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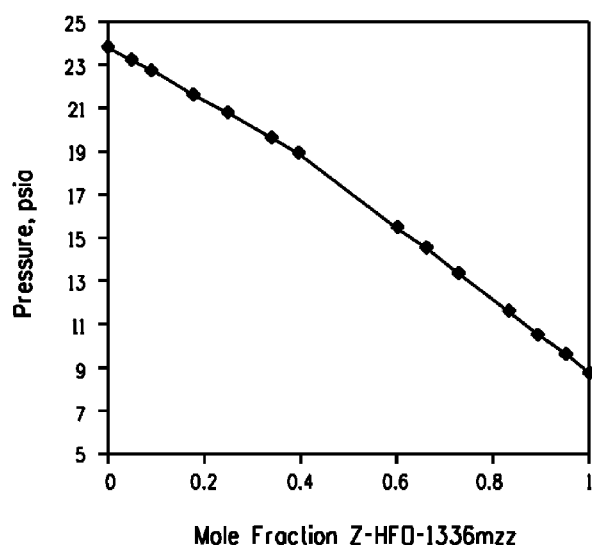
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(54) **Title:** AZEOTROPE-LIKE COMPOSITIONS OF Z-1,1,1,4,4,4-HEXAFLUORO-2-BUTENE AND E-1,1,1,4,4,4-HEXAFLUORO-2-BUTENE AND USES THEREOF

**FIG. 1**

(57) **Abstract:** Azeotrope-like compositions are disclosed. The azeotrope-like compositions are mixtures of Z-1,1,1,4,4,4-hexafluoro-2-butene and E-1,1,1,4,4,4-hexafluoro-2-butene. Also disclosed is a process of preparing a thermoplastic or thermoset foam by using such azeotrope-like compositions as blowing agents. Also disclosed is a process of producing refrigeration by using such azeotrope-like compositions. Also disclosed is a process of using such azeotrope-like compositions as solvents. Also disclosed is a process of producing an aerosol product by using such azeotrope-like compositions. Also disclosed is a process of using such azeotrope-like compositions as heat transfer media. Also disclosed is a process of extinguishing or suppressing a fire by using such azeotrope-like compositions. Also disclosed is a process of using such azeotrope-like compositions as dielectrics. Also disclosed is a foam-forming composition containing such azeotrope-like composition and an active hydrogen-containing compound having two or more active hydrogens.

**TITLE OF INVENTION**

AZEOTROPE-LIKE COMPOSITIONS OF  
Z-1,1,1,4,4,4-HEXAFLUORO-2-BUTENE AND E-1,1,1,4,4,4-  
5       HEXAFLUORO-2-BUTENE AND USES THEREOF

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

The present disclosure relates to azeotrope-like compositions of Z-  
10   1,1,1,4,4,4-hexafluoro-2-butene and 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  
replacements for the ozone depleting chlorofluorocarbons (CFCs) and  
hydrochlorofluorocarbons (HCFCs). The CFCs and HCFCs have been  
15   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  
dielectrics, fire extinguishing and suppression agents, power cycle working  
fluids, polymerization media, particulate removal fluids, carrier fluids,  
20   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).

The HFCs do not contribute to the destruction of stratospheric  
ozone, but are of concern due to their contribution to the "greenhouse  
25   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).  
30   Certain hydrofluoroolefins, such as 1,1,1,4,4,4-hexafluoro-2-butene  
( $\text{CF}_3\text{CH}=\text{CHCF}_3$ , FC-1336mzz, HFO-1336mzz), are believed to meet both  
goals.

Closed-cell polyisocyanate-based foams are widely used for insulation purposes, for example, in building construction and in the manufacture of energy efficient electrical appliances. In the construction industry, polyurethane/polyisocyanurate board stock is used in roofing and siding for its insulation and load-carrying capabilities. Poured and sprayed polyurethane foams are widely used for a variety of applications including insulating roofs, insulating large structures such as storage tanks, insulating appliances such as refrigerators and freezers, insulating refrigerated trucks and railcars, etc.

All of these various types of polyurethane/polyisocyanurate foams require blowing agents for their manufacture. Insulating foams depend on the use of halocarbon blowing agents, not only to foam the polymer, but primarily for their low vapor thermal conductivity, a very important characteristic for insulation value.

### **SUMMARY OF THE INVENTION**

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

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

FIG. 1 - FIG. 1 is a graphical representation of an azeotrope-like composition of Z-HFO-1336mzz and E-HFO-1336mzz at a temperature of about 20.0 °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 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, 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-CF<sub>3</sub>CH=CHCF<sub>3</sub>, Z-FC-1336mzz, Z-HFO-1336mzz) and E-1,1,1,4,4,4-hexafluoro-2-butene (E-CF<sub>3</sub>CH=CHCF<sub>3</sub>, E-FC-1336mzz, E-HFO-1336mzz).

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

HFO-1336mzz may exist as one of two configurational isomers, *E* or *Z*. HFO-1336mzz as used herein refers to the isomers, Z-HFO-1336mzz or E-HFO-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 ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control. 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. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

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 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.

Z-HFO-1336mzz is a known compound, and can be made by the selective hydrogenation of hexafluoro-2-butyne with a Lindlar catalyst and hydrogen, such as disclosed in U.S. Patent Publication No. 2008-0269532.

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

Azeotrope-like Compositions of Z-HFO-1336mzz and E-HFO-1336mzz

This application includes compositions consisting essentially of (a) Z-HFO-1336mzz and (b) E-HFO-1336mzz; wherein the E-HFO-1336mzz is present in an effective amount to form an azeotrope-like mixture with Z-HFO-1336mzz.

- 5 By effective amount is meant an amount of E-HFO-1336mzz, which, when combined with Z-HFO-1336mzz, results in the formation of an 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 azeotrope-like compositions continue to
- 10 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 azeotrope-like compositions at temperatures or pressures other than as described herein.
- 15 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
- 20 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).

- 25 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
- 30 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.,  
5 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  
10 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,  
15 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  
20 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. The vapor-liquid equilibrium  
25 (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  
30 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 Z-HFO-1336mzz/E-HFO-1336mzz 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-HFO-1336mzz and E-HFO-1336mzz 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 pressures measured versus the compositions in the PTx cell for Z-HFO-1336mzz/E-HFO-1336mzz mixtures are shown in FIG. 1, which graphically illustrates the formation of azeotrope-like compositions consisting essentially of 1-10 mole % Z-HFO-1336mzz and 99-90 mole % E-HFO-1336mzz at about 20.0 °C and pressures ranging from about 22 to about 24 psia, and also illustrates the formation of azeotrope-like compositions consisting essentially of 96-99 mole % Z-HFO-1336mzz and 4-1 mole % E-HFO-1336mzz at about 20.0 °C and pressures ranging from about 9 to about 10 psia.



According to calculation, azeotrope-like compositions consisting essentially of 1-28 mole % Z-HFO-1336mzz and 99-72 mole % E-HFO-1336mzz 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)). In addition, azeotrope-like compositions consisting essentially of 85-99 mole % Z-HFO-1336mzz and 15-1 mole % E-HFO-1336mzz 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)).

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

Table 1 Azeotrope-like compositions

COMPONENTS	T (°C)	Mole Percentage Range
Z-HFO-1336mzz/E-HFO-1336mzz	- 40	1-6/99-94 and 98-99/2-1
Z-HFO-1336mzz/E-HFO-1336mzz	- 20	1-7/99-93 and 97-99/3-1
Z-HFO-1336mzz/E-HFO-1336mzz	0	1-9/99-91 and 97-99/3-1
Z-HFO-1336mzz/E-HFO-1336mzz	20	1-10/99-90 and 96-99/4-1
Z-HFO-1336mzz/E-HFO-1336mzz	40	1-12/99-88 and 95-99/5-1
Z-HFO-1336mzz/E-HFO-1336mzz	60	1-15/99-85 and 94-99/6-1
Z-HFO-1336mzz/E-HFO-1336mzz	80	1-17/99-83 and 92-99/8-1
Z-HFO-1336mzz/E-HFO-1336mzz	100	1-22/99-78 and 90-99/10-1
Z-HFO-1336mzz/E-HFO-1336mzz	120	1-28/99-72 and 85-99/15-1

The 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 azeotrope-like composition can be prepared by weighing the desired component amounts and thereafter combining them in an appropriate container.

Applications of the Azeotrope-like Compositions of Z-HFO-1336mzz and E-HFO-1336mzz

The 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, 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.

One embodiment of this invention provides a process for preparing a thermoplastic or thermoset foam. The process comprises using an azeotrope-like composition as a blowing agent, wherein said azeotrope-like composition consists essentially of Z-HFO-1336mzz and E-HFO-1336mzz.

Another embodiment of this invention provides a process for producing refrigeration. The process comprises 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-HFO-1336mzz and E-HFO-1336mzz.

Another embodiment of this invention provides a process using an azeotrope-like composition as a solvent, wherein said azeotrope-like composition consists essentially of Z-HFO-1336mzz and E-HFO-1336mzz.

Another embodiment of this invention provides a process for producing an aerosol product. The process comprises using an azeotrope-like composition as a propellant, wherein said azeotrope-like composition consists essentially of Z-HFO-1336mzz and E-HFO-1336mzz.

Another embodiment of this invention provides a process using an azeotrope-like composition as a heat transfer media, wherein said azeotrope-like composition consists essentially of Z-HFO-1336mzz and E-HFO-1336mzz.

5 Another embodiment of this invention provides a process for extinguishing or suppressing a fire. The process comprises using an azeotrope-like composition as a fire extinguishing or suppression agent, wherein said azeotrope-like composition consists essentially of Z-HFO-1336mzz and E-HFO-1336mzz.

10 Another embodiment of this invention provides a process using an azeotrope-like composition as dielectrics, wherein said azeotrope-like composition consists essentially of Z-HFO-1336mzz and E-HFO-1336mzz.

Foam-forming Compositions Containing the Azeotrope-like Compositions of Z-HFO-1336mzz and E-HFO-1336mzz

This application also includes foam-forming compositions comprising: (a) azeotrope-like composition of Z-HFO-1336mzz and E-HFO-1336mzz as described in this disclosure; and (b) an active hydrogen-containing compound having two or more active hydrogens.

20 Azeotrope-like compositions of Z-HFO-1336mzz and E-HFO-1336mzz can be used as blowing agents for making polyurethane or polyisocyanurate polymer foams. Typically Z-HFO-1336mzz and E-HFO-1336mzz are combined prior to mixing with the other components in the foam-forming compositions. Alternatively, one can be mixed with some or  
25 all of the other components before the other is mixed in. For example, Z-HFO-1336mzz can be first mixed with the other components in the foam-forming compositions before E-HFO-1336mzz is added in.

The active hydrogen-containing compounds of this disclosure can comprise compounds having two or more groups that contain an active  
30 hydrogen atom reactive with an isocyanate group, such as described in U.S. Patent No. 4,394,491. Examples of such compounds have at least two hydroxyl groups per molecule, and more specifically comprise polyols, such as polyether or polyester polyols. Examples of such polyols are those which have an equivalent weight of about 50 to about 700, normally of

about 70 to about 300, more typically of about 90 to about 270, and carry at least 2 hydroxyl groups, usually 3 to 8 such groups.

Examples of suitable polyols comprise polyester polyols such as aromatic polyester polyols, e.g., those made by transesterifying  
5 polyethylene terephthalate (PET) scrap with a glycol such as diethylene glycol, or made by reacting phthalic anhydride with a glycol. The resulting polyester polyols may be reacted further with ethylene - and/or propylene oxide - to form an extended polyester polyol containing additional internal alkyleneoxy groups.

10 Examples of suitable polyols also comprise polyether polyols such as polyethylene oxides, polypropylene oxides, mixed polyethylene-propylene oxides with terminal hydroxyl groups, among others. Other suitable polyols can be prepared by reacting ethylene and/or propylene oxide with an initiator having 2 to 16, generally 3 to 8 hydroxyl groups as  
15 present, for example, in glycerol, pentaerythritol and carbohydrates such as sorbitol, glucose, sucrose and the like polyhydroxy compounds. Suitable polyether polyols can also include aliphatic or aromatic amine-based polyols.

This application also includes processes for producing a closed-cell  
20 polyurethane or polyisocyanurate polymer foam comprising: reacting an effective amount of the foam-forming composition of this disclosure with a suitable polyisocyanate.

Typically, before reacting with a suitable polyisocyanate, the active hydrogen-containing compound described hereinabove and optionally  
25 other additives are mixed with the blowing agent to form a foam-forming composition. Such foam-forming composition is typically known in the art as an isocyanate-reactive preblend, or B-side composition. The foam-forming composition of this invention can be prepared in any manner convenient to one skilled in this art, including simply weighing desired  
30 quantities of each component and, thereafter, combining them in an appropriate container at appropriate temperatures and pressures.

When preparing polyisocyanate-based foams, the polyisocyanate reactant is normally selected in such proportion relative to that of the active hydrogen-containing compound that the ratio of the equivalents of

isocyanate groups to the equivalents of active hydrogen groups, i.e., the foam index, is from about 0.9 to about 10 and in most cases from about 1 to about 4.

While any suitable polyisocyanate can be employed in the instant process, examples of suitable polyisocyanates useful for making polyisocyanate-based foam comprise at least one of aromatic, aliphatic and cycloaliphatic polyisocyanates, among others. Representative members of these compounds comprise diisocyanates such as meta- or paraphenylene diisocyanate, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, hexamethylene-1,6-diisocyanate, tetramethylene-1,4-diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotoluene diisocyanate (and isomers), naphthylene-1,5-diisocyanate, 1-methylphenyl-2,4-phenyldiisocyanate, diphenylmethane-4,4-diisocyanate, diphenylmethane-2,4-diisocyanate, 4,4'-biphenylenediisocyanate and 3,3-dimethoxy-4,4'-biphenylenediisocyanate and 3,3-dimethyldiphenylpropane-4,4-diisocyanate; triisocyanates such as toluene-2,4,6-triisocyanate and polyisocyanates such as 4,4'-dimethyldiphenylmethane-2,2,5,5-tetraisocyanate and the diverse polymethylenepoly-phenyloxy polyisocyanates, mixtures thereof, among others.

A crude polyisocyanate may also be used in the practice of this invention, such as the crude toluene diisocyanate obtained by the phosgenating a mixture comprising toluene diamines, or the crude diphenylmethane diisocyanate obtained by the phosgenating crude diphenylmethanediamine. Specific examples of such compounds comprise methylene-bridged polyphenylpolyisocyanates, due to their ability to crosslink the polyurethane.

It is often desirable to employ minor amounts of additives in preparing polyisocyanate-based foams. Among these additives comprise one or more members from the group consisting of catalysts, surfactants, flame retardants, preservatives, colorants, antioxidants, reinforcing agents, filler, antistatic agents, among others well known in this art.

Depending upon the composition, a surfactant can be employed to stabilize the foaming reaction mixture while curing. Such surfactants normally comprise a liquid or solid organosilicone compound. The surfactants are employed in amounts sufficient to stabilize the foaming reaction mixture against collapse and to prevent the formation of large, uneven cells. In one embodiment of this invention, about 0.1% to about 5% by weight of surfactant based on the total weight of all foaming ingredients (i.e. blowing agents + active hydrogen-containing compounds + polyisocyanates + additives) are used. In another embodiment of this invention, about 1.5% to about 3% by weight of surfactant based on the total weight of all foaming ingredients are used.

One or more catalysts for the reaction of the active hydrogen-containing compounds, e.g. polyols, with the polyisocyanate may be also employed. While any suitable urethane catalyst may be employed, specific catalyst comprise tertiary amine compounds and organometallic compounds. Exemplary such catalysts are disclosed, for example, in U.S. Patent No. 5,164,419, which disclosure is incorporated herein by reference. For example, a catalyst for the trimerization of polyisocyanates, such as an alkali metal alkoxide, alkali metal carboxylate, or quaternary amine compound, may also optionally be employed herein. Such catalysts are used in an amount which measurably increases the rate of reaction of the polyisocyanate. Typical amounts of catalysts are about 0.1% to about 5% by weight based on the total weight of all foaming ingredients.

In the process of making a polyisocyanate-based foam, the active hydrogen-containing compound (e.g. polyol), polyisocyanate and other components are contacted, thoroughly mixed, and permitted to expand and cure into a cellular polymer. The mixing apparatus is not critical, and various conventional types of mixing head and spray apparatus are used. By conventional apparatus is meant apparatus, equipment, and procedures conventionally employed in the preparation of isocyanate-based foams in which conventional isocyanate-based foam blowing agents, such as fluorotrichloromethane ( $\text{CCl}_3\text{F}$ , CFC-11), are employed. Such conventional apparatus are discussed by: H. Boden et al. in chapter

4 of the Polyurethane Handbook, edited by G. Oertel, Hanser Publishers, New York, 1985; a paper by H. Grunbauer et al. titled "Fine Celled CFC-Free Rigid Foam - New Machinery with Low Boiling Blowing Agents" published in Polyurethanes 92 from the Proceedings of the SPI 34th Annual Technical/Marketing Conference, October 21-October 24, 1992, New Orleans, Louisiana; and a paper by M. Taverna et al. titled "Soluble or Insoluble Alternative Blowing Agents? Processing Technologies for Both Alternatives, Presented by the Equipment Manufacturer", published in Polyurethanes World Congress 1991 from the Proceedings of the SPI/ISOPA September 24-26, 1991, Acropolis, Nice, France.

In one embodiment of this invention, a preblend of certain raw materials is prepared prior to reacting the polyisocyanate and active hydrogen-containing components. For example, it is often useful to blend the polyol(s), blowing agent, surfactant(s), catalysts(s) and other foaming ingredients, except for polyisocyanates, and then contact this blend with the polyisocyanate. Alternatively, all the foaming ingredients may be introduced individually to the mixing zone where the polyisocyanate and polyol(s) are contacted. It is also possible to pre-react all or a portion of the polyol(s) with the polyisocyanate to form a prepolymer.

The invention composition and processes are applicable to the production of all kinds of expanded polyurethane foams, including, for example, integral skin, RIM and flexible foams, and in particular rigid closed-cell polymer foams useful in spray insulation, as pour-in-place appliance foams, or as rigid insulating board stock and laminates.

This application also includes closed-cell polyurethane or polyisocyanurate polymer foams prepared from reaction of an effective amount of the foam-forming composition of this disclosure with a suitable polyisocyanate.

## EXAMPLES

The concepts described herein will be further described in the following examples, which do not limit the scope of the invention described in the claims.

VORANOL® 490 is a sucrose/glycerine initiated polyether polyol from Dow Chemical Co.

VORANOL® 391 is a toluene diamine (o-TDA) initiated aromatic polyether polyol from Dow Chemical Co.

5 STEPANPOL® PS2502A is a polyester polyol from Stepan Co.

NIAX Silicone L-6900 is a surfactant comprising 60-90% siloxane polyalkyleneoxide copolymer and 10-30% polyalkylene oxide available from Momentive Performance Materials.

10 POLYCAT® 8 is N,N-dimethylcyclohexylamine from Air Products Inc.

POLYCAT® 5 is pentamethyldiethylenetriamine from Air Products Inc.

CURITHANE® 52 is 2-methyl(n-methyl amino b-sodium acetate nonyl phenol) from Air Products Inc.

15 PAPI 27 is polymethylene polyphenyl isocyanate from Dow Chemical Co.

### EXAMPLE 1

20 In Example 1, a polyurethane foam was made using an azeotrope - like blowing agent composition of 3 weight % of E-1,1,1,4,4,4-hexafluoro-2-butene and 97 weight % of Z-1,1,1,4,4,4-hexafluoro-2-butene. The foam-forming composition is shown in Table 2. The k-factor and other properties of the resultant foam is shown in Table 3. The foam exhibited good dimensional stability and cell structure, and had a density of 1.7 pcf  
25 (pounds-per-cubic-feet).

By "cream time", it is meant to refer to the time period starting from the mixing of the active hydrogen-containing compound with polyisocyanate, and ending at when the foaming starts to occur and color of the mixture starts to change.

30 By "rise time", it is meant to refer to the time period starting from the mixing of the active hydrogen-containing compound with polyisocyanate, and ending at when the foam rising stops.

By "tack free time", it is meant to refer to the time period starting from the mixing of the active hydrogen-containing compound with



polyisocyanate, and ending at when the surface of the foam is no longer tacky.

- By “initial k-factor”, it is meant to refer to the polymer foam’s thermal conductivity measured at a mean temperature of 75 °F approximately one day after the foam is formed and becomes tack free.

Blowing agents Z-HFO-1336mzz and E-HFO-1336mzz were premixed to form an azeotrope -like mixture containing 3 weight % of E-HFO-1336mzz and 97 weight % of Z-HFO-1336mzz.

- Polyols, surfactant, catalysts, water and the above made blowing agent mixture (3 weight % of E-HFO-1336mzz and 97 weight % of Z-HFO-1336mzz) were pre-mixed by hand and then mixed with polyisocyanate. The amount of each component is illustrated in Table 2 as parts-by-weight (pbw) based on the total weight of the polyols. The resulting mixture was poured into a 8”x8”x2.5” paper box to form the polyurethane foam.

Table 2 Polyurethane formulation

Component	Quantity (pbw)
VORANOL® 490	40
VORANOL® 391	35
STEPANPOL® PS2502A	25
NIAX Silicone L-6900	6.0
POLYCAT® 8	3.0
POLYCAT® 5	0.38
CURITHANE® 52	0.50
Water	1.7
Blowing Agent Composition	42.1
Z-1,1,1,4,4,4-hexafluoro-2-butene	40.79
E-1,1,1,4,4,4-hexafluoro-2-butene	1.26
PAPI 27	148
Foam Index	1.2

Table 3. Polyurethane foam properties

Cream Time(second)	9
Rise Time(second)	65
Tack Free Time (second)	75
Foam density (pounds-per-cubic-feet)	1.7
Initial k-factor (Btu•in/ft <sup>2</sup> •h•°F)	0.136

CLAIMS

1. An azeotrope-like composition consisting essentially of:
  - (a) Z-1,1,1,4,4,4-hexafluoro-2-butene; and
  - 5 (b) E-1,1,1,4,4,4-hexafluoro-2-butene; wherein the E-1,1,1,4,4,4-hexafluoro-2-butene 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. A process for preparing a thermoplastic or thermoset foam comprising using the azeotrope-like composition of Claim 1 as a blowing  
10 agent.
3. 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.
4. A process comprising using the azeotrope-like composition of  
15 Claim 1 as a solvent.
5. A process for producing an aerosol product comprising using the azeotrope-like composition of Claim 1 as a propellant.
6. A process comprising using the azeotrope-like composition of Claim 1 as a heat transfer media.
- 20 7. A process for extinguishing or suppressing a fire comprising using the azeotrope-like composition of Claim 1 as a fire extinguishing or suppression agent.
8. A process comprising using the azeotrope-like composition of Claim 1 as dielectrics.
- 25 9. A foam-forming composition comprising:
  - (a) the azeotrope-like composition of Claim 1; and
  - (b) an active hydrogen-containing compound having two or more active hydrogens.
- 30 10. A process for producing a closed-cell polyurethane or polyisocyanurate polymer foam comprising: reacting an effective amount of the foam-forming composition of Claim 9 with a suitable polyisocyanate.

11. A closed-cell polyurethane or polyisocyanurate polymer foam prepared from reaction of an effective amount of the foam-forming composition of Claim 9 with a suitable polyisocyanate.

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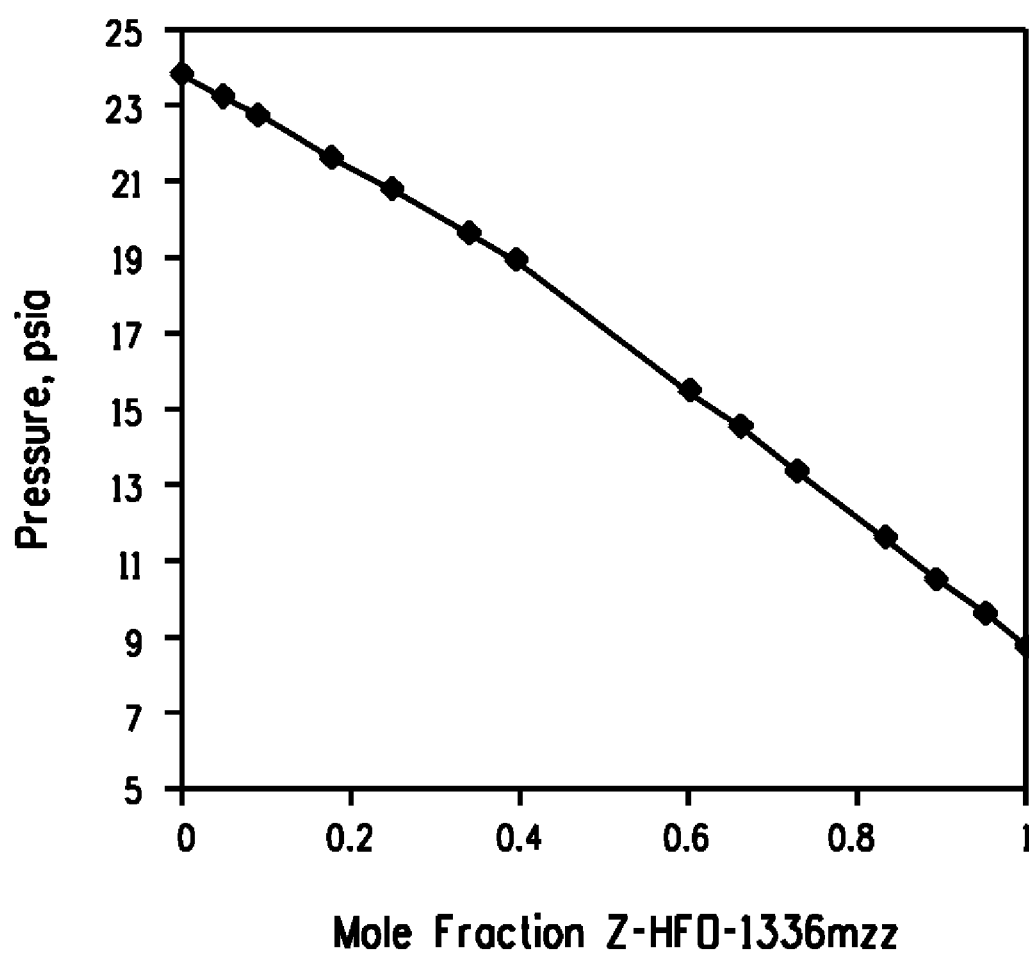


FIG. 1

## INTERNATIONAL SEARCH REPORT

International application No  
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. A62D1/00 C09K5/04 C09K3/30 C08J9/14 A62D1/02 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) A62D C09K C08J  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/014966 A1 (DU PONT [US]; LOH GARY [US]; CREAZZO JOSEPH ANTHONY [US]) 29 January 2009 (2009-01-29) claims page 1, lines 7-14 page 3, lines 18-26 example 2; table 3 -----	1,2,4, 9-11
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search  10 April 2013		Date of mailing of the international search report  19/04/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer  Schoenhentz, Jérôme

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PCT/US2013/026133

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 2009/012335 A1 (NAPPA MARIO JOSEPH [US] ET AL) 8 January 2009 (2009-01-08) examples 1-16; tables 1-14 -----	1-11
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International application No

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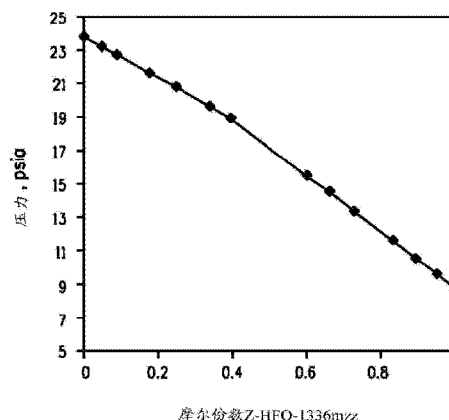
权利要求书1页 说明书9页 附图1页

### (54) 发明名称

Z-1,1,1,4,4,4-六氟-2-丁烯和E-1,1,1,4,4,4-六氟-2-丁烯的类共沸混合物及其用途

### (57) 摘要

本发明公开了类共沸混合物。所述类共沸混合物为 Z-1,1,1,4,4,4-六氟-2-丁烯和 E-1,1,1,4,4,4-六氟-2-丁烯的混合物。本发明还公开了通过使用此类类共沸混合物作为发泡剂来制备热塑性或热固性泡沫的方法。本发明还公开了通过使用此类类共沸混合物来制冷的方法。本发明还公开了使用此类类共沸混合物作为溶剂的方法。本发明还公开了通过使用此类类共沸混合物来制备气溶胶产品的方法。本发明还公开了使用此类类共沸混合物作为热传递介质的方法。本发明还公开了通过使用此类类共沸混合物来灭火或抑燃的方法。本发明还公开了使用此类类共沸混合物作为电介质的方法。本发明还公开了泡沫形成混合物,所述泡沫形成混合物包含此类类共沸混合物和具有两个或更多个活性氢的含活性氢的化合物。



1. 类共沸组合物,所述类共沸组合物基本上由以下组成:
  - (a) Z-1,1,1,4,4,4- 六氟 -2- 丁烯 ;和
  - (b) E-1,1,1,4,4,4- 六氟 -2- 丁烯 ;其中所述 E-1,1,1,4,4,4- 六氟 -2- 丁烯 以与所述 Z-1,1,1,4,4,4- 六氟 -2- 丁烯 形成类共沸组合的有效量存在。
2. 制备热塑性或热固性泡沫的方法,所述方法包括使用权利要求 1 所述的类共沸组合物作为发泡剂。
3. 制冷的方法,所述方法包括冷凝权利要求 1 所述的类共沸组合物,并且随后在待冷却的所述主体附近蒸发所述类共沸组合物。
4. 方法,所述方法包括使用权利要求 1 所述的类共沸组合物作为溶剂。
5. 制备气溶胶产品的方法,所述方法包括使用权利要求 1 所述的类共沸组合物作为推进剂。
6. 方法,所述方法包括使用权利要求 1 所述的类共沸组合物作为热传递介质。
7. 灭火或抑燃的方法,所述方法包括使用权利要求 1 所述的类共沸组合物作为灭火剂或抑燃剂。
8. 方法,所述方法包括使用权利要求 1 所述的类共沸组合物作为电介质。
9. 泡沫形成组合物,所述泡沫形成组合物包含:
  - (a) 权利要求 1 所述的类共沸组合物 ;和
  - (b) 具有两个或更多个活性氢的含活性氢的化合物。
10. 制备闭孔聚氨酯或聚异氰脲酸酯聚合物泡沫的方法,所述方法包括 :使有效量的权利要求 9 所述的泡沫形成组合物与适宜的多异氰酸酯反应。
11. 闭孔聚氨酯或聚异氰脲酸酯聚合物泡沫,所述闭孔聚氨酯或聚异氰脲酸酯聚合物泡沫由有效量的权利要求 9 所述的泡沫形成组合物与适宜的多异氰酸酯的反应制得。

## Z-1,1,1,4,4,4-六氟-2-丁烯和E-1,1,1,4,4,4-六氟-2-丁烯的类共沸组合物及其用途

### 技术领域

[0001] 本公开涉及 Z-1,1,1,4,4,4-六氟-2-丁烯和 E-1,1,1,4,4,4-六氟-2-丁烯的类共沸组合物。

### 背景技术

[0002] 在过去的几十年中,许多产业致力于寻找损耗臭氧的氯氟烃(CFC)和氢氯氟烃(HCFC)的替代物。CFC和HCFC已被用于范围广泛的应用中,包括它们用作气溶胶推进剂、制冷剂、清洁剂、热塑性和热固性泡沫的膨胀剂、热传递介质、气体电介质、灭火剂和阻燃剂、动力循环工作流体、聚合反应介质、颗粒移除流体、载液、抛光研磨剂、以及置换干燥剂。在寻求这些多功能化合物的替代物过程中,许多产业转向使用氢氟烃(HFC)。

[0003] HFC对同温层臭氧不具有破坏性,但是由于它们促进“温室效应”而受到关注,即它们促进全球变暖。由于它们会促进全球变暖,因此HFC已受到详细审查,并且它们的广泛应用将来也会受到限制。因此,需要对同温层臭氧不具有破坏性并且还具有低全球变暖潜势(GWP)的组合物。据信某些氢氟烯烃 1,1,1,4,4,4-六氟-2-丁烯( $\text{CF}_3\text{CH}=\text{CHCF}_3$ , FC-1336mzz, HFO-1336mzz)满足这两个要求。

[0004] 基于多异氰酸酯的闭孔泡沫被广泛用于绝缘用途,例如用于建筑构造以及用于制造节能电气设备。在建筑工业中,聚氨酯/聚异氰脲酸酯规格板材由于其隔热性能和承载能力而被用做屋顶材料和覆面材料。模浇和喷雾聚氨酯泡沫被广泛用于多种应用中,包括使屋顶隔热、使大型设备诸如储罐隔热、使设备诸如冷藏机和冷冻机隔热、使冷藏卡车和机械冷藏列车隔热等等。

[0005] 所有这些各种类型的聚氨酯/聚异氰脲酸酯泡沫的制造需要发泡剂来进行。绝热泡沫依赖于使用卤代烃发泡剂,不仅可使聚合物发泡,而且主要是由于它们具有低蒸气热导率(非常重要的隔热值特征)。

### 发明内容

[0006] 本公开提供了基本上由(a)Z-HFO-1336mzz和(b)E-HFO-1336mzz组成的组合物;其中所述E-HFO-1336mzz与Z-HFO-1336mzz形成类共沸混合物的有效量存在。

### 附图说明

[0007] 图1:图1为约20.0℃温度下Z-HFO-1336mzz和E-HFO-1336mzz的类共沸组合物的图示。

### 具体实施方式

[0008] 在许多应用中,期望使用单一的纯组分或共沸或类共沸混合物。例如,当发泡剂组合物(还被称为泡沫膨胀剂或泡沫膨胀组合物)不是单一的纯组分或共沸或类共沸混

合物时,所述组合物在其应用于成泡过程期间会发生变化。这种组成变化会不利地影响处理,或者在应用中导致性能变差。同样,在制冷应用中,制冷剂通常在操作期间经由轴密封件、软管连接、焊接接头和接折线中的裂缝而流失。此外,所述制冷剂可在制冷设备的维护过程期间,被释放到大气中。如果所述制冷剂不是单一的纯组分或共沸或类共沸组合物,则当从制冷设备渗漏或排放到大气中时,所述制冷剂组成会变化。制冷剂组成的变化会导致制冷剂变得易燃,或导致具有较差的制冷性能。因此,在这些和其它应用中需要使用共沸或类共沸混合物,例如包含 Z-1,1,1,4,4,4-六氟-2-丁烯 (Z-CF<sub>3</sub>CH = CHCF<sub>3</sub>, Z-FC-1336mzz, Z-HFO-1336mzz) 和 E-1,1,1,4,4,4-六氟-2-丁烯 (E-CF<sub>3</sub>CH = CHCF<sub>3</sub>, E-FC-1336mzz, E-HFO-1336mzz) 的共沸或类共沸混合物。

[0009] 在提出下述实施例详情之前,先定义或阐明一些术语。

[0010] HFO-1336mzz 可作为两种构型异构体 E 或 Z 中的一种存在。如本文所用, HFO-1336mzz 是指异构体 Z-HFO-1336mzz 或 E-HFO-1336mzz, 以及此类异构体的任何组合或混合物。

[0011] 如本文所用,术语“包含”、“包括”、“具有”或它们的任何其他变型均旨在涵盖非排他性的包括。例如,包括要素列表的工艺、方法、制品或设备不必仅限于那些要素,而是可以包括未明确列出的或该工艺、方法、制品或设备所固有的其它要素。此外,除非有相反的确说明,“或”是指包含性的“或”,而不是指排他性的“或”。例如,以下中任一者均满足条件 A 或 B : A 是真的 (或存在的) 且 B 是假的 (或不存在的)、A 是假的 (或不存在的) 且 B 是真的 (或存在的)、以及 A 和 B 都是真的 (或存在的)。

[0012] 同样,使用“一个”或“一种”来描述本文所描述的要素和组分。这样做仅是为了方便并且对本发明的范围给出一般含义。该描述应被理解为包括一个或至少一个,并且除非明显地另有所指,单数还包括复数。

[0013] 除非另有定义,本文所用的所有技术和科学术语的含义均与本发明所属领域的普通技术人员通常理解的一样。如发生矛盾,以本说明书及其包括的定义为准。尽管与本文所述的那些方法和材料的类似者或等同者均可用于本发明实施例的实践或检验,但合适的方法和材料是如下文所述的那些。此外,材料、方法和例子仅是例证性的,并且不旨在进行限制。

[0014] 当数量、浓度或其它数值或参数以范围、优选范围或优选上限数值和 / 或优选下限数值的列表形式给出时,它应理解为具体地公开由任何范围上限或优选数值和任何范围下限或优选数值的任何一对所构成的所有范围,而不管所述范围是否被单独地公开。凡在本文中给出某一数值范围之处,该范围都意在包括其端点,以及位于该范围内的所有整数和分数,除非另行指出。

[0015] Z-HFO-1336mzz 是已知化合物,并且可通过用林德乐催化剂和氢气选择性氢化六氟-2-丁炔来制得,如美国专利公布 2008-0269532 中所公开的。

[0016] E-HFO-1336mzz 也是已知的化合物,并能通过 1,2-氯-1,1,4,4,4-五氟丁烷与干燥的 KF 在蒸馏过的环丁砜中反应制得,如公开于美国专利 5,463,150 中。

[0017] Z-HFO-1336mzz 和 E-HFO-1336mzz 的类共沸组合物

[0018] 本申请包括基本上由 (a) Z-HFO-1336mzz 和 (b) E-HFO-1336mzz 组成的组合物;其中所述 E-HFO-1336mzz 以与 Z-HFO-1336mzz 形成类共沸混合物的有效量存在。

[0019] 有效量是指当与 Z-HF0-1336mzz 组合时导致形成类共沸混合物的 E-HF0-1336mzz 的量。该定义包括每种组分的量,所述量可根据施加在所述组合物上的压力而变化,前提条件是所述类共沸组合物在不同的压力下持续存在,但却具有可能不同的沸点。因此,有效量包括在不同于本文所述的温度或压力下形成类共沸组合物之本发明的组合物中每种组分的量,诸如以重量百分比或摩尔百分比表示的量。

[0020] 如本领域所认识到的,共沸组合物是两种或更多种不同组分的混合物,当在给定压力下为液体形式时,所述混合物将在基本上恒定的温度下沸腾,所述温度可以高于或低于单独组分的沸腾温度,并且将提供基本上与经历沸腾的整个液体组成相同的蒸气组成。(参见例如 M.F.Doherty 和 M.F.Malone 的“Conceptual Design of Distillation Systems”, McGraw-Hill (New York), 2001, 185-186, 351-359)。

[0021] 因此,共沸组合物基本特征是:在给定压力下,液体组合物的沸点是固定的,并且沸腾组合物上方的蒸气组成基本上就是整个沸腾液体组合物的组成(即,未发生液体组合物组分的分馏)。本领域还认识到,当共沸组合物在不同压力下经历沸腾时,共沸组合物中每种组分的沸点和重量百分比均可变化。因此,特征在于在特定压力下具有固定的沸点的共沸组合物可从以下几方面进行定义:存在于组分之间的独特关系、或所述组分的组成范围、或所述组合物中每种组分的精确重量百分比。

[0022] 对于本发明的目的而言,类共沸组合物是指行为类似共沸组合物之组合物(即沸腾或蒸发时具有恒沸特性或无分馏趋势)。因此,在沸腾或蒸发期间,如果蒸气和液体组成发生一些变化,则也仅发生最小程度或可忽略程度的变化。这与非类共沸组合物形成对比,在所述非类共沸组合物中,蒸气和液体组成在沸腾或蒸发期间发生显著程度的变化。

[0023] 此外,类共沸组合物表现出几乎无压差的露点压和泡点压。也就是说,给定温度下,露点压和泡点压的差值是很小的值。在本发明中,露点压和泡点压的差值小于或等于 5% (基于泡点压) 的组合物被认为是类共沸的。

[0024] 本领域认识到,当体系的相对挥发度接近 1.0 时,所述体系被定义为形成共沸或类共沸组合物。相对挥发度是组分 1 的挥发度与组分 2 的挥发度的比率。蒸气态的组分与液态的组分的摩尔份数的比率为所述组分的挥发度。

[0025] 可使用被称为 PTx 方法的方法来测定任何两种化合物的相对挥发度。可等温或等压测定汽-液平衡 (VLE),从而测定相对挥发度。等温方法需要测定已知组成的混合物在恒定温度下的总压力。在该方法中,测定两种化合物的不同组合物在恒定的温度下在已知体积的单元中的总绝对压力。等压方法需要测定已知组成的混合物在恒定压力下的温度。在此方法中,测定在恒定压力下含有两种化合物的不同组合物在已知体积的单元中的温度。PTx 方法的使用更详细地描述于由 Harold R. Null 撰写的“Phase Equilibrium in Process Design” (Wiley-Interscience Publisher, 1970 年) 第 124 至 126 页中。

[0026] 通过使用活度系数方程模型诸如非随机两液体 (Non-Random, Two-Liquid) (NRTL) 方程来表示液相非理想因素,可将这些量度转换成 PTx 单元中平衡蒸气和液体组成。活度系数方程诸如 NRTL 方程的应用更详细地描述于由 Reid、Prausnitz 和 Poling 撰写、由 McGraw Hill 公布的“The Properties of Gases and Liquids”第 4 版第 241 至 387 页,以及由 Stanley M. Walas 撰写、由 Butterworth Publishers 公布的“Phase Equilibria in Chemical Engineering”(1985 年) 第 165 至 244 页中。不受任何理论或解释的束缚,据信

NRTL 方程与 PTx 单元数据一起可足以预测本发明 Z-HFO-1336mzz/E-HFO-1336mzz 组合物的相对挥发度,因而可预测这些混合物在多级分离设备诸如蒸馏塔中的行为。

[0027] 通过实验发现, Z-HFO-1336mzz 和 E-HFO-1336mzz 形成类共沸混合物。

[0028] 使用上述的 PTx 方法来测定该二元对的相对挥发度。测定各种二元组合物在恒定的温度下在已知体积的 PTx 单元中的压力。然后使用 NRTL 方程将这些量度还原成所述单元中的平衡蒸气和液体组成。

[0029] Z-HFO-1336mzz/E-HFO-1336mzz 混合物在 PTx 单元中的所测压力与组成的关系曲线示于图 1 中,其以图形方式示出了在约 20.0°C 和约 22 至约 24psia 范围内的压力下形成基本上由 1-10 摩尔% Z-HFO-1336mzz 和 99-90 摩尔% E-HFO-1336mzz 组成的类共沸混合物,并且还示出在约 20.0°C 和约 9 至约 10psia 范围内的压力下形成基本上由 96-99 摩尔% Z-HFO-1336mzz 和 4-1 摩尔% E-HFO-1336mzz 组成的类共沸混合物。

[0030] 根据计算,基本上由 1-28 摩尔% Z-HFO-1336mzz 和 99-72 摩尔% E-HFO-1336mzz 组成的类共沸混合物在约 -40°C 至约 120°C 范围内的温度下形成(即超出该温度范围,所述组合物在特定温度下的露点压力与泡点压力之差小于或等于 5% (基于泡点压力))。此外,基本上由 85-99 摩尔% Z-HFO-1336mzz 和 15-1 摩尔% E-HFO-1336mzz 组成的类共沸混合物在约 -40°C 至约 120°C 范围内的温度下形成(即超出该温度范围,所述组合物在特定温度下的露点压力与泡点压力之差小于或等于 5% (基于泡点压力))。

[0031] 类共沸混合物的一些实施列列于表 1 中。

[0032] 表 1:类共沸混合物

[0033]

组分	T(°C)	摩尔百分比范围
Z-HFO-1336mzz/E-HFO-1336mzz	-40	1-6/99-94 和 98-99/2-1
Z-HFO-1336mzz/E-HFO-1336mzz	-20	1-7/99-93 和 97-99/3-1
Z-HFO-1336mzz/E-HFO-1336mzz	0	1-9/99-91 和 97-99/3-1
Z-HFO-1336mzz/E-HFO-1336mzz	20	1-10/99-90 和 96-99/4-1
Z-HFO-1336mzz/E-HFO-1336mzz	40	1-12/99-88 和 95-99/5-1
Z-HFO-1336mzz/E-HFO-1336mzz	60	1-15/99-85 和 94-99/6-1
Z-HFO-1336mzz/E-HFO-1336mzz	80	1-17/99-83 和 92-99/8-1
Z-HFO-1336mzz/E-HFO-1336mzz	100	1-22/99-78 和 90-99/10-1
Z-HFO-1336mzz/E-HFO-1336mzz	120	1-28/99-72 和 85-99/15-1

[0034] 本发明的类共沸混合物可由任何便利的方法来制成,包括混合或组合所需的量。在本发明的一个实施例中,通过称量所需的组分量,然后将它们合并适当的容器中来制备类共沸混合物。

[0035] Z-HFO-1336mzz 和 E-HFO-1336mzz 类共沸组合物的应用

[0036] 本发明的类共沸组合物可用于范围广泛的应用中,包括将它们用作气溶胶推进剂、制冷剂、溶剂、清洁剂、热塑性和热固性泡沫的发泡剂(泡沫膨胀剂)、热传递介质、气体电介质、灭火剂和抑燃剂、动力循环工作流体、聚合反应介质、颗粒移除流体、载液、抛光研磨剂、以及置换干燥剂。

[0037] 本发明的一个实施例提供了用于制备热塑性或热固性泡沫的方法。所述方法包括使用类共沸组合物作为发泡剂,其中所述类共沸组合物基本上由 Z-HFO-1336mzz 和 E-HFO-1336mzz 组成。

[0038] 本发明的另一个实施例提供了用于制冷的方法。所述方法包括冷凝类共沸组合物,然后在待冷却主体的附近蒸发所述类共沸组合物,其中所述类共沸组合物基本上由 Z-HFO-1336mzz 和 E-HFO-1336mzz 组成。

[0039] 本发明的另一个实施例提供了使用类共沸组合物作为溶剂的方法,其中所述类共沸组合物基本上由 Z-HFO-1336mzz 和 E-HFO-1336mzz 组成。

[0040] 本发明的另一个实施例提供了制备气溶胶产品的方法。所述方法包括使用类共沸组合物作为推进剂,其中所述类共沸组合物基本上由 Z-HFO-1336mzz 和 E-HFO-1336mzz 组成。

[0041] 本发明的另一个实施例提供了使用类共沸组合物作为热传递介质的方法,其中所述类共沸组合物基本上由 Z-HFO-1336mzz 和 E-HFO-1336mzz 组成。

[0042] 本发明的另一个实施例提供了用于灭火或阻燃的方法。所述方法包括使用类共沸组合物作为灭火剂或抑燃剂,其中所述类共沸组合物基本上由 Z-HFO-1336mzz 和 E-HFO-1336mzz 组成。

[0043] 本发明的另一个实施例提供了使用类共沸组合物作为电介质的方法,其中所述类共沸组合物基本上由 Z-HFO-1336mzz 和 E-HFO-1336mzz 组成。

[0044] 包含 Z-HFO-1336mzz 和 E-HFO-1336mzz 类共沸组合物的泡沫形成组合物

[0045] 本申请还包括泡沫形成组合物,所述组合物包含:(a)如本公开中所述的 Z-HFO-1336mzz 和 E-HFO-1336mzz 的类共沸组合物;和(b)具有两个或更多个活性氢的含活性氢的化合物。

[0046] Z-HFO-1336mzz 和 E-HFO-1336mzz 的类共沸组合物可用作用于制备聚氨酯或聚异氰脲酸酯聚合物泡沫的发泡剂。通常,使 Z-HFO-1336mzz 和 E-HFO-1336mzz 在与泡沫形成组合物中其它组分混合之前混合。作为另外一种选择,可使一种与部分或所有其它组分混合,然后混入另一种。例如,可使 Z-HFO-1336mzz 首先与泡沫形成组合物中的其它组分混合,然后加入 E-HFO-1336mzz。

[0047] 本公开的含活性氢化合物可包括具有两个或更多个包含与异氰酸酯基团反应的活性氢原子的基团的化合物,如美国专利公开 4,394,491 中描述的。此类化合物例子具有至少两个羟基每分子,并且更具体地讲包括多元醇,诸如聚醚或聚酯多元醇。此类多元醇例子是当量为约 50 至约 700,一般为约 70 至约 300,更典型为约 90 至约 270 并且带有至少 2 个羟基,一般 3 至 8 个此类基团的那些。

[0048] 适宜多元醇的例子包括聚酯多元醇,诸如芳族聚酯多元醇,例如由废聚对苯二甲酸乙二酯(PET)与二醇诸如二甘醇酯交换制得的那些,或由邻苯二甲酸酐与二醇反应制得

的那些。所得聚酯多元醇还可与乙烯-和/或环氧丙烷-反应形成包含额外的内部亚烷基氧基的扩展聚酯多元醇。

[0049] 适宜多元醇的例子还包括聚醚多元醇,诸如聚环氧乙烷、聚环氧丙烷、具有末端羟基的混合聚环氧乙烷-环氧丙烷等等。其它适宜多元醇可由环氧乙烷和/或环氧丙烷与引发剂的反应制得,所述引发剂具有2至16个,一般3至8个例如甘油、季戊四醇和碳水化合物诸如山梨醇、葡萄糖、蔗糖等多羟基化合物中存在的羟基。适宜的聚醚多元醇还包括基于脂肪族胺或芳族胺的多元醇。

[0050] 本申请还包括制备闭孔聚氨酯或聚异氰酸酯聚合物泡沫的方法,所述方法包括:使有效量的本公开泡沫形成组合物与适宜的多异氰酸酯反应。

[0051] 通常,在与适宜多异氰酸酯反应之前,使上文所述含活性氢的化合物以及任选的其它添加剂与发泡剂混合,以形成泡沫形成组合物。此类泡沫形成组合物通常在本领域被称为异氰酸酯反应预混物或B端组合物。本发明的泡沫形成组合物可以对本领域技术人员而言便捷的任何方式制得,包括简单称量所需量的每种组分,之后在适当的容器中,在适宜的温度和压力下将它们混合。

[0052] 当制备基于多异氰酸酯的泡沫时,多异氰酸酯反应物与含活性氢化合物的比例通常被选择成使得异氰酸酯基团当量与活性氢基团当量的比率(即泡沫指数)为约0.9至约10,并且在大多数情况下为约1至约4。

[0053] 虽然可在本发明方法中使用任何适宜的多异氰酸酯,但是可用于制备基于多异氰酸酯的泡沫的适宜多异氰酸酯例子包括至少一种芳族多异氰酸酯、脂族多异氰酸酯和脂环族多异氰酸酯等等。这些化合物的代表性成员包括二异氰酸酯,诸如间苯二异氰酸酯或对苯二异氰酸酯、甲苯-2,4-二异氰酸酯、甲苯-2,6-二异氰酸酯、环己烷-1,6-二异氰酸酯、环丁烷-1,4-二异氰酸酯、环己烷-1,4-二异氰酸酯、甲基环己烷二异氰酸酯(和异构体)、萘-1,5-二异氰酸酯、1-甲基苯基-2,4-苯基二异氰酸酯、二苯基甲烷-4,4'-二异氰酸酯、二苯基甲烷-2,4'-二异氰酸酯、4,4'-联苯二异氰酸酯和3,3'-二甲氧基-4,4'-联苯二异氰酸酯以及3,3'-二甲基二苯基丙烷-4,4'-二异氰酸酯;三异氰酸酯,诸如甲苯-2,4,6-三异氰酸酯,和多异氰酸酯诸如4,4'-二甲基二苯基甲烷-2,2,5,5'-四异氰酸酯,以及各种不同的多亚甲基多苯基多异氰酸酯,它们的混合物等等。

[0054] 在本发明的实践中,还可使用粗制多异氰酸酯,诸如通过将包含甲苯二胺的混合物光气化获得的粗制甲苯二异氰酸酯,或通过将粗制二苯基甲烷二胺光气化获得的粗制二苯基甲烷二异氰酸酯。此类化合物的具体例子包括亚甲基桥联的多苯基多异氰酸酯,这应归于它们交联聚氨酯的能力。

[0055] 在制备基于多异氰酸酯的泡沫中,通常期望使用微量添加剂。其中这些添加剂包括本领域熟知的下列一种或多种成员:催化剂、表面活性剂、阻燃剂、防腐剂、着色剂、抗氧化剂、增强剂、填料、抗静电剂等等。

[0056] 根据所述组合物,可使用表面活性剂以在固化时稳定发泡反应混合物。此类表面活性剂一般包含液体或固体有机硅氧烷化合物。所述表面活性剂的用量应足以稳定发泡反应混合物,防止塌缩,并且防止形成不均匀的大孔隙。在本发明的一个实施例中,使用按所有发泡成分(即发泡剂+含活性氢化合物+多异氰酸酯+添加剂)总重量计约0.1%至约5%的表面活性剂。在本发明的另一个实施例中,使用按所有发泡成分总重量计约1.5%至



约 3% 的表面活性剂。

[0057] 还可使用一种或多种用于含活性氢化合物例如多元醇与多异氰酸酯反应的催化剂。虽然可使用任何适宜的聚氨酯催化剂,但是具体的催化剂包括叔胺化合物和有机金属化合物。示例性的此类催化剂公开于例如美国专利公开 5,164,419 中,其公开内容以引用方式并入本文。例如,本文还可任选使用用于多异氰酸酯三聚反应的催化剂,诸如碱金属醇盐、碱金属羧酸盐、或季铵化合物。以可测定程度增加多异氰酸酯反应速率的量使用此类催化剂。催化剂的典型量按所有发泡成分总重量计为约 0.1% 至约 5%。

[0058] 在用于制备多异氰酸酯基泡沫的方法中,使含活性氢化合物(例如多元醇)、多异氰酸酯以及其它组分接触,充分混合,并且使其膨胀并且固化成泡沫状聚合物。混合设备不是关键性的,并且可使用各种常规类型的搅拌头和喷雾设备。常规设备是指常规用于制备基于异氰酸酯的泡沫的设备、器具和方法,其中使用常规的基于异氰酸酯的泡沫发泡剂,诸如三氯氟甲烷( $\text{CCl}_3\text{F}$ , CFC-11)。此类常规设备论述于:H. Boden 等人的 Polyurethane Handbook (G. Oertel 编辑, Hanser Publishers, New York, 1985) 第 4 章;H. Grunbauer 等人的题目为“Fine Celled CFC-Free Rigid Foam-New Machinery with Low Boiling Blowing Agents”的论文(公布于 1992 年 10 月 21 日-10 月 24 日“Proceedings of the SPI 34th Annual Technical/Marketing Conference”(New Orleans, Louisiana) 的“Polyurethanes 92”中);以及 1991 年 9 月 24 日至 26 日 Proceedings of the SPI/ISOPA (Acropolis, Nice, France) 在“Polyurethanes World Congress 1991”中公布的 M. Taverna 等人题目为“Soluble or Insoluble Alternative Blowing Agents? Processing Technologies for Both Alternatives, Presented by the Equipment Manufacturer”的论文中。

[0059] 在本发明的一个实施例中,在使多异氰酸酯与含活性氢组分反应之前制备某些原料的预混物。例如,通常有用的是,除多异氰酸酯以外,将多元醇、发泡剂、表面活性剂、催化剂以及其它发泡成分共混,然后使此共混物与多异氰酸酯接触。作为另外一种选择,将所有发泡成分单独引入到混合区域中,在所述混合区域使多异氰酸酯与多元醇接触。还可使所有或部分多元醇与多异氰酸酯预反应以形成预聚物。

[0060] 本发明的组合物和方法适于制备所有类型的膨胀聚氨酯泡沫,包括例如自成皮、RIM 且挠性的泡沫,具体地讲在喷雾式绝热中用作现场模浇设备泡沫,或用作刚性绝热规格板材和层压体的刚性闭孔聚合物泡沫。

[0061] 本申请还包括由有效量的本公开泡沫形成组合物与适宜的多异氰酸酯反应制得的闭孔聚氨酯或聚异氰脲酸酯聚合物泡沫。

#### [0062] 实例

[0063] 本文所描述的概念将在下列实例中进一步描述,所述实例不限制权利要求中描述的本发明的范围。

[0064] **VORANOL<sup>®</sup> 490** 为得自 Dow Chemical Co 的以蔗糖 / 甘油为起始的聚醚多元醇。

[0065] **VORANOL<sup>®</sup> 391** 为得自 Dow Chemical Co 的以甲苯二胺(o-TDA)为起始的芳族聚醚多元醇。

[0066] **STEPANPOL<sup>®</sup> PS2502A** 为得自 Stepan Co 的聚酯多元醇。

[0067] NIAx Silicone L-6900 为购自 Momentive Performance Materials 的表面活性剂,所述表面活性剂包含 60-90% 的硅氧烷聚亚烷基氧化物共聚物和 10-30% 的聚环氧烷。

[0068] POLYCAT<sup>®</sup> 8 为得自 Air Products Inc 的 N,N- 二甲基环己胺。

[0069] POLYCAT<sup>®</sup> 5 为得自 Air Products Inc 的五甲基二亚乙基三胺。

[0070] CURITHANE<sup>®</sup> 52 为得自 Air Products Inc 的 2- 甲基 (n- 甲基氨基 b- 乙酸钠壬基苯酚)。

[0071] PAPI 27 为得自 Dow Chemical Co 的多亚甲基多苯基异氰酸酯。

[0072] 实例 1

[0073] 在实例 1 中,使用 3 重量% E-1,1,1,4,4,4- 六氟 -2- 丁烯和 97 重量% Z-1,1,1,4,4,4- 六氟 -2- 丁烯的类共沸发泡剂组合物,制备聚氨酯泡沫。泡沫形成组合物示于表 2 中。所得泡沫的 k- 因子和其它性能示于表 3 中。所述泡沫表现出良好的尺寸稳定性和泡孔结构,并且具有 1.7pcf (磅 / 立方英尺) 的密度。

[0074] 所谓“乳稠时间”是指从含活性氢化合物与多异氰酸酯混合开始直到泡沫开始出现并且混合物颜色开始变化时结束的时间段。

[0075] “发泡时间”是指从含活性氢化合物与多异氰酸酯混合开始直到停止发泡时结束的时间段。

[0076] 所谓“不粘时间”是指从含活性氢化合物与多异氰酸酯混合开始直到泡沫表面不再发粘时结束的时间段。

[0077] “初始 k- 因子”旨在涉及聚合物泡沫的热导率,所述热导率在泡沫形成约 1 天并且变得无粘性后,在 75° F 平均温度下测得。

[0078] 发泡剂 Z-HFO-1336mzz 和 E-HFO-1336mzz 预混形成类共沸混合物,所述混合物包含 3 重量%的 E-HFO-1336mzz 和 97 重量%的 Z-HFO-1336mzz。

[0079] 用手将多元醇、表面活性剂、催化剂和上文制得的发泡剂混合物 (3 重量% E-HFO-1336mzz 和 97 重量% Z-HFO-1336mzz) 预混,然后与多异氰酸酯混合。每种组分的量以按所述多元醇总重量计的重量份 (pbw) 形式示于表 2 中。将所得混合物倒入到 8" × 8" × 2.5" 纸箱中以形成聚氨酯泡沫。

[0080] 表 2: 聚氨酯制剂

[0081]

组分	数量 (pbw)
VORANOL <sup>®</sup> 490	40
VORANOL <sup>®</sup> 391	35
STEPANPOL <sup>®</sup> PS2502A	25
NIAX Silicone L-6900	6.0
POLYCAT <sup>®</sup> 8	3.0
POLYCAT <sup>®</sup> 5	0.38
CURITHANE <sup>®</sup> 52	0.50
水	1.7
发泡剂组合物	42.1
Z-1,1,1,4,4,4-六氟-2-丁烯	40.79
E-1,1,1,4,4,4-六氟-2-丁烯	1.26
PAPI 27	148
泡沫指数	1.2

[0082] 表 3 : 聚氨酯泡沫特性

[0083]

乳稠时间 (秒)	9
发泡时间 (秒)	65
不粘时间 (秒)	75
泡沫密度 (磅每立方英尺)	1.7
初始 k- 因子 (Btu · in/ft <sup>2</sup> · h · ° F)	0.136

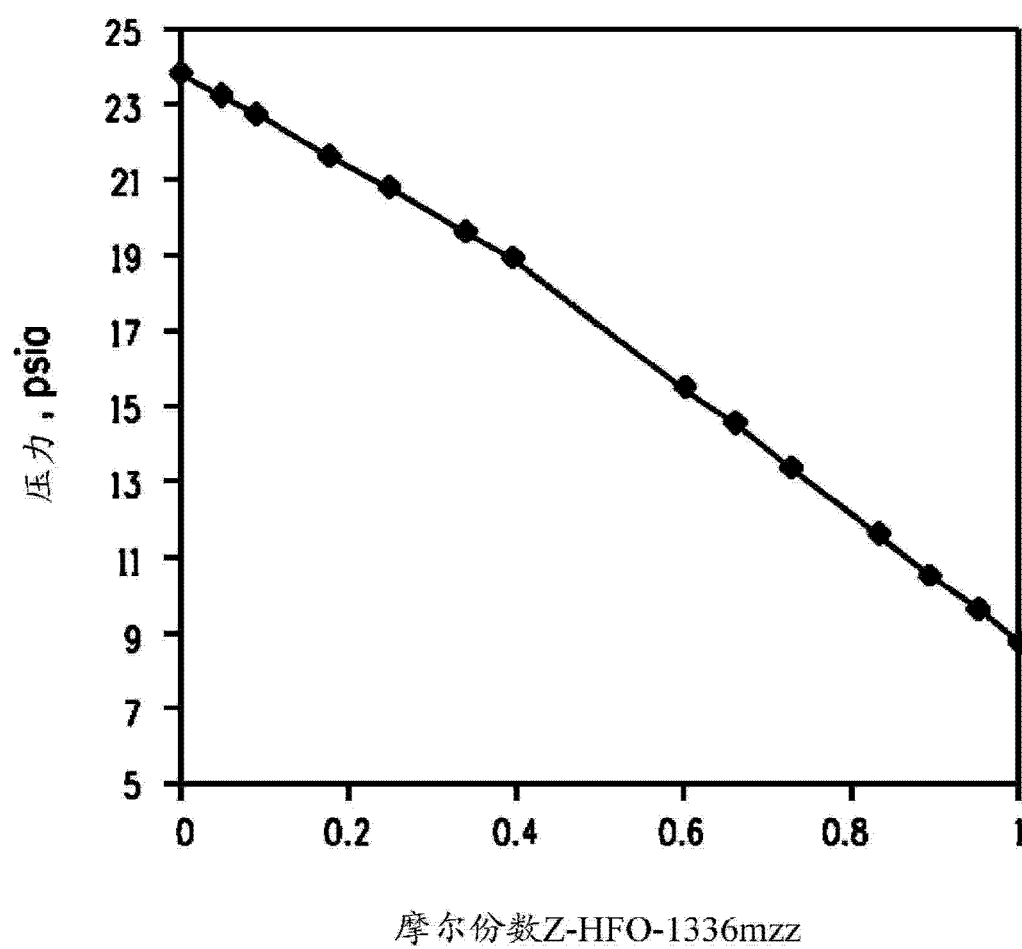


图 1