

TITLE OF INVENTION

AZEOTROPIC AND AZEOTROPE-LIKE COMPOSITIONS OF E-1,1,1,4,4,4-HEXAFLUORO-2-BUTENE

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This application claims priority of U.S. Patent Applications 60/934199 and 60/934209 filed June 12, 2007, U.S. Patent Application 60/936082 filed June 18, 2007, U.S. Patent Application 60/937590 filed June 28, 2007, U.S. Patent Applications 60/970387 and 60/970384 filed
10 September 6, 2007, and U.S. Patent Application 60/993241 filed September 11, 2007.

BACKGROUND OF THE INVENTION

Field of the Disclosure

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The present disclosure relates to azeotropic or azeotrope-like compositions of E-1,1,1,4,4,4-hexafluoro-2-butene.

Description of Related Art

Many industries have been working for the past few decades to find
20 replacements for the ozone depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). The CFCs and HCFCs have been employed in a wide range of applications, including their use as aerosol propellants, refrigerants, cleaning agents, expansion agents for thermoplastic and thermoset foams, heat transfer media, gaseous
25 dielectrics, fire extinguishing and suppression agents, power cycle working fluids, polymerization media, particulate removal fluids, carrier fluids, buffing abrasive agents, and displacement drying agents. In the search for replacements for these versatile compounds, many industries have turned to the use of hydrofluorocarbons (HFCs).

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The HFCs do not contribute to the destruction of stratospheric ozone, but are of concern due to their contribution to the "greenhouse effect", i.e., they contribute to global warming. As a result of their contribution to global warming, the HFCs have come under scrutiny, and

their widespread use may also be limited in the future. Thus, there is a need for compositions that do not contribute to the destruction of stratospheric ozone and also have low global warming potentials (GWPs). Certain hydrofluoroolefins, such as 1,1,1,4,4,4-hexafluoro-2-butene
5 (CF₃CH=CHCF₃, FC-1336mzz), are believed to meet both goals.

SUMMARY OF THE INVENTION

This application includes seven different types of azeotropic or azeotrope-like mixtures.

10 In a first aspect, there is provided a composition consisting essentially of (a) E-FC-1336mzz and (b) methyl formate; wherein the methyl formate is present in an effective amount to form an azeotrope-like mixture with E-FC-1336mzz.

In a second aspect, there is provided a composition consisting
15 essentially of (a) E-FC-1336mzz and (b) n-pentane; wherein the n-pentane is present in an effective amount to form an azeotropic or azeotrope-like mixture with E-FC-1336mzz.

In a third aspect, there is provided a composition consisting essentially of (a) E-FC-1336mzz and (b) 2-methylbutane (isopentane);
20 wherein the isopentane is present in an effective amount to form an azeotropic or azeotrope-like mixture with E-FC-1336mzz.

In a fourth aspect, there is provided a composition consisting essentially of (a) E-FC-1336mzz and (b) trans-1,2-dichloroethylene;
wherein the trans-1,2-dichloroethylene is present in an effective amount to
25 form an azeotrope-like mixture with E-FC-1336mzz.

In a fifth aspect, there is provided a composition consisting essentially of (a) E-FC-1336mzz and (b) 1,1,1,3,3-pentafluoropropane (CF₃CH₂CF₂H, HFC-245fa); wherein the HFC-245fa is present in an effective amount to form an azeotrope-like mixture with E-FC-1336mzz.

30 In a sixth aspect, there is provided a composition consisting essentially of (a) E-FC-1336mzz and (b) n-butane; wherein the n-butane is present in an effective amount to form an azeotropic or azeotrope-like mixture with E-FC-1336mzz.

In a seventh aspect, there is provided a composition consisting essentially of (a) E-FC-1336mzz and (b) 2-methyl-propane (isobutane); wherein the 2-methylpropane is present in an effective amount to form an azeotropic or azeotrope-like mixture with E-FC-1336mzz.

In an eighth aspect, there is provided a process for preparing a thermoplastic or thermoset foam comprising using an azeotropic or azeotrope-like composition as a blowing agent, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

In a ninth aspect, there is provided a process for producing refrigeration comprising condensing an azeotropic or azeotrope-like composition and thereafter evaporating said azeotropic or azeotrope-like composition in the vicinity of the body to be cooled, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

In a tenth aspect, there is provided a process comprising using an azeotropic or azeotrope-like composition as a solvent, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

In a eleventh aspect, there is provided a process for producing an aerosol product comprising using an azeotropic or azeotrope-like composition as a propellant, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-

pentafluoropropane, n-butane and isobutane.

In an twelfth aspect, there is provided a process comprising using an azeotropic or azeotrope-like composition as a heat transfer media, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

In a thirteenth aspect, there is provided a process for extinguishing or suppressing a fire comprising using an azeotropic or azeotrope-like composition as a fire extinguishing or suppression agent, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

In a fourteenth aspect, there is provided a process comprising using an azeotropic or azeotrope-like composition as dielectrics, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

BRIEF SUMMARY OF THE DRAWINGS

FIG. 1 - FIG. 1 is a graphical representation of azeotrope-like compositions consisting essentially of E-FC-1336mzz and methyl formate at a temperature of about 20.0 °C.

FIG. 2 - FIG. 2 is a graphical representation of an azeotrope and azeotrope-like compositions consisting essentially of E-FC-1336mzz and n-pentane at a temperature of about 20.0 °C.

FIG. 3 - FIG. 3 is a graphical representation of an azeotrope and azeotrope-like compositions consisting essentially of E-FC-1336mzz and isopentane at a temperature of about 20.0 °C.

FIG. 4 - FIG. 4 is a graphical representation of azeotrope-like compositions consisting essentially of E-FC-1336mzz and trans-1,2-dichloroethylene at a temperature of about 20.0 °C.

5 FIG. 5 - FIG. 5 is a graphical representation of azeotrope-like compositions consisting essentially of E-FC-1336mzz and HFC-245fa at a temperature of about 20.0 °C.

FIG. 6 - FIG. 6 is a graphical representation of an azeotrope and azeotrope-like compositions consisting essentially of E-FC-1336mzz and
10 n-butane at a temperature of about 20.0 °C.

FIG. 7 - FIG. 7 is a graphical representation of an azeotrope and azeotrope-like compositions consisting essentially of E-FC-1336mzz and isobutane at a temperature of about 20.0 °C.

15 **DETAILED DESCRIPTION OF THE INVENTION**

In many applications, the use of a pure single component or an azeotropic or azeotrope-like mixture is desirable. For example, when a blowing agent composition (also known as foam expansion agents or foam expansion compositions) is not a pure single component or an azeotropic
20 or azeotrope-like mixture, the composition may change during its

application in the foam forming process. Such change in composition could detrimentally affect processing or cause poor performance in the application. Also, in refrigeration applications, a refrigerant is often lost during operation through leaks in shaft seals, hose connections, soldered joints and broken lines. In addition, the refrigerant may be released to the atmosphere during maintenance procedures on refrigeration equipment. If the refrigerant is not a pure single component or an azeotropic or azeotrope-like composition, the refrigerant composition may change when leaked or discharged to the atmosphere from the refrigeration equipment.

10 The change in refrigerant composition may cause the refrigerant to become flammable or to have poor refrigeration performance. Accordingly, there is a need for using azeotropic or azeotrope-like mixtures in these and other applications, for example azeotropic or azeotrope-like mixtures containing E-1,1,1,4,4,4-hexafluoro-2-butene (E-CF₃CH=CHCF₃, E-FC-1336mzz).

Before addressing details of embodiments described below, some terms are defined or clarified.

FC-1336mzz may exist as one of two configurational isomers, E or Z. FC-1336mzz as used herein refers to the isomers, Z-FC-1336mzz or E-FC-1336mzz, as well as any combinations or mixtures of such isomers.

As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, use of "a" or "an" are employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the invention. This description

should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of
5 ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are
10 incorporated by reference in their entirety, unless a particular passage is cited. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

E-FC-1336mzz is a known compound, and its preparation method
15 has been disclosed, for example, in Dawoodi, et. al., Journal of the Chemical Society, Chemical Communications (1982), (12), 696-8, hereby incorporated by reference in its entirety.

This application includes azeotropic or azeotrope-like compositions comprising E-FC-1336mzz.

20 In some embodiments of this invention, the composition consists essentially of (a) E-FC-1336mzz and (b) methyl formate; wherein the methyl formate is present in an effective amount to form an azeotrope-like mixture with E-FC-1336mzz.

25 In some embodiments of this invention, the composition consists essentially of (a) E-FC-1336mzz and (b) n-pentane; wherein the n-pentane is present in an effective amount to form an azeotropic or azeotrope-like mixture with E-FC-1336mzz.

30 In some embodiments of this invention, the composition consists essentially of (a) E-FC-1336mzz and (b) isopentane; wherein the isopentane is present in an effective amount to form an azeotropic or azeotrope-like mixture with E-FC-1336mzz.

In some embodiments of this invention, the composition consists essentially of (a) E-FC-1336mzz and (b) trans-1,2-dichloroethylene;

wherein the trans-1,2-dichloroethylene is present in an effective amount to form an azeotrope-like mixture with E-FC-1336mzz.

In some embodiments of this invention, the composition consists essentially of (a) E-FC-1336mzz and (b) HFC-245fa; wherein the HFC-245fa is present in an effective amount to form an azeotrope-like mixture with E-FC-1336mzz.

In some embodiments of this invention, the composition consists essentially of (a) E-FC-1336mzz and (b) n-butane; wherein the n-butane is present in an effective amount to form an azeotropic or azeotrope-like mixture with E-FC-1336mzz.

In some embodiments of this invention, the composition consists essentially of (a) E-FC-1336mzz and (b) 2-methyl-propane (isobutane); wherein the 2-methylpropane is present in an effective amount to form an azeotropic or azeotrope-like mixture with E-FC-1336mzz.

By effective amount is meant an amount, which, when combined with E-FC-1336mzz, results in the formation of an azeotropic or azeotrope-like mixture. This definition includes the amounts of each component, which amounts may vary depending on the pressure applied to the composition so long as the azeotropic or azeotrope-like compositions continue to exist at the different pressures, but with possible different boiling points. Therefore, effective amount includes the amounts, such as may be expressed in weight or mole percentages, of each component of the compositions of the instant invention which form azeotropic or azeotrope-like compositions at temperatures or pressures other than as described herein.

As recognized in the art, an azeotropic composition is an admixture of two or more different components which, when in liquid form under a given pressure, will boil at a substantially constant temperature, which temperature may be higher or lower than the boiling temperatures of the individual components, and which will provide a vapor composition essentially identical to the overall liquid composition undergoing boiling. (see, e.g., M. F. Doherty and M.F. Malone, Conceptual Design of Distillation Systems, McGraw-Hill (New York), 2001, 185-186, 351-359).

Accordingly, the essential features of an azeotropic composition are that at a given pressure, the boiling point of the liquid composition is fixed and that the composition of the vapor above the boiling composition is

essentially that of the overall boiling liquid composition (i.e., no fractionation of the components of the liquid composition takes place). It is also recognized in the art that both the boiling point and the weight percentages of each component of the azeotropic composition may change when the azeotropic composition is subjected to boiling at different pressures. Thus, an azeotropic composition may be defined in terms of the unique relationship that exists among the components or in terms of the compositional ranges of the components or in terms of exact weight percentages of each component of the composition characterized by a fixed boiling point at a specified pressure.

For the purpose of this invention, an azeotrope-like composition means a composition that behaves like an azeotropic composition (i.e., has constant boiling characteristics or a tendency not to fractionate upon boiling or evaporation). Hence, during boiling or evaporation, the vapor and liquid compositions, if they change at all, change only to a minimal or negligible extent. This is to be contrasted with non-azeotrope-like compositions in which during boiling or evaporation, the vapor and liquid compositions change to a substantial degree.

Additionally, azeotrope-like compositions exhibit dew point pressure and bubble point pressure with virtually no pressure differential. That is to say that the difference in the dew point pressure and bubble point pressure at a given temperature will be a small value. In this invention, compositions with a difference in dew point pressure and bubble point pressure of less than or equal to 5 percent (based upon the bubble point pressure) is considered to be azeotrope-like.

It is recognized in this field that when the relative volatility of a system approaches 1.0, the system is defined as forming an azeotropic or azeotrope-like composition. Relative volatility is the ratio of the volatility of component 1 to the volatility of component 2. The ratio of the mole fraction of a component in vapor to that in liquid is the volatility of the component.

To determine the relative volatility of any two compounds, a method known as the PTx method can be used. In this procedure, the total absolute pressure in a cell of known volume is measured at a constant

temperature for various compositions of the two compounds. Use of the PTx Method is described in detail in "Phase Equilibrium in Process Design", Wiley-Interscience Publisher, 1970, written by Harold R. Null, on pages 124 to 126; hereby incorporated by reference.

5 These measurements can be converted into equilibrium vapor and liquid compositions in the PTx cell by using an activity coefficient equation model, such as the Non-Random, Two-Liquid (NRTL) equation, to represent liquid phase nonidealities. Use of an activity coefficient equation, such as the NRTL equation is described in detail in "The Properties of
10 Gases and Liquids," 4th edition, published by McGraw Hill, written by Reid, Prausnitz and Poling, on pages 241 to 387, and in "Phase Equilibria in Chemical Engineering," published by Butterworth Publishers, 1985, written by Stanley M. Walas, pages 165 to 244. Both aforementioned references are hereby incorporated by reference. Without wishing to be
15 bound by any theory or explanation, it is believed that the NRTL equation, together with the PTx cell data, can sufficiently predict the relative volatilities of the E-1,1,1,4,4,4-hexafluoro-2-butene-containing compositions of the present invention and can therefore predict the behavior of these mixtures in multi-stage separation equipment such as
20 distillation columns.

It was found through experiments that E-FC-1336mzz and n-pentane form azeotropic or azeotrope-like compositions.

To determine the relative volatility of this binary pair, the PTx method described above was used. The total absolute pressure in a PTx
25 cell of known volume was measured at constant temperature for various binary compositions. These measurements were then reduced to equilibrium vapor and liquid compositions in the cell using the NRTL equation.

The vapor pressure measured versus the compositions in the PTx
30 cell for E-FC-1336mzz/n-pentane mixture is shown in FIG. 2, which graphically illustrates the formation of an azeotropic and azeotrope-like composition consisting essentially of E-FC-1336mzz and n-pentane as indicated by a mixture of about 84.6 mole % E-1,1,1,4,4,4-hexafluoro-2-

- butene and 15.4 mole % n-pentane having the highest pressure over the range of compositions at this temperature. Based upon these findings, it has been calculated that E-FC-1336mzz and n-pentane form azeotropic compositions ranging from about 82.2 mole percent to about 95.3 mole percent E-FC-1336mzz and from about 17.8 mole percent to about 4.7 mole percent n-pentane (which form azeotropic compositions boiling at a temperature of from about -20 °C to about 80 °C and at a pressure of from about 4.5 psia (31 kPa) to about 139 psia (951 kPa)). Some embodiments of azeotropic compositions are listed in Table 1.

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Table 1 Azeotropic compositions

Azeotropic Temperature (°C)	Azeotropic Pressure (psia)	E-FC-1336mzz (mole %)	n-Pentane (mole %)
-20.0	4.55	82.2	17.8
-10.0	7.36	82.5	17.5
0.0	11.4	83.0	17.0
10.0	17.0	83.7	16.3
20.0	24.6	84.6	15.4
30.0	34.6	85.7	14.3
40.0	47.5	87.0	13.0
50.0	63.8	88.6	11.4
60.0	83.9	90.5	9.5
70.0	108.6	92.7	7.3
80.0	138.6	95.3	4.7

- Additionally, azeotrope-like compositions containing E-FC-1336mzz and n-pentane may also be formed. Such azeotrope-like compositions exist around azeotropic compositions. Some embodiments of azeotrope-like compositions are listed in Table 2. Additional embodiments of azeotrope-like compositions are listed in Table 3.

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Table 2 Azeotrope-like compositions

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COMPONENTS	T (°C)	Weight Percentage Range
E-FC-1336mzz/n-Pentane	-40	88-99/1-12
E-FC-1336mzz/n-Pentane	0	86-99/1-14
E-FC-1336mzz/n-Pentane	20	86-99/1-14
E-FC-1336mzz/n-Pentane	40	85-99/1-15
E-FC-1336mzz/n-Pentane	80	84-99/1-16
E-FC-1336mzz/n-Pentane	120	83-99/1-17

Table 3 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
E-FC-1336mzz/n-Pentane	-40	88-95/5-12
E-FC-1336mzz/n-Pentane	0	86-95/5-14
E-FC-1336mzz/n-Pentane	20	86-95/5-14
E-FC-1336mzz/n-Pentane	40	85-95/5-15
E-FC-1336mzz/n-Pentane	80	10-90/10-90 and 84-95/5-16
E-FC-1336mzz/n-Pentane	120	83-95/5-17

It was found through experiments that E-FC-1336mzz and methyl formate form azeotrope-like compositions. To determine the relative volatility of this binary pair, the PTx method described above was used. The total absolute pressure in a PTx cell of known volume was measured at constant temperature for various binary compositions. These measurements were then reduced to equilibrium vapor and liquid compositions in the cell using the NRTL equation.

The vapor pressure measured versus the compositions in the PTx cell for E-FC-1336mzz/methyl formate mixture is shown in FIG. 1, which

illustrates graphically the formation of azeotrope-like compositions consisting essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and methyl formate at 20.0 °C, as indicated by mixtures of about 83 mole % to about 99 mole % E-1,1,1,4,4,4-hexafluoro-2-butene and about 17 to about 1

5 mole % methyl formate.

Some embodiments of azeotrope-like compositions are listed in Table 4. Additional embodiments of azeotrope-like compositions are listed in Table 5.

10 Table 4. Azeotrope-like Compositions

COMPONENTS	T (°C)	Weight % Range
E-FC-1336mzz/Methyl formate	-40	96-99/1-4
E-FC-1336mzz/Methyl formate	0	95-99/1-5
E-FC-1336mzz/Methyl formate	40	92-99/1-8
E-FC-1336mzz/Methyl formate	80	86-99/1-14
E-FC-1336mzz/Methyl formate	120	73-100/1-27

15 Table 5. Azeotrope-like Compositions

COMPONENTS	T (°C)	Weight % Range
E-FC-1336mzz/Methyl formate	-40	98-99/1-2
E-FC-1336mzz/Methyl formate	0	97-99/1-3
E-FC-1336mzz/Methyl formate	40	95-99/1-5
E-FC-1336mzz/Methyl formate	80	92-99/1-8
E-FC-1336mzz/Methyl formate	120	87-99/1-13

It was found through experiments that E-FC-1336mzz and isopentane form azeotropic or azeotrope-like compositions. To determine

20 the relative volatility of this binary pair, the PTx method described above was used. The total absolute pressure in a PTx cell of known volume was measured at constant temperature for various binary compositions. These measurements were then reduced to equilibrium vapor and liquid compositions in the cell using the NRTL equation.

25 The vapor pressure measured versus the compositions in the PTx cell for E-FC-1336mzz/ isopentane mixture is shown in FIG. 3, which

illustrates graphically the formation of an azeotrope and azeotrope-like compositions of E-1,1,1,4,4,4-hexafluoro-2-butene and isopentane at 20.0 °C, as indicated by a mixture of about 77.2 mole % E-1,1,1,4,4,4-hexafluoro-2-butene and 22.8 mole % isopentane having the highest pressure over the range of compositions at this temperature.

Based upon these findings, it has been calculated that E-FC-1336mzz and isopentane form azeotropic compositions ranging from about 75.1 mole percent to about 95.4 mole percent E-FC-1336mzz and from about 24.9 mole percent to about 4.6 mole percent isopentane (which form azeotropic compositions boiling at a temperature of from about -40 °C to about 100 °C and at a pressure of from about 1.6 psia (11 kPa) to about 218 psia (1503 kPa)). Some embodiments of azeotropic compositions are listed in Table 6.

Table 6 Azeotropic compositions

Azeotropic Temperature (°C)	Azeotropic Pressure (psia)	E-FC-1336mzz (mole %)	Isopentane (mole %)
- 20.0	4.8	75.0	25.0
- 10.0	7.7	75.3	24.7
0.0	12.0	75.7	24.3
10.0	17.8	76.4	23.6
20.0	25.6	77.2	22.8
30.0	35.9	78.3	21.7
40.0	49.0	79.5	20.5
50.0	65.4	81.1	18.9
60.0	85.6	83.0	17.0
70.0	110.3	85.2	14.8
80.0	140.0	88.0	12.0
90.0	175.6	91.3	8.7
100.0	217.9	95.4	4.6

Additionally, azeotrope-like compositions containing E-FC-1336mzz and isopentane may also be formed. Such azeotrope-like compositions exist around azeotropic compositions. Some embodiments of azeotrope-

like compositions are listed in Table 7. Additional embodiments of azeotrope-like compositions are listed in Table 8.

Table 7. Azeotrope-like Compositions

COMPONENTS	T (°C)	Weight % Range
E-FC-1336mzz/isopentane	-40	81-94/6-19
E-FC-1336mzz/isopentane	0	80-99/1-20
E-FC-1336mzz/isopentane	40	80-99/1-20
E-FC-1336mzz/isopentane	80	79-99/1-21
E-FC-1336mzz/isopentane	100	77-99/1-23

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Table 8. Azeotrope-like Compositions

COMPONENTS	T (°C)	Weight % Range
E-FC-1336mzz/isopentane	-40	81-95/5-19
E-FC-1336mzz/isopentane	0	80-95/5-20
E-FC-1336mzz/isopentane	40	80-95/5-20
E-FC-1336mzz/isopentane	80	79-95/5-21
E-FC-1336mzz/isopentane	100	77-95/5-23

It was found through experiments that E-FC-1336mzz and trans-1,2-dichloroethylene form azeotrope-like compositions. To determine the relative volatility of this binary pair, the PTx method described above was used. The total absolute pressure in a PTx cell of known volume was measured at constant temperature for various binary compositions. These measurements were then reduced to equilibrium vapor and liquid compositions in the cell using the NRTL equation.

The vapor pressure measured versus the compositions in the PTx cell for E-FC-1336mzz/ trans-1,2-dichloroethylene mixture is shown in FIG. 4, which illustrates graphically the formation of azeotrope-like compositions of E-1,1,1,4,4,4-hexafluoro-2-butene and trans-1,2-dichloroethylene at 20.0 °C, as indicated by mixtures comprised of about 84 mole % to about 99 mole % E-1336mzz and from about 16 to about 1 mole % trans-1,2-dichloroethylene.

Some embodiments of azeotrope-like compositions are listed in Table 9. Additional embodiments of azeotrope-like compositions are listed in Table 10.

Table 9. Azeotrope-like Compositions

COMPONENTS	T (°C)	Weight % Range
E-FC-1336mzz/Trans-1,2-dichloroethylene	-40	92-99/1-8
E-FC-1336mzz/Trans-1,2-dichloroethylene	0	90-99/1-10
E-FC-1336mzz/Trans-1,2-dichloroethylene	40	90-99/1-10
E-FC-1336mzz/Trans-1,2-dichloroethylene	80	89-99/1-11
E-FC-1336mzz/Trans-1,2-dichloroethylene	120	88-99/1-12

Table 10. Azeotrope-like Compositions

COMPONENTS	T (°C)	Weight % Range,
E-FC-1336mzz/Trans-1,2-dichloroethylene	-40	94-99/1-6
E-FC-1336mzz/Trans-1,2-dichloroethylene	0	93-99/1-7
E-FC-1336mzz/Trans-1,2-dichloroethylene	40	92-99/1-8
E-FC-1336mzz/Trans-1,2-dichloroethylene	80	92-99/1-8
E-FC-1336mzz/Trans-1,2-dichloroethylene	120	93-99/1-7

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It was found through experiments that E-FC-1336mzz and HFC-245fa form azeotrope-like compositions. To determine the relative volatility of this binary pair, the PTx method described above was used. The total absolute pressure in a PTx cell of known volume was measured at constant temperature for various binary compositions. These measurements were then reduced to equilibrium vapor and liquid compositions in the cell using the NRTL equation.

The vapor pressure measured versus the compositions in the PTx cell for E-FC-1336mzz/ HFC-245fa mixture is shown in FIG. 5, which illustrates graphically the formation of azeotrope-like compositions of E-1,1,1,4,4,4-hexafluoro-2-butene and HFC-245fa at 20.0 °C, as indicated by mixtures of about 1 to 99 mole % E-1,1,1,4,4,4-hexafluoro-2-butene and about 99 to 1 mole % HFC-245fa.

Some embodiments of azeotrope-like compositions are listed in Table 11. Additional embodiments of azeotrope-like compositions are listed in Table 12.

Table 11. Azeotrope-like Compositions

COMPONENTS	T (°C)	Weight % Range
E-FC-1336mzz/HFC-245fa	-40	1-99/1-99
E-FC-1336mzz/HFC-245fa	0	1-99/1-99
E-FC-1336mzz/HFC-245fa	40	1-99/1-99
E-FC-1336mzz/HFC-245fa	80	1-99/1-99
E-FC-1336mzz/HFC-245fa	120	1-99/1-99

Table 12. Azeotrope-like Compositions

COMPONENTS	T (°C)	Weight % Range
E-FC-1336mzz/HFC-245fa	-40	10-90/10-90
E-FC-1336mzz/HFC-245fa	0	10-90/10-90
E-FC-1336mzz/HFC-245fa	40	10-90/10-90
E-FC-1336mzz/HFC-245fa	80	10-90/10-90
E-FC-1336mzz/HFC-245fa	120	10-90/10-90

5 It was found through experiments that E-FC-1336mzz and n-butane form azeotropic or azeotrope-like compositions. To determine the relative volatility of this binary pair, the PTx method described above was used. The total absolute pressure in a PTx cell of known volume was measured at constant temperature for various binary compositions. These
10 measurements were then reduced to equilibrium vapor and liquid compositions in the cell using the NRTL equation.

The vapor pressure measured versus the compositions in the PTx cell for E-FC-1336mzz/n-butane mixture is shown in FIG. 6, which illustrates graphically the formation of an azeotropic composition of E-
15 1,1,1,4,4,4-hexafluoro-2-butene and cyclopentane at 20.0 °C, as indicated by a mixture of about 38.1 mole % E-1,1,1,4,4,4-hexafluoro-2-butene and 61.9 mole % n-butane having the highest pressure over the range of compositions at this temperature.

Based upon these findings, it has been calculated that E-FC-
20 1336mzz and n-butane form azeotropic compositions ranging from about 29.5 mole percent to about 47.2 mole percent E-FC-1336mzz and from about 70.5 mole percent to about 52.8 mole percent n-butane (which form azeotropic compositions boiling at a temperature of from about -40 °C to

about 100 °C and at a pressure of from about 3.0 psia (21 kPa) to about 277 psia (1910 kPa)). Some embodiments of azeotropic compositions are listed in Table 13.

Table 13. Azeotropic Compositions

Azeotropic Temperature (°C)	Azeotropic Pressure (psia)	E-FC-1336mzz (mole %)	n-butane (mole %)
-40	3.0	29.5%	70.5%
-30	5.1	31.3%	68.7%
-20	8.2	33.0%	67.0%
-10	12.7	34.5%	65.5%
0	19.0	35.8%	64.2%
10	27.4	37.0%	63.0%
20	38.3	38.1%	61.9%
30	52.3	39.2%	60.8%
40	69.7	40.2%	59.8%
50	91.1	41.2%	58.8%
60	116.8	42.2%	57.8%
70	147.6	43.3%	56.7%
80	183.9	44.4%	55.6%
90	226.5	45.7%	54.3%
100	276.6	47.2%	52.8%

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Additionally, azeotrope-like compositions containing E-FC-1336mzz and n-butane may also be formed. Such azeotrope-like compositions exist around azeotropic compositions. Some embodiments of azeotrope-like compositions are listed in Table 14. Additional embodiments of

10 azeotrope-like compositions are listed in Table 15.

Table 14. Azeotrope-like Compositions

COMPONENTS	T (°C)	Weight % Range
E-FC-1336mzz/n-butane	-40	38-64/36-62
E-FC-1336mzz/n-butane	0	44-72/28-56
E-FC-1336mzz/n-butane	40	1-13/87-99 and 43-80/20-57 and 98-99/1-2
E-FC-1336mzz/n-butane	80	1-91/9-99 and 94-99/1-6
E-FC-1336mzz/n-butane	100	1-99/1-99

Table 15. Azeotrope-like Compositions

COMPONENTS	T (°C)	Weight % Range
E-FC-1336mzz/n-butane	-40	50-64/36-50

E-FC-1336mzz/n-butane	0	50-72/28-50
E-FC-1336mzz/n-butane	40	10-13/87-90 and 43-80/20-57
E-FC-1336mzz/n-butane	80	10-90/10-90
E-FC-1336mzz/n-butane	100	10-90/10-90

It was found through experiments that E-FC-1336mzz and isobutane form azeotropic or azeotrope-like compositions. To determine the relative volatility of this binary pair, the PTx method described above was used. The total absolute pressure in a PTx cell of known volume was measured at constant temperature for various binary compositions. These measurements were then reduced to equilibrium vapor and liquid compositions in the cell using the NRTL equation.

The vapor pressure measured versus the compositions in the PTx cell for E-FC-1336mzz/isobutane mixture is shown in FIG. 7, which illustrates graphically the formation of an azeotropic composition of E-1,1,1,4,4,4-hexafluoro-2-butene and cyclopentane at 20.0 °C, as indicated by a mixture of about 24.9 mole % E-1,1,1,4,4,4-hexafluoro-2-butene and 75.1 mole % isobutane having the highest pressure over the range of compositions at this temperature.

Based upon these findings, it has been calculated that E-FC-1336mzz and isobutane form azeotropic compositions ranging from about 19.4 mole percent to about 32.4 mole percent E-FC-1336mzz and from about 80.6 mole percent to about 67.6 mole percent isobutane (which form azeotropic compositions boiling at a temperature of from about -40 °C to about 80 °C and at a pressure of from about 4.5 psia (31 kPa) to about 218 psia (1503 kPa)). Some embodiments of azeotropic compositions are listed in Table 16.

Table 16. Azeotropic Compositions

Azeotropic Temperature (°C)	Azeotropic Pressure (psia)	E-FC-1336mzz (mole %)	isobutane (mole %)
-40	4.5	19.4%	80.6%
-30	7.3	20.3%	79.7%
-20	11.5	21.2%	78.8%
-10	17.2	22.1%	77.9%
0	25.0	23.0%	77.0%
10	35.2	24.0%	76.0%

20	48.4	24.9%	75.1%
30	64.9	25.9%	74.1%
40	85.3	27.0%	73.0%
50	110.1	28.1%	71.9%
60	140.0	29.3%	70.7%
70	175.7	30.7%	69.3%
80	218.2	32.4%	67.6%

Additionally, azeotrope-like compositions containing E-FC-1336mzz and isobutane may also be formed. Such azeotrope-like compositions exist around azeotropic compositions. Some embodiments of azeotrope-like compositions are listed in Table 17. Additional embodiments of azeotrope-like compositions are listed in Table 18.

Table 17. Azeotrope-like Compositions

COMPONENTS	T (°C)	Weight Range
E-FC-1336mzz/isobutane	-40	1 - 48.8/51.2 - 99
E-FC-1336mzz/isobutane	0	1 - 59.3/40.7 - 99
E-FC-1336mzz/isobutane	40	1 - 68.8/31.2 - 99
E-FC-1336mzz/isobutane	80	1 - 78.7/21.3 - 99
E-FC-1336mzz/isobutane	95	1 - 82.6/17.4 - 99

Table 18. Azeotrope-like Compositions

COMPONENTS	T (°C)	Weight Range, Preferred
E-FC-1336mzz/isobutane	-40	10 - 47.4/52.6 - 90
E-FC-1336mzz/isobutane	0	10 - 56.9/43.1 - 90
E-FC-1336mzz/isobutane	40	10 - 65.3/34.7 - 90
E-FC-1336mzz/isobutane	80	10 - 74.3/25.7 - 90
E-FC-1336mzz/isobutane	95	10 - 77.7/22.3 - 90

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The azeotropic or azeotrope-like compositions of the present invention can be prepared by any convenient method including mixing or combining the desired amounts. In one embodiment of this invention, an azeotropic or azeotrope-like composition can be prepared by weighing the desired component amounts and thereafter combining them in an appropriate container.

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The azeotropic or azeotrope-like compositions of the present invention can be used in a wide range of applications, including their use as aerosol propellants, refrigerants, solvents, cleaning agents, blowing agents (foam expansion agents) for thermoplastic and thermoset foams,

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heat transfer media, gaseous dielectrics, fire extinguishing and suppression agents, power cycle working fluids, polymerization media, particulate removal fluids, carrier fluids, buffing abrasive agents, and displacement drying agents.

5 One embodiment of this invention provides a process for preparing a thermoplastic or thermoset foam. The process comprises using an azeotropic or azeotrope-like composition as a blowing agent, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group
10 consisting of methyl formate, n-pentane, 2-methylbutane, , trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

Another embodiment of this invention provides a process for producing refrigeration. The process comprises condensing an azeotropic or azeotrope-like composition and thereafter evaporating said azeotropic
15 or azeotrope-like composition in the vicinity of the body to be cooled, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, , trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and
20 isobutane.

Another embodiment of this invention provides a process using an azeotropic or azeotrope-like composition as a solvent, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group
25 consisting of methyl formate, n-pentane, 2-methylbutane, , trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

Another embodiment of this invention provides a process for producing an aerosol product. The process comprises using an azeotropic or azeotrope-like composition as a propellant, wherein said azeotropic or
30 azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, , trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

Another embodiment of this invention provides a process using an azeotropic or azeotrope-like composition as a heat transfer media, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, 1, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

Another embodiment of this invention provides a process for extinguishing or suppressing a fire. The process comprises using an azeotropic or azeotrope-like composition as a fire extinguishing or suppression agent, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

Another embodiment of this invention provides a process using an azeotropic or azeotrope-like composition as dielectrics, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

CLAIMS

1. A composition consisting essentially of:
 - (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and
 - 5 (b) methyl formate; wherein the methyl formate is present in an effective amount to form an azeotrope-like combination with the E-1,1,1,4,4,4-hexafluoro-2-butene.
2. A composition consisting essentially of:
 - (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and
 - 10 (b) n-pentane; wherein the n-pentane is present in an effective amount to form an azeotropic combination with the E-1,1,1,4,4,4-hexafluoro-2-butene.
3. A composition consisting essentially of:
 - (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and
 - 15 (b) n-pentane; wherein the n-pentane is present in an effective amount to form an azeotrope-like combination with the E-1,1,1,4,4,4-hexafluoro-2-butene.
4. A composition consisting essentially of:
 - (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and
 - 20 (b) 2-methylbutane; wherein the 2-methylbutane is present in an effective amount to form an azeotropic combination with the E-1,1,1,4,4,4-hexafluoro-2-butene.
5. A composition consisting essentially of:
 - (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and
 - 25 (b) 2-methylbutane; wherein the 2-methylbutane is present in an effective amount to form an azeotrope-like combination with the E-1,1,1,4,4,4-hexafluoro-2-butene.
6. A composition consisting essentially of:
 - (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and
 - 30 (b) trans-1,2-dichloroethylene; wherein the trans-1,2-dichloroethylene is present in an effective amount to form an azeotrope-like combination with the E-1,1,1,4,4,4-hexafluoro-2-butene.
7. A composition consisting essentially of:
 - (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and

(b) 1,1,1,3,3-pentafluoropropane; wherein the 1,1,1,3,3-pentafluoropropane is present in an effective amount to form an azeotrope-like combination with the E-1,1,1,4,4,4-hexafluoro-2-butene.

8. A composition consisting essentially of:

- 5 (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and
(b) n-butane; wherein the n-butane is present in an effective amount to form an azeotropic combination with the E-1,1,1,4,4,4-hexafluoro-2-butene.

9. A composition consisting essentially of:

- 10 (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and
(b) n-butane; wherein the n-butane is present in an effective amount to form an azeotrope-like combination with the E-1,1,1,4,4,4-hexafluoro-2-butene.

10. A composition consisting essentially of:

- 15 (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and
(b) isobutane; wherein the isobutane is present in an effective amount to form an azeotropic combination with the E-1,1,1,4,4,4-hexafluoro-2-butene.

11. A composition consisting essentially of:

- 20 (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and
(b) isobutane; wherein the isobutane is present in an effective amount to form an azeotrope-like combination with the E-1,1,1,4,4,4-hexafluoro-2-butene.

12. A process for preparing a thermoplastic or thermoset foam

- 25 comprising using an azeotropic or azeotrope-like composition as a blowing agent, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

13. A process for producing refrigeration comprising condensing an azeotropic or azeotrope-like composition and thereafter evaporating said azeotropic or azeotrope-like composition in the vicinity of the body to be cooled, wherein said azeotropic or

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azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

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14. A process comprising using an azeotropic or azeotrope-like composition as a solvent, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

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15. A process for producing an aerosol product comprising using an azeotropic or azeotrope-like composition as a propellant, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

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16. A process comprising using an azeotropic or azeotrope-like composition as a heat transfer media, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

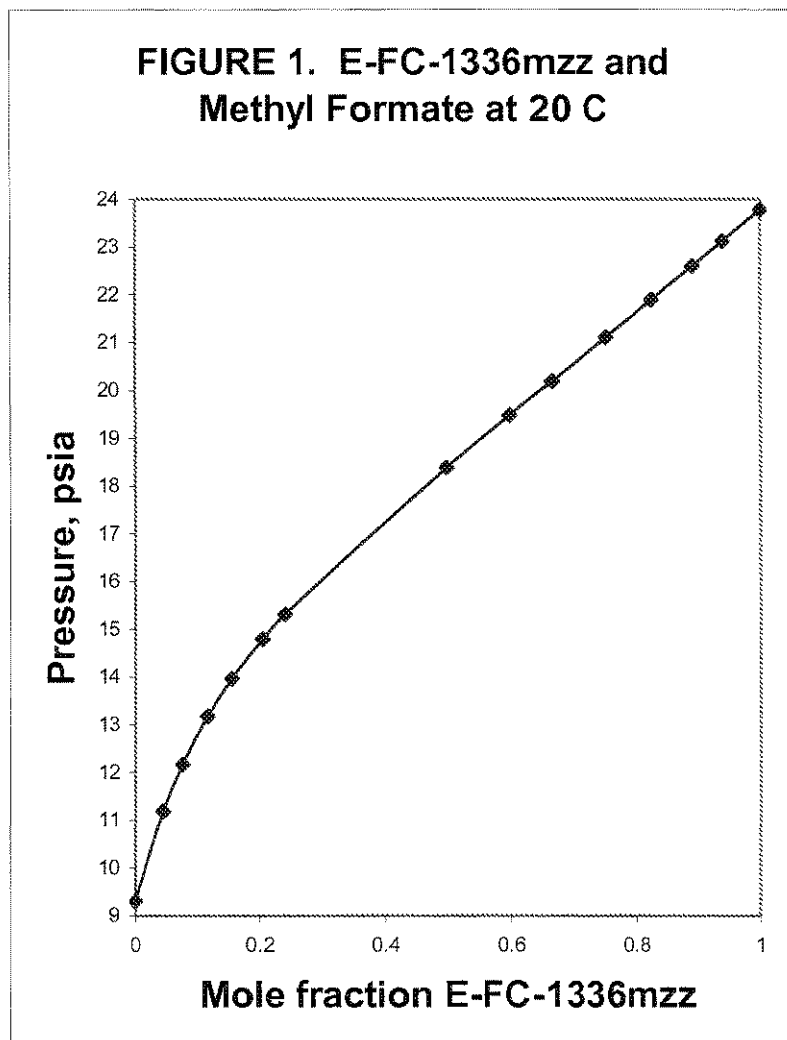
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17. A process for extinguishing or suppressing a fire comprising using an azeotropic or azeotrope-like composition as a fire extinguishing or suppression agent, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

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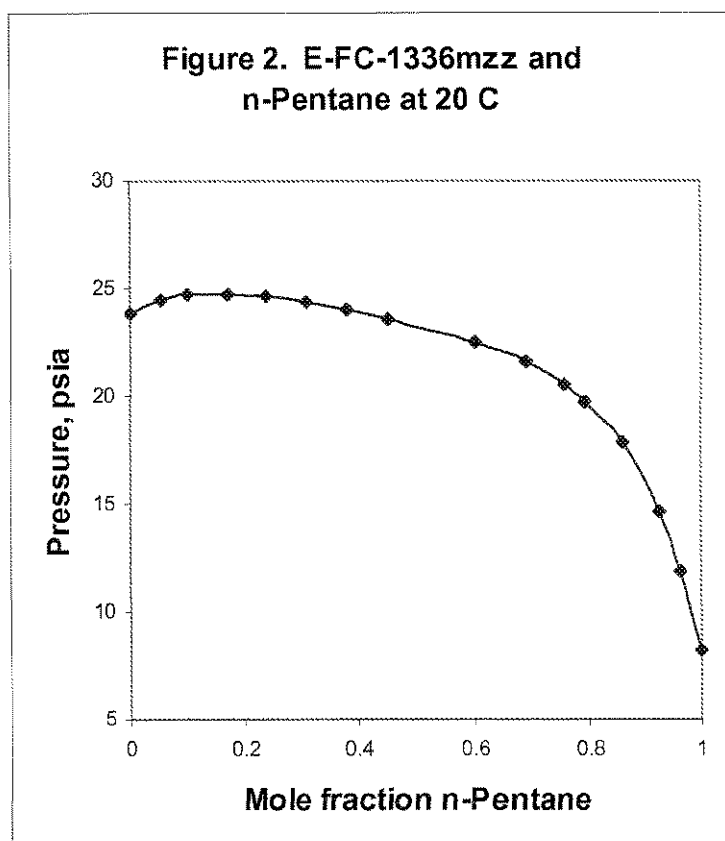
18. A process comprising using an azeotropic or azeotrope-like composition as dielectrics, wherein said azeotropic or azeotrope-like composition consists essentially of E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, n-pentane, 2-methylbutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, n-butane and isobutane.

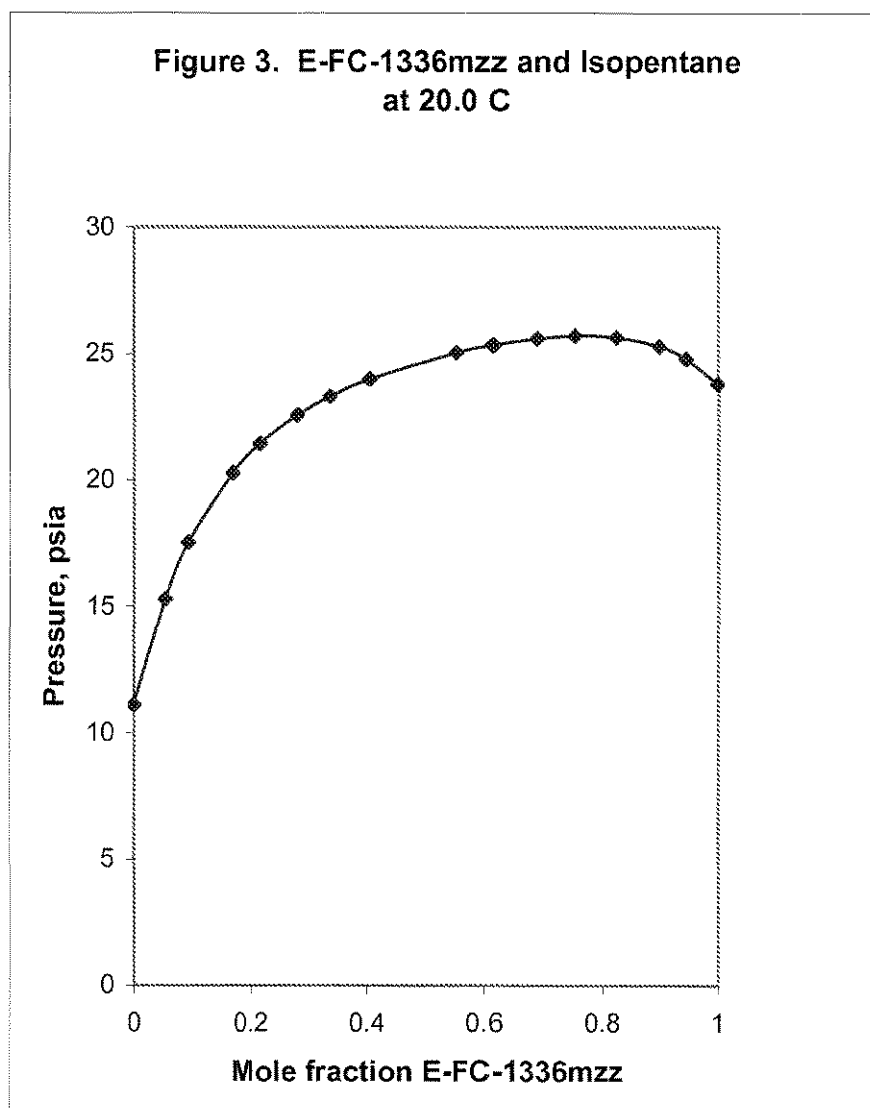


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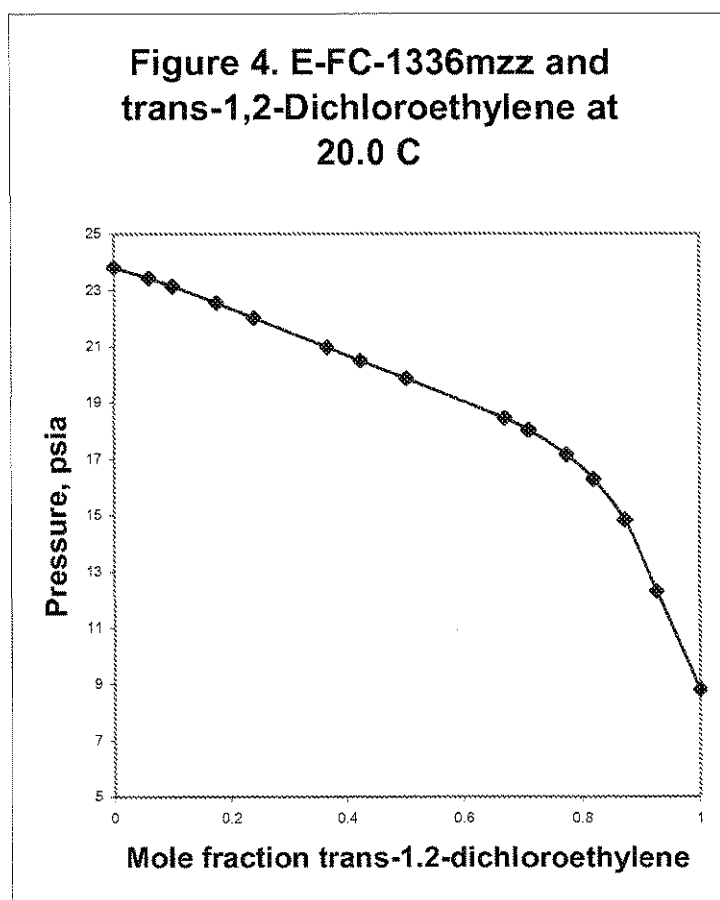
Figure 2. E-FC-1336mzz and
n-Pentane at 20 C





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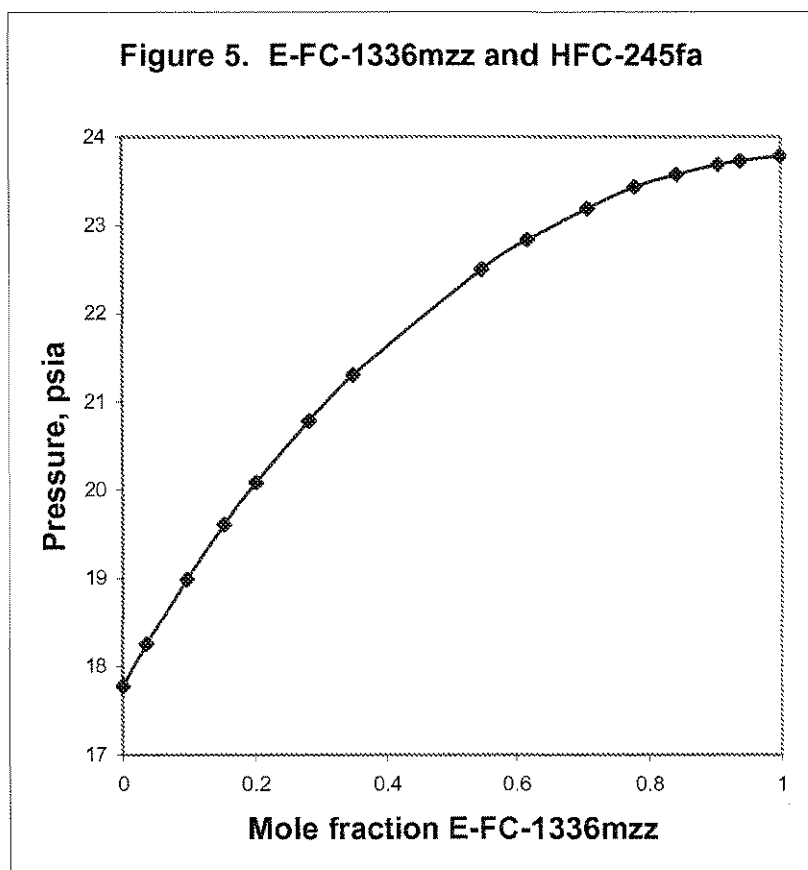
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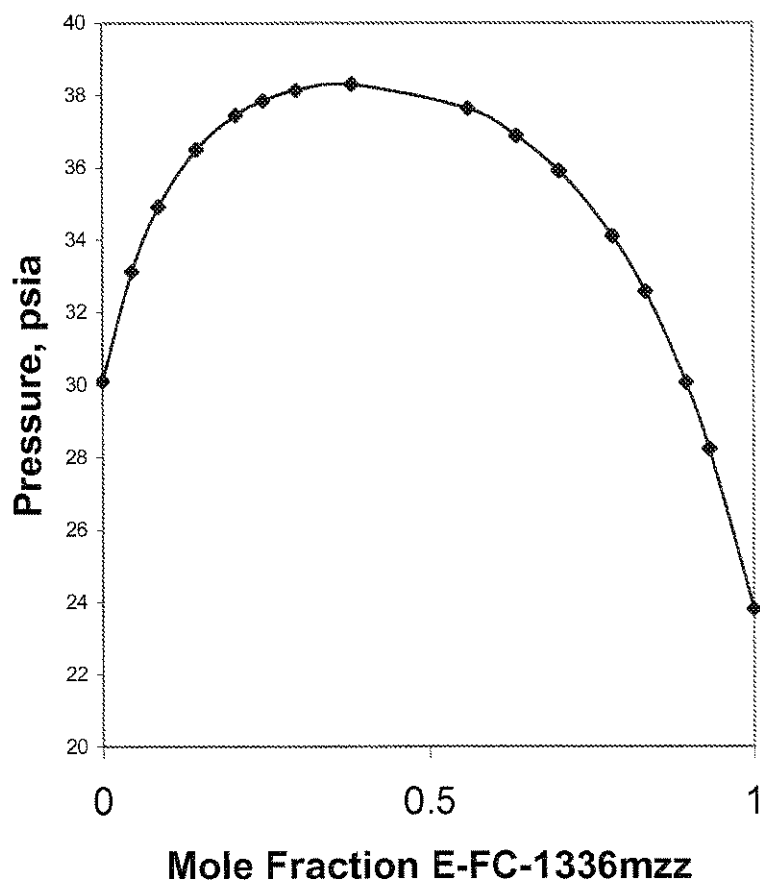


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**FIGURE 6. E-FC-1336mzz and
n-Butane at 20 C**



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