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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :		(11) International Publication Number:
C09K 5/04, C11D 7/50, B60H 1/00	A1	WO 97/16501
		(43) International Publication Date: 9 May 1997 (09.05.97)

(21) International Application Number: PCT/GB96/02574

(22) International Filing Date: 21 October 1996 (21.10.96)

(30) Priority Data:
9522377.2 1 November 1995 (01.11.95) GB

(71) Applicant *(for all designated States except US)*: IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: MORRISON, James, David [GB/GB]; 38 Sandown Crescent, Cuddington, Northwich, Cheshire CW8 2QN (GB).

(74) Agents: DEE, Ian, Mark et al.; ICI Chemicals & Polymers Limited, Intellectual Property Dept., P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: REFRIGERANT COMPOSITIONS

(57) Abstract

An azeotrope-like composition comprising: (A) 1,1,1,2-tetrafluoroethane and (B) n-pentane. Also described is a heat transfer device comprising the azeotrope-like composition.

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REFRIGERANT COMPOSITIONS

This invention relates to refrigerant compositions and to the use of such compositions in heat transfer devices such as refrigeration and air conditioning systems. The invention relates, in particular, to refrigerant compositions which can be used in the automobile air conditioning and refrigeration applications currently satisfied by dichlorodifluoromethane (refrigerant R-12).

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 for 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. In particular, refrigerant R-12 has found widespread use in automobile air conditioning and domestic refrigeration 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.

Replacements for some of the chlorofluorocarbon refrigerants presently in use have already been developed. These replacement refrigerants tend to comprise selected hydrofluorocarbons, 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).

In a heat transfer device, the refrigerant forms part of a working fluid composition which also comprises a lubricant. The lubricant circulates around the device along with the refrigerant and provides for continual lubrication of the compressor. In addition to possessing good lubricity in the presence of the refrigerant, the properties desired of a lubricant include good hydrolytic stability and good thermal stability. Moreover, in order to provide for the return of the lubricant to the compressor, the lubricant should be compatible with the refrigerant, which in practice means that the lubricant and refrigerant should possess a degree of mutual solubility, i.e. the lubricant and the refrigerant should be at least partially soluble in one another.

Hitherto, heat transfer devices have tended to use mineral oils as lubricants. The good solubility of chlorofluorocarbons with mineral oils allows the mineral oil to circulate around the heat transfer device together with the chlorofluorocarbon, and this in turn ensures effective lubrication of the compressor. Unfortunately, however, the replacement refrigerants tend to have different solubility characteristics to the chlorofluorocarbons presently in

use and tend to be insufficiently soluble in mineral oils to allow the latter to be used as lubricants.

Consequently, the need to replace the chlorofluorocarbon refrigerants has presented industry with very real difficulties, since not only is there the problem of finding a viable replacement refrigerant which has the required low or zero ozone depletion potential, but also, in many cases, there is also the problem of developing a lubricant which will perform satisfactorily with the replacement refrigerant.

The present invention provides a refrigerant composition comprising a mixture of compounds having zero ozone depletion potentials which may be used together with a mineral oil or alkyl benzene type lubricant in the automobile air conditioning and refrigeration applications currently satisfied by refrigerant R-12.

According to the present invention there is provided an azeotrope-like composition for use in heat transfer devices such as automobile air conditioning and domestic refrigeration systems comprising 1,1,1,2-tetrafluoroethane (R-134a) and n-pentane.

The present invention also provides a heat transfer device, such as a refrigeration or air conditioning system, comprising an evaporator, a condenser, a compressor and an expansion valve in which there is contained an azeotrope-like refrigerant composition comprising 1,1,1,2-tetrafluoroethane and n-pentane. The composition of the invention may, in particular, be used in domestic refrigeration systems and automobile air conditioning systems.

The azeotrope-like composition of the present invention comprises 1,1,1,2-tetrafluoroethane and n-pentane. The n-pentane is capable of dissolving in mineral oil or alkyl benzene lubricants and this property may allow the composition of the invention to transport such a lubricant around a heat transfer device and return it to the compressor. As a result, heat transfer devices which employ the composition of the invention as the refrigerant may be able to employ inexpensive lubricants based on mineral oils or alkyl benzenes to lubricate the compressor.

The term azeotropic is well known in the art of refrigeration and refers to compositions comprising two or more components which exhibit constant boiling behaviour and which tend not to fractionate or separate into their constituent components upon boiling or evaporation. Thus, when an azeotropic refrigerant is employed, the liquid and vapour phases that are encountered during the refrigeration cycle tend to have identical or substantially identical compositions. The term azeotrope-like as used herein refers to compositions that behave like the true azeotrope in that they exhibit constant boiling or essentially constant boiling behaviour and tend not to fractionate to any significant degree on boiling. Thus, with an azeotrope-like composition the liquid and vapour phases that are encountered during the refrigeration cycle will also tend to have similar compositions.

The azeotrope-like compositions of the invention will preferably comprise from 95.0 to 99.9 % by weight of the 1,1,1,2-tetrafluoroethane and from 0.1 to 5.0 % by weight of the n-pentane. Particularly preferred compositions are those comprising from 97.0 to 99.8 % by weight 1,1,1,2-tetrafluoroethane and from 0.2 to 3.0 % by weight n-pentane which exhibit azeotrope-like behaviour at the temperatures and pressures which are typically encountered in automobile air conditioning and domestic refrigeration systems, i.e. temperatures in the range of from -40 to +45°C and pressures in the range of from 0.5 to 12 bar ($0.5x10^5$ N/m^2 to $12x10^5$ N/m^2).

The azeotrope-like composition of the present invention may be used to provide the desired cooling in heat transfer devices such as automobile air conditioning and domestic refrigeration systems by a method which involves condensing the composition and thereafter evaporating it in a heat exchange relationship with a heat transfer fluid to be cooled such as air or water. In particular, the azeotrope-like composition of the invention may be employed as a replacement for refrigerant R-12. The composition of the invention may also be employed as a replacement for refrigerant R-500 which is

a mixture of refrigerant R-12 and 1,1-difluoroethane (R-152a) in specific proportions.

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

Example 1

A thermodynamic study was carried out on 1,1,1,2-tetrafluoroethane (hereinafter R-134a) and n-pentane in order to test for the existence of an azeotrope-like blend thereof. The vapour/liquid equilibrium (VLE) behaviour of a series of compositions containing R-134a and n-pentane in varying amounts was first measured. This measured VLE data was then used, together with the known properties of pure R-134a and pure n-pentane, to develop a modified Huron-Vidal (MHV-2) equation of state for the R-134a/n-pentane blend which was fitted to the measured VLE data in order to determine the various interaction parameters characterising the deviations from ideality of the blend. The resulting equation of state was then used to determine more closely the existence and composition of any azeotrope-like blends of R-134a and n-pentane at a number of different temperatures in the range of from -20°C to +30°C. This was achieved by varying the vapour pressure and composition of the R-134a/n-pentane blend at each temperature investigated until essentially identical liquid and vapour compositions were obtained. The results are given in Table 1. For each temperature specified in Table 1, the vapour pressure and composition of the R-134a/n-pentane blend which resulted in essentially identical liquid and vapour compositions (i.e. to the first decimal place in mole %) are recorded.

TABLE 1

Temperature (°C)	Pressure (Bar)	Composition of R-134a/n-pentane blend	
		Mole %	Weight %
-20.00	1.36	96.1/3.9	97.2/2.8
0.00	2.96	96.7/3.3	97.6/2.4
20.00	5.70	98.4/1.6	98.9/1.1
30.00	7.66	99.6/0.4	99.7/0.3

Claims:

1. An azeotrope-like composition comprising 1,1,1,2-tetrafluoroethane (R-134a) and n-pentane.

2. An azeotrope-like composition as claimed in claim 1 comprising from 95.0 to 99.9 % by weight 1,1,1,2-tetrafluoroethane and from 0.1 to 5.0 % by weight of n-pentane.

3. An azeotrope-like composition as claimed in claim 2 comprising from 97.0 to 99.8 % by weight 1,1,1,2-tetrafluoroethane and from 0.2 to 3.0 % by weight n-pentane.

4. An azeotrope-like composition as claimed in any one of claims 1 to 3 which exhibits azeotrope-like behaviour at the temperatures and pressures which are encountered in automobile air conditioning and domestic refrigeration systems.

5. An azeotrope-like composition as claimed in any one of claims 1 to 3 which exhibits azeotrope-like behaviour at temperatures in the range of from -40 to +45°C and pressures in the range of from 0.5 to 12 bar (0.5×10^5 N/m² to 12×10^5 N/m²).

6. A method of providing cooling which comprises condensing an azeotrope-like composition as claimed in any one of claims 1 to 5 and thereafter evaporating it in a heat exchange relationship with a heat transfer fluid to be cooled.

7. A method of providing cooling in an automobile air conditioning system or a domestic refrigeration system which method comprises condensing an azeotrope-like composition as claimed in any one of claims 1 to 5 and thereafter evaporating it in a heat exchange relationship with a heat transfer fluid to be cooled.

8. A heat transfer device comprising an evaporator, a condenser, a compressor and an expansion valve in which there is contained an azeotrope-like composition as claimed in any one of claims 1 to 5.

9. An air conditioning system or refrigeration system comprising an evaporator, a condenser, a compressor and an expansion valve in which there is contained an azeotrope-like composition as claimed in any one of claims 1 to 5.

10. An automobile air conditioning system or a domestic refrigeration system comprising an evaporator, a condenser, a compressor and an expansion valve in which there is contained an azeotrope-like composition as claimed in any one of claims 1 to 5.

11. The use of an azeotrope-like composition as claimed in any one of claims 1 to 5 as a replacement for refrigerant R-12.

INTERNATIONAL SEARCH REPORT

Interna al Application No
PCT/GB 96/02574

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K5/04 C11D7/50 B60H1/00

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 C11D

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.
X	EP,A,0 659 862 (SANYO ELECTRIC CO.) 28 June 1995 see column 3, line 8 - line 23 see column 4, line 2 - line 50 see column 6, line 28 - line 32 see column 8, line 10 - line 38 see claims 4,5 ---	1-3,6-8
X,P	CHEMICAL ABSTRACTS, vol. 124, no. 4, 22 January 1996 Columbus, Ohio, US; abstract no. 33550, SANYO ELECTRIC: "refrigerant compositions for protection of ozone layers" XP002024171 see abstract	1
X	& JP,A,07 252 473 (SANYO ELECTRIC) see column 2, line 42 - line 46 ---	1
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
30 January 1997	- 7. 02. 97

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,94 18282 (E.I.DU PONT DE NEMOURS) 18 August 1994 see claims 1,6 -----	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Interna. al Application No
PCT/GB 96/02574

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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