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(54) Title: COMPOSITIONS OF PENTAFLUOROMETHYL ETHER AND A HYDROCARBON (57) Abstract Azeotrope-like compositions of pentafluoromethyl ether and a hydrocarbon are provided. The compositions of the invention are stable and have utility as refrigerants for heating and cooling, blowing agents, solvents, and fire extinguishing agents.		

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COMPOSITIONS OF PENTAFLUOROMETHYL ETHER AND A HYDROCARBON

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Background of the Invention

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

The primary purpose of refrigeration is to remove energy at low
15 temperature. In contrast, 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 refrigeration evaporator.

20 Certain chlorofluoromethane and chlorofluoroethane derivatives have gained widespread use in refrigeration applications including air conditioning and heat pump applications owing to their unique combination of chemical and physical properties. The majority of refrigerants utilized in vapor compression systems are either single component fluids or azeotropic mixtures. Moreover, certain
25 applications, such as centrifugal chillers, can only use pure or azeotropic refrigerants because nonazeotropic mixtures will separate in pool boiling evaporators causing undesirable performance.

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Azeotropic or azeotrope-like compositions are used because they do not fractionate upon boiling. This behavior is desirable because, in the vapor compression equipment in which these refrigerants are employed, condensed material is generated in preparation for cooling or heating purposes. Unless the
5 refrigerant composition exhibits a constant boiling, i.e., azeotrope-like, behavior fractionation and segregation will occur on evaporation and condensation and undesirable refrigerant distribution may act to upset the cooling or heating. If a leak occurs in a refrigeration system during use or service, the composition of the azeotrope-like mixture does not change and, thus, system pressures and
10 performance remain unaffected.

The art continually is seeking new fluorocarbon based azeotrope-like mixtures that offer alternatives for refrigeration and heat pump applications. Currently of particular interest are fluorocarbon based azeotrope-like mixtures that
15 are considered environmentally safe substitutes for the presently used chlorofluorocarbons, CFC's, and hydrochlorofluorocarbons, HCFC's, such as monochlorodifluoromethane, R-502, and chlorodifluoromethane, R-22. The CFC's and HCFC's are suspected of causing environmental problems in connection with the earth's protective ozone layer.

20

The substitute materials must possess those properties unique to the materials that they replace including chemical stability, low toxicity, non-flammability, and efficiency in use. The latter characteristic is important in refrigeration and air conditioning especially in a case in which thermodynamic
25 performance or energy efficiency may have secondary environmental impacts as, for example, through an increase in fossil fuel use due to an increase in demand for electrical energy. Furthermore, the ideal substitute would not require engineering changes to conventional vapor compression technology used with CFC's and HCFC's.

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Mathematical models have substantiated that hydrofluoroethers, such as pentafluoromethyl ether, E-125, will not adversely affect atmospheric chemistry because it is a negligible contributor to ozone depletion and to green-house global warming in comparison to fully halogenated species.

Description of the Invention and Preferred Embodiments

In accordance with the invention, azeotrope-like compositions have been discovered comprising pentafluoromethyl ether, E-125, and at least one second component from the hydrocarbon family. Preferably, the hydrocarbon is a C₃ or C₄ hydrocarbon. More preferably, the hydrocarbon is propane (CH₃CH₂CH₃), cyclopropane (CH₂CH₂CH₂ -), or isobutane (CH₃CH(CH₃)CH₃).

The azeotrope-like compositions of the invention comprise effective amounts of pentafluoromethyl ether and at least one hydrocarbon. By "effective amount" is meant that the amount of each component is such that combination of the components results in the formation of an azeotrope-like composition. The preferred, more preferred, and most preferred compositions of this invention are set forth on Table I. The numerical ranges in Table I such as boiling point and pressure are to be understood to be prefaced by the term "about". The precise azeotropic compositions have not been determined, but have been ascertained to be within the listed ranges. Regardless of where the true azeotropes lie, all compositions within the indicated ranges, as well as certain compositions outside the indicated ranges, are azeotrope-like, as defined more particularly below.

Table I

	Preferred (wt %)	More Preferred (wt%)	Most Preferred (wt %)
E-125	99 - 50	95 - 70	95 - 80
Propane	1 - 50	5 - 30	5 - 20
E-125	99 - 50	95 - 70	95 - 80
Cyclopropane	1 - 50	5 - 30	5 - 20
E-125	99 - 50	95 - 70	95 - 80
Isobutane	1 - 50	5 - 30	5 - 20

Because the present compositions exhibit essentially constant vapor pressure characteristics as the liquid mixture is evaporated and show relatively minor shifts in composition during evaporation, the compositions are advantageous in a vapor compression cycle because they mimic the performance of a constant boiling single component or azeotropic mixture refrigerant.

From fundamental principles, the thermodynamic state of a fluid is defined by four variables: pressure (P); temperature (T); liquid composition (X); and vapor composition (Y). An azeotrope is a unique characteristic of a system of two or more components in which X and Y are equal at the state P and T. In practice, this means that the components of a mixture cannot be separated during a phase change and, therefore, are useful in cooling and heating applications.

15

For the purpose of this invention, azeotrope-like compositions are compositions that behave like an azeotrope, i.e., have constant boiling characteristics or a tendency not to fractionate on boiling or evaporation. In such compositions, the composition of the vapor formed during boiling or evaporation

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is identical, or substantially identical, to the original liquid composition. During boiling or evaporation, the liquid composition changes, if it at all, only to a minimal or negligible extent. This is to be contrasted with non-azeotrope-like compositions in which, during boiling or evaporation, the liquid composition changes to a
5 substantial degree.

The azeotrope-like compositions of the invention may include additional components that do not form new azeotropic or azeotrope-like systems, i.e., additional components that are not present in a first distillation cut. The first
10 distillation cut is the first cut taken after the distillation column displays steady state operations under total reflux conditions. One way to determine whether the addition of a component forms a new azeotropic or azeotrope-like system so as to be outside of this invention is to distill a sample of the composition with the component under conditions that would be expected to separate a nonazeotropic
15 mixture into its separate components. If the mixture containing the additional component is nonazeotropic or nonazeotrope-like, the additional component will fractionate or separate from the azeotropic or azeotrope-like components. If the mixture is azeotrope-like, some finite amount of a first distillation cut will be obtained that contains all of the mixture components and that is constant boiling or
20 behaves as a single substance.

It follows from this that another characteristic of azeotrope-like compositions is that there is a range of compositions containing the same components in varying proportions that are azeotrope-like or constant boiling. All
25 such compositions are intended to be covered by the terms "azeotrope-like" and "constant boiling". As an example, it is well known that at differing pressures, the composition of a given azeotrope will vary at least slightly as does the boiling point of the composition. Thus, an azeotrope of A and B represents a unique type of relationship, but with a variable composition depending on temperature and/or

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pressure. As is readily understood by one ordinarily skilled in the art, the boiling point of the azeotrope will vary with the pressure.

The compositions of the invention meet the need in the art for a refrigerant
5 that has a low ozone depletion potential and is a negligible contributor to green-house global warming compared with fully halogenated CFC refrigerants, is nonflammable, has a COP and a capacity comparable to that of presently used refrigerants including, without limitation, R-22 and R-502 and has a low
compressor discharge temperature. In a process embodiment, the azeotrope-like
10 compositions of the invention may be used in a method for producing refrigeration that comprises condensing a refrigerant comprising the azeotrope-like compositions and thereafter evaporating the refrigerant in the vicinity of a body to be cooled.

15 In yet another embodiment, the compositions of the invention may be used in a method of heating that comprises condensing a refrigerant comprising the azeotrope-like compositions of the invention in the vicinity of a body to be heated and thereafter evaporating the refrigerant. In yet another embodiment, the
compositions may be used in a method for producing foam comprising blending a
20 heat plasticized resin with a volatile blowing agent comprising the azeotrope-like compositions of the invention and introducing the resin/volatile blowing agent blend into a zone of lower pressure to cause foaming.

The azeotrope-like compositions of the invention may also be used in a
25 method of dissolving contaminants or removing contaminants from the surface of a substrate that comprises contacting the substrate with the azeotrope-like compositions of the present invention. The compositions of the invention may also be used as fire extinguishing agents.

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Pentafluoromethyl ether and the hydrocarbons useful in the invention are known materials. Preferably, these materials are sufficiently high in purity so as to avoid the introduction of adverse influences on the cooling or heating properties or constant boiling properties of the system.

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Additional components may be added to the compositions to tailor the properties of the composition as needed. For example, propane and pentane may be added to the compositions to aid solubility of the azeotrope-like refrigerant compositions of the invention. Nitromethane may also be added as a stabilizer.

10

The invention will be clarified further by a consideration of the following examples that are intended to be purely exemplary.

Examples

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Example 1

An ebulliometer that consisted of a vacuum jacketed tube with a condenser on the top was used. 13.85 g E-125 was charged into the ebulliometer and cyclopropane added in small measured increments. The temperature was measured using a platinum resistance thermometer. From about 0 to about 30 weight percent cyclopropane, the boiling point of the composition changed only 8° C. Therefore, the composition behaved as a constant boiling composition over this range.

20

Example 2

The procedure of Example 1 was used except that 17.75 g E-125 and isobutane were used. From about 0 to about 20 weight percent isobutane, the boiling point of the composition changed only 1.5° C. The composition behaved as a constant boiling composition over this range.

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Example 3

13.42 g of E-125 was charged to a ebulliometer and cyclopropane was added in small measured increments. Temperature was measured as for Example 1. From about 0 to about 12 weight percent cyclopropane, the boiling point of the composition changed only by 2.5°C. The composition behaved as a constant boiling composition over this range.

Example 4

10 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 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.

15 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 than a refrigerant with a lower capacity.

25 This type of calculation was performed for an air conditioning cycle in which the condenser temperature is typically 110° F and the evaporator temperature is typically 35° F. Compression efficiency of 85 % was assumed as well as superheat of 20° F and subcooling of 10° F. The calculations were performed for various combinations of E-125 and cyclopropane as well as for

R-22. Table II lists the COP's and capacities of the various blends relative to that of R-22.

Table II

E-125/hydrocarbon (wt%)	COP*	Capacity*
90/10	0.99	0.98
70/30	1.02	1.05

5 The asterixes indicate that the values are given relative to R-22.

Example 4 demonstrates that constant boiling E-125 and cyclopropane blends have certain advantages when compared to other refrigerants, such as R-22,
10 that are currently used in refrigeration cycles.

Example 5

Thermoset foams are made using the pentafluoromethyl ether and hydrocarbon compositions shown in Table III.

15

Table III

Components	Proportions (wt%)
E-125/cyclopropane	90/10
E-125/butane	90/10
E-125/isobutane	90/10

40 g of each of the azeotrope-like compositions is charged into each of three 200 cc sealed vessels containing 3 g of Dow styrene 685D. The
20 vessel is placed in a 250° F oven overnight and the pressure is released the next day. A good foam is obtained.

Having described the invention in detail and by reference to its preferred

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embodiments, it will be apparent that modifications and variations are possible without departing from the scope of the invention as defined in the following claims.

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What is claimed is:

1. Azeotrope-like compositions consisting essentially of about 50 to about 99 weight percent pentafluoromethyl ether and about 1 to about 50 weight percent
5 of a hydrocarbon.
2. The azeotrope-like compositions of claim 1 consisting essentially of about 70 to about 95 weight percent pentafluoromethyl ether and about 5 to about 30 weight percent of the hydrocarbon.
10
3. The azeotrope-like compositions of claim 1 consisting essentially of about 80 to 95 weight percent pentafluoromethyl ether and about 5 to about 20 weight percent of the hydrocarbon.
- 15 4. The compositions of claims 1, 2, or 3 wherein the hydrocarbon is a C₃ or C₄ hydrocarbon.
5. The compositions of claim 4 wherein the C₃ or C₄ hydrocarbon is propane, cyclopropane, or isobutane.
20
6. A method for producing refrigeration which comprises condensing a refrigerant comprising an azeotrope-like composition according to claims 1, 2, or 3 and thereafter evaporating the refrigerant in the vicinity of a body to be cooled.
25
7. A method for producing heating which comprises condensing a refrigerant comprising an azeotrope-like composition according to claims 1, 2, or 3, in the vicinity of a body to be heated and thereafter evaporating the composition.

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8. A method for producing foam comprising blending a heat plasticized resin with a volatile blowing agent comprising the azeotrope-like compositions of claims 1, 2, or 3 and introducing the blowing agent into a zone of lower pressure to cause foaming.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/16457

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K5/04 C08J9/14

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 C08J

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	US 3 922 228 A (HUTCHINSON) 25 November 1975 see abstract; claim 1 see column 4, line 6 - line 17 ---	1-8
Y	WO 93 14175 A (IMPERIAL CHEMICAL) 22 July 1993 see abstract; claims 1,10,11 ---	1-8
A	WO 93 14174 A (IMPERIAL CHEMICAL) 22 July 1993 see abstract; claims 1,16 ---	1-8
A	EP 0 385 737 A (GRACE & CO) 5 September 1990 see abstract; claims 1,9,10 -----	1-8

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

☒ Patent family members are listed in annex.

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Information on patent family members

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