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(54) Title: REFRIGERANT COMPOSITIONS

(57) Abstract

A non-azeotropic (zeotropic) refrigerant composition is described. The refrigerant composition comprises (A) a first component comprising fluoromethane (R-41), (B) a second component comprising at least one hydrofluorocarbon selected from the group consisting of 1,1,1,2-tetrafluoroethane (R-134a) and 1,1,2,2-tetrafluoroethane (R-134), and optionally (C) a third component comprising at least one hydrofluorocarbon selected from the group consisting of difluoromethane (R-32), 1,1,1-trifluoroethane (R-143a) and pentafluoroethane (R-125).

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REFRIGERANT COMPOSITIONS

The present invention relates to non-azeotropic refrigerant compositions and more particularly to non-azeotropic refrigerant compositions which boil over a wide temperature range and thus provide wide temperature glides in the heat exchangers of the heat transfer devices in which they are used.

Heat transfer devices of the mechanical compression type such as refrigerators, freezers, heat pumps and air conditioning systems are well known. In such devices a refrigerant liquid of a suitable boiling point evaporates at low pressure taking heat from a surrounding heat transfer fluid. The resulting vapour is then compressed and passes to a condenser where it condenses and gives off heat to another heat transfer fluid. The condensate is then returned through an expansion valve to the evaporator so completing the cycle. The mechanical energy required for compressing the vapour and pumping the liquid may be provided by an electric motor or an internal combustion engine.

In addition to having a suitable boiling point and a high latent heat of vaporisation, the properties preferred of a refrigerant include low toxicity, non-flammability, non-corrosivity, high stability and freedom from objectionable odour.

Hitherto, heat transfer devices have tended to use fully and partially halogenated chlorofluorocarbon refrigerants such as trichlorofluoromethane (Refrigerant R-11), dichlorodifluoromethane (Refrigerant R-12), chlorodifluoromethane (Refrigerant R-22) and the azeotropic mixture of chlorodifluoromethane and chloropentafluoroethane (Refrigerant R-115); the azeotrope being Refrigerant R-502. Refrigerant R-22, for example, is widely used in air conditioning systems.

However, the fully and partially halogenated chlorofluorocarbons have been implicated in the destruction of the earth's protective ozone layer and as a result the use and production thereof has been limited by international agreement.

Whilst heat transfer devices of the type to which the present invention relates are essentially closed systems, loss of refrigerant to the atmosphere can occur due to leakage during operation of the equipment or during maintenance procedures. It is important, therefore, to replace fully and partially halogenated chlorofluorocarbon refrigerants by materials having low or zero ozone depletion potentials.

In addition to the possibility of ozone depletion, it has been suggested that significant concentrations of chlorofluorocarbon refrigerants in the atmosphere might contribute to global warming (the so-called greenhouse effect). It is desirable, therefore, to use refrigerants which have relatively short atmospheric lifetimes as a result of their ability to react with other atmospheric constituents such as hydroxyl radicals.

Replacements for some of the chlorofluorocarbon refrigerants presently in use have already been developed. These replacement refrigerants tend to comprise selected hydrofluoroalkanes, i.e. compounds which contain only carbon, hydrogen and fluorine atoms in their structure. Thus, refrigerant R-12 is generally being replaced by 1,1,1,2-tetrafluoroethane (R-134a).

Although suitable replacement refrigerants are available, it could be beneficial in certain heat transfer devices to replace the chlorofluorocarbon refrigerant with a non-azeotropic refrigerant blend which not only exhibits a low or zero ozone depletion potential but which also boils over a reasonably wide temperature range, since in this way the energy efficiency (coefficient of performance) of the device may be increased leading to a reduction in indirect global warming.

The present invention provides a non-azeotropic refrigerant composition which comprises a mixture of compounds having low or zero ozone depletion potentials. The refrigerant composition of the invention can boil over a wide temperature range and this property can be exploited to increase the energy efficiency of the equipment in which the composition is used. Furthermore, the temperature range over which the refrigerant composition of the invention boils, i.e. the so-called temperature glide, can be adjusted by appropriate selection of the components and the amounts thereof forming the composition and in this way it is possible to tailor the composition to its intended application.

According to the present invention there is provided a non-azeotropic (zeotropic) refrigerant composition comprising:

(A) a first component comprising fluoromethane (R-41) optionally together with carbon dioxide (CO_2);

(B) a second component comprising at least one hydrofluorocarbon selected from the group consisting of 1,1,1,2-tetrafluoroethane (R-134a) and 1,1,2,2-tetrafluoroethane (R-134); and optionally

(C) a third component comprising at least one hydrofluorocarbon selected from the group consisting of difluoromethane (R-32), 1,1,1-trifluoroethane (R-143a) and pentafluoroethane (R-125).

The zeotropic refrigerant composition of the invention comprises at least the first and second components defined above.

The first component (component (A)) comprises fluoromethane (R-41) or a mixture of R-41 and carbon dioxide (CO_2). Both of these compounds have a low temperature refrigeration action, with CO_2 subliming at around -78.5°C and R-41 having a boiling point of around -78.4 °C.

The second component (component (B)) comprises at least one hydrofluorocarbon selected from the group consisting of 1,1,1,2-tetrafluoroethane (R-134a) and 1,1,2,2-tetrafluoroethane (R-134) which have boiling points of around -26.5°C and -19.7°C respectively. It is apparent that the boiling points of both R-134a and R-134 are appreciably higher than the boiling point of the R-41 and the sublimation temperature of the CO_2 (if included) making up the first component which means that the refrigerant composition of the invention is capable of boiling and condensing over a wide temperature range, i.e. it can exhibit a wide temperature glide in both the evaporator and condenser. Although the second component may contain a mixture of R-134a and R-134, it will preferably contain just one of these compounds and more preferably will contain just R-134a.

The refrigerant composition of the invention may also contain a third component (component (C)) comprising at least one hydrofluorocarbon selected from the group consisting of difluoromethane (R-32), 1,1,1-trifluoroethane (R-143a) and pentafluoroethane (R-125) which have boiling points of around -51.6°C, -47.6°C and -48.5°C respectively. The third component (if included) may contain just one of the three specified compounds or it may comprise a mixture, for example an azeotropic or azeotrope-like mixture, of any two or all three of these compounds. In a preferred embodiment, the third component (if included) is R-32, R-125 or a mixture comprising R-32 and R-125.

The amounts of the first and second components and the amount of the third component (if included) in the refrigerant composition may be varied within wide limits, but typically the refrigerant composition will comprise from 2 to 45 % by weight of the first component, from 15 to 98 % by weight of the second component and from 0 to 60 % by weight (for example, from 2 to 60 % by weight) of the third component. Preferably, the refrigerant composition will comprise from 2 to 35 % by weight of the first component, from 25 to 98 % by weight of the second component and from 0 to 50 % by weight (for example, from 2 to 50 % by weight) of the third component.

When the optional third component is not included and the second component is R-134a, then the refrigerant composition preferably comprises from 2 to 25 % by weight, more preferably from 2 to 10 % by weight, of the first component and from 75 to 98 % by weight, more preferably from 90 to 98 % by weight, of the second component.

When the optional third component is not included and the second component is R-134, then the refrigerant composition preferably comprises from 2 to 30 % by weight, more preferably from 2 to 15 % by weight, of the first component and from 70 to 98 % by weight, more preferably from 85 to 98 % by weight, of the second component.

When the optional third component is included, then the refrigerant composition preferably comprises from 2 to 25 % by weight, more preferably from 2 to 15 % by weight, of the first component, from 35 to 96 % by weight, more preferably from 75 to 96 % by weight, of the second component and from 2 to 40 % by weight, more preferably from 2 to 20 % by weight, of the third component.

The refrigerant composition of the invention may also be combined with one or more hydrocarbon compounds in an amount which is sufficient to allow the composition to transport a mineral oil or alkyl benzene type lubricant around a refrigeration circuit and return it to the compressor. In this way, inexpensive lubricants based on mineral oils or alkyl benzenes may be used to lubricate the compressor.

Suitable hydrocarbons for use with the refrigerant composition of the invention are those containing from 2 to 6 carbon atoms, with hydrocarbons containing from 3 to 5 carbon atoms being preferred. Propane and pentane are particularly preferred hydrocarbons, with pentane being especially preferred.

Where a hydrocarbon is combined with the refrigerant composition of the invention, it will preferably be present in an amount of from 1 to 10 % by weight on the total weight of the refrigerant composition.

The refrigerant composition of the invention may also be used in combination with the types of lubricants which have been specially developed for use with hydrofluorocarbon based refrigerants. Such lubricants include those comprising a polyoxyalkylene glycol base oil. Suitable polyoxyalkylene glycols include hydroxyl group initiated polyoxyalkylene glycols, e.g. ethylene and/or propylene oxide oligomers/polymers initiated on mono- or polyhydric alcohols such as methanol, butanol, pentaerythritol and glycerol. Such polyoxyalkylene glycols may also be end-capped with suitable terminal groups such as alkyl, e.g. methyl groups. Another class of lubricants which have been developed for use with hydrofluorocarbon based refrigerants and which may be used in combination with the present refrigerant compositions are those comprising a neopentyl polyol ester base oil derived from the reaction of at least one neopentyl polyol and at least one aliphatic carboxylic acid or an esterifiable derivative thereof. Suitable neopentyl polyols for the formation of the ester base oil include pentaerythritol, polypentaerythritols such as di- and tripentaerythritol, trimethylol alkanes such as trimethylol ethane and trimethylol propane, and neopentyl glycol. The esters may be formed with linear and/or branched aliphatic carboxylic acids, such as linear and/or branched alkanoic acids. Preferred acids are selected from the C_{5-8}, particularly the C_{5-7}, linear alkanoic acids and the C_{5-10}, particularly the C_{5-9}, branched alkanoic acids. A minor proportion of an aliphatic polycarboxylic acid, e.g. an aliphatic dicarboxylic acid, may also be used in the synthesis of the ester in order to increase the viscosity thereof. Usually, the amount of the carboxylic acid(s) which is used in the synthesis will be sufficient to esterify all of the hydroxyl groups contained in the polyol, although residual hydroxyl functionality may be acceptable.

The single fluid refrigerants and azeotropic refrigerant blends which are used in conventional heat transfer devices boil at a constant temperature in the evaporator under constant pressure conditions, and so produce an essentially constant temperature profile across the evaporator. The temperature of the heat transfer fluid being cooled, which may be air or water for example, drops fairly rapidly on first contacting the cold surfaces provided by the refrigerant evaporating in the evaporator owing to the large difference in temperature between that fluid and the evaporating refrigerant. However, since the temperature of the heat transfer fluid is progressively reduced as it passes along the length of the evaporator, there is a progressive reduction in the temperature differential between the fluid and the evaporating refrigerant and a consequent reduction in the heat transfer or cooling rate.

In contrast, the refrigerant composition of the invention is a non-azeotropic (zeotropic) composition which boils over a temperature range under constant pressure conditions so as to create a temperature glide in the evaporator which can be exploited to reduce the energy required to operate the heat transfer device, e.g. by making use of the Lorentz cycle. One technique for exploiting the temperature glide involves the use of a heat transfer device equipped with a counter current flow evaporator and/or condenser in which the refrigerant and the heat transfer fluid are caused to flow counter currently to each other. With such an arrangement, it is possible to minimise the temperature difference between the evaporating and condensing refrigerant whilst maintaining a sufficiently high temperature difference between the refrigerant and the external fluid(s) to cause the required heat transfer to take place.

The consequence of minimising the temperature difference between the evaporating and condensing refrigerant in the same system is that the pressure difference is also minimised. As a result, the overall energy efficiency of the system is improved as less energy is consumed to bring about the refrigerant pressure rise from evaporator to condenser conditions.

The zeotropic refrigerant composition of the present invention may be used to provide the desired cooling in heat transfer devices such as air conditioning and low temperature refrigeration systems by a method which involves condensing the refrigerant composition and thereafter evaporating it in a heat exchange relationship with a heat transfer fluid to be cooled. In particular, the refrigerant composition of the invention may be usefully employed as a replacement for refrigerant R-22.

The present invention is now illustrated but not limited with reference to the following example.

Example 1

The performance of seven refrigerant compositions of the invention in a refrigeration cycle of the type prevailing in an air conditioning system was evaluated using standard refrigeration cycle analysis techniques in order to assess the suitability thereof as a replacement for R-22. The operating conditions which were used for the analysis were chosen as being typical of those conditions which are found in an air conditioning system, and counter current flow at the heat exchangers was assumed.

In order to illustrate the benefit of the zeotropic refrigerant compositions of the invention in terms of their improved energy efficiency, it was first necessary to define the inlet and outlet temperatures of the heat transfer fluids at each heat exchanger (evaporator and condenser). The temperatures in the evaporator and condenser, assuming that a single fluid refrigerant was used in the cycle, were then chosen and these temperatures together with the inlet and outlet temperatures of the heat transfer fluids referred to above were used to determine a target log mean temperature difference for each heat exchanger. In the cycle analysis itself, the refrigerant inlet and outlet temperatures at both the evaporator and condenser were adjusted until the target log mean temperature difference was achieved for each heat exchanger. When the target log mean temperature difference for each heat exchanger was achieved, the various properties of the refrigerant composition in the cycle were recorded.

The following refrigerant compositions were subjected to the cycle analysis:

(1) A composition comprising 5 % by weight R-41 and 95 % by weight R-134a.

(2) A composition comprising 10 % by weight R-41 and 90 % by weight R-134a.

(3) A composition comprising 5 % by weight R-41, 5 % by weight R-125 and 90% by weight R-134a.

(4) A composition comprising 5 % by weight R-41, 10 % by weight R-125 and 85 % by weight R-134a.

(5) A composition comprising 5 % by weight R-41, 5 % by weight R-32 and 90 % by weight R-134a.

(6) A composition comprising 5 % by weight R-41, 5 % by weight R-32, 5 % by weight R-125 and 85 % by weight R-134a.

(7) A composition comprising 10 % by weight R-41, 5 % by weight R-125 and 85 % by weight R-134a.

The following operating conditions were used in the cycle analysis.

EVAPORATOR:

Evaporator Temperature:	10°C
Inlet Temperature of Heat Transfer Fluid	25°C
Outlet Temperature of Heat Transfer Fluid	15°C
Log Mean Temperature Difference for Evaporator	9.1°C

CONDENSER:

Condenser Temperature:	42°C
Inlet Temperature of Heat Transfer Fluid	30°C
Outlet Temperature of Heat Transfer Fluid	40°C
Log Mean Temperature Difference for Condenser	5.58°C

Amount of Superheat:	15°C
Amount of Subcooling:	5°C
Isentropic Compressor Efficiency:	75 %
Cooling Duty:	1 kW

The results of analysing the performance of the seven refrigerant compositions in an air conditioning cycle using these operating conditions are given in Table 1.

The performance parameters of the refrigerant compositions which are presented in Table 1, i.e. condenser pressure, evaporator pressure, discharge temperature, refrigeration capacity (by which is meant the cooling duty achieved per unit swept volume of the compressor), coefficient of performance (COP) (by which is meant the ratio of cooling duty achieved to mechanical energy supplied to the compressor), and the glides in the evaporator and condenser (the temperature range over which the refrigerant composition boils in the evaporator and condenses in the condenser), are all art recognised parameters.

The performance of refrigerant R-22 and R-134a under the same operating conditions is also shown in Table 1 by way of comparison.

It is apparent from Table 1 that the refrigerant compositions of the invention boiled over a wide temperature range in the evaporator and condensed over a wide temperature range in the condenser, i.e. they exhibited wide glide behaviour in both heat exchangers, and that this property enhanced the energy efficiency of the air conditioning cycle as is evident from the higher values recorded for the coefficient of performance in the case of the refrigerant compositions of the invention. It is also apparent from Table 1 that the refrigerant composition of the invention can exhibit a performance in an air conditioning system which, except for the wide glide behaviour and its attendant advantages, is comparable to that of refrigerant R-22.

TABLE 1

Refrigerant % by weight	R22 100	R134a 100	41/134a 5/95	41/134a 10/90	41/125/134a 5/5/90	41/125/134a 5/10/85	41/32/134a 5/5/90	41/32/125/134a 5/5/5/85	41/125/134a 10/5/85
Evaporator Pressure (bar)	6.79	4.14	5.44	6.67	5.63	5.83	5.85	6.04	6.87
Condenser Pressure (bar)	16.14	10.66	13.36	16.32	13.75	14.16	14.2	14.6	16.73
Discharge Temperature (°C)	79.7	79.7	72.4	78.5	72.3	72.2	74.3	74.1	78.1
Coefficient of Performance (COP)	5.34	5.36	5.77	5.64	5.75	5.74	5.77	5.76	5.63
COP Relative to R22	1	1.01	1.08	1.06	1.08	1.07	1.08	1.08	1.05
Refrigeration Capacity (KJ/m^3)	4,348	2,857	3,846	4,545	4,000	4,000	4,000	4,167	4,762
Refrigeration Capacity Relative to R-22	1	0.66	0.88	1.05	0.92	0.92	0.92	0.96	1.1
Evaporator Glide °C	0	0	7.2	8	7.5	7.7	7.9	8.1	12.1
Condenser Glide °C	0	0	9.8	14.8	9.9	9.9	10	10	14.5

Claims:

1. A non-azeotropic refrigerant composition comprising:

(A) a first component comprising fluoromethane; and

(B) a second component comprising at least one hydrofluorocarbon selected from the group consisting of 1,1,1,2-tetrafluoroethane and 1,1,2,2-tetrafluoroethane.

2. A non-azeotropic refrigerant composition as claimed in claim 1 wherein the first component (A) additionally comprises carbon dioxide.

3. A non-azeotropic refrigerant composition as claimed in claim 1 or claim 2 wherein the second component is 1,1,1,2-tetrafluoroethane.

4. A non-azeotropic refrigerant composition as claimed in claim 3 which comprises from 2 to 25 % by weight of the first component (A) and from 75 to 98 % by weight of the second component (B).

5. A non-azeotropic refrigerant composition as claimed in claim 4 which comprises from 2 to 10 % by weight of the first component (A) and from 90 to 98 % by weight of the second component (B).

6. A non-azeotropic refrigerant composition as claimed in claim 1 or claim 2 wherein the second component is 1,1,2,2-tetrafluoroethane.

7. A non-azeotropic refrigerant composition as claimed in claim 6 which comprises from 2 to 30 % by weight of the first component (A) and from 70 to 98 % by weight of the second component (B).

8. A non-azeotropic refrigerant composition as claimed in claim 7 which comprises from 2 to 15 % by weight of the first component (A) and from 85 to 98 % by weight of the second component (B).

9. A non-azeotropic (zeotropic) refrigerant composition comprising:

(A) a first component comprising fluoromethane;

(B) a second component comprising at least one hydrofluorocarbon selected from the group consisting of 1,1,1,2-tetrafluoroethane and 1,1,2,2-tetrafluoroethane; and optionally

(C) a third component comprising at least one hydrofluorocarbon selected from the group consisting of difluoromethane, 1,1,1-trifluoroethane and pentafluoroethane.

10. A non-azeotropic refrigerant composition as claimed in claim 9 wherein the first component (A) additionally comprises carbon dioxide.

11. A non-azeotropic refrigerant composition as claimed in claim 9 or claim 10 which comprises from 2 to 45 % by weight of the first component (A), from 15 to 98 % by weight of the second component (B) and from 0 to 60 % by weight of the third component (C).

12. A non-azeotropic refrigerant composition as claimed in claim 11 which comprises from 2 to 35 % by weight of the first component (A), from 25 to 98 % by weight of the second component (B) and from 0 to 50 % by weight of the third component (C).

13. A non-azeotropic refrigerant composition as claimed in claim 9 or claim 10 which comprises the optional third component (C).

14. A non-azeotropic refrigerant composition as claimed in claim 11 which comprises the optional third component (C) in an amount of from 2 to 60 % by weight on the total weight of the refrigerant composition.

15. A non-azeotropic refrigerant composition as claimed in claim 12 which comprises the optional third component (C) in an amount of from 2 to 50 % by weight on the total weight of the refrigerant composition.

16. A non-azeotropic refrigerant composition as claimed in claim 13 which comprises from 2 to 25 % by weight of the first component (A), from 35 to 96 % by weight of the second component (B) and from 2 to 40 % by weight of the third component (C).

17. A non-azeotropic refrigerant composition as claimed in claim 16 which comprises from 2 to 15 % by weight of the first component (A), from 75 to 96 % by weight of the second component (B) and from 2 to 20 % by weight of the third component (C).

18. A refrigeration or air conditioning system containing a non-azeotropic refrigerant composition as claimed in any one of claims 1 to 17.

19. The use in a refrigeration or air conditioning system of a non-azeotropic refrigerant composition as claimed in any one of claims 1 to 17.

20. A method for providing cooling which comprises condensing a non-azeotropic refrigerant composition as claimed in any one of claims 1 to 17 and thereafter evaporating it in a heat exchange relationship with a fluid to be cooled.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 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 6 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 299 614 (DU PONT DE NEMOURS) 18 January 1989 see abstract; claims 1-4; table 2 ---	1-20
Y,P	WO,A,94 17153 (IMPERIAL CHEMICAL INDUSTRIES) 4 August 1994 see page 8, line 17 - page 9, line 1; claims 1-11 see abstract ---	1-20
A,P	US,A,5 340 490 (DECAIRE) 23 August 1994 see abstract; claims 1-3; example 1 ---	1-20
A	DE,A,41 16 274 (FORSCHUNGSZENTRUM FUER KAELTE TECHNIK) 19 November 1992 see abstract; claims 1-4; example 1 --- -/--	1-20

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 12 September 1995	Date of mailing of the international search report 22.09.95.
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PCT/GB 95/01592

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO,A,93 14174 (IMPERIAL CHEMICAL INDUSTRIES) 22 July 1993 see page 3, line 1 - page 4, line 7; claims 1-8 see abstract	1-20

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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