed for refrigerant compositions containing mass fractions of R22 from 1.0 down to 0.0. The results are shown in Table 5 and the results plotted out in Chart 2 with the calculated points connected by smooth curves.

The following cycle conditions were used in the analysis:

EVAPORATOR

Midpoint fluid evaporation temperature	7.0 °C
Superheating	5.0 °C
Suction line pressure drop (in saturated temperature)	1.5 °C

CONDENSER

Midpoint fluid condensing temperature	45.0 °C
Subcooling	5.0 °C
Exhaust line pressure drop (in saturated temperature)	1.5 °C

LIQUID LINE/SUCTION LINE HEAT EXCHANGER

Efficiency	0.3
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COMPRESSOR

Electric motor efficiency	0.85
Compressor isentropic efficiency	0.7
Compressor volumetric efficiency	0.82

PARASITIC POWER

Indoor fan	0.3 kW
Outdoor fan	0.4 kW
Controls	0.1 kW

All blends containing the extender have lower exhaust temperatures than R22 and therefore meet the requirements of this specification. The COP (system) is essentially equal to that of R22 over the whole of the dilution range. The cooling capacity of the refrigerant is not less than 98% of that of R22 over the whole of the dilution range. For dilutions down to 20% of R22 the capacity is equal to or greater than that of R22. The exhaust pressure is less than the 0.5 bar above that of R22 over the whole of the dilution range.

The results of analysing the performance of an air-conditioning unit using these operating conditions are shown in Table 5.

R32/R134a 30/70 therefore meets the requirements of this invention.

EXAMPLE 6

An R32/R125/R134a/pentane composition was evaluated using standard refrigeration cycle analysis techniques program to assess its suitability as an extender for R22 in hermetic or semi-hermetic systems. The operating conditions selected for the analysis are typical of those conditions found in air conditioning systems. Since the blend was a zeotrope the midpoints of its temperature glides in the evaporator and condenser were chosen to define the temperature limits of the cycle. The same temperatures were also used to generate performance data for R22.

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The pentane was present at 4% by weight based on the total weight of the R32/R134a blend.

To simplify the calculation this small amount of pentane was omitted.

The following R22 extender composition was subjected to cycle analysis:

A composition comprising 23% by weight of R 32, 25%R125 by weight and 52% by weight R134a.

To establish the effect on unit performance resulting from successive dilutions of R22 by topping up with the above extender the cycle was analysed for refrigerant compositions containing mass fractions of R22 from 1.0 down to 0.0. The results are shown in Table 6 and the results plotted out in Chart 3 with the calculated points connected by smooth curves.

The following cycle conditions were used in the analysis:

EVAPORATOR

Midpoint fluid evaporation temperature	7.0 °C
Superheating	5.0 °C
Suction line pressure drop (in saturated temperature)	1.5 °C

CONDENSER

Midpoint fluid condensing temperature	45.0 °C
Subcooling	5.0 °C
Exhaust line pressure drop (in saturated temperature)	1.5 °C

LIQUID LINE/SUCTION LINE HEAT EXCHANGER

Efficiency	0.3
------------	-----

COMPRESSOR

Electric motor efficiency	0.8
Compressor isentropic efficiency	0.7
Compressor volumetric efficiency	0.82

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PARASITIC POWER

Indoor fan	0.3
Outdoor fan	0.4 kW
Controls	0.1 kW

The results of analysing the performance of an air-conditioning unit using these operating conditions are shown in Table 6.

All blends containing the extender have lower exhaust temperatures than R22 and therefore meet the requirements of this specification. The COP (system) is not less than 98% of that of R22 over the whole of the dilution range. The cooling capacity of the refrigerant is greater than of that of R22 over the whole of the dilution range. The exhaust pressure is less than the 2.0 bar above that of R22 over the whole of the dilution range.

R32/R134a in the ratio 30/70 therefore meets the requirements of this invention.

EXAMPLE 7

Refrigerant compositions comprising R 125, R 134a and hydrocarbon mixtures in commercial heat pump applications were assessed using a Comfort Aire model PHEC-60-1a 5 ton rooftop heat pump with a nominal cooling capacity of 56,000 btu and nominal heating capacity of 56,000 btu. An oil sight-glass was installed on the hermetic compressor and temperature sensors were installed on the suction and discharge lines and on the liquid line. Suction and discharge gauges were also installed.

The system was operated in both the cooling and heating mode with R 22 and the following data was recorded: voltage, amperage, suction pressure, suction temperature, discharge pressure, discharge temperature, liquid line temperature, evaporator temperature, ambient temperature, oil level and return supply air temperature. The R 22 charge was recovered and replaced successively with blends 1 to 6 of the following compositions.

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	R-125	R-134a	Pentane	Isopentane	Butane
Blend #1	64%	34%	2%		
Blend #2	70%	28%	2%		
Blend #3	55%	43%	2%		
Blend #4	60.5%	37.5%	2%		
Blend #5	45%	52%		1%	2%
Blend #6	55%	42%		1%	2%

It was observed that oil return was similar to R 22 operating levels with all of the blends employed, indicating that pentane and isopentane/butane additives provided proper oil return. Some blends required addition of up to 20% refrigerant to prevent icing of the evaporator. Capacities were found to vary with the composition employed. The energy consumption was generally lower with all blends. Discharge pressures were slightly higher on average with blends that exceeded 60.5% R 125 and lower with blends containing less than 60.5% R 125. The suction pressures and discharge temperatures were lower with all blends used. The superheat measured at the evaporator outlet was much higher than R 22 and the temperature difference across the evaporator was generally greater in the cooling mode and less in the heating mode. It was noted that pentane and isopentane/butane additives provided the necessary oil return. Blends #3, 5 and 6 provided the closest similarities to R 22 operational temperatures and pressures.

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CLAIMS

1. A refrigerant composition comprising 1,1,1,2-tetrafluoroethane (R 134a), pentafluoroethane (R 125) and an additive selected from a saturated hydrocarbon or mixture thereof boiling in the range -5 to $+70^{\circ}\text{C}$; wherein the weights of R 125 to R 134a is in the ranges:

R 125 50 - 80%

R 134a 50 - 20%

2. A refrigerant composition as claimed in claim 1, wherein the weights are in the ranges:

R 125 60 - 80%

R134a 40 - 20%

3. A refrigerant composition as claimed in claim 2, wherein the weights are in the ranges:

R 125 60 - 78%

R 134a 40 - 22%

4. A refrigerant composition as claimed in claim 3, wherein the weights are in the ranges:

R 125 64 - 76%

R 134a 36 - 24%

5. A refrigerant composition as claimed in claim 1, wherein the weights are in the ranges:

R 125 57 - 78%

R 134a 43 - 22%

6. A refrigerant composition as claimed in claim 5, wherein the weights are in the ranges:

R 125 63 - 76%

R 134a 37 - 24%

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7. A refrigerant composition as claimed in any preceding claim, wherein the hydrocarbon additive is selected from the group consisting of 2-methylpropane, 2,2-dimethylpropane, butane, pentane, 2-methylbutane, cyclopentane, hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, methylcyclopentane and mixtures thereof.
8. A refrigerant composition as claimed in any preceding claim, wherein the hydrocarbon additive has a boiling point in the range of 20 to 40°C.
9. A refrigerant composition as claimed in claim 8, wherein the hydrocarbon additive is selected from: n-pentane, cyclopentane, iso-pentane and mixtures thereof.
10. A refrigerant composition as claimed in claim 9, wherein the hydrocarbon additive is n-pentane.
11. A refrigerant composition as claimed in claim 9 or 10, wherein the additive further comprises butane.
12. A refrigerant compositions as claimed in claim 11, wherein the ratio of pentane : butane is 1 : 3 to 1 : 8, preferably about 1 : 5.
13. A refrigerant composition as claimed in any preceding claim, wherein the amount of hydrocarbon additive is from a trace to 10%.
14. A refrigerant composition as claimed in claim 13, wherein the amount of hydrocarbon additive is 1 to 8%.
15. A refrigerant composition as claimed in claim 14, wherein the amount of hydrocarbon additive is 2 to 4%.

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16. A refrigerant composition as claimed in any of claims 1 to 15 together with a proportion of R 22.

17. A refrigerant extender mixture comprising a refrigerant composition as claimed in any preceding claim.

18. A method of modifying a refrigerator or air conditioning system which incorporates R 22 as refrigerant, the method comprising the step of adding a refrigerant extender as claimed in claim 17 to the refrigerant of the system.

19. Use of a refrigerant composition as an extender to R 22, wherein the hydrofluorocarbon component comprises R 32, R 125 and R 134a wherein the ratio of weights of R 32, R 125 and R 134a are in the ranges:

R 32	18 - 28%
R 125	20 - 30%
R 134a	42 - 62%

Table 1

Refrigerant % by weight	R-22	1. 125/134a 44/56	2. 125/134a 56/44	3. 125/134a 64/36	4. 125/134a 76/24	5. 125/134a 80/20
Discharge pressure (bar)	17.91	15.89	17.19	18.13	19.68	20.23
Discharge temperature (°C)	104.68	79.75	78.51	77.60	76.07	75.51
COP (system)	2.49	2.50	2.47	2.45	2.41	2.40
Capacity (kW/m ³)	3066	2581	2747	2862	3041	3102
Glide in evaporator (°C)	0	3.06	3.17	3.03	2.47	2.19
Glide in condenser (°C)	0	2.97	2.94	2.71	2.09	1.81

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Table 2

Refrigerant % by weight	R-22	1. 125/134a 44/56	2. 125/134a 56/44	3. 125/134a 64/36	4. 125/134a 76/24	5. 125/134a 80/20
Discharge pressure (bar)	17.91	15.89	17.19	18.13	19.68	20.23
Discharge temperature (°C)	92.9	72.8	71.9	71.2	70.1	69.7
COP (system)	2.59	2.57	2.54	2.52	2.48	2.47
Capacity (kW/m ³)	3222	2669	2838	2956	3138	3200
Glide in evaporator (°C)	0	3.06	3.17	3.03	2.47	2.19
Glide in condenser (°C)	0	2.97	2.94	2.71	2.09	1.81

Table 3

Refrigerant % by weight	R-22	1. 125/134a 44/56	2. 125/134a 56/44	3. 125/134a 64/36	4. 125/134a 76/24	5. 125/134a 80/20
Discharge pressure (bar)	17.91	15.89	17.19	18.13	19.68	20.23
Discharge temperature (°C)	94.63	71.81	70.63	69.71	68.082	67.47
COP (system)	2.45	2.42	2.39	2.37	2.33	2.36
Capacity (kW/m ³)	3077	2535	2692	2800	2965	3021
Glide in evaporator (°C)	0	2.88	2.99	2.87	2.34	2.07
Glide in condenser (°C)	0	2.97	2.94	2.71	2.09	1.81

Table 4a R125/R134a 64%/36% as Extender for R22

Refrigerant % R22 by weight	0	10	20	30	40	50	60	70	80	90	100
Discharge pressure (bar)	18.13	18.47	18.69	18.81	18.84	18.80	18.70	18.56	18.37	18.15	17.91
Discharge temperature (°C)	77.6	79.7	81.8	84.0	86.4	89.0	91.7	94.6	97.8	101.1	104.7
COP (system)	2.45	2.45	2.46	2.46	2.47	2.47	2.48	2.48	2.49	2.49	2.49
Capacity (kW/m ³)	2862	2937	2996	3042	3074	3096	3107	3108	3101	3087	3069
Glide in evaporator (°C)	3.03	2.91	2.66	2.36	2.04	1.73	1.41	1.08	0.75	0.39	0
Glide in condenser (°C)	2.71	2.55	2.31	2.06	1.80	1.54	1.28	1.09	0.71	0.38	0

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Table 4b R125/R134a 44%/56% as Extender for R22

Refrigerant % R22 by weight	0	10	20	30	40	50	60	70	80	90	100
Discharge pressure (bar)	15.90	16.41	16.83	17.17	17.44	17.64	17.79	17.88	17.93	17.93	17.91
Discharge temperature (°C)	79.6	81.7	83.7	85.8	88.0	90.3	92.8	95.5	98.3	101.4	104.7
COP (system)	2.50	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49
Capacity (kW/m ³)	2581	2675	2756	2825	2885	2935	2977	3010	3036	3054	3066
Glide in evaporator (°C)	3.06	3.08	2.91	2.62	2.27	1.89	1.50	1.12	0.74	0.37	0
Glide in condenser (°C)	2.97	2.89	2.66	2.36	2.02	1.69	1.34	1.00	0.67	0.34	0

Table 5 R32/134a 30/70 as an Extender for R22

Refrigerant % R22 by weight	0	10	20	30	40	50	60	70	80	90	100
Discharge pressure (bar)	18.08	18.18	18.27	18.33	18.36	18.36	18.34	18.28	18.19	18.07	17.91
Discharge temperature (°C)	98.0	98.4	98.9	99.3	99.8	100.4	101.0	101.8	102.6	103.6	104.7
COP (system)	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49
Capacity (kW/m ³)	3030	3049	3066	3080	3091	3098	3101	3100	3094	3083	3066
Glide in evaporator (°C)	5.03	4.59	4.12	3.62	3.11	2.59	2.07	1.55	1.03	0.51	0
Glide in condenser (°C)	5.13	4.62	4.11	3.60	3.08	2.57	2.07	1.56	1.06	0.54	0

Table 6 R32/125/134a 23/25/52 as an Extender for R22

Refrigerant % R22 by weight	0	10	20	30	40	50	60	70	80	90	100
Discharge pressure (bar)	19.30	19.32	19.30	19.25	19.16	19.03	18.87	18.68	18.45	18.20	17.91
Discharge temperature (°C)	92.5	93.3	94.1	95.0	96.0	97.1	98.4	99.7	101.2	102.9	104.7
COP (system)	2.47	2.47	2.47	2.47	2.47	2.48	2.48	2.48	2.49	2.49	2.49
Capacity (kW/m ³)	3172	3183	3190	3193	3191	3183	3171	3157	3129	3101	3066
Glide in evaporator (°C)	4.8	4.4	3.9	3.4	2.9	2.4	1.9	1.5	1.0	0.5	0
Glide in condenser (°C)	4.7	4.2	3.8	3.3	2.8	2.4	1.9	1.5	1.0	0.5	0

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TABLE 7

COMMERCIAL ROOF TOP HEAT PUMP 5 TON

	R-22	BLEND 1	BLEND 3	BLEND 4	BLEND 5	BLEND 6	BLEND 7
WT% COMPOSITION		64/34/2	70/28/2	55/43/2	60.5/37.5/2	45/52/1/2	55/42/1/2
COOLING MODE							
ADDITIONAL REFR. REQ'D		.9 KG	.9 KG	NONE	.9 KG	NONE	NONE
SUCTION PRESSURE	4.48	3.5	3.37	3.03	3.45	2.69	3.1
SUCTION TEMPERATURE	18	22	19.4	27	20	22	21.7
DISCHARGE PRESSURE	13.1	13.5	13.17	12.68	12.42	11.25	12.42
DISCHARGE TEMP.	90	80	73	81	72	76	76
LIQ. LINE TEMP.	31	29	26	32	26	26	26
AMBIENT TEMPERATURE	22	24	21.7	26	21.2	22	22
OIL LEVEL	10.8CM	10.8 CM	10.8 CM	10.8 CM	10.8 CM	10.8 CM	10.8 CM
AMPERAGE	22.27	19.86	19.64	17.72	19.06	16.13	17.83
VOLTAGE	200	201	199	200	199	203	200
EVAPORATOR TEMP.	7.2	3.9	2.2	4	5	1.7	2.3
AIR TEMP. DIFFERENCE	12.2	17.7	16.1	19.7	14.4	17.3	16.1
SUPERHEAT	9.1	21	19.4	28	20	26	23.3
HEATING MODE							
SUCTION PRESSURE	4.82	4.97	4.9	3.6	4.69	3.45	3.72
SUCTION TEMP.	25	23	23	26	22	23	22
DISCHARGE PRESSURE	20.34	25.5	25.6	19.3	24	17.94	19.3
DISCHARGE TEMP.	120	98	98	95	94	91	91
LIQ. LINE TEMP.	32.2	30	30	32	29	27	26
AMBIENT TEMP.	24.2	24	22.2	25	22.4	22	20
OIL LEVEL	10.8CM	10.8 CM	10.8 CM	10.8 CM	10.8 CM	10.8 CM	10.8 CM
AMPERAGE	28.97	28.08	27.63	21.9	26.72	20.77	22.54
VOLTAGE	198	199	198	199	198	203	199
EVAPORATOR TEMP.	41	36.2	36.1	36.1	34	32	31
AIR TEMP. DIFFERENCE	11.1	7.8	7.8	6.3	7.6	7.2	7.5
SUPERHEAT	NA	NA	NA	NA	NA	NA	NA

PRESSURES ARE IN BARS GAUGE PRESSURE

TEMPERATURES ARE IN CELSIUS

ALL READINGS ARE AVERAGES OVER SEVERAL HOURS OF OPERATION

OIL LEVEL MEASURED IN CENTIMETRES

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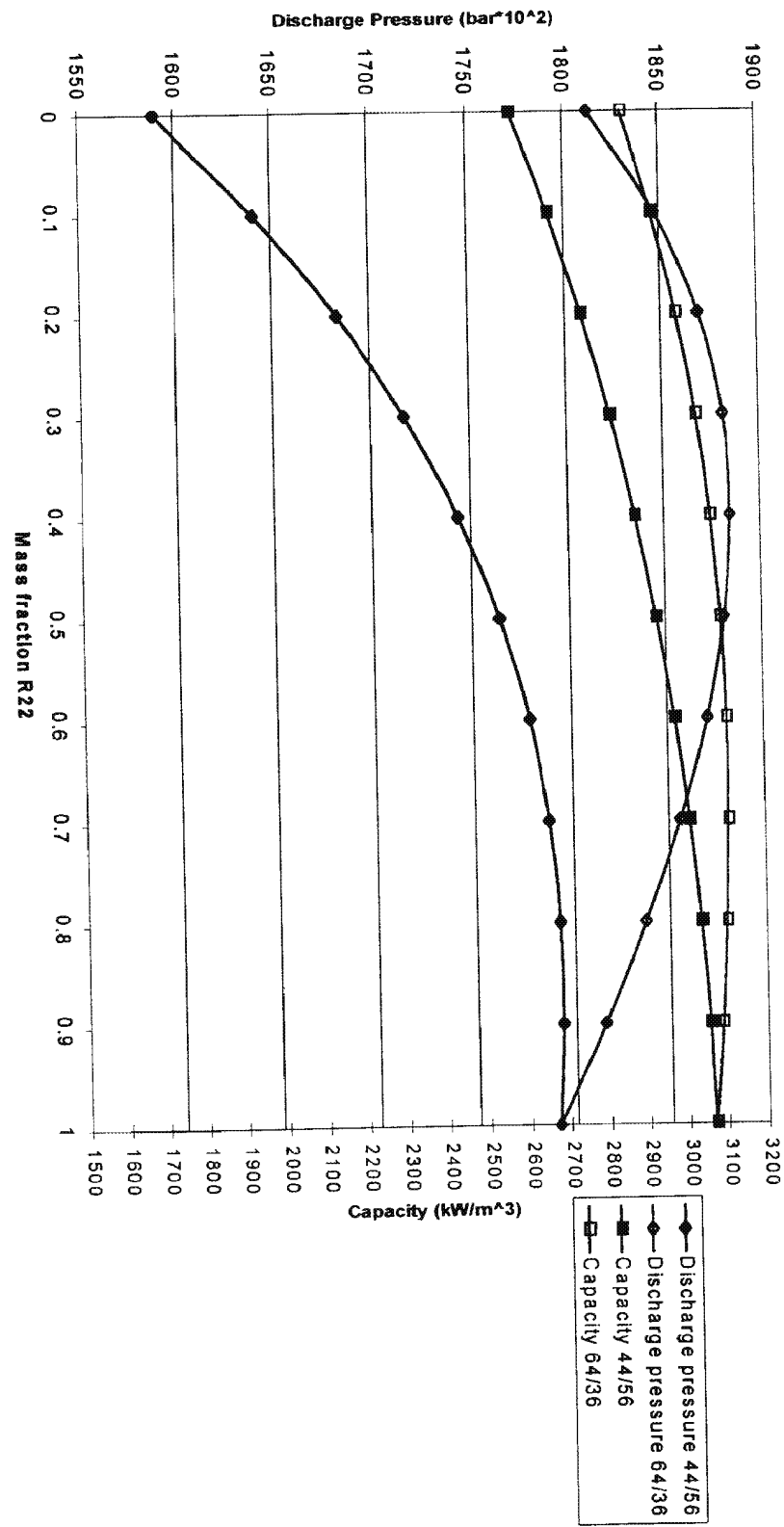
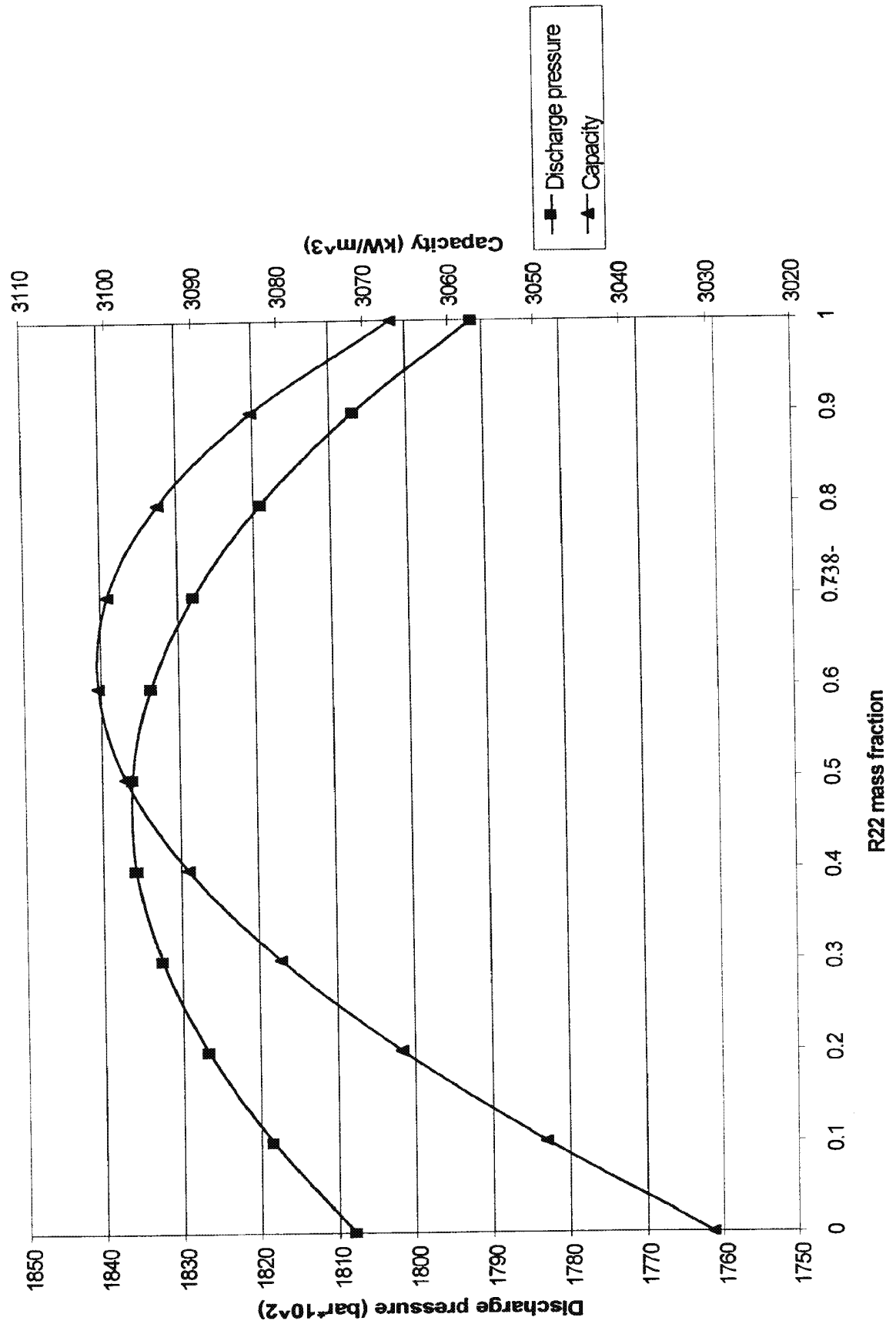
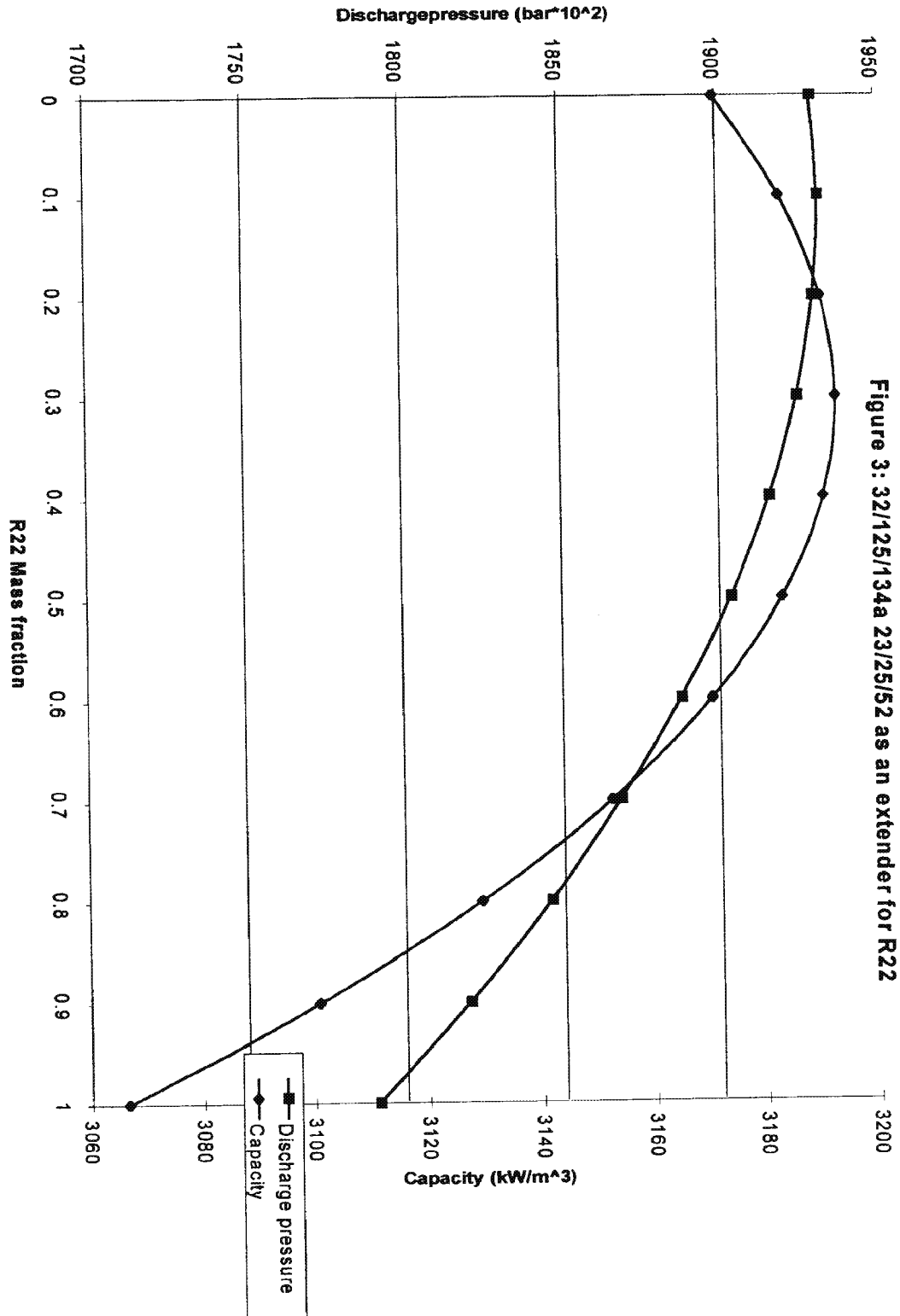


Figure 1: R125/134a 64/36 and 44/56 as R22 Extenders

Figure 2: R32(30)/R134a(70) as an extender for R22



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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/03725

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 539 952 A (MATSUSHITA ELECTRIC IND CO LTD) 5 May 1993 (1993-05-05) table 3	1-19
A	EP 0 811 670 A (MATSUSHITA ELECTRIC IND CO LTD) 10 December 1997 (1997-12-10) abstract	1-19
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *O* document referring to an oral disclosure, use, exhibition or other means
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- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

1 December 2000

Date of mailing of the international search report

19/12/2000

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/03725

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Bibliographic data: JPH08319479 (A) — 1996-12-03**REFRIGERANT**

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Classification: - **international:** **C07C19/08; C09K5/04; F25B1/00;**
(IPC1-7): C07C19/08; C09K5/04; F25B1/00
- **cooperative:**

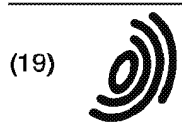
Application number: JP19950325342 19951214

Priority number (s): JP19950325342 19951214

Also published as: JP2867932 (B2)

Abstract of JPH08319479 (A)

PURPOSE: To obtain refrigerants free from the possibility of causing ozonosphere depletion and excellent in refrigerating performance, especially coefficient of performance. **CONSTITUTION:** A refrigerant consisting of HCFC-125 and HFC-134a, of which HCFC-125 accounts for more than 40wt.% to less than 90wt.% and HFC-134a accounts for more than 10wt.% to less than 60wt.%, or of which HCFC-125 accounts for more than 90wt.% to less than 100wt.% and HFC-134a accounts for more than 0wt.% to less than 10wt.%. A refrigerant consisting of HCFC-125 and HFC-134, of which HCFC-125 accounts for more than 40wt.% to less than 90wt.% and HFC-134 accounts for more than 10wt.% to less than 60wt.%, or of which HCFC-125 accounts for more than 90wt.% to less than 100wt.% and HFC-134 accounts for more than 0wt.% to less than 10wt.%.



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Office européen des brevets



(11) EP 0 811 670 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
10.12.1997 Bulletin 1997/50

(51) Int. Cl.⁶: C09K 5/04

(21) Application number: 97106576.8

(22) Date of filing: 21.04.1997

(84) Designated Contracting States:
BE ES IT NL

(30) Priority: 05.06.1996 JP 143056/96

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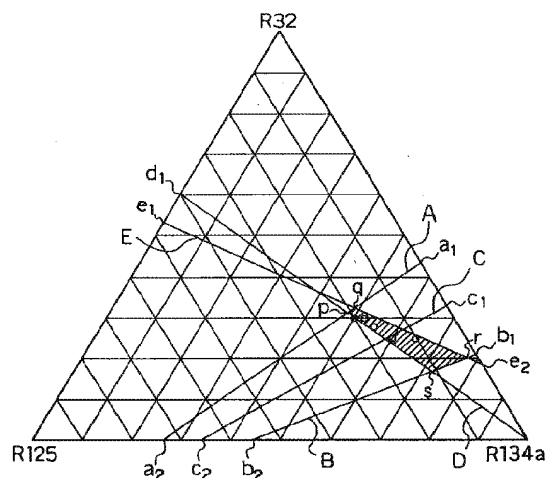
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(54) Ternary mixture refrigerant and heat pump apparatus utilizing the same

(57) A ternary mixture refrigerant having a high efficiency which can be used as a substitute for R22 and a heat pump apparatus utilizing the same are disclosed. The ternary mixture refrigerant is in a composition range defined by a straight line A which connects a point a_1 ($R32/R134a = 43/57$ wt%) and a point a_2 ($R125/R134a = 73/27$ wt%), a line B which connects a point b_1 ($R32/R134a = 21/79$ wt%) and a point b_2 ($R125/R134a = 55/45$ wt%), a line D which connects a point d_1 ($R32/R125 = 60/40$ wt%) and a vertex of R134a, and a line E which connects a point e_1 ($R32/R125 = 53/47$ wt%) and a point e_2 ($R32/R134a = 19/81$ wt%) in a ternary composition diagram of R32, R125 and R134a represented by a triangular coordinate in FIG. 1.

FIG. 1



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Description

BACKGROUND OF THE INVENTION

5 The present invention relates to a ternary mixture refrigerant which can be used as a substitute for chlorodifluoromethane and a heat pump apparatus utilizing the same.

Conventional heat pump apparatuses in air conditioners, freezers, refrigerators and the like comprise a power refrigerating cycle formed by connecting a compressor, a condenser, a squeezing device such as capillary tube, expansion valve or the like, and an evaporator or the like together through pipe lines, and perform a cooling operation or a heating operation by circulating a refrigerant or working fluid through the connected components and pipe lines. The above-mentioned refrigerating cycle may include a four-way valve or cock. In these heat pump apparatuses, halogenated hydrocarbons derived from methane or ethane (hereinafter referred to as R-- or R---, as stipulated in the U.S. ASHRAE 34 Standard of the United States) are usually used as their refrigerants or working fluids. Among them, chlorodifluoromethane (CHClF_2 , R22, b.p. -40.8°C) has been widely used as a refrigerant in a refrigerating system such as air conditioner, freezer, refrigerator and the like.

However, depletion of the ozone layer in the stratosphere with chlorofluorohydrocarbons is seriously discussed as one of the global environmental problems in recent years, and the usage and volume of production of some chlorofluorohydrocarbons which have high ozone depletion potential are limited by the Montreal Protocol. In future, their use and production will be completely banned. In order to substantially obviate the influence on the ozone layer in the stratosphere, it is an essential requirement for the refrigerant to contain no chlorine atom in its molecular structure. As one having a possibility of obviating the influence on the ozone layer in the stratosphere, fluorohydrocarbons containing no chlorine (HFCs) are proposed. Fluorohydrocarbons containing no chlorine may be exemplified as difluoromethane (CH_2F_2 , R32, b.p. -52°C), pentafluoroethane ($\text{CF}_3\text{-CHF}_2$, R125, b.p. -48°C), 1,1,1-trifluoroethane ($\text{CF}_3\text{-CH}_3$, R143a, b.p. -48°C), 1,1,1,2-tetrafluoroethane ($\text{CF}_3\text{-CH}_2\text{F}$, R134a, b.p. -27°C), 1,1-difluoroethane ($\text{CHF}_2\text{-CH}_3$, R152a, b.p. -25°C), and the like.

In addition to this problem, the refrigerants of fluorohydrocarbons have another serious environmental problem of global warming and are regarded as having global warming potential (hereinafter referred to as "GWP") indicating the influence on the global warming of the same degree as R22. According to the report on IPCC (Intergovernmental Panel on Climate Change) in 1994 which defines the GWP of carbon dioxide (CO_2) as 1, it is estimated that relative values of GWP of R22 are 4300, 1700 and 520 for 20 years, 100 years, and 500 years, respectively; and with the fluorinated hydrocarbons containing no chlorine, the corresponding relative values for R32 are 1800, 580 and 180; the corresponding relative values for R125 are 4800, 3200 and 1100; the corresponding relative values for R143a are 5200, 4400 and 1600; the corresponding relative values for R134a are 3300, 1300 and 420; and the corresponding relative values for R152a are 460, 140 and 44, respectively.

Among the fluorinated hydrocarbons containing no chlorine, R32, R125 and R143a have a lower boiling point than that of R22 and thus raise the condensing pressure in the heat pump apparatus very high, and thus it is difficult to use them singly as a substitute for R22. Since R134a and R152a have a higher boiling point than that of R22 and lower the refrigerating capacity of the heat pump apparatus, it is also difficult to use them singly as a substitute for R22. In addition, R32, R143a and R152a have a disadvantage that they are flammable.

In order to overcome the disadvantage, a binary mixture refrigerant comprising R32/R125 or a ternary mixture refrigerant comprising R32/R125/R134a has been proposed as a promising substitute for R22. U.S. Patent No. 4,978,467 discloses that the binary mixture refrigerant comprising R32/R125 acts as an azeotropic mixture refrigerant. Since the disclosed mixture refrigerant has a high vapor pressure, it is difficult to apply the refrigerant as it is to the heat pump apparatus which has been operated with R22.

For this reason, the ternary mixture refrigerant comprising R32/R125/R134a which has a vapor pressure of the same degree as that of R22 is disclosed in U.S. Patent No. 5,370,811, U.S. Patent No. 5,185,094, EP A 451,692 and EP A 509,673 as a promising refrigerant. In addition, a composition of R32/R125/R134a of 23/25/52 wt% is proposed [Request for Refrigerant Safety Classification and Nomenclature for Zeotropic Ternary Refrigerant Mixture: HFC-32/HFC-125/HFC-134a, by E.I. du Pont de Nemours and Company, Wilmington, Del., U.S.A., applied on May 18, 1994].

The above-mentioned ternary mixture refrigerant is however a non-azeotropic mixture refrigerant and its boiling point differs from its dew point. In addition, the refrigerant shows a temperature gradient in the condenser or the evaporator. Namely, the temperature of the mixture refrigerant lowers by its temperature gradient as the refrigerant is condensed in the condenser and the temperature of the refrigerant rises by its temperature gradient as it is evaporated in the evaporator. Therefore, low boiling point components such as R32 and R125 are liable to be concentrated in the vapor phase whereas a high boiling point component such as R134a in the liquid phase. In addition, since the mixture refrigerant is prepared by blending a plurality of components, it is necessary to specify an error in the proportion of the respective components as a definite composition error. For that reason, a further research will be required for clarifying what composition will give a suitable refrigerant for the heat pump apparatus.

Summaries of the prior art literature which disclose the above-mentioned ternary mixture refrigerant are as follows.

U.S. Patent No. 5,370,811 which is a senior application by some of the inventors of the present invention specifies a composition range of the ternary mixture refrigerant comprising R32/R125/R134s wherein the mixture can demonstrate a substantially equal vapor pressure to that of R22.

U.S. Patent No. 5,185,094 discloses characteristics of the refrigerant in terms of coefficient of performance and refrigerating capacity obtained by using this ternary mixture refrigerant for a heat pump apparatus, and a change in the composition resulting from repeated leakages as a non-azeotropic mixture refrigerant.

EP A 451,692 discloses in Example 3 a general tendency of the coefficient of performance and refrigerating capacity during the application of this ternary mixture refrigerant to a heat pump apparatus, and outlines the nonflammable range of the composition.

Similarly, EP A 509,673 discloses some examples of the coefficient of performance and refrigerating capacity during the application of this ternary mixture refrigerant to a heat pump apparatus. In addition, in Attachment 2, Exhibit 7 of the above-mentioned Request by E.I. du Pont, there is disclosed a most recently published nonflammable range of this R32/R125/R134a.

Based on the above disclosures of the prior art literature, although it is possible to analogize a suitable composition range of this R32/R125/R134a, it is not clarified which composition is actually preferable as the refrigerant of the heat pump apparatus.

In addition, relative values of GWP of the promising composition of R32/R125/R134a of 23/25/52 wt% (R407C), calculated by defining the GWP of carbon dioxide (CO₂) as 1, are estimated to be 3300, 1600 and 530, for 20 years, 100 years and 500 years, respectively. The values are smaller than those of R22 as GWPs for 20 years and 100 years but have a possibility of becoming larger than that of R22 if compared for a long span of 500 years. From this point of view, it is desired to propose a more promising new composition.

BRIEF SUMMARY OF THE INVENTION

The present invention proposes a further restricted composition range of a ternary mixture refrigerant comprising R32/R125/R134a on the basis of a detailed experimental study using a heat pump apparatus which utilizes air as its heat source and various investigations based on the most recently published nonflammable range of R32/R125/R134a.

The object of the present invention is to provide a ternary mixture refrigerant which is more suitable for a working fluid for the heat pump apparatus and has substantially equal refrigerating capacity and higher coefficient of performance compared with the promising composition of 23/25/52 wt% (R407C).

Another object of the present invention is to provide a ternary mixture refrigerant which is nonflammable even in the vapor phase composition in addition to the liquid phase composition and has lower GWP compared with R407C.

The mixture refrigerant in accordance with the present invention comprising R32/R125/R134a is in a composition range defined by a straight line A which connects a point a₁ (R32/R134a = 43/57 wt%) and a point a₂ (R125/R134a = 73/27 wt%), a line B which connects a point b₁ (R32/R134a = 21/79 wt%) and a point b₂ (R125/R134a = 55/45 wt%), a line D which connects a point d₁ (R32/R125 = 60/40 wt%) and a vertex of R134a, and a line E which connects a point e₁ (R32/R125 = 53/47 wt%) and a point e₂ (R32/R134a = 19/81 wt%) in a ternary composition diagram represented by a triangular coordinate in FIG. 1.

In the triangular coordinate, which is depicted by disposing R32, R125 and R134a at the respective vertexes of a triangle in the counterclockwise direction from the top vertex, single components are assigned on the vertexes from a compound having the lowest boiling point to one having the highest boiling point. A composition (ratio by weight) of the three compounds at one point on the triangular coordinate is expressed by a ratio of distances between the point and the opposite sides. The distance between the point and the opposite side corresponds to a proportion of the compound which is assigned on the vertex which faces the side.

While the novel features of the invention are set forth particularly in the appended claims, the invention, both as to organization and content, will be better understood and appreciated, along with other objects and features thereof, from the following detailed description taken in conjunction with the drawings.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

FIG. 1 is a composition diagram represented by a triangular coordinate for describing the composition of the ternary mixture refrigerant comprising R32/R125/R134a in accordance with the present invention.

FIG. 2 is a diagram showing a relationship between percent by weight of R32 in a binary mixture refrigerant comprising R32/R125 and saturation temperature gradient.

FIG. 3 is a schematic diagram showing the refrigerating cycle in the heat pump apparatus which utilizes the mixture refrigerant in accordance with the present invention.

FIG. 4 is a composition diagram represented by a triangular coordinate for describing the nonflammable region of the ternary mixture refrigerant comprising R32/R125/R134a in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The ternary mixture refrigerant in accordance with the present invention is in the composition range defined by lines A, B, D and E, namely a hatched area of a quadrilateral formed by connecting vertexes of points p, q, r and s, in the ternary composition diagram represented by the triangular coordinate in FIG. 1. The points p and q are the intersecting points at which the line A intersects the lines D and E, respectively, and the points r and s are the intersecting points at which the line B intersects the lines E and D, respectively. In FIG. 1, the compositions of the five specific examples of the mixture refrigerant in accordance with the present invention, namely, the mixture refrigerants Nos. 4, 3, 2, 9 and 10 in the specific examples which will be described below are indicated by white circles in turn from the left side of the diagram.

The heat pump apparatus in accordance with the present invention has a power refrigerating cycle which utilizes the above-mentioned ternary mixture refrigerant as a working fluid. In particular, a refrigerating cycle comprising a compressor driven by an inverter unit is suitable.

Of the mixture refrigerant of R32/R125/R134a, compositions in a region between the line A and the line B have a vapor pressure which is substantially equal to that of R22 and thus have substantially equal refrigerating capacity. Compositions containing R32 in a larger quantity than those on the line D have a higher coefficient of performance than that of the composition of R32/R125/R134a = 23/25/52 wt% (R407C). In compositions containing R32 in a smaller quantity than those on the line E, it is believed that not only a liquid phase composition but also its equilibrium vapor phase composition are nonflammable even if the composition at room temperature is placed in an atmospheric temperature at 100°C. In addition, since the mixture refrigerants of R32/R125/R134a in this composition range contain a smaller proportion of R125 which has a high GWP as compared with R407C, it is possible to lower their GWPs.

Among the compositions in the quadrilateral formed by connecting the vertexes of the above-mentioned points p, q, r and s, compositions in the region between a line C connecting a point c_1 (R32/R134a = 33/67 wt%) and a point c_2 (R125/R134a = 65/35 wt%) and the line A have larger refrigerating capacity than that of R407C, and thus are preferable for improving the coefficient of performance in the heat pump apparatus comprising a compressor driven by an inverter unit in both the cooling mode and heating mode operations. This ambi-utility heat pump apparatus is preferably used in a household air conditioner or the like.

In addition, among the compositions in the quadrilateral formed by connecting the vertexes of the above-mentioned points p, q, r and s, although compositions in the region between the line C and the line B have substantially the same as or smaller refrigerating capacity than that of R407C, the compositions are preferable for improving the coefficient of performance in the heat pump apparatus mainly for the cooling mode operation. This heat pump apparatus is used in a commercial air-conditioner, an automatic vendor or the like.

Further, mixture refrigerants having a composition of R32/R125/R134a of about 25/10/65 wt% or about 25/15/60 wt% can lower the condensing pressure. These compositions are suitable for such a heat pump apparatus in which refrigerating cycle is designed to work under a mode of counter flow heat transfer in cooling mode operation.

In the following paragraphs, specific examples of the present invention will be described.

EXAMPLE 1

Table 1 and Table 2 below show ideal refrigerating capacity of some specific examples of mixture refrigerants comprising R32/R125/R134a in accordance with the present invention together with those of mixture refrigerants of some comparative examples. The performance was measured under conditions of an average condensing temperature of 50°C, an average evaporating temperature of 0°C, a degree of supercool of 0 deg at an outlet of the condenser and a degree of superheat of 0 deg at an outlet of the evaporator. The refrigerants Nos. 2, 3, 4, 9 and 10 are specific examples of the present invention and the other refrigerants are comparative examples.

Table 1

Refrigerant No.		1	2	3	4	5
Composition (wt%)	R32	23	28	30	30	33
	R125	25	17	18	20	17
	R134a	52	55	52	50	50
Refrigerating capacity (Ratio to R407C)		1.000	1.031	1.059	1.065	1.090
Coefficient of performance (Ratio to R407C)		1.000	1.012	1.010	1.007	1.013
Condensing pressure (MPa)		2.091	2.108	2.161	2.185	2.212
Evaporating pressure (MPa)		0.495	0.498	0.513	0.520	0.528
Discharge temperature (°C)		67.29	69.81	70.57	70.39	71.70
Condensing temperature gradient (deg)		4.74	4.94	4.86	4.78	4.80
Evaporating temperature gradient (deg)		4.24	4.43	4.44	4.40	4.45

As listed in Table 1 above, the refrigerants No. 2 through No.5 have slightly higher condensing pressure, evaporating pressure and discharge temperature, compared with those of R 407C (R32/R125/R134a = 23/25/52 wt%), because the proportion of R32 having a higher vapor pressure than that of R22 is large, but both their refrigerating capacity and coefficient of performance are more favorable than those of R407C.

Table 2

Refrigerant No.		6	7	8	9	10
Composition (wt%)	R32	30	30	25	25	25
	R125	0	10	20	15	10
	R134a	70	60	55	60	65
Refrigerating capacity (Ratio to R407C)		0.989	1.027	1.006	0.987	0.969
Coefficient of performance (Ratio to R407C)		1.045	1.029	1.008	1.022	1.028
Condensing pressure (MPa)		1.965	2.071	2.077	2.022	1.968
Evaporating pressure (MPa)		0.455	0.486	0.490	0.473	0.457
Discharge temperature (°C)		71.30	70.84	68.39	68.51	68.80
Condensing temperature gradient (deg)		5.22	5.10	4.88	5.00	5.08
Evaporating temperature gradient (deg)		4.46	4.52	4.34	4.36	4.33

As listed in Table 2 above, the refrigerants No. 6 through No.10 have slightly lower condensing pressure and evaporating pressure, compared with those of R407C, because the proportion of R125 having a higher vapor pressure than that of R22 is small, and their refrigerating capacity remains substantially equal to that of R407C but their coefficients of performance are more favorable than that of R407C.

In this context, the compositions of the refrigerants No.2 through No.5 and the compositions of the refrigerants No.6 through No.10 are classified into two regions as follows. In the triangular coordinate representing the composition of the mixture refrigerant comprising R32/R125/R134a of the above-mentioned U.S. Patent No. 5,370,811, three lines are depicted: namely, a saturated vapor phase line of the mixture refrigerant which coincides with the saturation pressure of R22 at 0°C, a saturated vapor phase line of the mixture refrigerant which coincides with the saturation pressure of R22 at 50°C, and a saturated liquid phase line of the mixture refrigerant which coincides with the saturation pressure of R22 at 50°C (which also substantially coincides with a saturated liquid phase line at the saturation pressure of R22 at 0°C).

The position of the composition on the saturated vapor phase line of the mixture refrigerant which coincides with

the saturation pressure of R22 at 50°C is substantially midway in a region between the saturated liquid phase line and the saturated vapor phase line of the mixture refrigerant which coincides with the saturation pressure of R22 at 0°C. For that reason, at the same pressure as that of R22, the mixture refrigerant has a boiling point lower than 0°C and a dew point higher than 0°C, and demonstrates an average evaporation temperature of 0°C when it is utilized as a working fluid in a heat pump apparatus.

Since it is known that the refrigerating capacity of a refrigerant is substantially proportional to its evaporation temperature, it is appreciated that the refrigerating capacity of a composition which is on the saturated vapor phase line of the mixture refrigerant, which coincides with the saturation pressure of R22 at 50°C, is in substantial agreement with the refrigerating capacity of R22. That is, the compositions of the refrigerants No. 2 through No.5 and the compositions of the refrigerants No. 6 through No.10 are classified into two regions by taking the saturated vapor phase line of the mixture refrigerant which coincides with the saturation pressure of R22 at 50°C as borderline, and the composition of 23/25/52 wt% (R407C) is substantially on this borderline.

And, the refrigerating capacity of the refrigerants No.2 through No.5 having a larger proportion of R32 than that of the composition on this borderline is larger than that of R407C. In addition, the refrigerating capacity of the refrigerants No.6 through No.10 which are on this borderline or have a smaller proportion of R32 than that of the composition on this borderline is substantially the same as or smaller than that of R407C. These facts are clearly seen from Table 1 and Table 2.

That is, among the composition ranges specified by U.S. Patent No. 5,370,811, the saturated vapor phase line of the mixture refrigerant which coincides with the saturation pressure of R22 at 0°C approximates to the line A which connects the point a_1 (R32/R134a = 43/57 wt%) and the point a_2 (R125/R134a = 73/27 wt%). The saturated liquid phase line of the mixture refrigerant which coincides with the saturation pressure of R22 at 50°C approximates to the line B which connects the point b_1 (R32/R134a = 21/79 wt%) and the point b_2 (R125/R134a = 55/45 wt%). In addition, the saturated vapor phase line of the mixture refrigerant positioned substantially midway which coincides with the saturation pressure of R22 at 50°C approximates to the line C which connects the point c_1 (R32/R134a = 33/67 wt%) and the point c_2 (R125/R134a = 65/35 wt%). For that reason, the compositions No.2 through No.5 are substantially in a region between the line A and the line C, and their refrigerating capacity increases more than that of R407C. In addition, the compositions of the refrigerants No.6 through No.10 are substantially in a region between the line C and the line B, and their refrigerating capacity is substantially the same as or decreases lower than that of R407C.

In addition, the composition of the ternary mixture refrigerant comprising R32/R125/R134a as discussed above is a combination of a binary azeotropic mixture refrigerant comprising R32/R125 and R134a, and a temperature gradient of the binary azeotropic mixture refrigerant comprising R32/R125 at an average saturation temperature of 0°C shown by the diagram in FIG. 2 is obtained. From FIG. 2, it is appreciated that the composition of 23/25/52 wt% (R407C) is a combination of a mixture refrigerant of R32/R125 (48/52 wt%) having non-azeotropic property and R134a. By contrast, it is appreciated that the compositions of the refrigerant No. 2 through No. 10 which demonstrate favorable coefficient of performance have a larger proportion of R32 than those on the line D which connects the point of R32/R125 (60/40 wt%) and the vertex for R134a, and are a combination of the mixture refrigerant comprising R32/R125 which can be handled almost as a single refrigerant and R134a.

On the basis of the above discussion, a more restricted suitable composition range has been classified. In the case of applying a mixture refrigerant having a condensing temperature gradient and an evaporation temperature gradient to a practical heat pump apparatus, an actual condensing temperature gradient in a condenser becomes larger by a pressure loss than the condensing temperature gradient shown in Table 1 and Table 2, and an actual evaporating temperature gradient in an evaporator becomes smaller by a pressure loss than the evaporating temperature gradient shown in Table 1 and Table 2. For that reason, the operation temperature of the refrigerating cycle changes from the data shown in Table 1 and Table 2, and thus it is necessary to grasp the actual characteristics of the refrigerants in the practical heat pump apparatus.

EXAMPLE 2

A description will be made on an example wherein some specific examples of the ternary mixture refrigerant in accordance with the present invention are applied to a heat pump apparatus utilizing air as its heat source.

The air-heat source heat pump apparatus shown by FIG. 3 comprises a refrigerating cycle configured by connecting a compressor 2 driven by an inverter unit 1, an accumulator 3, a four-way valve 4, an outdoor unit 7 including an outdoor heat transfer unit 5 which acts as a condenser or an evaporator and an expansion valve 6, and an indoor unit 9 including an indoor heat transfer unit 8 which acts as a condenser or an evaporator, together with pipe lines. The ternary mixture refrigerant is injected into this refrigerating cycle as a working fluid and sealed, and an oil of an ester which is suited for the fluorohydrocarbons containing no chlorine is injected into the compressor 1 and sealed.

In this refrigerating cycle, the refrigerant circulates in the direction of dashed arrows during the cooling mode operation and in the direction of the solid arrows during the heating mode operation. The outdoor heat transfer unit 5 is an air-cooled heat transfer unit having two rows of 6 paths and the indoor heat transfer unit 8 is an air-cooled heat transfer

unit having four rows of four paths, and the flow of the refrigerant is designed to be a counter flow against the air flow during the cooling mode operation.

Table 3 summarizes characteristics of the previously described mixture refrigerants No. 1 through No.10 comprising R32/R125/R134a when they are utilized in the heat pump apparatus shown by FIG. 3 during cooling mode and heating mode operations. The disclosed characteristics are obtained by adjusting the charging amounts of the mixture refrigerant and the openings of the expansion valve 6 so as to maximize the coefficients of performance. The disclosed characteristics are represented by the coefficient of performance measured by taking the value for R407C as reference and finely adjusting the rotational frequency of the compressor 2 driven by the inverter unit 1 so as to correct fine differences in capacity shown in Table 1 and Table 2 and make the capacity equal.

Table 3

Refrigerant No.	1	2	3	4	5
COP in cooling mode (Ratio to R407C)	1.000	1.075	1.076	1.084	1.049
COP in heating mode (Ratio to R407C)	1.000	1.026	1.051	1.075	1.042
Refrigerant No.	6	7	8	9	10
COP in cooling mode (Ratio to R407C)	1.041	1.068	1.024	1.036	1.041
COP in heating mode (Ratio to R407C)	0.996	1.007	0.995	0.998	1.021
COP: coefficient of performance					

As clearly appreciated from Table 3 above, coefficients of performance of the mixture refrigerants No.2 through No.5 during both the cooling and heating mode operations are greatly improved, compared with the ideal coefficients of performance shown in Table 1, because their increasing performance compared with that of R407C is made to be the same by finely adjusting the rotational frequency of the compressor 2 in the direction of decreasing the frequency by the inverter unit 1.

In addition, with the mixture refrigerants No.6 through No.10, their coefficients of performance during the cooling mode operation are also greatly improved compared with the ideal coefficients of performance shown in Table 2 and increased compared with that of R407C. During the heating mode operation, however, only substantially the same coefficients of performance as that of R407C can be expected with the mixture refrigerants, because the decreased performance is made to be the same by finely adjusting the rotational frequency of the compressor 2 by the inverter unit 1 to the same or in the direction of increasing the frequency.

In particular, it is appreciated that, among the tested mixture refrigerants shown in Table 3, the refrigerants whose coefficients of performance during the cooling mode operation are greatly improved compared with their ideal values are those of the compositions having a larger proportion of R32 than those substantially on the line D, i.e., the refrigerants No.2 through No.5, and No.7 through No.10. In addition, among the tested mixture refrigerants shown in Table 3, with the refrigerants whose coefficients of performance during the cooling mode operation are greatly improved compared with their ideal values and whose refrigerating capacity is increased, the effects of decreased condensing pressure, increased evaporating pressure and decreased compression ratio are great. The ideal evaporation temperature gradients listed in Table 1 and Table 2 are larger than those of R407C. These facts are suited for the air-cooled heat transfer unit which is designed to be a counter flow during the cooling mode operation. The disclosed results were first found during the process of the research and development to this invention.

In addition, among the mixture refrigerants No.6 through No.10, since No.9 or No.10 is effective for improving the coefficient of performance during the cooling mode operation and has smaller proportions of R32 and R125 having a high vapor pressure as compared with that of R407C, the condensing pressure can be made low, and thus is suited for the heat pump apparatus mainly for the cooling mode operation. However, if the proportion of R32 is decreased more than that, the refrigerating capacity of the mixture refrigerant decreases as shown in Table 2 and an improvement in the coefficient of performance becomes hard to expect because an input increases in order to make the capacity the same. In addition, all the tested mixture refrigerants shown in Table 3 suggest that small differences of not more than 2 - 5% in the proportions of R32, R125 and R134a to be incorporated in the mixture have an influence on the performance of the heat pump apparatus, and thus it is desirable that the respective components are in the composition error of not more than $\pm 2\%$.

EXAMPLE 3

FIG. 4 is a composition diagram of the mixture refrigerant comprising R32/R125/R134a represented by a triangular coordinate. In this figure, each of the white circles indicates the respective compositions of the previously described mixture refrigerants No.1 through No.10, and each of the black circles indicates the respective saturated vapor phase compositions of the respective saturated liquid phases of the compositions indicated by the white circles which are in an equilibrium state at 23°C. Lines connecting the white circles and the black circles are tie lines for indicating that the pairs are in equilibrium state.

In addition, FIG. 4 further incorporates by reference nonflammable borderlines of the composition R32/R125/R134a shown in Attachment 2, Exhibit 7 of the previously described Request for Refrigerant Safety Classification and Nomenclature for Zeotropic Ternary Refrigerant Mixture by E.I. du Pont de Nemours and Company. In this diagram, the solid line indicates a nonflammability borderline at an atmospheric temperature of 100°C and the dot-dashed line indicates a nonflammability borderline at room temperature (about 23°C), respectively. The broken line indicates the saturated liquid phase composition in a state in equilibrium with the saturated vapor phase composition at 23°C which coincides with the solid line.

It is believed that a mixture refrigerant having a smaller proportion of R32 than that on the broken line is nonflammable in both its liquid phase composition and equilibrium vapor phase composition, even if R32 having a flammability is concentrated in its vapor phase and the composition in an environment at room temperature of 23°C is subjected to a flammability test at an atmospheric temperature of 100°C. This nonflammable composition is specified as a composition having a smaller proportion of R32 than that on the line E which connects the point e_1 (R32/R125 = 53/47 wt%) and the point e_2 (R32/R134a = 19/81 wt%). Therefore, it is believed that among the mixture refrigerants which demonstrate favorable coefficient of performance as shown in Table 3, the refrigerants No.1 (R407C), Nos.2 - 4 and Nos.8 - 10 are nonflammable.

By contrast, the mixture refrigerants No.5 through No.7 have a possibility that their vapor phase compositions in equilibrium state with their liquid phase compositions become flammable when the compositions at room temperature such as 23°C are placed at an atmospheric temperature of 100°C, and thus should be excluded. In addition, the composition at an intersecting point r at which the line B intersects the line E shown in Example 1 can reduce the flammability of R32, because the composition contains at least R125 which has a large nonflammable effect.

EXAMPLE 4

Investigation was made on the global warming potential (GWP) of the ternary mixture refrigerant in accordance with the present invention.

Table 4 summarizes the relative values of GWP of the mixture refrigerants No.1 through No.10 for 20 years, 100 years and 500 years, respectively, calculated by defining GWP of carbon dioxide (CO₂) as 1.

Table 4

Refrigerant No.	1	2	3	4	5
GWP of 20 years (Ratio to CO ₂)	3300	3100	3100	3200	3100
GWP of 100 years (Ratio to CO ₂)	1600	1400	1400	1500	1400
GWP of 500 years (Ratio to CO ₂)	530	470	470	480	460
Refrigerant No.	6	7	8	9	10
GWP of 20 years (Ratio to CO ₂)	2900	3000	3200	3200	3100
GWP of 100 years (Ratio to CO ₂)	1100	1300	1500	1400	1300
GWP of 500 years (Ratio to CO ₂)	350	420	500	460	430

The mixture refrigerants No.2 through No.10 shown above have a small GWP for the entire time periods as compared with R407C having a composition No.1 of 23/25/52 wt% because their proportions of R125 having a high GWP are small. In addition to this, it is possible to make GWP of the mixture refrigerants No.2 through No.10 smaller than that of R22 even if a comparison is made at a long term of 500 years. However, it should be noted here that although the mixture refrigerant No.6 or No.7 has small GWP and is favorable from the viewpoint of only GWP, it may have a possibility of having a flammable property if the proportion of R125 having a large nonflammable effect is too small compared with R32 having a flammable property, as appreciated from the description of Example 3.

As described previously, the mixture refrigerants No.2, No.3, No.4, No.9 and No.10 specified by Example 1, Example 2 and Example 3 have favorable coefficient of performance, and are considered to be nonflammable, and, in addition, it is possible to lower GWP as compared with the promising R407C.

As described previously, in accordance with the present invention, it is possible to provide a mixture refrigerant having substantially equal refrigerating capacity, high coefficient of performance, low GWP and nonflammable even in its vapor phase composition in addition to its liquid phase composition, compared with the promising composition of 23/25/52 wt% (R407C), by further restricting a composition range of a ternary mixture refrigerant comprising R32/R125/R134a, which has hitherto been proposed as a substitute for R22, more suitably for a working fluid for a heat pump apparatus.

It is understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the scope and spirit of the present invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the description as set forth herein, but rather that the claims be construed as encompassing all the features of patentable novelty that reside in the present invention, including all features that would be treated as equivalents thereof by those skilled in the art to which this invention pertains.

Claims

1. A ternary mixture refrigerant comprising R32/R125/R134a in a composition range defined by a straight line A which connects a point a_1 (R32/R134a = 43/57 wt%) and a point a_2 (R125/R134a = 73/27 wt%), a line B which connects a point b_1 (R32/R134a = 21/79 wt%) and a point b_2 (R125/R134a = 55/45 wt%), a line D which connects a point d_1 (R32/R125 = 60/40 wt%) and a vertex of R134a, and a line E which connects a point e_1 (R32/R125 = 53/47 wt%) and a point e_2 (R32/R134a = 19/81 wt%) in a ternary composition chart of R32, R125 and R134a represented by a triangular coordinate in FIG. 1.
2. A heat pump apparatus comprising a refrigerating cycle which utilizes the ternary mixture refrigerant in accordance with claim 1.
3. The heat pump apparatus in accordance with claim 2, wherein said mixture refrigerant is in a composition range defined by a line C which connects a point c_1 (R32/R134a = 33/67 wt%) and a point c_2 (R125/R134a = 65/35 wt%) and the line A, and wherein said refrigerating cycle comprises an inverter unit for driving a compressor and performs both cooling mode and heating mode operations.
4. The heat pump apparatus in accordance with claim 2, wherein said mixture refrigerant is in a composition range defined by a line C which connects a point c_1 (R32/R134a = 33/67 wt%) and a point c_2 (R125/R134a = 65/35 wt%) and the line B, and wherein said refrigerating cycle performs a cooling mode operation.
5. The heat pump apparatus in accordance with claim 2, wherein said mixture refrigerant consists essentially of R32/R125/R134a of about 25/10/65 wt%, and wherein said refrigerating cycle is so designed as to perform a counter flow heat transfer in a cooling mode operation.
6. The heat pump apparatus in accordance with claim 2, wherein said mixture refrigerant consists essentially of R32/R125/R134a of about 25/15/60 wt%, and wherein said refrigerating cycle is so designed as to perform a counter flow heat transfer in a cooling mode operation.

FIG. 1

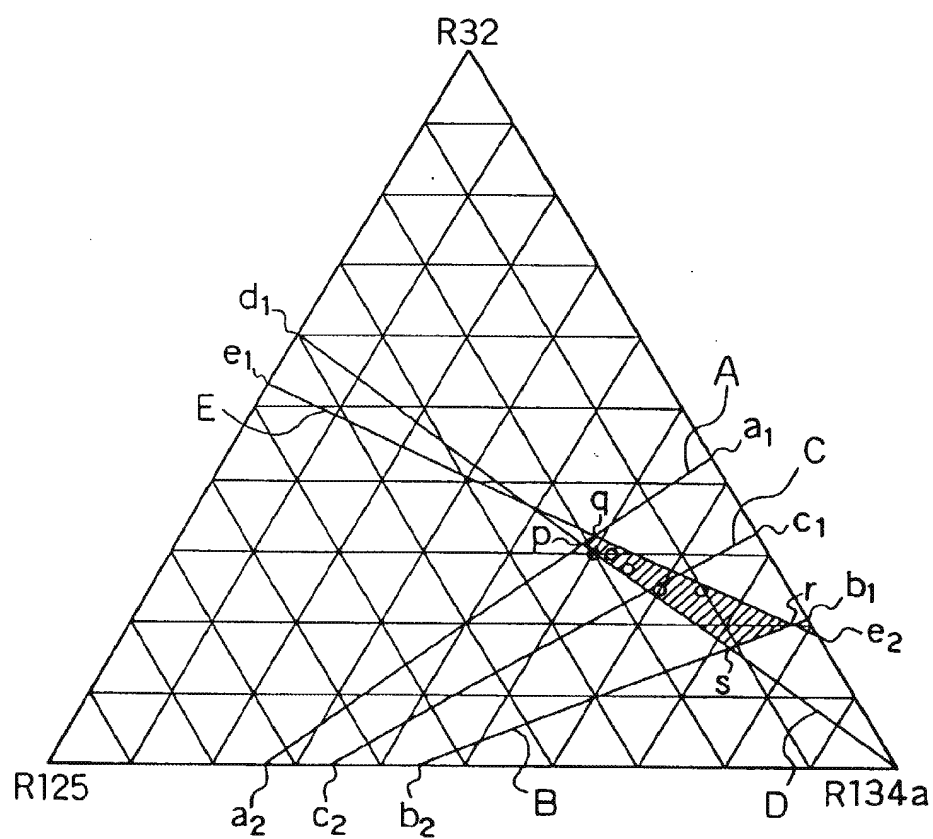


FIG. 2

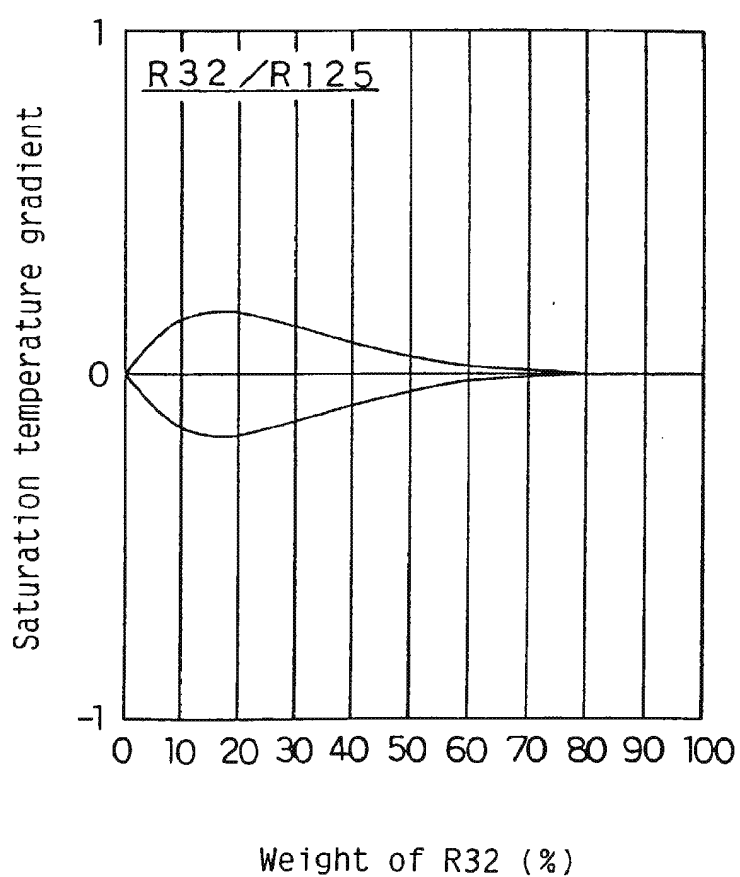


FIG. 3

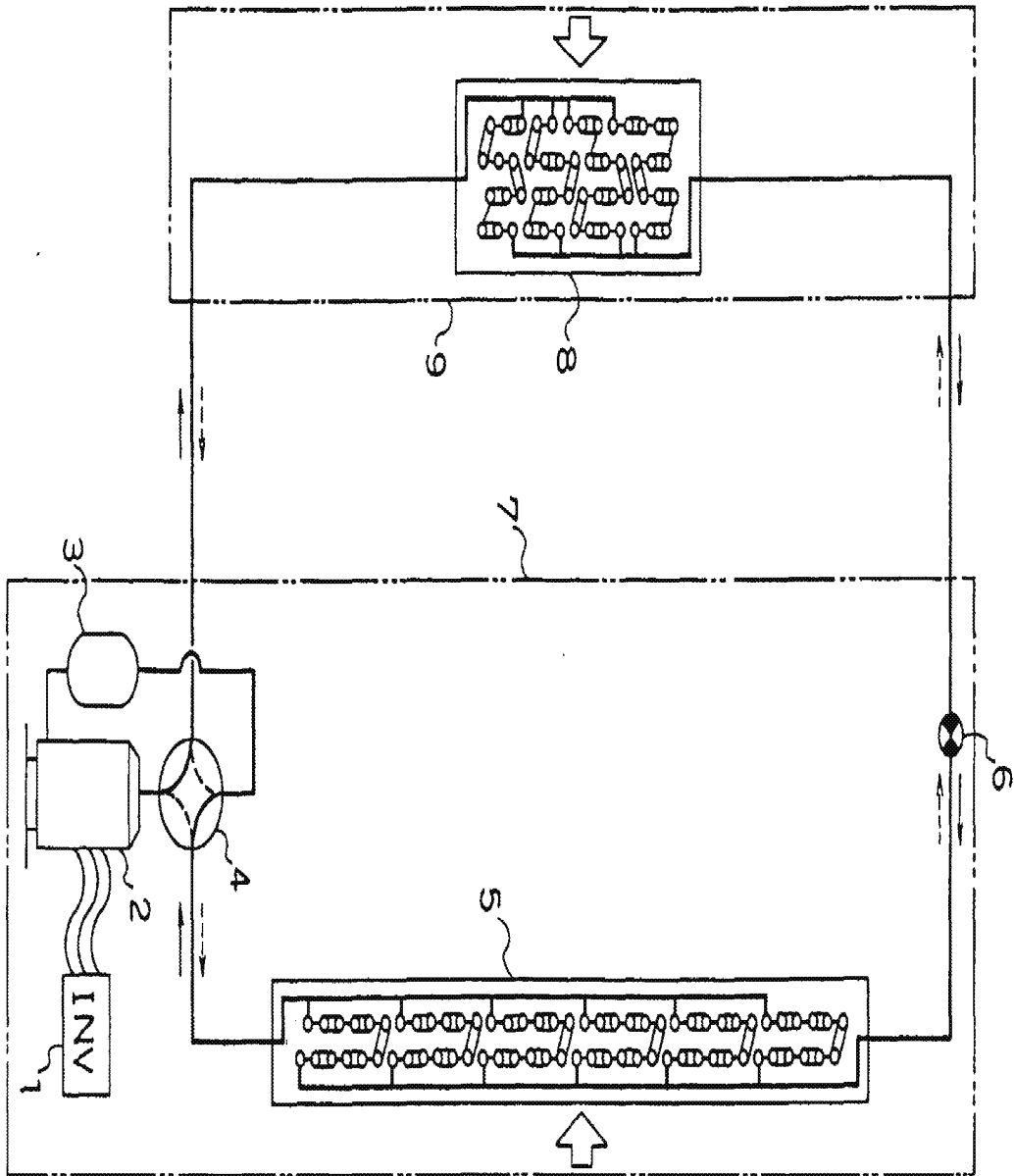
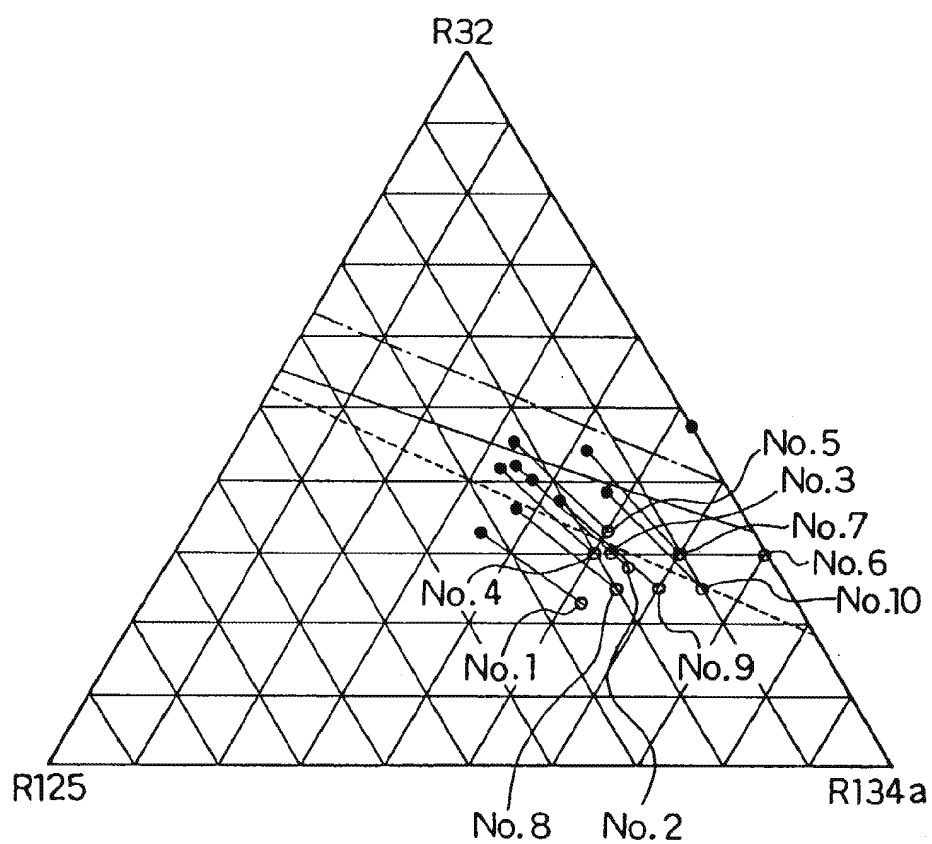


FIG. 4





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 97 10 6576

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X	EP 0 509 673 A (ICI PLC) 21 October 1992 * page 5, line 12 - line 20 * * example 1 * ---	1-3	C09K5/04
D,X	WO 92 11339 A (DU PONT) 9 July 1992 * page 3, line 1 - line 26 * * example 6 * ---	1,2,4	
D,X	EP 0 430 169 A (MATSUSHITA ELECTRIC IND CO LTD) 5 June 1991 * examples 7,A1 * ---	1-4	
X	DATABASE WPI Section Ch, Week 9441 Derwent Publications Ltd., London, GB; Class E16, AN 94-330370 XP002039438 & JP 06 256 757 A (DAIKIN KOGYO KK) , 13 September 1994 * abstract * ---	1-3	
D,A	EP 0 451 692 A (DAIKIN IND LTD) 16 October 1991 * page 2, line 20 - line 38 * * figure 3; example 3 * -----	1,2	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 2 September 1997	Examiner Puetz, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

EPO FORM 1503.03.92 (P04C01)

Electronic Acknowledgement Receipt

EFS ID:	34376553
Application Number:	15989655
International Application Number:	
Confirmation Number:	5897
Title of Invention:	REFRIGERANT WITH LUBRICATING OIL FOR REPLACEMENT OF R22 REFRIGERANT
First Named Inventor/Applicant Name:	Kenneth M. Ponder
Customer Number:	24504
Filer:	Todd Deveau./Sheila Gray
Filer Authorized By:	Todd Deveau.
Attorney Docket Number:	821920-1033
Receipt Date:	21-NOV-2018
Filing Date:	25-MAY-2018
Time Stamp:	14:43:32
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no
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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	821920-1033__SIDS.pdf	1034848	no	4
			702e2e9c41f63258948f3da2a082a1b9127e3f68		

Warnings: