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(54) Title: AZEOTROPIC AND AZEOTROPE-LIKE COMPOSITIONS OF E-1,1,1,4,4,4-HEXAFLUORO-2-BUTENE

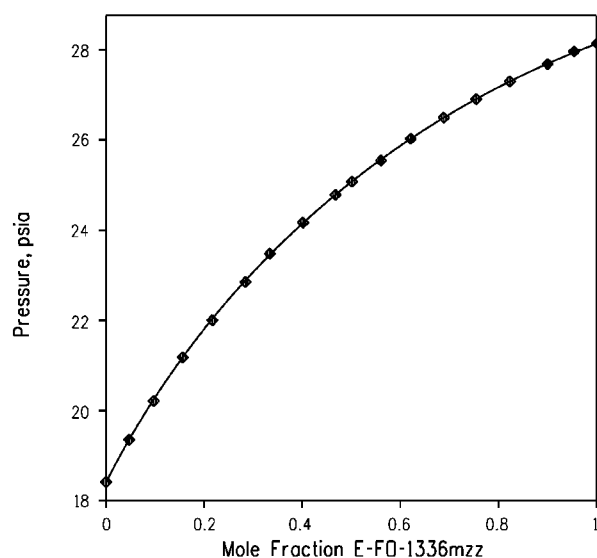


FIG. 1

(57) Abstract: Azeotropic or azeotrope-like compositions are disclosed. The azeotropic or azeotrope-like compositions are mixtures of E-1,1,1,4,4,4-hexafluoro-2-butene with E-1-chloro-3,3,3-trifluoropropene or 2-chloro-3,3,3-trifluoropropene. 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.

**TITLE OF INVENTION**

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

5

This application claims priority of U.S. Patent Application 61/327746 filed April 26, 2010, and U.S. Patent Application 61/435875 filed January 25, 2011.

10

**BACKGROUND OF THE INVENTION****Field of the Disclosure**

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

15

**Description of Related Art**

Many industries have been working for the past few decades to find 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  
20 propellants, refrigerants, cleaning agents, expansion agents for thermoplastic and thermoset foams, 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. In the search  
25 for replacements for these versatile compounds, many industries have turned to the use of hydrofluorocarbons (HFCs).

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  
30 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, FO-1336mzz), are believed to meet both goals.

5

### **SUMMARY OF THE INVENTION**

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

This disclosure provides a composition consisting essentially of (a) E-FO-1336mzz and (b) E-HCFO-1233zd (E-1-chloro-3,3,3-trifluoropropene,  $\text{E-CF}_3\text{CH}=\text{CHCl}$ ); wherein the E-HCFO-1233zd is present in an effective amount to form an azeotrope-like mixture with E-FO-1336mzz.

This disclosure also provides a composition consisting essentially of (a) E-FO-1336mzz and (b) HCFO-1233xf (2-chloro-3,3,3-trifluoropropene,  $\text{CF}_3\text{CCl}=\text{CH}_2$ ); wherein the HCFO-1233xf is present in an effective amount to form an azeotropic or azeotrope-like mixture with E-FO-1336mzz.

### **BRIEF SUMMARY OF THE DRAWINGS**

FIG. 1 - FIG. 1 is a graphical representation of azeotrope-like compositions consisting essentially of E-FO-1336mzz and E-HCFO-1233zd at a temperature of about 24.7 °C.

FIG. 2 - FIG. 2 is a graphical representation of an azeotropic composition consisting essentially of E-FO-1336mzz and HCFO-1233xf at a temperature of about 25.7 °C.

### **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 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  
5 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. The change in refrigerant composition may cause the refrigerant to become flammable or to have poor refrigeration performance. Accordingly,  
10 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-CF<sub>3</sub>CH=CHCF<sub>3</sub>, E-FC-1336mzz, E-FO-1336mzz).

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

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

HCFO-1233zd (1-chloro-3,3,3-trifluoropropene, CF<sub>3</sub>CH=CHCl) may  
20 exist as one of two configurational isomers, *E* or *Z*. HCFO-1233zd as used herein refers to the isomers, Z-HCFO-1233zd or E-HCFO-1233zd, 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  
25 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  
30 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  
5 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 ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control. Although  
10 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. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

15 When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and/or lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of  
20 whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

E-FO-1336mzz is a known compound, and can be made by the  
25 reaction of 1,2-dichloro-1,1,4,4,4-pentafluorobutane with dried KF in distilled tetramethylene sulphone, which is disclosed in U.S. Patent No. 5,463,150.

E-HCFO-1233zd is a known compound and can be made by the fluorination of  $\text{CCl}_3\text{CH}_2\text{CHCl}_2$  with HF in the presence of  $\text{SnCl}_4$ , such as  
30 disclosed by Van Der Puy et al. in US Patent Number 5,777,184.

HCFO-1233xf is a known compound and can be made by the addition of HF to  $\text{CH}_2\text{ClCCl}=\text{CCl}_2$  in a gas phase reaction using di-isopropyl amine as a stabilizer and  $\text{Cr}_2\text{O}_3$  as a catalyst, such as disclosed

by Merkel et al. in US Patent Application Publication Number 2011/0004035.

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

5           In some embodiments of this invention, the composition consists essentially of (a) E-FO-1336mzz and (b) E-HCFO-1233zd; wherein the E-HCFO-1233zd is present in an effective amount to form an azeotrope-like mixture with E-FO-1336mzz.

10           In some embodiments of this invention, the composition consists essentially of (a) E-FO-1336mzz and (b) HCFO-1233xf; wherein the HCFO-1233xf is present in an effective amount to form an azeotropic or azeotrope-like mixture with E-FO-1336mzz.

15           By effective amount is meant an amount, which, when combined with E-FO-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, 20 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.

25           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. 30 (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  
5 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  
10 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  
15 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  
20 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  
25 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  
30 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. The vapor-liquid equilibrium (VLE), and hence relative volatility, can be determined either isothermally

or isobarically. The isothermal method requires measurement of the total pressure of mixtures of known composition at constant temperature. 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. The isobaric method requires measurement of the temperature of mixtures of known composition at constant pressure. In this procedure, the temperature in a cell of known volume is measured at a constant pressure 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.

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. 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 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 distillation columns.

It was found through experiments that E-FO-1336mzz and E-HCFO-1233zd form azeotrope-like compositions.

To determine the relative volatility of this binary pair, the PTx method described above was used. The 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-FO-1336mzz/E-HCFO-1233zd 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 E-HCFO-1233zd at 24.7 °C, as indicated by mixtures of about 1 to about 19 mole % E-1,1,1,4,4,4-hexafluoro-2-butene and about 99 to about 81 mole % E-HCFO-1233zd, and by mixtures of about 38 to about 99 mole % E-1,1,1,4,4,4-hexafluoro-2-butene and about 62 to about 1 mole % E-HCFO-1233zd.

According to calculation, azeotrope-like compositions consisting essentially of from about 1 to about 99 mole percent E-FO-1336mzz and from about 99 to about 1 mole percent E-HCFO-1233zd are formed at temperatures ranging from about -40 °C to about 140 °C (i.e., over this temperature range, the difference in dew point pressure and bubble point pressure of the composition at a particular temperature is less than or equal to 5 percent (based upon the bubble point pressure)).

Some embodiments of azeotrope-like compositions are listed in Table 1. Additional embodiments of azeotrope-like compositions are listed in Table 2.

Table 1. Azeotrope-like Compositions

COMPONENTS	T (°C)	Mole % Range
E-FO-1336mzz/E-HCFO-1233zd	-40	1-5/99-95 and 67-99/33-1
E-FO-1336mzz/E-HCFO-1233zd	-20	1-8/99-92 and 56-99/44-1
E-FO-1336mzz/E-HCFO-1233zd	0	1-12/99-88 and 47-99/53-1
E-FO-1336mzz/E-HCFO-1233zd	20	1-17/99-83 and 40-99/60-1
E-FO-1336mzz/E-HCFO-1233zd	40	1-99/99-1
E-FO-1336mzz/E-HCFO-1233zd	50	1-99/99-1
E-FO-1336mzz/E-HCFO-1233zd	60	1-99/99-1
E-FO-1336mzz/E-HCFO-1233zd	80	1-99/99-1
E-FO-1336mzz/E-HCFO-1233zd	100	1-99/99-1
E-FO-1336mzz/E-HCFO-1233zd	120	1-99/99-1
E-FO-1336mzz/E-HCFO-1233zd	140	1-99/99-1

Table 2. Azeotrope-like Compositions

COMPONENTS	T (°C)	Mole % Range
E-FO-1336mzz/E-HCFO-1233zd	-40	67-95/33-5
E-FO-1336mzz/E-HCFO-1233zd	-20	5-8/95-92 and 56-95/44-5
E-FO-1336mzz/E-HCFO-1233zd	0	5-12/95-88 and 47-95/53-5
E-FO-1336mzz/E-HCFO-1233zd	20	5-17/95-83 and 40-95/60-5
E-FO-1336mzz/E-HCFO-1233zd	40	5-95/95-5
E-FO-1336mzz/E-HCFO-1233zd	50	5-95/95-5
E-FO-1336mzz/E-HCFO-1233zd	60	5-95/95-5
E-FO-1336mzz/E-HCFO-1233zd	80	5-95/95-5
E-FO-1336mzz/E-HCFO-1233zd	100	5-95/95-5
E-FO-1336mzz/E-HCFO-1233zd	120	5-95/95-5
E-FO-1336mzz/E-HCFO-1233zd	140	5-95/95-5

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It was found through experiments that E-FO-1336mzz and HCFO-1233xf form azeotropic or azeotrope-like compositions. To determine the relative volatility of this binary pair, the PTx method described above was used. The pressure in a PTx cell of known volume was measured at  
 10 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-FO-1336mzz/HCFO-1233xf mixture is shown in FIG. 2, which  
 15 illustrates graphically the formation of an azeotropic composition consisting essentially of E-FO-1336mzz and HCFO-1233xf as indicated by a mixture of about 81.6 mole % E-FO-1336mzz and 18.4 mole % HCFO-1233xf having the highest pressure over the range of compositions at about 25.7 °C.

20 Based upon these findings, it has been calculated that E-FO-1336mzz and HCFO-1233xf form azeotropic compositions ranging from about 60.2 mole percent to about 98.8 mole percent E-FO-1336mzz and from about 39.8 mole percent to about 1.2 mole percent HCFO-1233xf (which form azeotropic compositions boiling at a temperature of from

about -40 °C to about 120 °C and at a pressure of from about 1.5 psia (10 kPa) to about 328 psia (2261 kPa)). For example, at about 25.7 °C and about 29.4 psia (203 kPa) the azeotropic composition consists essentially of about 81.6 mole % E-FO-1336mzz and about 18.4 mole % HCFO-1233xf. For another example, at about 7.0 °C and about atmospheric pressure (14.7 psia, 101 kPa) the azeotropic composition consists essentially of about 76.3 mole % E-FO-1336mzz and about 23.7 mole % HCFO-1233xf. Some embodiments of azeotropic compositions are listed in Table 3.

10

Table 3 Azeotropic compositions

Azeotropic Temperature (°C)	Azeotropic Pressure (psia)	E-FO-1336mzz (mole %)	HCFO-1233xf (mole %)
- 40.0	1.46	60.2	39.8
- 30.0	2.60	64.1	35.9
- 20.0	4.40	67.7	32.3
- 10.0	7.11	71.1	28.9
0.0	11.0	74.2	25.8
10.0	16.5	77.2	22.8
20.0	24.0	80.0	20.0
25.7	29.4	81.6	18.4
30.0	33.9	82.7	17.3
40.0	46.7	85.2	14.8
50.0	63.0	87.7	12.3
60.0	83.3	90.1	9.9
70.0	108	92.3	7.7
80.0	138	94.5	5.5
90.0	175	96.4	3.6
100.0	218	97.9	2.1
110.0	268	98.8	1.2
120.0	328	98.2	1.8

Additionally, azeotrope-like compositions containing E-FO-1336mzz and HCFO-1233xf may also be formed. According to calculation, azeotrope-like compositions consisting essentially of from about 1 to about 99 mole percent E-FO-1336mzz and from about 99 to about 1 mole percent HCFO-1233xf are formed at temperatures ranging from about -40 °C to about 120 °C (i.e., over this temperature range, the difference in dew point pressure and bubble point pressure of the composition at a particular

temperature is less than or equal to 5 percent (based upon the bubble point pressure)).

- Such azeotrope-like compositions exist around azeotropic compositions. Some embodiments of azeotrope-like compositions are listed in Table 4. Some more embodiments of azeotrope-like compositions are listed in Table 5.

Table 4. Azeotrope-like Compositions

COMPONENTS	T (°C)	Mole Percentage Range
E-FO-1336mzz/HCFO-1233xf	- 40	1 – 99/99 - 1
E-FO-1336mzz/HCFO-1233xf	- 20	1 – 99/99 - 1
E-FO-1336mzz/HCFO-1233xf	0	1 – 99/99 - 1
E-FO-1336mzz/HCFO-1233xf	40	1 – 99/99 - 1
E-FO-1336mzz/HCFO-1233xf	80	1 – 99/99 - 1
E-FO-1336mzz/HCFO-1233xf	120	1 – 99/99 - 1

Table 5. Azeotrope-like Compositions

COMPONENTS	T (°C)	Mole Percentage Range
E-FO-1336mzz/HCFO-1233xf	- 40	5 – 95/95 - 5
E-FO-1336mzz/HCFO-1233xf	- 20	5 – 95/95 - 5
E-FO-1336mzz/HCFO-1233xf	0	5 – 95/95 - 5
E-FO-1336mzz/HCFO-1233xf	40	5 – 95/95 - 5
E-FO-1336mzz/HCFO-1233xf	80	5 – 95/95 - 5
E-FO-1336mzz/HCFO-1233xf	120	5 – 95/95 - 5

10

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.

The azeotropic or azeotrope-like compositions of the present invention can be used in a wide range of applications, including their use  
5 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, particulate removal fluids, carrier fluids, buffing abrasive agents, and  
10 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 azeotropic or azeotrope-like composition consists essentially of E-  
15 1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of E-HCFO-1233zd and HCFO-1233xf.

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  
20 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 E-HCFO-1233zd and HCFO-1233xf.

Another embodiment of this invention provides a process using an  
25 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 E-HCFO-1233zd and HCFO-1233xf.

Another embodiment of this invention provides a process for  
30 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 E-1,1,1,4,4,4-hexafluoro-2-butene and a component selected from the group consisting of E-HCFO-1233zd and HCFO-1233xf.

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 E-HCFO-1233zd and HCFO-1233xf.

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 E-HCFO-1233zd and HCFO-1233xf.

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 E-HCFO-1233zd and HCFO-1233xf.

CLAIMS

1. A composition consisting essentially of:  
    (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and  
5      (b) a component selected from the group consisting of E-1-chloro-3,3,3-trifluoropropene and 2-chloro-3,3,3-trifluoropropene; wherein said component 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      2. A composition consisting essentially of:  
    (a) E-1,1,1,4,4,4-hexafluoro-2-butene; and  
    (b) 2-chloro-3,3,3-trifluoropropene; wherein the 2-chloro-3,3,3-trifluoropropene is present in an effective amount to form an azeotropic combination with the E-1,1,1,4,4,4-hexafluoro-2-butene.
- 15      3. The azeotrope-like composition of claim 1 consisting essentially of from about 1 to about 99 mole percent E-1,1,1,4,4,4-hexafluoro-2-butene and from about 99 to about 1 mole percent E-1-chloro-3,3,3-trifluoropropene, characterized by: at a temperature of from  
20      about -40 °C to about 140 °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.
- 25      4. The azeotrope-like composition of claim 1 consisting essentially of from about 5 to about 99 mole percent E-1,1,1,4,4,4-hexafluoro-2-butene and from about 99 to about 5 mole percent E-1-chloro-3,3,3-trifluoropropene, characterized by: at a temperature of from about -40 °C to about 140 °C, said composition having a  
30      difference in dew point pressure and bubble point pressure of less than or equal to 5 percent based upon the bubble point pressure.
- 35      5. The azeotrope-like composition of claim 1 consisting essentially of from about 1 to about 99 mole percent E-1,1,1,4,4,4-hexafluoro-2-butene and from about 99 to about 1 mole percent 2-chloro-3,3,3-trifluoropropene, characterized by: at a temperature of from about -40 °C to about 120 °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.

- 5           6. The azeotrope-like composition of claim 1 consisting essentially of  
from about 5 to about 99 mole percent E-1,1,1,4,4,4-hexafluoro-2-  
butene and from about 99 to about 5 mole percent 2-chloro-3,3,3-  
trifluoropropene, characterized by: at a temperature of from about  
-40 °C to about 120 °C, said composition having a difference in  
10           dew point pressure and bubble point pressure of less than or  
equal to 5 percent based upon the bubble point pressure.
- 15           7. The azeotropic composition of claim 2 consisting essentially of  
from about 60.2 mole percent to about 98.8 mole percent E-  
1,1,1,4,4,4-hexafluoro-2-butene and from about 39.8 mole percent  
to about 1.2 mole percent 2-chloro-3,3,3-trifluoropropene, which  
has boiling point temperature of from about -40 °C to about 120  
°C at a pressure of from about 1.5 psia to about 328 psia.
- 20           8. A process for preparing a thermoplastic or thermoset foam  
comprising using the azeotrope-like composition of Claim 1 as a  
blowing agent.
- 25           9. A process for preparing a thermoplastic or thermoset foam  
comprising using the azeotropic composition of Claim 2 as a  
blowing agent.
- 30           10. A process for producing refrigeration comprising condensing the  
azeotrope-like composition of Claim 1 and thereafter evaporating  
said azeotrope-like composition in the vicinity of the body to be  
cooled.
- 35           11. A process for producing refrigeration comprising condensing the  
azeotropic composition of Claim 2 and thereafter evaporating said  
azeotropic composition in the vicinity of the body to be cooled.



12. A process comprising using the azeotrope-like composition of Claim 1 as a solvent.
- 5 13. A process comprising using the azeotropic composition of Claim 2 as a solvent.
14. A process for producing an aerosol product comprising using the azeotrope-like composition of Claim 1 as a propellant.
- 10 15. A process for producing an aerosol product comprising using the azeotropic composition of Claim 2 as a propellant.
16. A process comprising using the azeotrope-like composition of Claim 1 as a heat transfer media.
- 15 17. A process comprising using the azeotropic composition of Claim 2 as a heat transfer media.
- 20 18. A process for extinguishing or suppressing a fire comprising using the azeotrope-like composition of Claim 1 as a fire extinguishing or suppression agent.
- 25 19. A process for extinguishing or suppressing a fire comprising using the azeotropic composition of Claim 2 as a fire extinguishing or suppression agent.
20. A process comprising using the azeotrope-like composition of Claim 1 as dielectrics.
- 30 21. A process comprising using the azeotropic composition of Claim 2 as dielectrics.

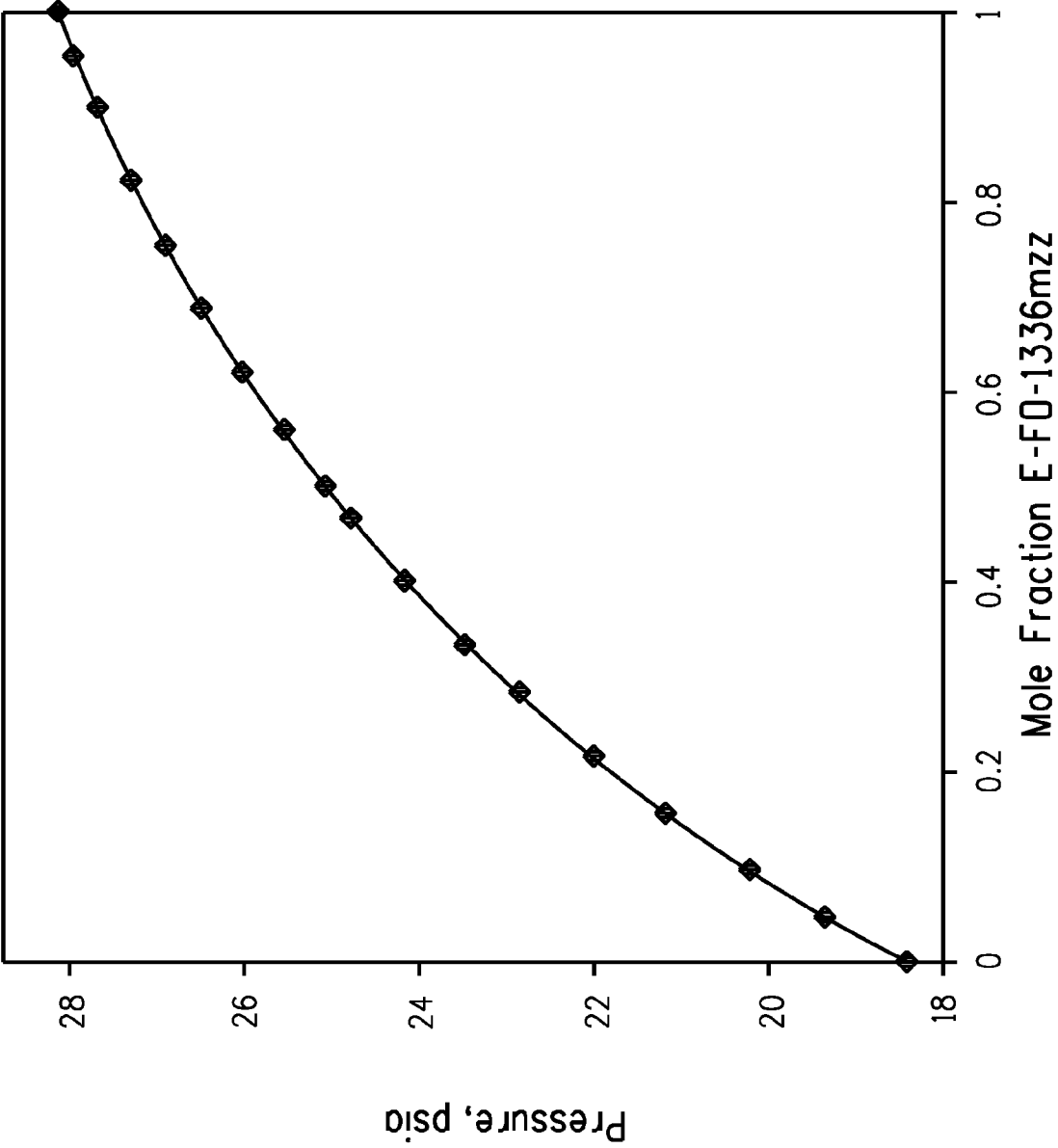


FIG. 1

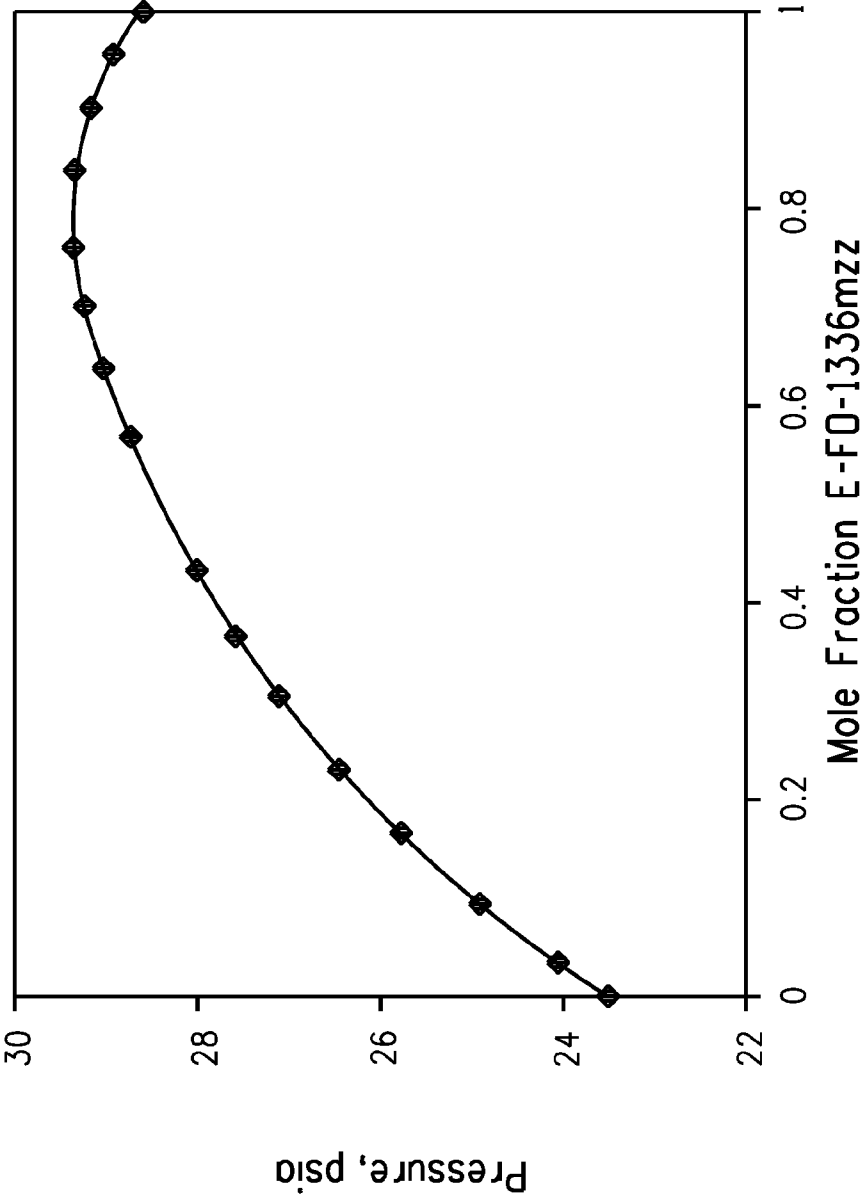


FIG. 2

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2011/033843

A. CLASSIFICATION OF SUBJECT MATTER  
INV. A62D1/00 C08J9/14 C09K3/30 C09K5/04 C11D7/50  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
A62D C08J C09K C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2009/114397 A2 (ARKEMA INC [US]; VAN HORN BRETT L [US]; ELSHEIKH MAHER Y [US]; CHEN BE) 17 September 2009 (2009-09-17) page 1, lines 5-10 page 5, line 1 - page 6, line 7 -----	1-16
A	WO 2009/155490 A1 (DU PONT [US]; ROBIN MARK L [US]) 23 December 2009 (2009-12-23) page 1, lines 10-12 page 15, lines 8-15 -----	1-21
X,P	WO 2010/062888 A2 (DU PONT [US]; KONTOMARIS KONSTANTINOS [US]) 3 June 2010 (2010-06-03) page 19, lines 6-31 -----	1-7,10, 11,16,17



Further documents are listed in the continuation of Box C.



See patent family annex.

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

"&" document member of the same patent family

Date of the actual completion of the international search

19 July 2011

Date of mailing of the international search report

26/07/2011

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/033843

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