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(54) Title: AZEOTROPE-LIKE COMPOSITIONS OF DIFLUOROMETHANE AND 1,1,1-TRIFLUOROETHANE

(57) Abstract

The invention relates to azeotrope-like compositions of difluoromethane and 1,1,1-trifluoroethane which are useful as refrigerants for heating and cooling applications and as blowing agents for the preparation of thermal plastic foam and polyurethane foam.

AZEOTROPE-LIKE COMPOSITIONS OF DIFLUOROMETHANE AND 1,1,1-TRIFLUOROETHANE

Background of the Invention

Fluorocarbon based fluids have found widespread use in industry for refrigeration, 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.

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 refrigeration evaporator.

Certain chlorofluorocarbons 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. Single component fluids and azeotropic mixtures are characterized as constant-boiling because they exhibit isothermal and isobaric evaporation and condensation. The use of azeotropic mixtures as refrigerants is known in the art. See, for example, R.C. Downing, "Fluorocarbon Refrigerants Handbook", pp. 139-158, Prentice-Hall, 1988, and U.S. Patents 2,101,993 and 2,641,579.

Azeotropic or azeotrope-like compositions are desired because they do not fractionate upon boiling or evaporation. 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, and unless the refrigerant composition is constant boiling, i.e., is azeotrope-like, fractionation and segregation will occur upon evaporation and condensation and undesirable refrigerant distribution may act to upset cooling or heating.

The art is continually seeking new fluorocarbon based azeotrope-like mixtures which offer alternatives for refrigeration and heat pump applications. Currently, fluorocarbon and hydrofluorocarbon based refrigerants are of particular interest because they are considered to be environmentally acceptable substitutes for the fully halogenated chlorofluorocarbons which are suspected of causing environmental problems associated with the depletion of the earth's protective ozone layer. Mathematical models have substantiated that partially halogenated species, such as difluoromethane (HFC-32) and 1,1,1-trifluoroethane (HFC-143a), will not adversely affect atmospheric chemistry since they contribute negligibly to stratospheric ozone depletion and global warming in comparison to the fully halogenated species.

Substitute refrigerants must also possess those properties unique to the CFC's including chemical stability, low toxicity, and efficiency in-use. Efficiency in-use is important, for example, in refrigeration applications like air conditioning where a loss in refrigerant thermodynamic performance or energy efficiency may produce secondary environmental effects due to increased fossil fuel 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.

Description of the Invention

Our solution to the need in the art for stratospherically safer substitutes for CFC-based refrigerant compositions is mixtures comprising from about 10 to about 99 weight percent difluoromethane (HFC-32) and from about 1 to about 90 weight percent 1,1,1-trifluoroethane (HFC-143a) which boil at about -51°C ± about 5°C at 760 mm Hg. These compositions are azeotrope-like because they exhibit a minimum in the boiling point versus composition curve.

HFC-32 has been proposed as an environmentally acceptable refrigerant however, it is not a particularly efficient refrigerant especially at higher condensing temperatures because it has a relatively low critical temperature. HFC-143a is a good refrigerant on a thermodynamic basis but has a lower vapor pressure than HFC-32. This results in a lower refrigeration capacity than HFC-32. Applicants have discovered, however, that when these compounds are combined in effective amounts, surprisingly an azeotrope-like composition results which has a higher refrigeration capacity than both HFC-32 and HFC-143a.

We have also discovered that the azeotrope-like compositions of the invention are useful as blowing agents for extruded thermal plastic foams such as polyethylene and polystyrene foams and for certain polyurethane type foams. When the compositions of the invention are used as blowing agents, they may be used alone or in combination with another liquid blowing agent such as 1,1-dichloro-1-fluoroethane (HCFC-141b) or other hydrochlorofluorocarbon or hydrofluorocarbon liquids.

The compositions of the more preferred and most preferred azeotrope-like compositions of the invention are summarized in Table I below. Note that the composition ranges reported are in weight percent.

Table I

Components	HFC-32	HFC-143a	Vpr.Pressure (psia) at 25°C
More Preferred Composition	60 - 98	2 - 40	about 240 ± about 10
Most Preferred Composition	90 - 98	2 - 10	about 243 ± about 2

The precise or true azeotrope compositions have not been determined but have been ascertained to be within the indicated ranges. Regardless of where the true azeotrope lie, all compositions within the indicated ranges, as well as certain compositions outside the indicated ranges, are azeotrope-like, as defined more particularly below.

For purposes of this discussion, by azeotrope-like composition is intended to mean that the composition behaves like a true azeotrope in terms of its constant boiling characteristics or tendency not to fractionate upon boiling or evaporation. Thus, in such a system, the composition of the vapor formed during evaporation is identical or substantially identical to the original liquid composition. Hence, during boiling or evaporation, the liquid composition, if it changes at all, changes only slightly. This is contrasted with non-azeotrope-like compositions in which the liquid and vapor compositions change substantially during evaporation or condensation.

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 the body to be cooled.

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

In still another process embodiment of the invention, the azeotrope-like compositions of the invention may be used as a blowing agent in a process for making extruded thermal plastic foams comprising blending heat plasticized polyolefin resin with a blowing agent and introducing the resin/blowing agent blend into a zone of lower pressure to cause foaming. Generally, about 1 - 15 parts of blowing agent are utilized per 100 parts resin.

In still another process embodiment, the azeotrope-like compositions of the invention may be used as a blowing agent in a process for preparing polyurethane foams comprising reacting and foaming a mixture of ingredients which will form the polymeric foam in the presence of a blowing agent. In such a process, approximately 30 parts of blowing agent is used per 100 parts of polyol.

The difluoromethane and 1,1,1-trifluoroethane components of the novel azeotrope-like compositions of the invention are known materials. Preferably they should be used in sufficiently high purity so as to avoid the introduction of adverse influences upon the constant boiling properties of the system.

Example 1

This example shows that a minimum occurs in the boiling point versus composition curve for the HFC-32/ HFC-143a system, confirming the existence of an azeotrope. The azeotropic properties of the HFC-32/ HFC-143a system were measured using an ebulliometric technique similar to that described by W. Swietoslawski in Ebulliometric Measurements, p. 4, Reinhold Publishing Corp. (1945).

The ebulliometer was first charged with a weighed amount of HFC-32. The system was brought to total reflux by gently warming the lower part of the ebulliometer. A carbon dioxide ice/methanol mixture was used to cool the condenser. The temperature of the boiling liquid was measured using a precision 25 ohm platinum resistance thermometer. The thermometer recorded the boiling point measurements with a precision of ± 0.01°C. Boiling temperature and atmospheric pressure were recorded after steady-state had been attained. A weighed aliquot of HFC-143a was then introduced into the ebulliometer and the temperature and pressure recorded again after the attainment of steady-state. This process was repeated with additional aliquots of HFC-143a.

By the above-described method, we discovered that mixtures comprising from about 10 to about 99 weight percent HFC-32 and from about 1 to about 90 weight percent HFC-143a are constant boiling at about -51°C ± 5°C at 760 mm Hg.

Example 2

This example shows that azeotrope-like compositions of HFC-32 and HFC-143a have certain performance advantages when compared to HFC-32 alone.

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, "Fluorocarbons Refrigerants Handbook", ch. 3, Prentice-Hall, (1988) by R.C. Downing. 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.

We have performed this type of calculation for a medium to low temperature refrigeration cycle where the condenser temperature is typically 125°F and the evaporator temperature is typically -40°F. We have further assumed isentropic compression and a compressor inlet temperature of 65°F. Such calculations were performed for a 95/5 weight percent blend of HFC-32/ HFC-143a respectively and HFC-32 alone.

Under the conditions specified above, the COP of the 95/5 weight percent HFC-32/HFC-143a blend was 1.52 and that of HFC-32 alone was 1.5. Thus, the energy efficiency of the mixture was higher than that of pure HFC-32. Similarly the capacity of the azeotropic blend was higher than that of HFC-32 and HFC-143a by 3%.

Another important parameter for refrigeration is the compressor discharge temperature. High discharge temperatures cause a decrease in compressor reliability and are therefore preferably avoided. Under the conditions specified above, we calculated the discharge temperature for the 95/5 weight percent HFC-32/HFC-143a blend. The discharge temperature for the mixture was 406°F. This is lower than the discharge temperature for HFC-32 which, under the conditions specified above, was determined to be 416°F.

Example 3

Free-rise rigid polyurethane foams are prepared using the formulations specified in Table II below using a Martin Sweets Co. Modern Module III urethane foam machine at a delivery rate of 15 lbs./min. This formulation is an example of a pour-in-place rigid polyurethane formulation which might be used as appliance insulation.

In the present Example, the HFC-32/HFC-143a composition of Example 1 is metered into the Martin Sweets machine as a third stream. Alternately, it may be preblended with the polyol and held in solution under pressure and a two stream foam machine used.

Table II

Component	Parts by Weight
Pluracol 11141 (420-OH)[1]	100
Silicone L-5340[2]	1.5
Thancat TD-33[3]	0.5
Thancat DME[4]	0.2
Catalyst T-12[5]	0.1
Example 1	<35
Lupranate M20SR (1.29 Index)[6]	129

[1]Pluracol 11141 is a polyether polyol manufactured by BASF Wyandotte Corp.

[2]Silicone L-5340 is a silicone surfactant manufactured by Union Carbide Corp.

[3]Thancat TD-33 is 33% triethylenediamine in propylene glycol manufactured by Texaco Inc.

[4]Thancat DME is N,N-dimethylethanolamine manufactured by Texaco Inc.

[5]Catalyst T-12 is dibutyl dilaurate manufactured by Metal + Thermit Co.

[6]Lupranate M20S is polyethylene polyphenylisocyanate manufactured by BASF Wandotte Corp.

The froth foams produced using the above formulation are closed-cell, low density foams with good insulation characteristics indicating that the composition of Example 1 is a good blowing agent for polyurethane foams.

Example 4

A small 304 grade stainless steel pressure vessel is constructed using schedule 40 pipe which is 4 inches in length and 2 inches in diameter. The vessel has top and bottom flanges which are used to close the ends of the cell. A pressure tight seal is maintained between the ends of the pipe and the flanges using Teflon o-rings. The vessel is closed by tightening 4 bolts which run the length of the cell through the top and bottom flanges. The design pressure limit for the apparatus is 1700 psi at 200°C; the operational limit is set at 1000 psi.

Three grams of very finely ground Dow Styrene 685D is placed into a 3 inch x 1.5 inch open glass jar. The glass jar is then placed in the pressure vessel and the pressure vessel is closed and evacuated.

Twenty two and one half grams of the composition of Example 1 is charged into the sealed vessel. The vessel is placed in a 250°F oven overnight. The vessel is removed from the oven, rapidly depressurized and then immersed in water. The glass jar is removed from the vessel. The resulting foam has a density of 3 - 4 lbs/ft^3 indicating that the composition of Example 1 is a good blowing agent for thermal plastic foam.

In summary, we have discovered that compositions of HFC-32 and HFC-143a are azeotrope-like, useful as blowing agents for thermal plastic foam and polyurethane foam and exhibit improved refrigeration properties.

What is Claimed:

1. Azeotrope-like compositions consisting essentially of from about 10 to about 99 weight percent difluoromethane and from about 1 to about 90 weight percent 1,1,1-trifluoroethane which boil at about -51°C ± about 5°C, at 760 mm Hg.

2. The azeotrope-like compositions of claim 1 consisting essentially of from about 60 to about 98 weight percent difluoromethane and from about 2 to about 40 weight percent 1,1,1-trifluoroethane.

3. The azeotrope-like compositions of claim 3 consisting essentially of from about 90 to about 98 weight percent difluoromethane and from about 2 to about 10 weight percent 1,1,1-trifluoroethane.

4. The azeotrope-like compositions of claim 3 wherein said compositions have a vapor pressure of about 240 psia at 25°C.

5. The azeotrope-like compositions of claim 4 wherein said compositions have a vapor pressure of about 243 psia at 25°C.

6. A method for producing refrigeration which comprises condensing a composition of claim 1 and thereafter evaporating said composition in the vicinity of a body to be cooled.

7. A method for producing heating which comprises condensing a composition of claim 1 in the vicinity of a body to be heated and thereafter evaporating said composition.

8. A process for making extruded thermal plastic foams comprising blending heat plasticized polyolefin resin with a composition of claim 1 and introducing the blend into a zone of lower pressure to cause foaming.

9. A process for preparing polyurethane foams comprising reacting and foaming a mixture of ingredients which will form the polymeric foam in the presence of a composition of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/07390

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C09K5/04; C08J9/14

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C09K ; C08J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
P,X	WO,A,9 307 232 (DU PONT DE NEMOURS) 15 April 1993 see claims 1-5,13-19 see page 3, line 34 - page 4, line 10 ---	1-9
A	DATABASE WPI Week 9136, Derwent Publications Ltd., London, GB; AN 91-262362 & JP,A,3 170 592 (MATSUSHITA) 24 July 1991 see abstract ---	1-7
A	DATABASE WPI Week 9136, Derwent Publications Ltd., London, GB; AN 91-262359 & JP,A,317 059 (MATSUSHITA) 24 July 1991 see abstract ---	1-7

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° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

1

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
26 OCTOBER 1993	- 2. 11. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	NICOLAS H.J.F.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	DATABASE WPI Week 9136, Derwent Publications Ltd., London, GB; AN 91-262357 & JP,A,3 170 586 (MATSUSHITA) 24 July 1991 see abstract	1-7

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9307390
SA 77952

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9307232	15-04-93	US-A- 5232618	03-08-93
		AU-A- 2756992	03-05-93

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82