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<p>(21) International Application Number: PCT/US94/06003</p> <p>(22) International Filing Date: 27 May 1994 (27.05.94)</p> <p>(30) Priority Data: 08/092,317 14 July 1993 (14.07.93) US</p> <p>(71) Applicant: ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).</p> <p>(72) Inventors: DECAIRE, Barbara, Ruth; 200-L Sunshine Drive, West Amherst, NY 14228 (US). LOGSDON, Peter, Brian; 1536 Kingston Avenue, North Tonawanda, NY 14120 (US). LUND, Earl, August, Eugene; 404 Reserve Road, West Seneca, NY 14224 (US). SHANKLAND, Ian, Robert; 200 Forest Hill Drive, Williamsville, NY 14221 (US). SINGH, Rajiv, Ratna; 18 Foxfire Drive, Getzville, NY 14221 (US). WILSON, David, Paul; 118 Waxwing Court, East Amherst, NY 14051 (US). THOMAS, Raymond, Hilton, Percival; 131 Sunset Court, Amherst, NY 14228 (US).</p> <p>(74) Agent: CRISS, Roger, H.; AlliedSignal Inc., Law Dept. (C.A. McNally), 101 Columbia Road, P.O. Box 2245R, Morristown, NJ 07962-2245 (US).</p>	<p>(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, HU, JP, KP, KR, KZ, LK, LV, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, 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).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: AZEOTROPE-LIKE COMPOSITIONS OF TRIFLUOROMETHANE AND CARBON DIOXIDE OR HEXAFLUOROETHANE AND CARBON DIOXIDE</p>		
<p>(57) Abstract</p> <p>Azeotrope-like compositions comprising trifluoromethane and carbon dioxide or hexafluoroethane and carbon dioxide are stable and have utility as refrigerants for heating and cooling as well as fire extinguishing compositions.</p>		

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AZEOTROPE-LIKE COMPOSITIONS OF
TRIFLUOROMETHANE AND CARBON DIOXIDE OR
5 HEXAFLUOROETHANE AND CARBON DIOXIDE

BACKGROUND OF THE INVENTION

This invention relates to azeotrope-like or constant-boiling mixtures of
10 trifluoromethane and carbon dioxide or hexafluoroethane and carbon dioxide.
These mixtures are useful as refrigerants for heating and cooling and also as
fire extinguishing compositions.

Fluorocarbon based fluids have found widespread use in industry for
15 refrigeration applications such as air conditioning and heat pump
applications. Vapor compression is one form of refrigeration. In its simplest
form, vapor compression involves changing the refrigerant from the liquid to
the vapor phase through heat absorption at a low pressure and then from
the vapor to the liquid phase through heat removal at an elevated pressure.

20 While the primary purpose of refrigeration is to remove energy at low
temperature, the primary purpose of a heat pump is to add energy at higher
temperature. Heat pumps are considered reverse cycle systems because for
heating, the operation of the condenser is interchanged with that of the
25 refrigeration evaporator.

Certain chlorofluoromethane and chlorofluoroethane derivatives have
gained widespread use as refrigerants in applications including air
conditioning and heat pump applications owing to their unique combination
30 of chemical and physical properties. The majority of refrigerants utilized in

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vapor compression systems are either single components fluids or azeotropic mixtures.

Azeotropic or azeotrope-like compositions are desired as refrigerants
5 because they do not fractionate upon boiling. This behavior is desirable
because in the previously described vapor compression equipment with
which these refrigerants are employed, condensed material is generated in
preparation for cooling or for heating purposes. Unless the refrigerant
composition exhibits a constant boiling point, i.e. is azeotrope-like,
10 fractionation and segregation will occur upon evaporation and condensation
and undesirable refrigerant distribution may act to upset the cooling or
heating.

The art is continually seeking new fluorocarbon and
15 hydrofluorocarbon based azeotrope-like mixtures which offer alternatives for
refrigeration and heat pump applications. Fluorocarbon and
hydrofluorocarbon based azeotrope-like mixtures are of particular interest
because they are considered to be environmentally safe substitutes for the
presently used fully halogenated chlorofluorocarbons (CFC's) which are
20 suspected of causing environmental problems in connection with the earth's
protective ozone layer. R-503 is an azeotropic blend which consists of
trifluoromethane (HFC-23) and chlorotrifluoromethane (CFC-13), a fully
halogenated chlorofluorocarbon (U.S. Patents 2,101,993 and 2,641,579).

25 Substitute refrigerants must also possess those properties unique to
the CFC's refrigerants including similar refrigeration characteristics, chemical
stability, low toxicity, non-flammability, and efficiency in-use. The latter
characteristic is important in refrigeration and air-conditioning especially
where a loss in refrigerant thermodynamic performance or energy efficiency
30 may have secondary environmental impacts through increased fossil fuel

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usage arising from an increased demand for electrical energy. Furthermore, the ideal CFC refrigerant substitute would not require major engineering changes to conventional vapor compression technology currently used with CFC refrigerants. Mathematical models have substantiated that

5 hydrofluorocarbons, such as trifluoromethane (HFC-23), will not adversely affect atmospheric chemistry, being a negligible contributor to ozone depletion and to green-house global warming in comparison to the fully halogenated species. HFC-23 alone is not useful as a refrigerant because of a reduction in low evaporator temperature capability.

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JO-3,255,189-A published November 14, 1991 teaches a refrigerant composition of HFC-23 and n-pentane.

Bromofluoromethane and bromochlorofluoromethane derivatives,

15 particularly bromotrifluoromethane (Halon 1301) and bromochlorodifluoromethane (Halon 1211) have gained widespread use as fire extinguishing agents in enclosed areas such as airplane cabins and computer rooms. However, the use of these materials is being phased out due to their high ozone depletion. Moreover, as Halons are frequently used

20 in areas where humans are present, suitable replacements must also be safe to humans at concentrations necessary to suppress or extinguish fire.

Low or non-ozone depleting hydrochlorofluorocarbons have been disclosed to be suitable replacements for various Halons in fire

25 extinguishing. For example, U.S. Patent No. 5,040,609 discloses a process for preventing and controlling fires using a composition containing trifluoromethane. CO₂ is a common fire extinguishing agent used in household fire extinguishers. However, there remains a need for suitable Halon replacements.

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DETAILED DESCRIPTION OF THE INVENTION

We have discovered novel azeotrope-like or constant-boiling compositions comprising trifluoromethane (HFC-23) and carbon dioxide or
5 trifluoromethane, hexafluoroethane (FC-116) and carbon dioxide.

The present binary azeotrope-like compositions consist essentially of about 35 to about 85 weight percent trifluoromethane and about 15 to about 65 weight percent carbon dioxide which have a vapor pressure of
10 about 15 psia (103 kPa) at $-85 \pm 1^\circ\text{C}$. The present ternary azeotrope-like compositions consist essentially of about 30 to about 43 weight percent trifluoromethane, about 33 to about 43 weight percent hexafluoroethane and about 14 to about 37 weight percent carbon dioxide which have a vapor pressure of about 15 psia at about $-87 \pm 1^\circ\text{C}$.

15

The present azeotrope-like compositions are advantageous for the following reasons. Each component is a negligible contributor to ozone depletion. Also, because the present compositions exhibit essentially constant-vapor pressure characteristics as the liquid mixture is evaporated
20 and show relatively minor shifts in composition during evaporation, the compositions are advantageous in a vapor compression cycle as they mimic the performance of a constant-boiling single component or azeotropic mixture refrigerant.

25 The preferred azeotrope-like compositions are in the following Table. In the Table, the numerical ranges are understood to be prefaced by "about":

COMPONENTS	PREFERRED RANGE (WT.%)	MORE-PREFERRED RANGE (WT.%)	MOST PREFERRED RANGE (WT.%)	VAPOR PRESSURE (PSIA) (kPa)
HFC-23	35-85	40-80	50-70	15 at -85 ± 1°C
CO ₂	15-65	20-60	30-50	
HFC-23	30-43	33-43	36-40	15 at -87 ± 1°C
FC-116	33-43	33-43	36-40	
CO ₂	14-37	14-34	20-28	

Since CO₂, FC-116 and HFC-23 are individually non-flammable materials, their mixtures in all proportions are likewise non-flammable.

15 Additional components may be added to the mixture to tailor the properties of the mixture according to the need. For example, in the art, propane has been added to refrigerant compositions to aid oil solubility. Similar materials may be added to the present mixture.

20 All compositions within the indicated ranges, as well as certain compositions outside the indicated ranges, are azeotrope-like, as defined more particularly below.

25 The term "azeotrope-like composition" as used herein is intended to mean that the composition behaves like an azeotrope, i.e. has constant-boiling characteristics or a tendency not to fractionate upon boiling or evaporation. Thus, in such compositions, the composition of the vapor formed during boiling or evaporation is identical or substantially identical to the original liquid composition. Hence, during boiling or evaporation, the
30 liquid composition, if it changes at all, changes only to a minimal or

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negligible extent. This is to be contrasted with non-azeotrope-like compositions in which during boiling or evaporation, the liquid composition changes to a substantial degree.

5 In one process embodiment of the invention, the azeotrope-like compositions of the invention may be used in a method for producing refrigeration which comprises condensing a refrigerant comprising the azeotrope-like compositions and thereafter evaporating the refrigerant in the vicinity of a body to be cooled.

10

 In another process embodiment of the invention, the azeotrope compositions of the invention may be used in a method for producing heating which comprises condensing a refrigerant comprising the azeotrope-like compositions in the vicinity of a body to be heated and thereafter
15 evaporating the refrigerant.

 In the fire extinguishing embodiment of the invention, the azeotrope-like compositions may be used to extinguish a fire by releasing an effective amount of the composition in an enclosed area containing the fire. As used
20 herein the term effective amount is an amount which will impart to the modified air a heat capacity per mole of total oxygen present sufficient to suppress or prevent combustion of the flammable, non-self-sustaining materials in the enclosed environment. The minimum heat capacities required to prevent or suppress combustion of a variety of materials are
25 generally known in the art and are disclosed in U.S. Patent No. 5,141,654, incorporated herein by reference. The fire extinguishing compositions of the present invention may also be directly applied to a fire.

 The compositions of the present invention may be released via any
30 method known in the art, such as controlled release into the environment of

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the enclosed space or propelling from a portable or fixed fire extinguisher. Other methods for releasing or applying the fire extinguishing compositions are well known in the art and need not be repeated here.

5 The compositions may be controllingly released any time that it appears desirable. For example, the modified air can be continuously released at a level sufficient to prevent the start of a fire in environments where the chance of fire must be kept at an absolute minimum or where the threat of fire is constant. Alternatively, the compositions of the present
10 invention may be released as an emergency measure when a fire develops.

 The trifluoromethane, hexafluoroethane and carbon dioxide of the novel azeotrope-like compositions of the invention are known materials and are commercially available. Preferably, the materials should be used in
15 sufficiently high purity so as to avoid the introduction of adverse influences upon the cooling or heating properties or constant-boiling properties of the system.

EXAMPLE 1

20

 This Example shows the azeotrope-like nature of a mixture of trifluoromethane and carbon dioxide.

 A 50:50 weight percent mixture of HFC-23 and CO₂ was charged into
25 a packed distillation column with about 150 theoretical separation stages. The overhead composition of the distillate remained at about 42 weight percent CO₂ and about 58 weight percent HFC-23; i.e. these two components could not be separated. Further, the boiling point of the mixture was noted to be about -85°C, which is lower than that of
30 trifluoroethane (-82°C). Carbon dioxide is a solid at this temperature.

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EXAMPLE 2

This Example shows that constant-boiling HFC-23/carbon dioxide blends have certain advantages when compared to other refrigerants which are currently used in certain refrigeration cycles.

The theoretical performance of a refrigerant at specific operating conditions can be estimated from the thermodynamic properties of the refrigerant using standard refrigeration cycle analysis techniques; see for example, R.C. Downing, FLUOROCARBON REFRIGERANTS HANDBOOK, Chapter 3, Prentice-Hall, 1988. The coefficient of performance (COP) is a universally accepted measure, especially useful in representing the relative thermodynamic efficiency of a refrigerant in a specific heating or cooling cycle involving evaporation or condensation of the refrigerant. In refrigeration engineering, this term expresses the ratio of useful refrigeration to the energy applied by the compressor in compressing the vapor. The capacity of a refrigerant represents the volumetric efficiency of the refrigerant. To a compressor engineer, this value expresses the capability of a compressor to pump quantities of heat for a given volumetric flow rate of refrigerant. In other words, given a specific compressor, a refrigerant with a higher capacity will deliver more cooling or heating power.

This type of calculation was performed for a medium to low temperature refrigeration cycle where the condenser temperature is typically -20°F and the evaporator temperature is typically -120°F. We have further assumed isentropic compression and a superheat of 20°F (18.3°C). Such calculations were performed for various combinations of HFC-23 and carbon dioxide as well as for R-503. Table II lists the COP and capacity of the various blends relative to that of R-503. In Table II, "*" means that the COP and capacity are given relative to R-503.

Table II

THERMODYNAMIC PERFORMANCE		
Composition HFC-23/carbon dioxide (by weight)	COP*	Capacity*
100%	1.02	0.83
58%	1.03	0.91
0%	Carbon dioxide is a solid at the operating conditions and cannot act as a refrigerant.	

As can be seen, the 58 weight percent HFC-23 mixture (azeotrope) has improved refrigeration properties over either HFC-23 or carbon dioxide alone and is a good R-503 alternate.

EXAMPLE 3

This Example shows that the HFC-23/carbon dioxide blends of the invention have utility as fire extinguishing agents.

The fire extinguishing concentrations of CHF₃ and CO₂ blends are determined by the cup burner method. This method is described in Measurement of Flame-Extinguishing Concentrations, R. Hirst and K. Booth, Fire Technology, Vol. 13, 269-315 (1977). Specifically, an air stream is passed at 40 liters/minute through an outer chimney from a distributor at its base. A fuel cup burner is positioned within the chimney below the top edge of the chimney. The fire extinguishing agent is added to the air stream

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prior to its entry into the distributor. The air and agent flow rates are measured using calibrated rotameters.

Each test is conducted by adjusting the fuel level in the reservoir to bring the liquid fuel level in the cup burner just even with the ground glass lip on the burner cup. With the air flow rate maintained at 10 liters/minute, the fuel in the cup burner is ignited. The fuels are heptane or methanol. A 50:50 weight percent mixture of HFC-23 and CO₂ is added by increments until the flame is extinguished.

10

Example 4

This example shows that a mixture of HFC-23, FC-116 and carbon dioxide form a three component azeotrope, i.e., they can not be separated by distillation and the boiling point of the mixture is lower than the boiling point of the HFC-23/carbon dioxide binary azeotrope (boiling point -85.5°C) or FC-116 (-78.1°C).

A mixture of approximately 200 g of 30 weight percent HFC-23, 40 weight percent FC-116 and 30 weight percent CO₂ is charged in a low temperature still with approximately 150 theoretical separation stages. The distillation is started at total reflux and at atmospheric pressure. After an hour equilibrium is reached. The refluxing condensate is sampled and analyzed by gas chromatography. The temperature of the condensate is stable at approximately -87°C, lower than that of the binary azeotrope of Example 1 (-85.5°C). The overhead composition remains constant at approximately 38±% wt% HFC-23, 38±5 wt% FC-116, with the balance being CO₂.

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The fact that the boiling point of the ternary is lower than the binary azeotrope or FC-116 establishes that the system is a positive azeotrope. The fact that the ternary cannot be separated into its components, even in a very efficient distillation column, confirms azeotropy.

WHAT IS CLAIMED IS:

1. Azeotrope-like compositions consisting essentially of trifluoromethane and carbon dioxide or hexafluoroethane and carbon dioxide wherein said
5 compositions consist essentially of

about 35 to about 85 weight percent trifluoromethane and about 15 to about 65 weight percent carbon dioxide which have a vapor pressure of about 15 psia at about $85 \pm 1^\circ\text{C}$ when the azeotrope-
10 like components consist of trifluoromethane and carbon dioxide; and

about 30 to about 43 weight percent trifluoromethane, about 33 to about 43 weight percent hexafluoroethane and about 24 to about 37 weight
15 percent carbon dioxide which have a vapor pressure of about 15 psia at about $-87 \pm 1^\circ\text{C}$.

2. The azeotrope-like compositions of claim 1 consisting essentially of about 40 to about 80 weight percent said trifluoromethane and about 60 to about 20
20 weight percent said carbon dioxide.

3. The azeotrope-like compositions of claim 1 consisting essentially of about 50 to about 70 weight percent said trifluoromethane and about 30 to about 50
weight percent said carbon dioxide.

4. The azeotrope-like compositions of claim 1 consisting essentially of about 30 to about 43 weight percent said trifluoromethane, about 33 to about 43
hexafluoroethane and about 14 to about 37 weight percent said carbon dioxide.

5. The azeotrope-like compositions of claim 1 consisting essentially of about 33 to about 43 weight percent said trifluoromethane, about 33 to about 43
hexafluoroethane and about 14 to about 34 weight percent said carbon dioxide.

6. The azeotrope-like compositions of claim 1 consisting essentially of about 36 to about 40 weight percent said trifluoromethane, about 36 to about 40

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hexafluoroethane and about 20 to about 28 weight percent said carbon dioxide.

5 7. A method for producing refrigeration which comprises condensing a refrigerant comprising the azeotrope-like compositions of claims 1 through 6 and thereafter evaporating said refrigerant in the vicinity of a body to be cooled.

10 8. A method for producing heating which comprises condensing a refrigerant comprising the azeotrope-like compositions of claims 1-6 in the vicinity of a body to be heated and thereafter evaporating said composition.

15 9. A method for extinguishing fire which comprises releasing an amount of the azeotrope-like compositions of claims 1-6 sufficient to suppress combustion in an enclosed area containing a fire.

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 94/06003

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09K5/04 A62D1/00

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 A62D

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.
P,X	WO,A,94 01512 (E.I.DU PONT DE NEMOURS AND COMPANY) 20 January 1994 see claims 1,4,6,7 see page 16, line 30 - line 34 see examples 11,9 ---	1-8
Y	DE,A,41 16 274 (FORSCHUNGSZENTRUM FUER KAELETETECNIK UND WAERMEPUMPEN) 19 November 1992 see claim 1 see column 2, line 40 - line 44 ---	1-8
Y	US,A,3 804 759 (BECKER) 16 April 1974 see claim 1 see abstract; figure ---	1-9
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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 :

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

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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.
P,Y	US,A,5 275 751 (DECAIRE) 1 April 1994 see claims 1,2 see example 1; table 1 -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/US 94/06003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9401512	20-01-94	NONE	
DE-A-4116274	19-11-92	NONE	
US-A-3804759	16-04-74	CA-A- 989362	18-05-76
		DE-A- 2264201	12-07-73
		JP-A- 48077692	18-10-73
		US-A- 3721300	20-03-73
US-A-5275751	04-01-94	NONE	