

TITLE OF INVENTION

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

5

This application claims priority of U.S. Patent Application 60/926617
filed April 27, 2007, U.S. Patent Applications 60/930467, 60/930445 and
60/930383 filed May 16, 2007, U.S. Patent Applications 60/931960 and
60/931875 filed May 24, 2007, U.S. Patent Application 60/967874 filed
10 September 7, 2007, U.S. Patent Application 60/962203 filed October 5,
2007, U.S. Patent Application 60/999871 filed October 22, 2007.

BACKGROUND OF THE INVENTION

Field of the Disclosure

15

The present disclosure relates to azeotropic or azeotrope-like
compositions of Z-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).

30

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 ($\text{CF}_3\text{CH}=\text{CHCF}_3$, FC-1336mzz), are believed to meet both goals.

SUMMARY OF THE INVENTION

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

This disclosure provides a composition consisting essentially of (a) Z-FC-1336mzz and (b) methyl formate; wherein the methyl formate is present in an effective amount to form an azeotropic or azeotrope-like mixture with Z-FC-1336mzz.

This disclosure also provides a composition consisting essentially of (a) Z-FC-1336mzz and (b) pentane; wherein the pentane is present in an effective amount to form an azeotropic or azeotrope-like mixture with Z-FC-1336mzz.

This disclosure also provides a composition consisting essentially of (a) Z-FC-1336mzz and (b) 2-methylbutane (isopentane); wherein the isopentane is present in an effective amount to form an azeotropic or azeotrope-like mixture with Z-FC-1336mzz.

In one aspect, there is provided a composition consisting essentially of (a) Z-FC-1336mzz and (b) 1,1,1,3,3-pentafluorobutane ($\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3$, HFC-365mfc); wherein the HFC-365mfc is present in an effective amount to form an azeotrope-like mixture with Z-FC-1336mzz.

This disclosure also provides a composition consisting essentially of (a) Z-FC-1336mzz and (b) trans-1,2-dichloroethylene; wherein the trans-1,2-dichloroethylene is present in an effective amount to form an azeotropic or azeotrope-like mixture with Z-FC-1336mzz.

This disclosure also provides a composition consisting essentially of (a) Z-FC-1336mzz and (b) 1,1,1,3,3-pentafluoropropane ($\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$),

HFC-245fa); wherein the HFC-245fa is present in an effective amount to form an azeotrope-like mixture with Z-FC-1336mzz.

This disclosure also provides a composition consisting essentially of (a) Z-FC-1336mzz and (b) dimethoxymethane ($\text{CH}_3\text{OCH}_2\text{OCH}_3$, methylal); wherein the dimethoxymethane is present in an effective amount to form an azeotrope-like mixture with Z-FC-1336mzz.

This disclosure also provides a composition consisting essentially of (a) Z-FC-1336mzz and (b) cyclopentane ($\text{c-C}_5\text{H}_{10}$); wherein the cyclopentane is present in an effective amount to form an azeotropic or azeotrope-like mixture with Z-FC-1336mzz.

In another aspect, there is provided a process for preparing a thermoplastic or thermoset foam comprising using an azeotrope-like composition as a blowing agent, wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.

In another aspect, there is provided a process for producing refrigeration comprising condensing an azeotrope-like composition and thereafter evaporating said azeotrope-like composition in the vicinity of the body to be cooled, wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.

In another aspect, there is provided a process comprising using an azeotrope-like composition as a solvent, wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.

In another aspect, there is provided a process for producing an aerosol product comprising using an azeotrope-like composition as a propellant, wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.

In another aspect, there is provided a process comprising using an azeotrope-like composition as a heat transfer media, wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.

In another aspect, there is provided a process for extinguishing or suppressing a fire comprising using an azeotrope-like composition as a fire extinguishing or suppression agent, wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.

In another aspect, there is provided a process comprising using an azeotrope-like composition as dielectrics, wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.

BRIEF SUMMARY OF THE DRAWINGS

FIG. 1 - FIG. 1 is a graphical representation of an azeotrope and azeotrope-like compositions consisting essentially of Z-FC-1336mzz and methyl formate at a temperature of about 50.1 °C.

FIG. 2 - FIG. 2 is a graphical representation of an azeotrope and azeotrope-like compositions consisting essentially of Z-FC-1336mzz and pentane at a temperature of about 19.9 °C.

FIG. 3 - FIG. 3 is a graphical representation of an azeotrope and azeotrope-like compositions consisting essentially of Z-FC-1336mzz and isopentane at a temperature of about 19.9 °C.

FIG. 4 - FIG. 4 is a graphical representation of azeotrope-like compositions consisting essentially of Z-FC-1336mzz and HFC-365mfc at a temperature of about 50.0 °C.

FIG. 5 - FIG. 5 is a graphical representation of an azeotrope and azeotrope-like compositions consisting essentially of Z-FC-1336mzz and trans-1,2-dichloroethylene at a temperature of about 50.1 °C.

FIG. 6 - FIG. 6 is a graphical representation of azeotrope-like compositions consisting essentially of Z-FC-1336mzz and HFC-245fa at a temperature of about 20,0 °C.

- 5 FIG. 7 - FIG. 7 is a graphical representation of azeotrope-like compositions consisting essentially of Z-FC-1336mzz and dimethoxymethane at a temperature of about 50.0 °C.

- FIG. 8 - FIG. 8 is a graphical representation of an azeotrope and
10 azeotrope-like compositions consisting essentially of Z-FC-1336mzz and cyclopentane at a temperature of about 50 °C.

DETAILED DESCRIPTION OF THE INVENTION

15

- 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
25 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.
- 30 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 Z-1,1,1,4,4,4-hexafluoro-2-butene (Z-CF₃CH=CHCF₃, Z-FC-1336mzz).

5 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.

10 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
15 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).

20 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.

25 Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of 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
30 methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are 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.

Z-FC-1336mzz is a known compound, and its preparation method has been disclosed, for example, in U.S. Patent Application No.

5 60/926293 [FL1346 US PRV] filed April/26/2007, hereby incorporated by reference in its entirety.

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

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

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

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

In some embodiments of this invention, the composition consists essentially of (a) Z-FC-1336mzz and (b) HFC-365mfc; wherein the HFC-365mfc is present in an effective amount to form an azeotrope-like mixture with Z-FC-1336mzz.

25 In some embodiments of this invention, the composition consists essentially of (a) Z-FC-1336mzz and (b) trans-1,2-dichloroethylene; wherein the trans-1,2-dichloroethylene is present in an effective amount to form an azeotropic or azeotrope-like mixture with Z-FC-1336mzz.

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

In some embodiments of this invention, the composition consists essentially of (a) Z-FC-1336mzz and (b) dimethoxymethane; wherein the

dimethoxymethane is present in an effective amount to form an azeotrope-like mixture with Z-FC-1336mzz.

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

By effective amount is meant an amount, which, when combined with Z-FC-1336mzz, results in the formation of an azeotropic or azeotrope-like mixture. This definition includes the amounts of each component,
10 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
15 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
20 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
25 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
30 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
35 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
5 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
10 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
15 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
20 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
25 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
30 pages 124 to 126; hereby incorporated by reference.

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 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
5 aforementioned references are hereby incorporated by reference. Without wishing to be bound by any theory or explanation, it is believed that the NRTL equation, together with the PTx cell data, can sufficiently predict the
10 relative volatilities of the Z-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 distillation columns.

It was found through experiments that Z-FC-1336mzz and methyl
15 formate 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
20 equilibrium vapor and liquid compositions in the cell using the NRTL equation.

The vapor pressure measured versus the compositions in the PTx cell for Z-FC-1336mzz/methyl formate mixture is shown in FIG. 1, which graphically illustrates the formation of an azeotropic and azeotrope-like
25 composition consisting essentially of Z-FC-1336mzz and methyl formate as indicated by a mixture of about 20.4 mole % Z-1,1,1,4,4,4-hexafluoro-2-butene and 79.6 mole % methyl formate having the highest pressure over the range of compositions at this temperature. Based upon these findings, it has been calculated that Z-FC-1336mzz and methyl formate
30 form azeotropic compositions ranging from about 25.4 mole percent to about 15.6 mole percent Z-FC-1336mzz and from about 74.6 mole percent to about 84.4 mole percent methyl formate (which form azeotropic compositions boiling at a temperature of from about -20 °C to about 100 °C and at a pressure of from about 1.4 psia (10 kPa) to about 113 psia

(779 kPa)). Some embodiments of azeotropic compositions are listed in Table 1.

Table 1 Azeotropic compositions

Azeotropic Temperature (°C)	Azeotropic Pressure (psia)	Z-FC-1336mzz (mole %)	Methyl formate (mole %)
- 20.0	1.38	25.4	74.6
- 10.0	2.40	25.2	74.8
0.0	3.97	24.8	75.2
10.0	6.30	24.3	75.7
20.0	9.64	23.7	76.3
30.0	14.3	22.9	77.1
40.0	20.5	22.1	77.9
50.0	28.7	21.2	78.8
60.0	39.2	20.2	79.8
70.0	52.4	19.1	80.9
80.0	68.9	18.0	82.0
90.0	89.0	16.8	83.2
100.0	113.3	15.6	84.4

5

Additionally, azeotrope-like compositions containing Z-FC-1336mzz and methyl formate 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

10 azeotrope-like compositions are listed in Table 3

15

Table 2 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/Methyl formate	-40	1-99/1-99
Z-FC-1336mzz/Methyl formate	0	1-99/1-99
Z-FC-1336mzz/Methyl formate	20	1-99/1-99
Z-FC-1336mzz/Methyl formate	40	1-99/1-99
Z-FC-1336mzz/Methyl formate	80	1-99/1-99
Z-FC-1336mzz/Methyl formate	120	1-99/1-99

5

Table 3 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/Methyl formate	-40	10-90/10-90
Z-FC-1336mzz/Methyl formate	0	10-90/10-90
Z-FC-1336mzz/Methyl formate	20	10-90/10-90
Z-FC-1336mzz/Methyl formate	40	10-90/10-90
Z-FC-1336mzz/Methyl formate	80	10-90/10-90
Z-FC-1336mzz/Methyl formate	120	10-90/10-90

10 It was found through experiments that Z-FC-1336mzz and 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 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 Z-FC-1336mzz/pentane mixture is shown in FIG. 2, which illustrates graphically the formation of an azeotropic and azeotrope-like composition consisting essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and pentane at 19.9 °C, as indicated by a mixture of about 50.0 mole % Z-1,1,1,4,4,4-hexafluoro-2-butene and 50.0 mole % pentane having the highest pressure over the range of compositions at this temperature.

Based upon these findings, it has been calculated that Z-FC-1336mzz and pentane form azeotropic compositions ranging from about 48.2 mole percent to about 58.7 mole percent Z-FC-1336mzz and from about 51.8 mole percent to about 41.3 mole percent pentane (which form azeotropic compositions boiling at a temperature of from about -20 °C to about 120 °C and at a pressure of from about 2.2 psia (15 kPa) to about 182 psia (1255 kPa)). Some embodiments of azeotropic compositions are listed in Table 4.

Table 4 Azeotropic compositions

Azeotropic Temperature (°C)	Azeotropic Pressure (psia)	Z-FC-1336mzz (mole %)	Pentane (mole %)
-20.0	2.20	48.2	51.8
-10.0	3.70	48.9	51.1
0.0	5.91	49.5	50.5
10.0	9.07	50.1	49.9
20.0	13.4	50.7	49.3
30.0	19.2	51.2	48.8
40.0	26.7	51.8	48.2
50.0	36.2	52.3	47.7
60.0	48.0	52.9	47.1
70.0	62.4	53.6	46.4
80.0	79.6	54.3	45.7
90.0	100	55.1	44.9
100.0	124	56.0	44.0
110.0	151	57.2	42.8
120.0	182	58.7	41.3

Additionally, azeotrope-like compositions containing Z-FC-1336mzz and pentane may also be formed. Such azeotrope-like compositions exist around azeotropic compositions. Some embodiments of azeotrope-like compositions are listed in Table 5. Additional embodiments of azeotrope-like compositions are listed in Table 6.

Table 5 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/Pentane	-40	60-75/25-40
Z-FC-1336mzz/Pentane	0	60-80/20-40
Z-FC-1336mzz/Pentane	20	60-82/28-40
Z-FC-1336mzz/Pentane	40	60-85/15-40
Z-FC-1336mzz/Pentane	80	55-90/10-45
Z-FC-1336mzz/Pentane	120	45-99/1-55

5

Table 6 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/Pentane	-40	62-70/30-38
Z-FC-1336mzz/Pentane	0	64-74/26-36
Z-FC-1336mzz/Pentane	20	64-76/24-36
Z-FC-1336mzz/Pentane	40	64-78/22-36
Z-FC-1336mzz/Pentane	80	62-84/16-38
Z-FC-1336mzz/Pentane	120	57-99/1-43

It was found through experiments that Z-FC-1336mzz and isopentane 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 Z-FC-1336mzz/ isopentane mixture is shown in FIG. 3, which illustrates graphically the formation of an azeotrope and azeotrope-like

compositions of Z-1,1,1,4,4,4-hexafluoro-2-butene and isopentane at 19.9 °C, as indicated by a mixture of about 40.0 mole % Z-1,1,1,4,4,4-hexafluoro-2-butene and 60.0 mole % isopentane having the highest pressure over the range of compositions at this temperature.

- 5 Based upon these findings, it has been calculated that Z-FC-1336mzz and isopentane form azeotropic compositions ranging from about 37.1 mole percent to about 48.6 mole percent Z-FC-1336mzz and from about 62.9 mole percent to about 51.4 mole percent isopentane (which form azeotropic compositions boiling at a temperature of from about -20 °C to about 120 °C and at a pressure of from about 2.7 psia (19 kPa) to about 199 psia (1372 kPa)). Some embodiments of azeotropic compositions are listed in Table 7.

Table 7 Azeotropic compositions

Azeotropic Temperature (°C)	Azeotropic Pressure (psia)	Z-FC-1336mzz (mole %)	Isopentane (mole %)
- 20.0	2.72	37.1	62.9
- 10.0	4.47	38.3	61.7
0.0	7.01	39.4	60.6
10.0	10.6	40.4	59.6
20.0	15.4	41.2	58.8
30.0	21.9	42.0	58.0
40.0	30.1	42.8	57.2
50.0	40.5	43.5	56.5
60.0	53.4	44.2	55.8
70.0	69.0	44.8	55.2
80.0	87.6	45.5	54.5
90.0	110	46.2	53.8
100.0	135	46.9	53.1
110.0	165	47.7	52.3
120.0	199	48.6	51.4

- 15 Additionally, azeotrope-like compositions containing Z-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 8. Additional embodiments of azeotrope-like compositions are listed in Table 9.

5

Table 8 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/Isopentane	-40	40-65/35-60
Z-FC-1336mzz/Isopentane	0	45-70/30-55
Z-FC-1336mzz/Isopentane	20	45-75/25-55
Z-FC-1336mzz/Isopentane	40	45-75/25-55
Z-FC-1336mzz/Isopentane	80	40-85/15-60
Z-FC-1336mzz/Isopentane	120	1-99/1-99

Table 9 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/Isopentane	-40	49-58/42-51
Z-FC-1336mzz/Isopentane	0	53-65/35-47
Z-FC-1336mzz/Isopentane	20	53-68/32-47
Z-FC-1336mzz/Isopentane	40	53-71/29-47
Z-FC-1336mzz/Isopentane	80	52-77/23-48
Z-FC-1336mzz/Isopentane	120	43-89/11-57

- 10 It was found through experiments that Z-FC-1336mzz and HFC-365mfc 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.

5 The vapor pressure measured versus the compositions in the PTx cell for Z-FC-1336mzz/ HFC-365mfc mixture is shown in FIG. 4, which illustrates graphically the formation of azeotrope-like compositions of Z-1,1,1,4,4,4-hexafluoro-2-butene and HFC-365mfc at 50.1 °C, as indicated by a mixtures of about 1 to 99 mole % Z-1,1,1,4,4,4-hexafluoro-2-butene and about 1 to 99 mole % HFC-365mfc.

10 Some embodiments of azeotrope-like compositions are listed in Table 10. Additional embodiments of azeotrope-like compositions are listed in Table 11.

Table 10 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/HFC-365mfc	-40	1-99/1-99
Z-FC-1336mzz/HFC-365mfc	0	1-99/1-99
Z-FC-1336mzz/HFC-365mfc	40	1-99/1-99
Z-FC-1336mzz/HFC-365mfc	80	1-99/1-99
Z-FC-1336mzz/HFC-365mfc	120	1-99/1-99
Z-FC-1336mzz/HFC-365mfc	160	1-99/1-99

Table 11 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/HFC-365mfc	-40	10-99/10-90
Z-FC-1336mzz/HFC-365mfc	0	10-99/10-90
Z-FC-1336mzz/HFC-365mfc	40	10-99/10-90
Z-FC-1336mzz/HFC-365mfc	80	10-90
Z-FC-1336mzz/HFC-365mfc	120	10-90
Z-FC-1336mzz/HFC-365mfc	160	10-90

It was found through experiments that Z-FC-1336mzz and trans-1,2-dichloroethylene form azeotropic or azeotrope-like compositions.

5 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.

10 The vapor pressure measured versus the compositions in the PTx cell for Z-FC-1336mzz/ trans-1,2-dichloroethylene mixture is shown in FIG. 5, which illustrates graphically the formation of an azeotropic composition of Z-1,1,1,4,4,4-hexafluoro-2-butene and trans-1,2-dichloroethylene at 50.1 °C, as indicated by a mixture of about 64.8 mole % Z-1,1,1,4,4,4-
15 hexafluoro-2-butene and 35.2 mole % trans-1,2-dichloroethylene having the highest pressure over the range of compositions at this temperature.

Based upon these findings, it has been calculated that Z-FC-1336mzz and trans-1,2-dichloroethylene form azeotropic compositions ranging from about 62.4 mole percent to about 71.0 mole percent Z-FC-
20 1336mzz and from about 37.6 mole percent to about 29.0 mole percent trans-1,2-dichloroethylene (which form azeotropic compositions boiling at a temperature of from about -20 °C to about 120 °C and at a pressure of

from about 1.6 psia (11 kPa) to about 170 psia (1172 kPa)). Some embodiments of azeotropic compositions are listed in Table 12.

Table 12 Azeotropic compositions

Azeotropic Temperature (°C)	Azeotropic Pressure (psia)	Z-FC-1336mzz (mole %)	trans-1,2-dichloroethylene (mole %)
- 20.0	1.60	62.4	37.6
- 10.0	2.74	62.4	37.6
0.0	4.47	62.5	37.5
10.0	6.98	62.8	37.2
20.0	10.5	63.1	36.9
30.0	15.3	63.6	36.4
40.0	21.7	64.2	35.8
50.0	29.9	64.8	35.2
60.0	40.3	65.5	34.5
70.0	53.2	66.3	33.7
80.0	69.0	67.2	32.8
90.0	88.2	68.1	31.9
100.0	111	69.0	31.0
110.0	138	70.0	30.0
120.0	170	71.0	29.0

5 Additionally, azeotrope-like compositions containing Z-FC-1336mzz and trans-1,2-dichloroethylene may also be formed. Such azeotrope-like compositions exist around azeotropic compositions. Some embodiments of azeotrope-like compositions are listed in Table 13. Additional embodiments of azeotrope-like compositions are listed in Table 14.

10

Table 13 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/trans-1,2-dichloroethylene	-40	71-82/18-29
Z-FC-1336mzz/trans-1,2-dichloroethylene	0	67-86/14-33
Z-FC-1336mzz/trans-1,2-dichloroethylene	20	65-93/7-35
Z-FC-1336mzz/trans-1,2-dichloroethylene	40	65-99/1-35
Z-FC-1336mzz/trans-1,2-dichloroethylene	80	63-99/1-37
Z-FC-1336mzz/trans-1,2-dichloroethylene	120	61-99/1-39
Z-FC-1336mzz/trans-1,2-dichloroethylene	160	58-99/1-42

Table 14 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/trans-1,2-dichloroethylene	-40	72-80/20-38
Z-FC-1336mzz/trans-1,2-dichloroethylene	0	69-83/17-31
Z-FC-1336mzz/trans-1,2-dichloroethylene	20	68-86/14-32
Z-FC-1336mzz/trans-1,2-dichloroethylene	40	68-90/10-32
Z-FC-1336mzz/trans-1,2-dichloroethylene	80	66-99/1-34
Z-FC-1336mzz/trans-1,2-dichloroethylene	120	65-99/1-35
Z-FC-1336mzz/trans-1,2-dichloroethylene	160	65-99/1-35

5 It was found through experiments that Z-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
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 Z-FC-1336mzz/ HFC-245fa mixture is shown in FIG. 6, which
illustrates graphically the formation of azeotrope-like compositions of Z-
15 1,1,1,4,4,4-hexafluoro-2-butene and HFC-245fa at 19.9 °C, as indicated

by mixtures of about 1 to 21 mole % Z-1,1,1,4,4,4-hexafluoro-2-butene and about 79 to 99 mole % HFC-245fa with vapor pressure of approximately 17 psia (117 kPa), and by mixtures of about 94 to 99 mole percent Z-1,1,1,4,4,4-hexafluoro-2-butene and 1 to 6 mole % HFC-245fa with vapor pressure of approximately 9 psia (62 kPa).

Some embodiments of azeotrope-like compositions are listed in Table 15. Additional embodiments of azeotrope-like compositions are listed in Table 16.

Table 15 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/HFC-245fa	-40	1-19/81-99 and 97-99/1-3
Z-FC-1336mzz/HFC-245fa	0	1-22/78-99 and 95-99/1-5
Z-FC-1336mzz/HFC-245fa	40	1-26/74-99 and 94-99/1-6
Z-FC-1336mzz/HFC-245fa	80	1-35/65-99 and 90-99/1-10
Z-FC-1336mzz/HFC-245fa	120	1-58/42-99 and 76-99/1-24

10

Table 16 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/HFC-245fa	-40	10-13/87-90 and 98-99/1-2
Z-FC-1336mzz/HFC-245fa	0	10-14/86-90 and 97-99/1-3
Z-FC-1336mzz/HFC-245fa	40	10-17/83-90 and 96-99/1-4
Z-FC-1336mzz/HFC-245fa	80	10-22/78-90 and 95-99/1-5
Z-FC-1336mzz/HFC-245fa	120	10-33/67-90 and 90-99/1-10

It was found through experiments that Z-FC-1336mzz and dimethoxymethane 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 Z-FC-1336mzz/dimethoxymethane mixture is shown in FIG. 7, which illustrates graphically the formation of azeotrope-like compositions of Z-1,1,1,4,4,4-hexafluoro-2-butene and dimethoxymethane at 49.99 °C and about 22.5 psia (155 kPa), as indicated by mixtures of about 1 to 99 mole % Z-1,1,1,4,4,4-hexafluoro-2-butene and about 1 to 99 mole % dimethoxymethane.

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 Percentage Range
Z-FC-1336mzz/Dimethoxymethane	-40	1-99/1-99
Z-FC-1336mzz/Dimethoxymethane	0	1-99/1-99
Z-FC-1336mzz/Dimethoxymethane	40	1-99/1-99
Z-FC-1336mzz/Dimethoxymethane	80	1-99/1-99
Z-FC-1336mzz/Dimethoxymethane	120	1-99/1-99
Z-FC-1336mzz/Dimethoxymethane	160	1-99/1-99

Table 18 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/Dimethoxymethane	-40	5-95/5-95
Z-FC-1336mzz/Dimethoxymethane	0	5-95/5-95
Z-FC-1336mzz/Dimethoxymethane	40	5-95/5-95
Z-FC-1336mzz/Dimethoxymethane	80	5-95/5-95
Z-FC-1336mzz/Dimethoxymethane	120	5-95/5-95
Z-FC-1336mzz/Dimethoxymethane	160	5-95/5-95

It was found through experiments that Z-FC-1336mzz and cyclopentane 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.

- 5 The vapor pressure measured versus the compositions in the PTx cell for Z-FC-ISS β mzz/cyclopentane mixture is shown in FIG. 8, which illustrates graphically the formation of an azeotropic composition of Z-1,1,1,4,4,4-hexafluoro-2-butene and cyclopentane at 49.97 °C, as indicated by a mixture of about 63.9 mole % Z-1,1,1,4,4,4-hexafluoro-2-
- 10 butene and 36.1 mole % cyclopentane having the highest pressure over the range of compositions at this temperature.

- Based upon these findings, it has been calculated that Z-FC-1336mzz and cyclopentane form azeotropic compositions ranging from about 64.2 mole percent to about 74.4 mole percent Z-FC-1336mzz and
- 15 from about 35.8 mole percent to about 25.6 mole percent cyclopentane (which form azeotropic compositions boiling at a temperature of from about -20 °C to about 150 °C and at a pressure of from about 1.7 psia (12 kPa) to about 302 psia (2082 kPa)). Some embodiments of azeotropic compositions are listed in Table 19.

Table 19 Azeotropic compositions

Azeotropic Temperature (°C)	Azeotropic Pressure (psia)	Z-FC-1336mzz (mole %)	Cyclopentane (mole %)
- 20.0	1.74	64.2	35.8
- 10.0	2.98	63.9	36.1
0.0	4.86	63.7	36.3
10.0	7.59	63.6	36.4
20.0	11.4	63.5	36.5
30.0	16.6	63.6	36.4
40.0	23.4	63.7	36.3
49.97	32.1	63.9	36.1
50.0	32.1	63.9	36.1
60.0	43.1	64.2	35.8
70.0	56.7	64.6	35.4
80.0	73.2	65.1	34.9
90.0	92.9	65.8	34.2
100.0	116	66.6	33.4
110.0	144	67.6	32.4
120.0	175	68.9	31.1
130.0	211	70.4	29.6
140.0	254	72.3	27.7
150.0	302	74.4	25.6

Additionally, azeotrope-like compositions containing Z-FC-1336mzz and cyclopentane may also be formed. Such azeotrope-like compositions exist around azeotropic compositions. Some embodiments of azeotrope-like compositions are listed in Table 20. Additional embodiments of azeotrope-like compositions are listed in Table 21.

Table 20 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/cyclopentane	- 20	77 - 86/14 - 23
Z-FC-1336mzz/cyclopentane	0	76 - 87/13 - 24
Z-FC-1336mzz/cyclopentane	40	74 - 90/10 - 26
Z-FC-1336mzz/cyclopentane	80	72 - 99/1 - 28
Z-FC-1336mzz/cyclopentane	120	70 - 99/1 - 30
Z-FC-1336mzz/cyclopentane	150	68 - 99/1 - 32

Table 21 Azeotrope-like compositions

COMPONENTS	T (°C)	Weight Percentage Range
Z-FC-1336mzz/cyclopentane	- 20	80 - 86/14 - 20
Z-FC-1336mzz/cyclopentane	0	80 - 87/13 - 20
Z-FC-1336mzz/cyclopentane	40	80- 90/10 - 206
Z-FC-1336mzz/cyclopentane	80	80 - 95/5 - 20
Z-FC-1336mzz/cyclopentane	120	80 - 95/5 - 20
Z-FC-1336mzz/cyclopentane	150	80 - 99/5 - 20

The azeotropic or azeotrope-like compositions of the present invention can be prepared by any convenient method including mixing or
5 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.

The azeotropic or azeotrope-like compositions of the present
10 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, heat transfer media, gaseous dielectrics, fire extinguishing and suppression agents, power cycle working fluids, polymerization media,
15 particulate removal fluids, carrier fluids, buffing abrasive agents, and displacement drying agents.

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
20 azeotropic or azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, pentane, 2-methylbutane, 1,1,1,3,3-pentafluorobutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, dimethoxymethane and cyclopentane.

25 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

or azeotrope-like composition in the vicinity of the body to be cooled, wherein said azeotropic or azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, pentane, 2-methylbutane, 1,1,1,3,3-
5 pentafluorobutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, dimethoxymethane and cyclopentane.

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 Z-
10 1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, pentane, 2-methylbutane, 1,1,1,3,3-pentafluorobutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, dimethoxymethane and cyclopentane.

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

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
25 of Z-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, pentane, 2-methylbutane, 1,1,1,3,3-pentafluorobutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, dimethoxymethane and cyclopentane.

Another embodiment of this invention provides a process for
30 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 Z-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of methyl formate, pentane, 2-

methylbutane, 1,1,1,3,3-pentafluorobutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, dimethoxymethane and cyclopentane.

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

10

CLAIMS

1. A composition consisting essentially of:
 - (a) Z-1,1,1,4,4,4-hexafluoro-2-butene; and
 - 5 (b) 1,1,1,3,3-pentafluorobutane; wherein the 1,1,1,3,3-pentafluorobutane is present in an effective amount to form an azeotrope-like combination with the Z-1,1,1,4,4,4-hexafluoro-2-butene.
2. The azeotrope-like composition of claim 1 consisting essentially of from 1 to 99 weight percent Z-1,1,1,4,4,4-hexafluoro-2-butene and from 99 to 1
10 weight percent 1,1,1,3,3-pentafluorobutane, characterized by: at a temperature of from -40 °C to 160 °C, said composition having a difference in dew point pressure and bubble point pressure of less than or equal to 5 percent based upon the bubble point pressure.
3. A process for preparing a thermoplastic or thermoset foam comprising
15 using an azeotrope-like composition as a blowing agent, wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.
4. A process for producing refrigeration comprising condensing an
20 azeotrope-like composition and thereafter evaporating said azeotrope-like composition in the vicinity of the body to be cooled, wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.
5. A process comprising using an azeotrope-like composition as a solvent,
25 wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.
6. A process for producing an aerosol product comprising using an azeotrope-like composition as a propellant, wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.
- 30 7. A process comprising using an azeotrope-like composition as a heat transfer media, wherein said azeotrope-like composition consists

essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.

- 5
8. A process for extinguishing or suppressing a fire comprising using an azeotrope-like composition as a fire extinguishing or suppression agent, wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.
9. A process comprising using an azeotrope-like composition as dielectrics, wherein said azeotrope-like composition consists essentially of Z-1,1,1,4,4,4-hexafluoro-2-butene and 1,1,1,3,3-pentafluorobutane.

10

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

Abstract

5

Azeotropic or azeotrope-like compositions are disclosed. The azeotropic or azeotrope-like compositions are mixtures of Z-1,1,1,4,4,4-hexafluoro-2-butene with methyl formate, pentane, 2-methylbutane, 1,1,1,3,3-pentafluorobutane, trans-1,2-dichloroethylene, 1,1,1,3,3-pentafluoropropane, dimethoxymethane, or cyclopentane. Also disclosed is a process of preparing a thermoplastic or thermoset foam by using such azeotropic or azeotrope-like compositions as blowing agents. Also disclosed is a process of producing refrigeration by using such azeotropic or azeotrope-like compositions. Also disclosed is a process of using such azeotropic or azeotrope-like compositions as solvents. Also disclosed is a process of producing an aerosol product by using such azeotropic or azeotrope-like compositions. Also disclosed is a process of using such azeotropic or azeotrope-like compositions as heat transfer media. Also disclosed is a process of extinguishing or suppressing a fire by using such azeotropic or azeotrope-like compositions. Also disclosed is a process of using such azeotropic or azeotrope-like compositions as dielectrics

20

(Figure 8)