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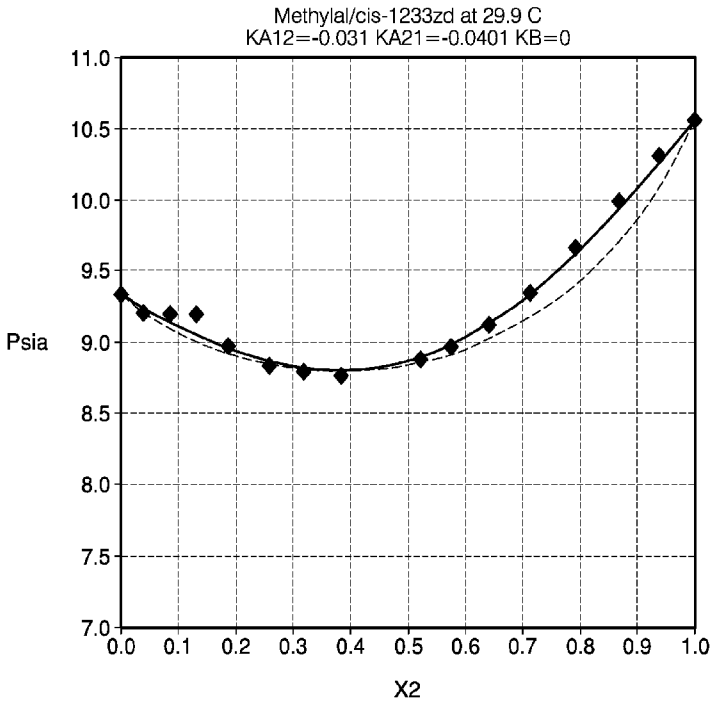
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[Continued on next page]

(54) Title: AZEOTROPIC AND AZEOTROPE-LIKE COMPOSITIONS OF Z-1233zd

FIG. 2



(57) Abstract: This application provides azeotropic and near-azeotropic compositions of Z-1233zd and a second component selected from the group consisting of methyl formate, dimethoxymethane, HFC-43-10-mee and HFC-245fa. The inventive compositions are useful as aerosol propellants, refrigerants, cleaning agents, expansion agents for thermoplastic and thermoset foams, solvents, 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. The compositions were modeled based on Vapor-Liquid Equilibria data such as those illustrated in the figures.

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TITLE OF INVENTION

AZEOTROPIC AND AZEOTROPE-LIKE COMPOSITIONS OF Z-1233zd

BACKGROUND OF THE INVENTION

Field of the Disclosure

The present invention relates to the discovery of azeotropic or azeotrope-like compositions which include Z -1-chloro-3,3,3-trifluoropropene. These compositions are useful as aerosol propellants, refrigerants, cleaning agents, expansion agents ("blowing agents") for the production of thermoplastic and thermoset foams, heat transfer media, gaseous dielectrics, solvents, fire extinguishing and suppression agents, power cycle working fluids, polymerization media, particulate removal fluids, carrier fluids, buffing abrasive agents, and displacement drying agents.

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 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 for replacements for these versatile compounds, many industries have turned to the use of hydrofluorocarbons (HFCs), hydrofluoroolefins (HFOs), and hydrochlorofluoroolefins (HCFOs).

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, they have come under scrutiny, and their widespread use may also be limited in the future. Unlike HFCs, many HFOs and HCFOs do not contribute to the greenhouse effect, as they react and decompose in the atmosphere relatively quickly. However, HFOs such as HFO-1234ze and HCFOs such as E-HCFO-1233zd have been found to be too unstable for many applications.

SUMMARY OF THE INVENTION

Mixtures of certain hydrocarbons or fluorocarbons that include Z-1-chloro-3,3,3-trifluoropropene (Z-$CF_3CH=CHCl$, Z-1233zd) are believed to function as potential candidates for replacement of CFCs and HCFCs, but to display low global warming potentials ("GWPs"), and not contribute to the destruction of stratospheric ozone.

In Embodiment 1.0, there is provided a composition comprising Z-1233zd and a second component selected from the group consisting of:

a) Methyl formate;

b) Dimethoxymethane;

c) HFC-43-10-mee; and,

d) HFC-245fa,

wherein the second component is present in an effective amount to form an azeotrope or azeotrope-like mixture with the Z-1233zd.

In Embodiment 2.0, there is provided the composition according to Embodiment 1.0, wherein the second component is methyl formate.

In Embodiment 3.0, there is provided the composition according to Embodiment 1.0, wherein the second component is dimethoxymethane.

In Embodiment 4.0, there is provided the composition according to Embodiment 1.0, wherein the second component is HFC-43-10-mee.

In Embodiment 5.0, there is provided the composition according to Embodiment 1.0, wherein the second component is HFC-245fa.

In Embodiment 6.0, there is provided the composition according to Embodiment 1.0, further comprising an additive selected from the group consisting of lubricants, pour point modifiers, anti-foam agents, viscosity improvers, emulsifiers dispersants, oxidation inhibitors, extreme pressure agents, corrosion inhibitors, detergents, catalysts, surfactants, flame retardants, preservatives, colorants, antioxidants, reinforcing agents, fillers, antistatic agents, solubilizing agents, IR attenuating agents, nucleating agents, cell controlling agents, extrusion aids, stabilizing agents, thermally insulating agents, plasticizers, viscosity modifiers, impact modifiers, gas barrier resins, polymer modifiers, rheology modifiers, antibacterial agents, vapor pressure modifiers, UV absorbers, cross-linking agents, permeability modifiers, bitterants, propellants and acid catchers.

In Embodiment 6.1, there is provided the composition according to Embodiment 2.0, further comprising an additive selected from the group consisting of lubricants, pour point modifiers, anti-foam agents, viscosity improvers, emulsifiers dispersants, oxidation inhibitors, extreme pressure agents, corrosion inhibitors, detergents, catalysts, surfactants, flame retardants, preservatives, colorants, antioxidants, reinforcing agents, fillers, antistatic agents, solubilizing agents, IR attenuating agents, nucleating agents, cell controlling agents, extrusion aids, stabilizing agents, thermally insulating agents, plasticizers, viscosity modifiers, impact modifiers, gas barrier resins, polymer modifiers, rheology modifiers, antibacterial agents, vapor pressure modifiers, UV absorbers, cross-linking agents, permeability modifiers, bitterants, propellants and acid catchers.

In Embodiment 6.2, there is provided the composition according to Embodiment 3.0, further comprising an additive selected from the group consisting of lubricants, pour point modifiers, anti-foam agents, viscosity improvers, emulsifiers dispersants, oxidation inhibitors, extreme pressure agents, corrosion inhibitors, detergents, catalysts, surfactants, flame retardants, preservatives, colorants, antioxidants, reinforcing agents, fillers, antistatic agents, solubilizing agents, IR attenuating agents, nucleating agents, cell controlling agents, extrusion aids, stabilizing agents, thermally insulating agents, plasticizers, viscosity modifiers, impact modifiers, gas barrier resins, polymer modifiers, rheology modifiers, antibacterial agents, vapor pressure modifiers, UV absorbers, cross-linking agents, permeability modifiers, bitterants, propellants and acid catchers.

In Embodiment 6.3, there is provided the composition according to Embodiment 4.0, further comprising an additive selected from the group consisting of lubricants, pour point modifiers, anti-foam agents, viscosity improvers, emulsifiers dispersants, oxidation inhibitors, extreme pressure agents, corrosion inhibitors, detergents, catalysts, surfactants, flame retardants, preservatives, colorants, antioxidants, reinforcing agents, fillers, antistatic agents, solubilizing agents, IR attenuating agents, nucleating agents, cell controlling agents, extrusion aids, stabilizing agents, thermally insulating agents, plasticizers, viscosity modifiers, impact modifiers, gas barrier resins, polymer modifiers, rheology modifiers, antibacterial agents, vapor pressure modifiers, UV absorbers, cross-linking agents, permeability modifiers, bitterants, propellants and acid catchers.

In Embodiment 6.4, there is provided the composition according to Embodiment 5.0, further comprising an additive selected from the group consisting of lubricants, pour point modifiers, anti-foam agents, viscosity improvers, emulsifiers dispersants, oxidation inhibitors, extreme pressure agents, corrosion inhibitors, detergents, catalysts, surfactants, flame retardants, preservatives, colorants, antioxidants, reinforcing agents, fillers, antistatic agents, solubilizing agents, IR attenuating agents, nucleating agents, cell controlling agents, extrusion aids, stabilizing agents, thermally insulating agents, plasticizers, viscosity modifiers, impact modifiers, gas barrier resins, polymer modifiers, rheology modifiers, antibacterial agents, vapor pressure modifiers, UV absorbers, cross-linking agents, permeability modifiers, bitterants, propellants and acid catchers.

In Embodiment 7.0, there is provided a process of forming a foam comprising:

(a) adding a foamable composition to a blowing agent; and,

(b) reacting said foamable composition under conditions effective to form a foam,

wherein said blowing agent comprises the composition according to Embodiment 1.0.

In Embodiment 7.1, there is provided a process of forming a foam comprising:

(a) adding a foamable composition to a blowing agent; and,

(b) reacting said foamable composition under conditions effective to form a foam,

wherein said blowing agent comprises the composition according to Embodiment 2.0.

In Embodiment 7.2, there is provided a process of forming a foam comprising:

(a) adding a foamable composition to a blowing agent; and,

(b) reacting said foamable composition under conditions effective to form a foam,

wherein said blowing agent comprises the composition according to Embodiment 3.0.

In Embodiment 7.3, there is provided a process of forming a foam comprising:

(a) adding a foamable composition to a blowing agent; and,

(b) reacting said foamable composition under conditions effective to form a foam,

wherein said blowing agent comprises the composition according to Embodiment 4.0.

In Embodiment 7.4, there is provided a process of forming a foam comprising:

(a) adding a foamable composition to a blowing agent; and,

(b) reacting said foamable composition under conditions effective to form a foam,

wherein said blowing agent comprises the composition according to Embodiment 5.0.

In Embodiment 8.0, there is provided a foam formed by the process according to any of Embodiments 7.1 to 7.4.

In Embodiment 9.0, there is provided a foam comprising a polymer and the composition according to any of Embodiments 2.0-5.0.

In Embodiment 10.0, there is provided a pre-mix composition comprising a foamable component and a composition according to any of Embodiments 2.0-5.0 as a blowing agent.

In Embodiment 11.0, there is provided a process for producing refrigeration comprising condensing the composition according to any of Embodiments 2.0-5.0, and thereafter evaporating said composition in the vicinity of the body to be cooled.

In Embodiment 12.0, there is provided a heat transfer system comprising the composition according to any of Embodiments 2.0-5.0 as a heat transfer medium.

In Embodiment 13.0, there is provided a method of cleaning a surface comprising bringing the composition according to any of Embodiments 2.0-5.0 into contact with said surface.

In Embodiment 14.0, there is provided an aerosol product comprising a component to be dispensed and the composition according to any of Embodiment 2.0-5.0 as a propellant.

In Embodiment 15.0, there is provided a method for extinguishing or suppressing a flame comprising dispensing the composition according to any of Embodiments 2.0-5.0 at said flame.

In Embodiment 16.0, there is provided a system for preventing or suppressing a flame comprising a vessel containing the composition according to any of Embodiments 2.0-5.0 and a nozzle to dispense said composition toward an anticipated or actual location of said flame.

In Embodiment 17.0, there is provided a process for dissolving a solute comprising contacting and mixing said solute with a sufficient quantity of the composition according to any of Embodiments 2.0-5.0.

In Embodiment 18.0, there is provided a method for preventing or rapidly quenching an electric discharge in a space in a high voltage device comprising injecting the composition according to any of Embodiments 2.0-5.0 into said space as a gaseous dielectric.

In Embodiment 19.0, there is provided a high voltage device comprising the composition according to any of Embodiments 2.0-5.0 as a gaseous dielectric.

In Embodiment 20.0, there is provided the high voltage device according to Embodiment 19.0 selected from the group consisting of a transformer, a circuit breaker, a switch and a radar waveguide.

In Embodiment 21.0, there is provided an azeotropic or near-azeotropic composition according to any of the line entries of any of Tables 1.2, 1.3, 2.2, 2.3, 2.4, 3.2, 3.3, 4.2 and 4.3.

In Embodiment 22.0, there is provided the composition according to any of Embodiments 21.0, 21.1, 21.2, 21.3, 21.4 and 22.0, further comprising an additive selected from the group consisting of lubricants, pour point modifiers, anti-foam agents, viscosity improvers, emulsifiers dispersants, oxidation inhibitors, extreme pressure agents, corrosion inhibitors, detergents, catalysts, surfactants, flame retardants, preservatives, colorants, antioxidants, reinforcing agents, fillers, antistatic agents, solubilizing agents, IR attenuating agents, nucleating agents, cell controlling agents, extrusion aids, stabilizing agents, thermally insulating

agents, plasticizers, viscosity modifiers, impact modifiers, gas barrier resins, polymer modifiers, rheology modifiers, antibacterial agents, vapor pressure modifiers, UV absorbers, cross-linking agents, permeability modifiers, bitterants, propellants and acid catchers.

BRIEF SUMMARY OF THE DRAWINGS

FIG. 1 displays the vapor/liquid equilibrium curve for a mixture of Z-1233zd (cis-1233zd) and methyl formate at a temperature of 30 °C.

FIG. 2 displays the vapor/liquid equilibrium curve for a mixture of Z-1233zd (cis-1233zd) and dimethoxymethane (methylal) at 29.9 °C.

FIG. 3 displays the vapor/liquid equilibrium curve for a mixture of Z-1233zd (cis-1233zd) and HFC-43-10-mee (FC4310mee) at a temperature of 30 °C.

FIG. 4 displays the vapor/liquid equilibrium curve for a mixture of Z-1233zd (cis-1233zd) and HFC-245fa (FC245fa) at a temperature of 30 °C.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to azeotropic and near-azeotropic compositions of Z-1233zd with each of methyl formate, dimethoxymethane, HFC-43-10-mee and HFC-245fa.

Alternate designations for Z-1233zd include Z-1-chloro-3,3,3-trifluoropropene (Z-$CF_3CH=CHCl$), cis-1-chloro-3,3,3-trifluoropropene, cis-1233zd, Z-HFO-1233zd and cis-HFO-1233zd. Alternate designations for methyl formate ($C_2H_4O_2$) include MF and methyl methanoate. Alternate designations for dimethoxymethane ($CH_3OCH_2OCH_3$) include DMM, methylal and dimethylformal. Alternate designations for HFC-43-10-mee include 1,1,1,2,2,3,4,5,5,5-decafluoropentane and FC4310mee. Alternate designations for HFC-245fa include 1,1,1,3,3-pentafluoropropane and FC245fa.

The azeotrope or azeotrope-like compositions of the present invention can be prepared by any convenient method including mixing or combining the desired amounts. A preferred method is to weigh the desired component amounts and thereafter combine them in an appropriate container.

The inventive compositions 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.

As used herein, the terms "inventive compositions" and "compositions of the present invention" shall be understood to mean the azeotropic and near-azeotropic compositions of Z-1233zd and, a second component selected from the group consisting of methyl formate, dimethoxymethane, HFC-43-10-mee and HFC-245fa.

Uses as a Heat Transfer Medium

The disclosed compositions can act as a working fluid used to carry heat from a heat source to a heat sink. Such heat transfer compositions may also be useful as a refrigerant in a cycle wherein the fluid undergoes a phase change; that is, from a liquid to a gas and back, or vice versa.

Examples of heat transfer systems include but are not limited to air conditioners, freezers, refrigerators, heat pumps, water chillers, flooded evaporator chillers, direct expansion chillers, walk-in coolers, heat pumps, mobile refrigerators, mobile air conditioning units and combinations thereof.

In one embodiment, the compositions comprising Z-1233zd are useful in mobile heat transfer systems, including refrigeration, air conditioning, or heat pump systems or apparatus. In another embodiment, the compositions are useful in stationary heat transfer systems, including refrigeration, air conditioning, or heat pump systems or apparatus.

As used herein, the term "mobile heat transfer system" shall be understood to mean any refrigeration, air conditioner, or heating apparatus incorporated into a transportation unit for the road, rail, sea or air. In addition, mobile refrigeration or air conditioner units, include those apparatus that are independent of any moving carrier and are known as "intermodal" systems. Such intermodal systems include "containers' (combined sea/land transport) as well as "swap bodies" (combined road/rail transport).

As used herein, the term "stationary heat transfer system" shall be understood to mean a system that is fixed in place during operation. A stationary heat transfer system may be located within or attached to a building, or may be a stand-alone device located out of doors, such as a soft drink vending machine. Such a stationary application may be a stationary air conditioning device or heat pump, including but not limited to a chiller, a high temperature heat pumps, which may be a trans-critical heat pump (one that operates with a condenser temperature above 50ºC, 70ºC, 80ºC, 100ºC, 120ºC, 140ºC, 160ºC, 180ºC, or 200ºC), a residential, commercial or industrial air conditioning system, and may be window-mounted, ductless, ducted, packaged terminal, a chiller, and one that is exterior but connected to a building, such as a rooftop system. In stationary refrigeration applications, the disclosed compositions may be useful in high temperature, medium temperature and/or low temperature refrigeration equipment including commercial, industrial or residential refrigerators and freezers, ice machines, self-contained coolers and freezers, flooded evaporator chillers, direct expansion chillers, walk-in and reach-in coolers and freezers, and combination systems. In some embodiments, the disclosed compositions may be used in supermarket refrigerator systems.

Therefore in accordance with the present invention, the compositions as disclosed herein containing Z-1233zd may be useful in methods for producing cooling, producing heating, and transferring heat.

In one embodiment, a method is provided for producing cooling comprising evaporating any of the present compositions comprising Z-1233zd in the vicinity of a body to be cooled, and thereafter condensing said composition.

In another embodiment, a method is provided for producing heating comprising condensing any of the present compositions comprising Z-1233zd in the vicinity of a body to be heated, and thereafter evaporating said compositions.

In another embodiment, disclosed is a method of using the present compositions comprising Z-1233zd as a heat transfer fluid composition. The method comprises transporting said composition from a heat source to a heat sink.

Any one of the compositions disclosed herein may be useful as a replacement for a currently used ("incumbent") refrigerant, including but not limited to R-123 (or HFC-123, 2,2-dichloro-1,1,1-trifluoroethane), R-11 (or CFC-11, trichlorofluoromethane), R-12 (or CFC-12, dichlorodifluoromethane), R-22 (chlorodifluoromethane), R-245fa (or HFC-245fa, 1,1,1,3,3-pentafluoropropane), R-114 (or CFC-114, 1,2-dichloro-1,1,2,2-tetrafluoroethane), R-236fa (or HFC-236fa, 1,1,1,3,3,3-hexafluoropropane), R-236ea (or HFC-236ea, 1,1,1,2,3,3-hexafluoropropane), R-124 (or HCFC-124, 2-chloro-1,1,1,2-tetrafluoroethane), among others.

As used herein, the term "incumbent refrigerant" shall be understood to mean the refrigerant for which the heat transfer system was designed to operate, or the refrigerant that is resident in the heat transfer system.

In another embodiment is provided a method for operating a heat transfer system or for transferring heat that is designed to operate with an incumbent refrigerant by charging an empty system with a composition of the present invention, or by substantially replacing said incumbent refrigerant with a composition of the present invention.

As used herein, the term "substantially replacing" shall be understood to mean allowing the incumbent refrigerant to drain from the system, or pumping the incumbent refrigerant from the system, and then charging the system with a composition of the present invention. The system may be flushed with one or more quantities of the replacement refrigerant before being charged. It shall be understood that some small quantity of the incumbent refrigerant may be present in the system after the system has been charged with the composition of the present invention.

In another embodiment is provided a method for recharging a heat transfer system that contains an incumbent refrigerant and a lubricant, said method comprising substantially removing the incumbent refrigerant from the heat transfer system while retaining a substantial portion of the lubricant in said system and introducing one of the present compositions comprising Z-1233zd to the heat transfer system. In some embodiments, the lubricant in the system is partially replaced.

In another embodiment, the compositions of the present invention comprising Z-1233zd may be used to top-off a refrigerant charge in a chiller. For instance, if a chiller using HCFC-123 has diminished

performance due to leakage of refrigerant, the compositions as disclosed herein may be added to bring performance back up to specification.

In another embodiment, a heat exchange system containing any of the present compositions comprising Z-1233zd is provided, wherein said system is selected from the group consisting of air conditioners, freezers, refrigerators, heat pumps, water chillers, flooded evaporator chillers, direct expansion chillers, walk-in coolers, heat pumps, mobile refrigerators, mobile air conditioning units, and systems having combinations thereof. Additionally, the compositions comprising Z-1233zd may be useful in secondary loop systems wherein these compositions serve as the primary refrigerant thus providing cooling to a secondary heat transfer fluid that thereby cools a remote location.

Each of a vapor-compression refrigeration system, an air conditioning system, and a heat pump system includes as components an evaporator, a compressor, a condenser, and an expansion device. A vapor-compression cycle re-uses refrigerant in multiple steps producing a cooling effect in one step and a heating effect in a different step. The cycle can be described simply as follows. Liquid refrigerant enters an evaporator through an expansion device, and the liquid refrigerant boils in the evaporator, by withdrawing heat from the environment, at a low temperature to form a vapor and produce cooling. The low-pressure vapor enters a compressor where the vapor is compressed to raise its pressure and temperature. The higher-pressure (compressed) vapor refrigerant then enters the condenser in which the refrigerant condenses and discharges its heat to the environment. The refrigerant returns to the expansion device through which the liquid expands from the higher-pressure level in the condenser to the low-pressure level in the evaporator, thus repeating the cycle.

In one embodiment, there is provided a heat transfer system containing any of the present compositions comprising Z-1233zd. In another embodiment is disclosed a refrigeration, air-conditioning or heat pump apparatus containing any of the present compositions comprising Z-1233zd. In another embodiment, is disclosed a stationary refrigeration or air-conditioning apparatus containing any of the present compositions comprising Z-1233zd. In yet another embodiment is disclosed a mobile refrigeration or air conditioning apparatus containing a composition as disclosed herein.

Lubricants and Additives

In one embodiment, there is provided one of the present compositions comprising Z-1233zd and at least one additive. The most common additive is a lubricant. Lubricants and other additives are discussed in *Fuels and Lubricants Handbook: Technology, Properties, Performance and Testing*, Ch. 15, "Refrigeration Lubricants – Properties and Applications," Michels, H. Harvey and Seinel, Tobias H., MNL37WCD-EB, ASTM International, June 2003, which is incorporated by reference. Lubricants include polyolesters ("POEs"), naphthenic mineral oils ("NMOs") and polyalkylene glycols ("PAGs"), and synthetic lubricants. Other additives are selected from the group that are chemically active in the sense that they can react with metals in the system or with contaminants in the lubricant, including dispersants, oxidation inhibitors, extreme pressure agents, corrosion inhibitors, detergents, acid catchers. The selection of oxidation inhibitor can be dependent on the selection of lubricant. Alkyl phenols (e.g., dibutylhydroxytoluene) may be useful for polyolester lubricants. Nitrogen containing inhibitors (e.g., arylamines and phenols) may be useful for mineral oil lubricants. Acid catchers can be especially important in synthetic lubricant systems, and include alkanolamines, long chain amides and imines, carbonates and epoxides. Still other additives are selected from the group that change physical property characteristics selected from the group consisting of pour point modifiers, anti-foam agents, viscosity improvers, and emulsifiers. Anti-foam agents include the polydimethyl siloxanes, polyalkoxyamines and polyacrylates.

Methods of Forming a Foam

The present invention further relates to a method of forming a foam comprising: (a) adding to a foamable composition a composition of the present invention; and (b) reacting the foamable composition under conditions effective to form a foam.

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.

A second type of insulating foam is thermoplastic foam, primarily polystyrene foam. Polyolefin foams (e.g., polystyrene, polyethylene, and polypropylene) are widely used in insulation and packaging applications. These thermoplastic foams were generally made with CFC-12 (dichlorodifluoromethane) as the blowing agent. More recently HCFCs (HCFC-22, chlorodifluoromethane) or blends of HCFCs (HCFC-22/HCFC-142b) or HFCs (HFC-152a) have been employed as blowing agents for polystyrene.

A third important type of insulating foam is phenolic foam. These foams, which have very attractive flammability characteristics, were generally made with CFC-11 (trichlorofluoromethane) and CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane) blowing agents

In addition to closed-cell foams, open-cell foams are also of commercial interest, for example in the production of fluid-absorbent articles. U.S. Patent no. 6,703,431 (Dietzen, et. al.) describes open-cell foams based on thermoplastics polymers that are useful for fluid-absorbent hygiene articles such as wound contact materials. U.S. Patent no, 6,071,580 (Bland, et. al.) describes absorbent extruded thermoplastic foams which can be employed in various absorbency applications. Open-cell foams have also found application in evacuated or vacuum panel technologies, for example in the production of evacuated insulation panels as described in U.S. Patent no. 5,977,271 (Malone). Using open-cell foams in evacuated insulation panels, it has been possible to obtain R-values of 10 to 15 per inch of thickness depending upon the evacuation or vacuum level, polymer type, cell size, density, and open cell content of the foam. These open-cell foams have traditionally been produced employing CFCs, HCFCs, or more recently, HFCs as blowing agents.

Multimodal foams are also of commercial interest, and are described, for example, in U.S. Patent nos. 6,787,580 (Chonde, et. al.) and 5,332,761 (Paquet, et. al.). A multimodal foam is a foam having a multimodal cell size distribution, and such foams have particular utility in thermally insulating articles since they often have higher insulating values (R-values) than analogous foams having a generally uniform cell size distribution.

These foams have been produced employing CFCs, HCFCs, and, more recently, HFCs as the blowing agent.

All of these various types of foams require blowing (expansion) 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.

Other embodiments provide foamable compositions, and preferably thermoset or thermoplastic foam compositions, prepared using the compositions of the present disclosure. In such foam embodiments, one or more of the present compositions are included as or part of a blowing agent in a foamable composition, which composition preferably includes one or more additional components capable of reacting and/or foaming under the proper conditions to form a foam or cellular structure. Another aspect relates to foam, and preferably closed cell foam, prepared from a polymer foam formulation containing a blowing agent comprising the compositions of the present disclosure.

Certain embodiments provide methods of preparing foams. In such foam embodiments, a blowing agent comprising a composition of the present disclosure is added to and reacted with a foamable composition, which foamable composition may include one or more additional components capable of reacting and/or foaming under the proper conditions to form a foam or cellular structure. Any of the methods well known in the art, such as those described in “Polyurethanes Chemistry and Technology,” Volumes I and II, Saunders and Frisch, 1962, John Wiley and Sons, New York, N.Y., which is incorporated herein by reference, may be used or adapted for use in accordance with the foam embodiments.

In certain embodiments, it is often desirable to employ certain other ingredients in preparing foams. Among these additional ingredients are , catalysts, surfactants, flame retardants, preservatives, colorants, antioxidants, reinforcing agents, fillers, antistatic agents, solubilizing agents, IR attenuating agents, nucleating agents, cell controlling agents, extrusion aids, stabilizing agents, thermally insulating agents, plasticizers, viscosity modifiers, impact modifiers, gas barrier resins, polymer modifiers, rheology modifiers, antibacterial agents, vapor pressure modifiers, UV

absorbers, cross-linking agents, permeability modifiers, bitterants, propellants and the like.

Polyurethane foams are generally prepared by combining and reacting an isocyanate with a polyol in the presence of a blowing or expanding agent and auxiliary chemicals added to control and modify both the polyurethane reaction itself and the properties of the final polymer. For processing convenience, these materials can be premixed into two non-reacting parts typically referred to as the "A-side" and the "B-side."

The term “A-side” is intended to mean isocyanate or isocyanate containing mixture. An isocyanate containing mixture may include the isocyanate, the blowing or expanding agent and auxiliary chemicals, like catalysts, surfactants, stabilizers, chain extenders, cross-linkers, water, fire retardants, smoke suppressants, pigments, coloring materials, fillers, etc.

The term “B-side” is intended to mean polyol or polyol containing mixture. A polyol containing mixture usually includes the polyol, the blowing or expanding agent and auxiliary chemicals, like catalysts, surfactants, stabilizers, chain extenders, cross-linkers, water, fire retardants, smoke suppressants, pigments, coloring materials, fillers, etc.

To prepare the foam, appropriate amounts of A-side and B-side are then combined to react.

When preparing a foam by a process disclosed herein, it is generally preferred to employ a minor amount of a surfactant to stabilize the foaming reaction mixture until it cures. Such surfactants may comprise a liquid or solid organosilicone compound. Other, less preferred surfactants include polyethylene glycol ethers of long chain alcohols, tertiary amine or alkanolamine salts of long chain alkyl acid sulfate esters, alkyl sulfonic esters and alkyl arylsulfonic acids. The surfactants are employed in amounts sufficient to stabilize the foaming reaction mixture against collapse and to prevent the formation of large, uneven cells. About 0.2 to about 5 parts or even more of the surfactant per 100 parts by weight of polyol are usually sufficient.

One or more catalysts for the reaction of the polyol with the polyisocyanate may also be used. Any suitable urethane catalyst may be used, including tertiary amine compounds and organometallic compounds. Such catalysts are used in an amount which measurably increases the

rate of reaction of the polyisocyanate. Typical amounts are about 0.1 to about 5 parts of catalyst per 100 parts by weight of polyol.

Thus, in one aspect, the invention is directed to a closed cell foam prepared by foaming a foamable composition in the presence of a blowing agent described above.

Another aspect is for a foam premix composition comprising a polyol and a blowing agent described above.

Additionally, one aspect is for a method of forming a foam comprising:

(a) adding to a foamable composition a blowing agent described above; and

(b) reacting the foamable composition under conditions effective to form a foam.

In the context of polyurethane foams, the terms “foamable composition” and “foamable component” shall be understood herein to mean isocyanate or an isocyanate-containing mixture. In the context of polystyrene foams, the terms “foamable composition” and “foamable component” shall be understood herein to mean a polyolefin or a polyolefin-containing mixture.

A further aspect is for a method of forming a polyisocyanate-based foam comprising reacting at least one organic polyisocyanate with at least one active hydrogen-containing compound in the presence of a blowing agent described above. Another aspect is for a polyisocyanate foam produced by said method.

Propellants

Another embodiment of the present invention relates to the use of an inventive composition as described herein for use as a propellant in sprayable composition. Additionally, the present invention relates to a sprayable composition comprising an inventive composition as described herein. The active ingredient to be sprayed together with inert ingredients, solvents and other materials may also be present in a sprayable composition. Preferably, the sprayable composition is an aerosol. Suitable active materials to be sprayed include, without limitations, cosmetic materials, such as deodorants, perfumes, hair sprays, cleaners, and polishing agents as well as medicinal materials such as anti-asthma and anti-halitosis medications.

The present invention further relates to a process for producing aerosol products comprising the step of adding an inventive composition as described herein to active ingredients in an aerosol container, wherein said composition functions as a propellant.

Flame Suppression and Inerting

A further aspect provides methods of suppressing a flame, said methods comprising contacting a flame with a fluid comprising an inventive composition of the present disclosure. Any suitable methods for contacting the flame with the present composition may be used. For example, an inventive composition of the present disclosure may be sprayed, poured, and the like onto the flame, or at least a portion of the flame may be immersed in the flame suppression composition. In light of the teachings herein, those of skill in the art will be readily able to adapt a variety of conventional apparatus and methods of flame suppression for use in the present disclosure.

A further embodiment provides methods of extinguishing or suppressing a fire in a total-flood application comprising providing an agent comprising an inventive composition of the present disclosure; disposing the agent in a pressurized discharge system; and discharging the agent into an area to extinguish or suppress fires in that area.

Another embodiment provides methods of inerting a space to prevent a fire or explosion comprising providing an agent comprising an inventive composition of the present disclosure; disposing the agent in a pressurized discharge system; and discharging the agent into the space to prevent a fire or explosion from occurring.

The term “extinguishment” is usually used to denote complete elimination of a fire; whereas, “suppression” is often used to denote reduction, but not necessarily total elimination, of a fire or explosion. As used herein, terms “extinguishment” and “suppression” will be used interchangeably. There are four general types of halocarbon fire and explosion protection applications:

1) In total-flood fire extinguishment and/or suppression applications, the agent is discharged into a space to achieve a concentration sufficient to extinguish or suppress an existing fire. Total flooding use includes protection of enclosed, potentially occupied spaces such, as computer rooms as well as specialized, often unoccupied

spaces such as aircraft engine nacelles and engine compartments in vehicles.

2) In streaming applications, the agent is applied directly onto a fire or into the region of a fire. This is usually accomplished using manually operated wheeled or portable units. A second method, included as a streaming application, uses a "localized" system, which discharges the agent toward a fire from one or more fixed nozzles. Localized systems may be activated either manually or automatically.

3) In explosion suppression, an inventive composition of the present disclosure is discharged to suppress an explosion that has already been initiated. The term "suppression" is normally used in this application because the explosion is usually self-limiting. However, the use of this term does not necessarily imply that the explosion is not extinguished by the agent. In this application, a detector is usually used to detect an expanding fireball from an explosion, and the agent is discharged rapidly to suppress the explosion. Explosion suppression is used primarily, but not solely, in defense applications.

4) In inertion, an inventive composition of the present disclosure is discharged into a space to prevent an explosion or a fire from being initiated. Often, a system similar or identical to that used for total-flood fire extinguishment or suppression is used. Usually, the presence of a dangerous condition (for example, dangerous concentrations of flammable or explosive gases) is detected, and the inventive composition of the present disclosure is then discharged to prevent the explosion or fire from occurring until the condition can be remedied.

The extinguishing method can be carried out by introducing the composition into an enclosed area surrounding a fire. Any of the known methods of introduction can be utilized provided that appropriate quantities of the composition are metered into the enclosed area at appropriate intervals. For example, a composition can be introduced by streaming, e.g., using conventional portable (or fixed) fire extinguishing equipment; by misting; or by flooding, e.g., by releasing (using appropriate piping, valves, and controls) the composition into an enclosed area surrounding a fire. The composition can optionally be combined with an inert propellant, e.g.,

nitrogen, argon, decomposition products of glycidyl azide polymers or carbon dioxide, to increase the rate of discharge of the composition from the streaming or flooding equipment utilized.

Preferably, the extinguishing process involves introducing an inventive composition of the present disclosure to a fire or flame in an amount sufficient to extinguish the fire or flame. One skilled in this field will recognize that the amount of flame suppressant needed to extinguish a particular fire will depend upon the nature and extent of the hazard. When the flame suppressant is to be introduced by flooding, cup burner test data are useful in determining the amount or concentration of flame suppressant required to extinguish a particular type and size of fire.

Laboratory tests useful for determining effective concentration ranges of an inventive composition when used in conjunction with extinguishing or suppressing a fire in a total-flood application or fire inertion are described, for example, in U.S. Patent no. 5,759,430.

Gaseous Dielectrics

A dielectric gas, or insulating gas, is a dielectric material in gaseous state. Its main purpose is to prevent or rapidly quench electric discharges. Dielectric gases are used as electrical insulators in high voltage applications, e.g., transformers, circuit breakers, switchgear (namely high voltage switchgear), and radar waveguides. As used herein, the term “high voltage” shall be understood to mean above 1000 V for alternating current, and at least 1500 V for direct current. The inventive compositions can be useful as gaseous dielectrics in high voltage applications.

Solvents

The inventive compositions may also be used as inert media for polymerization reactions, fluids for removing particulates from metal surfaces, as carrier fluids that may be used, for example, to place a fine film of lubricant on metal parts or as buffing abrasive agents to remove buffing abrasive compounds from polished surfaces such as metal. They are also used as displacement drying agents for removing water, such as from jewelry or metal parts, as resist developers in conventional circuit manufacturing techniques including chlorine-type developing agents, or as strippers for photoresists when used with, for example, a

chlorohydrocarbon such as 1,1,1-trichloroethane or trichloroethylene. It is desirable to identify new agents for these applications with reduced global warming potential.

Binary azeotropic or azeotrope-like compositions of substantially constant-boiling mixtures can be characterized, depending upon the conditions chosen, in a number of ways. For example, it is well known by those skilled in the art, that, at different pressures the composition of a given azeotrope or azeotrope-like composition will vary at least to some degree, as will the boiling point temperature. Thus, an azeotropic or azeotrope-like composition of two compounds represents a unique type of relationship but with a variable composition that depends on temperature and/or pressure. Therefore, compositional ranges, rather than fixed compositions, are often used to define azeotropes and azeotrope-like compositions.

As used herein, the term "azeotropic composition" shall be understood to mean a composition where at a given temperature at equilibrium, the boiling point pressure (of the liquid phase) is identical to the dew point pressure (of the vapor phase), i.e., $X_2 = Y_2$. One way to characterize an azeotropic composition is that the vapor produced by partial evaporation or distillation of the liquid has the same composition as the liquid from which it was evaporated or distilled, that is, the admixture distills/refluxes without compositional change. Constant boiling compositions are characterized as azeotropic because they exhibit either a maximum or minimum boiling point, as compared with that of the non-azeotropic mixtures of the same components. Azeotropic compositions are also characterized by a minimum or a maximum in the vapor pressure of the mixture relative to the vapor pressure of the neat components at a constant temperature.

As used herein, the terms "azeotrope-like composition" and "near-azeotropic composition" shall be understood to mean a composition wherein the difference between the bubble point pressure ("BP") and dew point pressure ("DP") of the composition at a particular temperature is less than or equal to 5 percent based upon the bubble point pressure, i.e., $[(BP-VP)/BP] \times 100 \leq 5$. As used herein, the terms "3 percent azeotrope-like composition" and "3 percent near-azeotropic composition" shall be understood to mean a composition wherein the difference between the bubble point pressure ("BP") and dew point pressure ("DP") of the

composition at a particular temperature is less than or equal to 3 percent based upon the bubble point pressure, i.e., [(BP-VP)/BP] x 100 ≤ 3.

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

As used herein, the term “mole fraction” shall be understood to mean the ratio of the number of moles of one component in the binary composition to the sum of the numbers of moles of each of the two components in said composition (e.g., $X_2 = m_2/(m_1 + m_2)$.

To determine the relative volatility of any two compounds, a method known as the PTx method can be used. In this procedure, the total absolute pressure in a cell of known volume is measured at a constant temperature for various compositions of the two compounds. Use of the PTx Method is described in detail in "Phase Equilibrium in Process Design", Wiley-Interscience Publisher, 1970, written by Harold R. Null, on pages 124 to 126; hereby incorporated by reference. The resulting pressure v. liquid composition data are alternately referred to as Vapor Liquid Equilibria data (or “VLE data.”)

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. The collection of VLE data, the determination of interaction parameters by regression and the

use of an equation of state to predict non-ideal behavior of a system are taught in "Double Azeotropy in Binary Mixtures of NH_3 and CHF_2CF_2," C.-P. Chai Kao, M.E. Paulaitis, A. Yokozeki, *Fluid Phase Equilibria*, 127 (1997) 191-203. All of the 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 relative volatilities of the Z-1233zd-containing compositions of the present invention and can therefore predict the behavior of these mixtures in multi-stage separation equipment such as distillation columns.

For economy of space in the tables that follow, "Z-1233zd" may be abbreviated to "Z1233zd."

EXAMPLE 1: Z-1233zd/Methyl Formate

The binary system of Z-1233zd/methyl formate was explored for potential azeotropic and near-azeotropic behavior. To determine the relative volatility of this binary system, the PTx method described above was used. The pressure in a PTx cell of known volume was measured at constant temperature of 30ºC for various binary compositions. The collected experimental data are displayed in Table 1.1 below.

Table 1.1. Experimental VLE Data on the Z-1233zd/Methyl Formate System at 30ºC.

X2	Y2	Pexp (psia)	Pcalc (psia)	Pcalc - Pexp (psia)
0.000	0.000	13.832		
0.025	0.018	13.665	13.724	0.0043
0.055	0.039	13.575	13.597	0.0016
0.087	0.063	13.469	13.464	-0.0003
0.128	0.096	13.312	13.294	-0.0014
0.181	0.139	13.103	13.080	-0.0017
0.229	0.180	12.881	12.893	0.0009
0.285	0.229	12.681	12.684	0.0003
0.446	0.383	12.136	12.115	-0.0017
0.522	0.460	11.861	11.870	0.0007
0.606	0.548	11.598	11.614	0.0013
0.689	0.638	11.363	11.373	0.0009
0.776	0.736	11.133	11.135	0.0002
0.861	0.835	10.928	10.913	-0.0013
0.939	0.926	10.743	10.724	-0.0018
1.000	1.000	10.580		

X_2 = liquid mole fraction of Z-1233zd.

Y_2 = vapor mole fraction of Z-1233zd.

P_{exp} = experimentally measured pressure.

P_{calc} = pressure as calculated by NRTL model.

Figure 1 displays a plot of the pressure vs composition data over the compositional range of 0-1 liquid mole fraction of Z-1233zd. The top curve represents the bubble point ("BP") locus, and the bottom curve represents the dew point ("DP") locus.

Based on these VLE data, interaction coefficients were extracted. These coefficients were then used in the NRTL model to predict the behavior of the Z-1233zd/methyl formate system at various temperatures

and pressures. The NRTL model was run over the temperature range of -40 to 140 deg. C in increments of 20 deg. C (as well as at 29.9 deg. C) and increments of 0.002 liquid mole fraction of Z-1233zd. For purposes of brevity, the listing of the 5511 combinations (501 compositions x 11 temperatures) was edited to reflect increments of 0.100 Z-1233zd liquid molar composition, or the boundaries of near-azeotropic behavior. The resulting abridged listing of near-azeotropes of the Z-1233zd/methyl formate system is presented in Table 1.2

Table 1.2. Predictions of Near-Azeotropes of the Z-1233zd/Methyl Formate System from -40 to 140 deg. C.

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. MF	Vapor mol. frac. MF	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/BP] x 100
-40.0	0.000	0	1	1	0.359	0.359	0.00%
-40.0	0.002	0.001	0.998	0.999	0.359	0.359	0.03%
-40.0	0.100	0.073	0.9	0.927	0.348	0.344	1.09%
-40.0	0.200	0.154	0.8	0.846	0.338	0.332	1.59%
-40.0	0.300	0.242	0.7	0.758	0.328	0.322	1.72%
-40.0	0.400	0.339	0.6	0.661	0.319	0.313	1.61%
-40.0	0.500	0.441	0.5	0.559	0.310	0.306	1.38%
-40.0	0.600	0.547	0.4	0.453	0.303	0.300	1.09%
-40.0	0.700	0.657	0.3	0.343	0.296	0.294	0.81%
-40.0	0.800	0.769	0.2	0.231	0.290	0.289	0.54%
-40.0	0.900	0.883	0.1	0.117	0.285	0.284	0.29%
-40.0	0.998	0.998	0.002	0.002	0.279	0.279	0.01%
-40.0	1	1.000	0	0.000	0.279	0.279	0.00%
-20.0	0	0.000	1	1.000	1.299	1.299	0.00%
-20.0	0.002	0.001	0.998	0.999	1.298	1.298	0.03%
-20.0	0.1	0.073	0.9	0.927	1.260	1.247	1.04%
-20.0	0.2	0.154	0.8	0.846	1.222	1.203	1.54%
-20.0	0.3	0.243	0.7	0.757	1.187	1.167	1.68%
-20.0	0.4	0.339	0.6	0.661	1.154	1.136	1.60%
-20.0	0.5	0.440	0.5	0.560	1.124	1.109	1.40%
-20.0	0.6	0.546	0.4	0.454	1.097	1.085	1.14%
-20.0	0.7	0.656	0.3	0.344	1.073	1.064	0.86%
-20.0	0.8	0.768	0.2	0.232	1.050	1.044	0.58%
-20.0	0.9	0.882	0.1	0.118	1.029	1.026	0.31%
-20.0	0.998	0.998	0.002	0.002	1.009	1.009	0.01%
-20.0	1	1.000	0	0.000	1.009	1.009	0.00%
0.0	0.000	0.000	1	1.000	3.773	3.773	0.00%
0.0	0.002	0.001	0.998	0.999	3.770	3.769	0.03%
0.0	0.100	0.074	0.9	0.926	3.659	3.623	1.01%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. MF	Vapor mol. frac. MF	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/BP] x 100
0.0	0.200	0.155	0.8	0.845	3.552	3.498	1.51%
0.0	0.300	0.244	0.7	0.756	3.450	3.392	1.67%
0.0	0.400	0.339	0.6	0.661	3.355	3.301	1.62%
0.0	0.500	0.440	0.5	0.560	3.268	3.221	1.43%
0.0	0.600	0.545	0.4	0.455	3.188	3.150	1.18%
0.0	0.700	0.655	0.3	0.345	3.115	3.087	0.90%
0.0	0.800	0.767	0.2	0.233	3.048	3.029	0.62%
0.0	0.900	0.882	0.1	0.118	2.984	2.974	0.33%
0.0	0.998	0.998	0.002	0.002	2.924	2.923	0.01%
	1	1.000	0	0.000	2.922	2.922	0.00%
20.0	0	0.000	1	1.000	9.243	9.243	0.00%
20.0	0.002	0.001	0.998	0.999	9.237	9.235	0.03%
20.0	0.1	0.074	0.9	0.926	8.967	8.878	0.99%
20.0	0.2	0.155	0.8	0.845	8.703	8.572	1.50%
20.0	0.3	0.244	0.7	0.756	8.453	8.311	1.68%
20.0	0.4	0.339	0.6	0.661	8.220	8.084	1.65%
20.0	0.5	0.439	0.5	0.561	8.003	7.885	1.48%
20.0	0.6	0.545	0.4	0.455	7.804	7.708	1.23%
20.0	0.7	0.654	0.3	0.346	7.620	7.548	0.95%
20.0	0.8	0.766	0.2	0.234	7.450	7.401	0.66%
20.0	0.9	0.881	0.1	0.119	7.290	7.264	0.35%
20.0	0.998	0.998	0.002	0.002	7.137	7.136	0.01%
20.0	1	1.000	0	0.000	7.134	7.134	0.00%
29.9	0	0.000	1	1.000	13.735	13.735	0.00%
29.9	0.002	0.001	0.998	0.999	13.727	13.724	0.03%
29.9	0.1	0.074	0.9	0.926	13.325	13.194	0.99%
29.9	0.2	0.155	0.8	0.845	12.932	12.738	1.50%
29.9	0.3	0.244	0.7	0.756	12.560	12.347	1.69%
29.9	0.4	0.339	0.6	0.661	12.211	12.008	1.66%
29.9	0.5	0.439	0.5	0.561	11.887	11.709	1.50%
29.9	0.6	0.544	0.4	0.456	11.588	11.442	1.25%
29.9	0.7	0.653	0.3	0.347	11.311	11.201	0.97%
29.9	0.8	0.766	0.2	0.234	11.054	10.980	0.67%
29.9	0.9	0.881	0.1	0.119	10.812	10.774	0.36%
29.9	0.998	0.998	0.002	0.002	10.582	10.581	0.01%
29.9	1	1.000	0	0.000	10.577	10.577	
40.0	0.000	0.000	1	1.000	19.817	19.817	0.00%
40.0	0.002	0.001	0.998	0.999	19.805	19.800	0.03%
40.0	0.100	0.074	0.9	0.926	19.223	19.034	0.98%
40.0	0.200	0.156	0.8	0.844	18.654	18.374	1.50%
40.0	0.300	0.244	0.7	0.756	18.115	17.807	1.70%
40.0	0.400	0.339	0.6	0.661	17.608	17.313	1.68%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. MF	Vapor mol. frac. MF	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/BP] x 100
40.0	0.500	0.439	0.5	0.561	17.137	16.877	1.52%
40.0	0.600	0.544	0.4	0.456	16.701	16.488	1.28%
40.0	0.700	0.653	0.3	0.347	16.297	16.135	0.99%
40.0	0.800	0.765	0.2	0.235	15.921	15.812	0.69%
40.0	0.900	0.881	0.1	0.119	15.567	15.510	0.36%
40.0	0.998	0.998	0.002	0.002	15.231	15.230	0.01%
40.0	1.000	1.000	0	0.000	15.224	15.224	0.00%
60.0	0	0.000	1	1.000	38.211	38.211	0.00%
60.0	0.002	0.001	0.998	0.999	38.188	38.178	0.02%
60.0	0.1	0.075	0.9	0.925	37.056	36.695	0.97%
60.0	0.2	0.156	0.8	0.844	35.949	35.409	1.50%
60.0	0.3	0.244	0.7	0.756	34.897	34.300	1.71%
60.0	0.4	0.339	0.6	0.661	33.907	33.331	1.70%
60.0	0.5	0.439	0.5	0.561	32.983	32.473	1.55%
60.0	0.6	0.544	0.4	0.456	32.125	31.705	1.31%
60.0	0.7	0.653	0.3	0.347	31.328	31.009	1.02%
60.0	0.8	0.765	0.2	0.235	30.586	30.370	0.71%
60.0	0.9	0.881	0.1	0.119	29.886	29.775	0.37%
60.0	0.998	0.998	0.002	0.002	29.226	29.223	0.01%
60.0	1	1.000	0	0.000	29.212	29.212	0.00%
80.0	0.000	0.000	1	1.000	67.665	67.665	0.00%
80.0	0.002	0.001	0.998	0.999	67.623	67.607	0.02%
80.0	0.100	0.075	0.9	0.925	65.596	64.967	0.96%
80.0	0.200	0.157	0.8	0.843	63.612	62.667	1.48%
80.0	0.300	0.246	0.7	0.754	61.727	60.678	1.70%
80.0	0.400	0.340	0.6	0.660	59.951	58.933	1.70%
80.0	0.500	0.440	0.5	0.560	58.290	57.387	1.55%
80.0	0.600	0.545	0.4	0.455	56.745	56.000	1.31%
80.0	0.700	0.654	0.3	0.346	55.309	54.743	1.02%
80.0	0.800	0.766	0.2	0.234	53.972	53.590	0.71%
80.0	0.900	0.881	0.1	0.119	52.714	52.518	0.37%
80.0	0.998	0.998	0.002	0.002	51.530	51.526	0.01%
	1	1.000	0	0.000	51.507	51.507	
100.0	0	0.000	1	1.000	111.844	111.844	0.00%
100.0	0.002	0.001	0.998	0.999	111.773	111.747	0.02%
100.0	0.1	0.076	0.9	0.924	108.378	107.371	0.93%
100.0	0.2	0.159	0.8	0.841	105.060	103.544	1.44%
100.0	0.3	0.248	0.7	0.752	101.909	100.222	1.66%
100.0	0.4	0.342	0.6	0.658	98.943	97.304	1.66%
100.0	0.5	0.442	0.5	0.558	96.169	94.714	1.51%
100.0	0.6	0.547	0.4	0.453	93.589	92.391	1.28%
100.0	0.7	0.656	0.3	0.344	91.194	90.286	1.00%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. MF	Vapor mol. frac. MF	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/BP] x 100
100.0	0.8	0.767	0.2	0.233	88.967	88.357	0.69%
100.0	0.9	0.882	0.1	0.118	86.878	86.569	0.36%
100.0	0.998	0.998	0.002	0.002	84.925	84.918	0.01%
100.0	1	1.000	0	0.000	84.885	84.885	0.00%
120.0	0	0.000	1	1.000	174.772	174.772	0.00%
120.0	0.002	0.001	0.998	0.999	174.660	174.621	0.02%
120.0	0.1	0.077	0.9	0.923	169.285	167.795	0.88%
120.0	0.2	0.161	0.8	0.839	164.045	161.802	1.37%
120.0	0.3	0.251	0.7	0.749	159.081	156.588	1.57%
120.0	0.4	0.346	0.6	0.654	154.419	152.002	1.56%
120.0	0.5	0.446	0.5	0.554	150.069	147.930	1.43%
120.0	0.6	0.551	0.4	0.449	146.033	144.280	1.20%
120.0	0.7	0.659	0.3	0.341	142.298	140.978	0.93%
120.0	0.8	0.770	0.2	0.230	138.837	137.959	0.63%
120.0	0.9	0.884	0.1	0.116	135.609	135.168	0.33%
120.0	0.998	0.998	0.002	0.002	132.610	132.601	0.01%
	1	1.000	0	0.000	132.550	132.550	
140.0	0.000	0.000	1	1.000	260.836	260.836	0.00%
140.0	0.002	0.002	0.998	0.998	260.667	260.613	0.02%
140.0	0.100	0.079	0.9	0.921	252.540	250.500	0.81%
140.0	0.200	0.164	0.8	0.836	244.651	241.590	1.25%
140.0	0.300	0.255	0.7	0.745	237.212	233.824	1.43%
140.0	0.400	0.351	0.6	0.649	230.256	226.992	1.42%
140.0	0.500	0.451	0.5	0.549	223.796	220.932	1.28%
140.0	0.600	0.556	0.4	0.444	217.835	215.514	1.07%
140.0	0.700	0.664	0.3	0.336	212.353	210.628	0.81%
140.0	0.800	0.774	0.2	0.226	207.311	206.182	0.54%
140.0	0.900	0.886	0.1	0.114	202.647	202.091	0.27%
140.0	0.998	0.998	0.002	0.002	198.361	198.349	0.01%
	1	1.000	0	0.000	198.275	198.275	0.00%

The NRTL model was run at a pressure of 1 atm in increments of 0.002 liquid mole fraction of Z-1233zd. For purposes of brevity, the listing was edited to reflect increments of 0.100 Z-1233zd liquid molar composition, or the boundaries of near-azeotropic behavior. The resulting abridged listing of near-azeotropes of the Z-1233zd/methyl formate system is presented in Table 1.3.

Table 1.3. Predicted Near-Azeotropes of the Z-1233zd/MF System at 1 Atm.

Pressure (atm)	Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. MF	Vapor mol. frac. MF	Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
1.00	31.787	0.000	0.000	1.000	1.000	14.696	14.696	0.00%
1.00	31.804	0.002	0.001	0.998	0.999	14.696	14.692	0.03%
1.00	32.599	0.100	0.074	0.900	0.926	14.696	14.551	0.98%
1.00	33.404	0.200	0.155	0.800	0.845	14.696	14.475	1.50%
1.00	34.195	0.300	0.244	0.700	0.756	14.696	14.447	1.69%
1.00	34.965	0.400	0.339	0.600	0.661	14.696	14.450	1.67%
1.00	35.705	0.500	0.439	0.500	0.561	14.696	14.474	1.51%
1.00	36.414	0.600	0.544	0.400	0.456	14.696	14.510	1.27%
1.00	37.090	0.700	0.653	0.300	0.347	14.696	14.551	0.99%
1.00	37.739	0.800	0.765	0.200	0.235	14.696	14.596	0.68%
1.00	38.369	0.900	0.881	0.100	0.119	14.696	14.643	0.36%
1.00	38.984	0.998	0.998	0.002	0.002	14.696	14.695	0.01%
1.00	38.996	1.000	1.000	0.000	0.000	14.696	14.696	0.00%

The detailed data in Tables 1.2 and 1.3 are broadly summarized in Tables 1.4 and 1.5 below. The broad ranges of azeotrope-like compositions (based on [(BP-VP)/BP] x 100 ≤ 5) are listed in Table 1.4.

Table 1.4. Summaries of Near-Azeotropes of the Z-1233zd/MF System.

Components	T (°C)	Z-1233zd /Methyl formate Liquid Mole Percentage Range
Z-1233zd / methyl formate	-40	1-99 / 99-1
Z-1233zd / methyl formate	-20	1-99 / 99-1
Z-1233zd / methyl formate	0	1-99 / 99-1
Z-1233zd / methyl formate	20	1-99 / 99-1
Z-1233zd / methyl formate	29.9	1-99 / 99-1
Z-1233zd / methyl formate	40	1-99 / 99-1
Z-1233zd / methyl formate	60	1-99 / 99-1
Z-1233zd / methyl formate	80	1-99 / 99-1
Z-1233zd / methyl formate	100	1-99 / 99-1
Z-1233zd / methyl formate	120	1-99 / 99-1
Z-1233zd / methyl formate	140	1-99 / 99-1

The broad ranges of 3% azeotrope-like compositions (based on [(BP-VP)/BP] x 100 ≤ 3) are listed in Table 1.5.

Table 1.5. Summaries of 3% Near-Azeotropes of the Z-1233zd/MF System.

Components	T (°C)	Z-1233zd/Methyl formate Liquid Mole Percentage Range
Z-1233zd / methyl formate	-40	1-99 / 99-1
Z-1233zd / methyl formate	-20	1-99 / 99-1
Z-1233zd / methyl formate	0	1-99 / 99-1
Z-1233zd / methyl formate	20	1-99 / 99-1
Z-1233zd / methyl formate	29.9	1-99 / 99-1
Z-1233zd / methyl formate	40	1-99 / 99-1
Z-1233zd / methyl formate	60	1-99 / 99-1
Z-1233zd / methyl formate	80	1-99 / 99-1
Z-1233zd / methyl formate	100	1-99 / 99-1
Z-1233zd / methyl formate	120	1-99 / 99-1
Z-1233zd / methyl formate	140	1-99 / 99-1

At atmospheric pressure, all compositions were found to be 3% near azeotropes.

EXAMPLE 2: Z-1233zd/Dimethoxymethane

The binary system of Z-1233zd/dimethoxymethane was explored for potential azeotropic and near-azeotropic behavior. To determine the relative volatility of this binary system, the PTx method described above was used. The pressure in a PTx cell of known volume was measured at constant temperature of 29.9 °C for various binary compositions. The collected experimental data are displayed in Table 2.1 below.

Table 2-1. VLE Data for the Z-1233zd/Dimethoxymethane System.

X2	Y2	Pexp psia	Pcalc psia	Pcalc-Pexp psia
0.000	0.000	9.329		
0.038	0.030	9.197	9.241	0.005
0.085	0.069	9.191	9.140	-0.006
0.131	0.110	9.192	9.050	-0.015
0.188	0.165	8.964	8.956	-0.001
0.259	0.240	8.827	8.865	0.004
0.318	0.307	8.790	8.818	0.003
0.384	0.385	8.760	8.799	0.005
0.522	0.552	8.877	8.892	0.002
0.576	0.617	8.970	8.980	0.001
0.642	0.694	9.118	9.128	0.001
0.715	0.772	9.354	9.340	-0.002
0.793	0.848	9.657	9.621	-0.004
0.869	0.913	9.991	9.940	-0.005
0.939	0.963	10.307	10.259	-0.005
1.000	1.000	10.556		

X_2 = liquid mole fraction of Z-1233zd.

Y_2 = vapor mole fraction of Z-1233zd.

P_{exp} = experimentally measured pressure.

P_{calc} = pressure as calculated by NRTL model.

The above vapor pressure v. Z-1233zd liquid mole fraction data are plotted in Figure 2. The experimental data points are shown in Figure 2 as solid points. The solid line represents bubble point predictions using the NRTL equation. The dashed line represents predicted dew points.

Based on these VLE data, interaction coefficients were extracted. The NRTL model was run over the temperature range of -40 to 140 deg. C in increments of 10 deg. C allowing pressure to vary such that the azeotropic condition ($X_2 = Y_2$) was met. The resulting predictions of azeotropes in the Z-1233zd/DMM system are displayed in Table 2.2.

Table 2.2. Predicted Azeotropes of the Z-1233zd/DMM System from -40 to 140 deg. C.

Temp. (deg. C)	Pressure (psia)	Z1233zd Vapor mol. frac.	DMM Vapor mol. frac.	Z1233zd Liquid mol. frac.	DMM Liquid mol. frac.	Z1233zd Liquid wt. frac.	DMM Liquid wt. frac.
-40	0.18	0.394	0.606	0.394	0.606	0.527	0.473
-30	0.38	0.389	0.611	0.389	0.611	0.522	0.478
-20	0.73	0.385	0.615	0.385	0.615	0.518	0.482
-10	1.33	0.382	0.618	0.382	0.618	0.515	0.485
0	2.28	0.381	0.619	0.381	0.619	0.513	0.487
10	3.72	0.380	0.620	0.380	0.620	0.513	0.487
20	5.84	0.382	0.618	0.382	0.618	0.514	0.486
29.9	8.78	0.385	0.615	0.385	0.615	0.517	0.483
30	8.82	0.385	0.615	0.385	0.615	0.517	0.483
40	12.90	0.389	0.611	0.389	0.611	0.522	0.478
50	18.33	0.395	0.605	0.395	0.605	0.529	0.471
60	25.37	0.403	0.597	0.403	0.597	0.536	0.464
70	34.31	0.411	0.589	0.411	0.589	0.545	0.455
80	45.44	0.421	0.579	0.421	0.579	0.555	0.445
90	59.05	0.431	0.569	0.431	0.569	0.565	0.435
100	75.45	0.440	0.560	0.440	0.560	0.574	0.426
110	94.94	0.450	0.550	0.450	0.550	0.583	0.417
120	117.82	0.458	0.542	0.458	0.542	0.592	0.408
130	144.38	0.465	0.535	0.465	0.535	0.599	0.401
140	174.86	0.471	0.529	0.471	0.529	0.605	0.395

The model was used to predict azeotropes over a pressure range of 1-31 atm at 1 atm increments, the results of which are displayed in Table 2.3.

Table 2.3. Predicted Azeotropes of the A-1233zd/DMM System from 1 to 31 Atm.

Pressure (atm)	Temp. (deg. C)	Z1233zd Vapor mol. frac.	DMM Vapor mol. frac.	Z1233zd Liquid mol. frac.	DMM Liquid mol. frac.	Z1233zd Liquid wt. frac.	DMM Liquid wt. frac.
1	43.6	0.391	0.609	0.391	0.609	0.524	0.476
2	64.8	0.407	0.593	0.407	0.593	0.540	0.460
3	78.9	0.420	0.580	0.420	0.580	0.554	0.446
4	89.8	0.431	0.569	0.431	0.569	0.565	0.435
5	98.9	0.439	0.561	0.439	0.561	0.573	0.427
6	106.7	0.447	0.553	0.447	0.553	0.581	0.419
7	113.6	0.453	0.547	0.453	0.547	0.587	0.413
8	119.9	0.458	0.542	0.458	0.542	0.591	0.409
9	125.6	0.462	0.538	0.462	0.538	0.596	0.404
10	130.9	0.466	0.534	0.466	0.534	0.599	0.401
11	135.8	0.469	0.531	0.469	0.531	0.602	0.398
12	140.5	0.472	0.528	0.472	0.528	0.605	0.395
13	144.8	0.474	0.526	0.474	0.526	0.607	0.393
14	149.0	0.476	0.524	0.476	0.524	0.609	0.391
15	152.9	0.478	0.522	0.478	0.522	0.611	0.389
16	156.7	0.480	0.520	0.480	0.520	0.613	0.387
17	160.4	0.481	0.519	0.481	0.519	0.614	0.386
18	163.9	0.483	0.517	0.483	0.517	0.616	0.384
19	167.3	0.484	0.516	0.484	0.516	0.617	0.383
20	170.6	0.486	0.514	0.486	0.514	0.618	0.382
21	173.8	0.487	0.513	0.487	0.513	0.620	0.380
22	176.9	0.489	0.511	0.489	0.511	0.621	0.379
23	180.0	0.491	0.509	0.491	0.509	0.623	0.377
24	183.0	0.493	0.507	0.493	0.507	0.625	0.375
25	186.0	0.495	0.505	0.495	0.505	0.627	0.373
26	189.0	0.497	0.503	0.497	0.503	0.629	0.371
27	192.0	0.501	0.499	0.501	0.499	0.632	0.368
28	195.1	0.505	0.495	0.505	0.495	0.636	0.364
29	198.5	0.513	0.487	0.513	0.487	0.644	0.356
30	202.0	0.522	0.478	0.522	0.478	0.652	0.348
31	205.8	0.528	0.472	0.528	0.472	0.657	0.343

The model was run over a temperature range from -40 to 140 deg. C in 20 deg. increments, and also at 29.9 deg. for the purpose of comparison to experimentally measured results. At each temperature, the model was run over the full range from 0 to 1 of Z-1233zd liquid molar composition in increments of 0.002. Thus the model was run at a total of 5511 combinations of temperature and Z-1233zd liquid molar composition (11 temperatures x 501 compositions = 5511). Among those 5511

combinations, some qualify as azeotropic or near-azeotropic, and it is these combinations that Applicant claims. For purposes of brevity, the listing of the 5511 combinations was edited to reflect increments of 0.10 Z-1233zd liquid molar composition, or the boundaries of near-azeotropic behavior. The resulting abridged listing is presented in Table 2.4.

Table 2.4. Predicted Near-Azeotropes of the Z-1233zd/DMM System.

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac DMM	Vapor mol. frac DMM	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
-40.00	0.000	0.000	1.000	1.000	0.211	0.211	0.00%
-40.00	0.002	0.001	0.998	0.999	0.211	0.211	0.08%
-40.00	0.100	0.063	0.900	0.937	0.202	0.198	2.02%
-40.00	0.200	0.151	0.800	0.849	0.193	0.190	1.66%
-40.00	0.300	0.264	0.700	0.736	0.187	0.186	0.56%
-40.00	0.400	0.403	0.600	0.597	0.185	0.185	0.00%
-40.00	0.500	0.555	0.500	0.445	0.188	0.186	1.01%
-40.00	0.600	0.702	0.400	0.298	0.198	0.190	3.88%
-40.00	0.628	0.740	0.372	0.260	0.202	0.192	4.94%
-40.00	0.630	0.742	0.370	0.258	0.202	0.192	5.02%
-40.00	0.966	0.990	0.034	0.010	0.272	0.259	5.05%
-40.00	0.968	0.990	0.032	0.010	0.273	0.260	4.81%
-40.00	0.998	0.999	0.002	0.001	0.279	0.278	0.34%
-40.00	1.000	1.000	0.000	0.000	0.279	0.279	0.00%
-20.00	0.000	0.000	1.000	1.000	0.813	0.813	0.00%
-20.00	0.002	0.001	0.998	0.999	0.813	0.812	0.05%
-20.00	0.100	0.070	0.900	0.930	0.783	0.773	1.28%
-20.00	0.200	0.161	0.800	0.839	0.757	0.749	1.01%
-20.00	0.300	0.274	0.700	0.726	0.739	0.737	0.30%
-20.00	0.400	0.406	0.600	0.594	0.734	0.734	0.01%
-20.00	0.500	0.547	0.500	0.453	0.745	0.739	0.75%
-20.00	0.600	0.683	0.400	0.317	0.774	0.754	2.63%
-20.00	0.696	0.797	0.304	0.203	0.819	0.778	5.00%
-20.00	0.698	0.799	0.302	0.201	0.820	0.779	5.04%
-20.00	0.700	0.801	0.300	0.199	0.821	0.779	5.09%
-20.00	0.928	0.969	0.072	0.031	0.964	0.915	5.05%
-20.00	0.930	0.970	0.070	0.030	0.965	0.917	4.96%
-20.00	0.998	0.999	0.002	0.001	1.007	1.005	0.18%
-20.00	1.000	1.000	0.000	0.000	1.009	1.009	0.00%
0.00	0.000	0.000	1.000	1.000	2.470	2.470	0.00%
0.00	0.002	0.001	0.998	0.999	2.469	2.468	0.03%
0.00	0.100	0.075	0.900	0.925	2.392	2.372	0.84%
0.00	0.200	0.169	0.800	0.831	2.328	2.313	0.65%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac DMM	Vapor mol. frac DMM	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
0.00	0.300	0.280	0.700	0.720	2.287	2.282	0.18%
0.00	0.400	0.406	0.600	0.594	2.276	2.276	0.01%
0.00	0.500	0.538	0.500	0.462	2.303	2.291	0.52%
0.00	0.600	0.667	0.400	0.333	2.371	2.330	1.74%
0.00	0.700	0.781	0.300	0.219	2.479	2.397	3.31%
0.00	0.800	0.875	0.200	0.125	2.617	2.502	4.38%
0.00	0.900	0.946	0.100	0.054	2.769	2.665	3.77%
0.00	0.998	0.999	0.002	0.001	2.919	2.916	0.11%
	1.000	1.000	0.000	0.000	2.922	2.922	0.00%
20.00	0.000	0.000	1.000	1.000	6.249	6.249	0.00%
20.00	0.002	0.001	0.998	0.999	6.246	6.244	0.02%
20.00	0.100	0.079	0.900	0.921	6.079	6.044	0.58%
20.00	0.200	0.174	0.800	0.826	5.944	5.918	0.45%
20.00	0.300	0.284	0.700	0.716	5.859	5.851	0.12%
20.00	0.400	0.404	0.600	0.596	5.837	5.836	0.01%
20.00	0.500	0.530	0.500	0.470	5.889	5.869	0.34%
20.00	0.600	0.654	0.400	0.346	6.022	5.953	1.14%
20.00	0.700	0.766	0.300	0.234	6.231	6.096	2.16%
20.00	0.800	0.861	0.200	0.139	6.502	6.316	2.86%
20.00	0.900	0.939	0.100	0.061	6.811	6.645	2.45%
20.00	0.998	0.999	0.002	0.001	7.127	7.122	0.07%
20.00	1.000	1.000	0.000	0.000	7.134	7.134	0.00%
29.93	0.000	0.000	1.000	1.000	9.364	9.364	0.00%
29.93	0.002	0.001	0.998	0.999	9.359	9.357	0.02%
29.93	0.100	0.081	0.900	0.919	9.127	9.081	0.50%
29.93	0.200	0.176	0.800	0.824	8.939	8.904	0.39%
29.93	0.300	0.285	0.700	0.715	8.820	8.810	0.11%
29.93	0.400	0.403	0.600	0.597	8.787	8.786	0.00%
29.93	0.500	0.527	0.500	0.473	8.854	8.830	0.27%
29.93	0.600	0.648	0.400	0.352	9.029	8.946	0.92%
29.93	0.700	0.759	0.300	0.241	9.307	9.143	1.76%
29.93	0.800	0.856	0.200	0.144	9.670	9.443	2.35%
29.93	0.900	0.936	0.100	0.064	10.091	9.887	2.02%
29.93	0.998	0.999	0.002	0.001	10.528	10.522	0.06%
29.93	1.000	1.000	0.000	0.000	10.537	10.537	
40.00	0.000	0.000	1.000	1.000	13.703	13.703	0.00%
40.00	0.002	0.002	0.998	0.998	13.696	13.693	0.02%
40.00	0.100	0.082	0.900	0.918	13.375	13.317	0.44%
40.00	0.200	0.177	0.800	0.823	13.118	13.073	0.34%
40.00	0.300	0.285	0.700	0.715	12.953	12.939	0.10%
40.00	0.400	0.402	0.600	0.598	12.903	12.903	0.00%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac DMM	Vapor mol. frac DMM	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
40.00	0.500	0.523	0.500	0.477	12.986	12.959	0.21%
40.00	0.600	0.643	0.400	0.357	13.210	13.113	0.74%
40.00	0.700	0.754	0.300	0.246	13.572	13.377	1.44%
40.00	0.800	0.851	0.200	0.149	14.051	13.778	1.94%
40.00	0.900	0.933	0.100	0.067	14.615	14.367	1.70%
40.00	0.998	0.999	0.002	0.001	15.212	15.204	0.05%
40.00	1.000	1.000	0.000	0.000	15.224	15.224	0.00%
60.00	0.000	0.000	1.000	1.000	26.837	26.837	0.00%
60.00	0.002	0.002	0.998	0.998	26.824	26.821	0.01%
60.00	0.100	0.084	0.900	0.916	26.251	26.158	0.35%
60.00	0.200	0.179	0.800	0.821	25.788	25.713	0.29%
60.00	0.300	0.285	0.700	0.715	25.484	25.458	0.10%
60.00	0.400	0.400	0.600	0.600	25.373	25.373	0.00%
60.00	0.500	0.517	0.500	0.483	25.480	25.449	0.12%
60.00	0.600	0.634	0.400	0.366	25.821	25.695	0.49%
60.00	0.700	0.744	0.300	0.256	26.395	26.131	1.00%
60.00	0.800	0.843	0.200	0.157	27.182	26.801	1.40%
60.00	0.900	0.929	0.100	0.071	28.139	27.782	1.27%
60.00	0.998	0.999	0.002	0.001	29.190	29.178	0.04%
60.00	1.000	1.000	0.000	0.000	29.212	29.212	0.00%
80.00	0.000	0.000	1.000	1.000	48.031	48.031	0.00%
80.00	0.002	0.002	0.998	0.998	48.009	48.003	0.01%
80.00	0.100	0.085	0.900	0.915	47.027	46.879	0.31%
80.00	0.200	0.180	0.800	0.820	46.227	46.100	0.28%
80.00	0.300	0.285	0.700	0.715	45.683	45.632	0.11%
80.00	0.400	0.397	0.600	0.603	45.443	45.441	0.00%
80.00	0.500	0.512	0.500	0.488	45.549	45.520	0.06%
80.00	0.600	0.627	0.400	0.373	46.030	45.879	0.33%
80.00	0.700	0.737	0.300	0.263	46.897	46.552	0.74%
80.00	0.800	0.838	0.200	0.162	48.134	47.609	1.09%
80.00	0.900	0.926	0.100	0.074	49.696	49.178	1.04%
80.00	0.998	0.999	0.002	0.001	51.468	51.450	0.04%
	1.000	1.000	0.000	0.000	51.507	51.507	
100.00	0.000	0.000	1.000	1.000	79.955	79.955	0.00%
100.00	0.002	0.002	0.998	0.998	79.919	79.910	0.01%
100.00	0.100	0.085	0.900	0.915	78.280	78.042	0.30%
100.00	0.200	0.181	0.800	0.819	76.930	76.712	0.28%
100.00	0.300	0.284	0.700	0.716	75.977	75.876	0.13%
100.00	0.400	0.395	0.600	0.605	75.495	75.485	0.01%
100.00	0.500	0.509	0.500	0.491	75.552	75.528	0.03%
100.00	0.600	0.623	0.400	0.377	76.203	76.022	0.24%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac DMM	Vapor mol. frac DMM	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
100.00	0.700	0.733	0.300	0.267	77.483	77.027	0.59%
100.00	0.800	0.834	0.200	0.166	79.394	78.655	0.93%
100.00	0.900	0.924	0.100	0.076	81.894	81.125	0.94%
100.00	0.998	0.999	0.002	0.001	84.822	84.792	0.03%
100.00	1.000	1.000	0.000	0.000	84.885	84.885	0.00%
120.00	0.000	0.000	1.000	1.000	125.531	125.531	0.00%
120.00	0.002	0.002	0.998	0.998	125.471	125.457	0.01%
120.00	0.100	0.086	0.900	0.914	122.767	122.375	0.32%
120.00	0.200	0.180	0.800	0.820	120.514	120.140	0.31%
120.00	0.300	0.283	0.700	0.717	118.878	118.686	0.16%
120.00	0.400	0.393	0.600	0.607	117.972	117.941	0.03%
120.00	0.500	0.506	0.500	0.494	117.906	117.887	0.02%
120.00	0.600	0.620	0.400	0.380	118.781	118.558	0.19%
120.00	0.700	0.730	0.300	0.270	120.678	120.049	0.52%
120.00	0.800	0.832	0.200	0.168	123.637	122.555	0.88%
120.00	0.900	0.923	0.100	0.077	127.636	126.452	0.93%
120.00	0.998	0.999	0.002	0.001	132.444	132.397	0.04%
	1.000	1.000	0.000	0.000	132.550	132.550	
140.00	0.000	0.000	1.000	1.000	187.944	187.944	0.00%
140.00	0.002	0.002	0.998	0.998	187.845	187.822	0.01%
140.00	0.100	0.086	0.900	0.914	183.369	182.711	0.36%
140.00	0.200	0.180	0.800	0.820	179.618	178.970	0.36%
140.00	0.300	0.282	0.700	0.718	176.846	176.489	0.20%
140.00	0.400	0.391	0.600	0.609	175.222	175.146	0.04%
140.00	0.500	0.504	0.500	0.496	174.924	174.910	0.01%
140.00	0.600	0.618	0.400	0.382	176.130	175.834	0.17%
140.00	0.700	0.728	0.300	0.272	179.002	178.083	0.51%
140.00	0.800	0.832	0.200	0.168	183.659	181.991	0.91%
140.00	0.900	0.923	0.100	0.077	190.128	188.224	1.00%
140.00	0.998	0.999	0.002	0.001	198.098	198.018	0.04%
	1.000	1.000	0.000	0.000	198.275	198.275	0.00%

The data in Table 2.4 are broadly summarized in Tables 2.5 and 2.6 below. Azeotrope-like compositions (based on [(BP-VP)/BP] x 100 ≤ 5), are summarized in Table 2.5, and 3% near-azeotropic compositions (where [(BP-VP)/BP] x 100 ≤ 3) are listed in Table 2.6.

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Table 2.5. Predicted Near-Azeotropes of the Z-1233zd/DMM System.

Components	T (°C)	Z-1233zd /DMM Liquid Mole Percentage Range
Z-1233zd / DMM	-40	1-62 / 99-38 97-99 / 3-1
Z-1233zd / DMM	-20	1-69 /99-31 93-99 / 7-1
Z-1233zd / DMM	0	1-99 / 99-1
Z-1233zd / DMM	20	1-99 / 99-1
Z-1233zd / DMM	29.9	1-99 / 99-1
Z-1233zd / DMM	40	1-99 / 99-1
Z-1233zd / DMM	60	1-99 / 99-1
Z-1233zd / DMM	80	1-99 / 99-1
Z-1233zd / DMM	100	1-99 / 99-1
Z-1233zd / DMM	120	1-99 / 99-1
Z-1233zd / DMM	140	1-99 / 99-1

Table 2.6. Predicted 3% Near-Azeotropes of the Z-1233zd/DMM System.

Components	T (°C)	Z-1233zd/DMM Liquid Mole Percentage Range
Z-1233zd / DMM	-40	1-57 / 99-43
Z-1233zd / DMM	-20	1-61 /99-39
Z-1233zd / DMM	0	1-68 / 99-32
Z-1233zd / DMM	20	1-99 / 99-1
Z-1233zd / DMM	29.9	1-99 / 99-1
Z-1233zd / DMM	40	1-99 / 99-1
Z-1233zd / DMM	60	1-99 / 99-1
Z-1233zd / DMM	80	1-99 / 99-1
Z-1233zd / DMM	100	1-99 / 99-1
Z-1233zd / DMM	120	1-99 / 99-1
Z-1233zd / DMM	140	1-99 / 99-1

At atmospheric pressure, all compositions were found to be 3% near azeotropes.

EXAMPLE 3: Z-1233zd/HFC-43-10-mee

The binary system of Z-1233zd/ HFC-43-10-mee was explored for potential azeotropic and near-azeotropic behavior. To determine the relative volatility of this binary system, the PTx method described above was used. The pressure in a PTx cell of known volume was measured at constant temperature of 30 ºC for various binary compositions. The collected experimental data are displayed in Table 3.1 below.

Table 3.1. VLE Data for Z-1233zd/ HFC-43-10-mee System at 30 ^{0}C.

X2	Y2	Pexp (psia)	Pcalc (psia)	Pcalc - Pexp (psia)
0.0000	0.0000	5.8500		
0.0610	0.1322	6.3480	6.3498	0.0003
0.1381	0.2660	6.9310	6.9332	0.0003
0.2243	0.3849	7.5230	7.5241	0.0001
0.3099	0.4811	8.0510	8.0518	0.0001
0.3924	0.5594	8.5070	8.5089	0.0002
0.4711	0.6247	8.9020	8.9015	-0.0001
0.5326	0.6713	9.1930	9.1809	-0.0013
0.6549	0.7558	9.6750	9.6676	-0.0008
0.7124	0.7936	9.8670	9.8666	0.0000
0.7659	0.8286	10.0380	10.0349	-0.0003
0.8143	0.8605	10.1560	10.1728	0.0017
0.8673	0.8967	10.2940	10.3077	0.0013
0.9172	0.9328	10.4030	10.4173	0.0014
0.9620	0.9677	10.5020	10.4988	-0.0003
1.0000	1.0000	10.5530		99.6% purity

X_2 = liquid mole fraction of Z-1233zd.

Y_2 = vapor mole fraction of Z-1233zd.

P_{exp} = experimentally measured pressure.

The above vapor pressure v. Z-1233zd liquid mole fraction data are plotted in Figure 3. The experimental data points are shown in Figure 3 as solid points. The solid line represents bubble point predictions using the NRTL equation (see below). The dashed line represents predicted dew points.

The model was run over a temperature range from -40 to 140 deg. C in 20 deg. Increments as well as at 29.93 deg. C. At each temperature, the model was run over the full range from 0 to 1 of Z1233zd liquid molar composition in increments of 0.002. Thus the model was run at a total of 5511 combinations of temperature and Z-1233zd liquid molar composition

(11 temperatures x 501 compositions = 5511). Among those 5511 combinations, some qualify as azeotropic or near-azeotropic, and it is these combinations that Applicant claims. For purposes of brevity, the listing of the 5511 combinations was edited to reflect increments of 0.100 Z-1233zd liquid molar composition, or the boundaries of near-azeotropic behavior. The resulting abridged listing is presented in Table 3.2. HFC-43-10mee is abbreviated to "4310mee" in the table headings.

Table 3.2. Predicted Near-Azeotropes of the Z-1233zd/HFC-43-10mee System from -40 to 140 deg. C.

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. 4310mee	Vapor mol. frac. 4310mee	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
-40.00	0.000	0.000	1.000	1.000	0.0680	0.0680	0.00%
-40.00	0.002	0.013	0.998	0.987	0.0687	0.0681	0.96%
-40.00	0.010	0.063	0.990	0.937	0.0718	0.0685	4.54%
-40.00	0.012	0.075	0.988	0.925	0.0726	0.0687	5.37%
-40.00	0.100	0.407	0.900	0.593	0.1036	0.0743	28.32%
-40.00	0.200	0.587	0.800	0.413	0.1339	0.0819	38.88%
-40.00	0.300	0.691	0.700	0.309	0.1599	0.0911	43.02%
-40.00	0.400	0.760	0.600	0.240	0.1824	0.1027	43.71%
-40.00	0.500	0.811	0.500	0.189	0.2021	0.1174	41.89%
-40.00	0.600	0.852	0.400	0.148	0.2196	0.1367	37.72%
-40.00	0.700	0.888	0.300	0.112	0.2355	0.1627	30.90%
-40.00	0.800	0.922	0.200	0.078	0.2503	0.1977	21.00%
-40.00	0.900	0.958	0.100	0.042	0.2647	0.2409	8.97%
-40.00	0.936	0.972	0.064	0.028	0.2698	0.2562	5.04%
-40.00	0.938	0.973	0.062	0.027	0.2701	0.2570	4.84%
-40.00	0.998	0.999	0.002	0.001	0.2788	0.2784	0.11%
-40.00	1.000	1.000	0.000	0.000	0.2790	0.2790	0.00%
-20.00	0.000	0.000	1.000	1.000	0.3319	0.3319	0.00%
-20.00	0.002	0.009	0.998	0.991	0.3343	0.3324	0.57%
-20.00	0.018	0.078	0.982	0.922	0.3534	0.3366	4.75%
-20.00	0.020	0.086	0.980	0.914	0.3558	0.3372	5.23%
-20.00	0.100	0.326	0.900	0.674	0.4447	0.3601	19.01%
-20.00	0.200	0.503	0.800	0.497	0.5424	0.3935	27.45%
-20.00	0.300	0.616	0.700	0.384	0.6272	0.4333	30.92%
-20.00	0.400	0.697	0.600	0.303	0.7012	0.4814	31.34%
-20.00	0.500	0.759	0.500	0.241	0.7662	0.5405	29.45%
-20.00	0.600	0.811	0.400	0.189	0.8237	0.6136	25.50%
-20.00	0.700	0.856	0.300	0.144	0.8754	0.7041	19.58%
-20.00	0.800	0.900	0.200	0.100	0.9228	0.8115	12.06%
-20.00	0.892	0.942	0.108	0.058	0.9635	0.9142	5.12%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. 4310mee	Vapor mol. frac. 4310mee	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
-20.00	0.894	0.943	0.106	0.057	0.9644	0.9163	4.98%
-20.00	0.998	0.999	0.002	0.001	1.0077	1.0072	0.05%
-20.00	1.000	1.000	0.000	0.000	1.0086	1.0086	0.00%
0.00	0.000	0.000	1.000	1.000	1.1959	1.1959	0.00%
0.00	0.002	0.007	0.998	0.993	1.2020	1.1976	0.36%
0.00	0.030	0.097	0.970	0.903	1.2853	1.2223	4.90%
0.00	0.032	0.103	0.968	0.897	1.2912	1.2241	5.19%
0.00	0.100	0.270	0.900	0.730	1.4811	1.2885	13.00%
0.00	0.200	0.439	0.800	0.561	1.7318	1.3957	19.41%
0.00	0.300	0.557	0.700	0.443	1.9520	1.5207	22.10%
0.00	0.400	0.645	0.600	0.355	2.1454	1.6674	22.28%
0.00	0.500	0.716	0.500	0.284	2.3156	1.8404	20.52%
0.00	0.600	0.776	0.400	0.224	2.4660	2.0434	17.14%
0.00	0.700	0.830	0.300	0.170	2.5997	2.2765	12.43%
0.00	0.800	0.882	0.200	0.118	2.7197	2.5269	7.09%
0.00	0.840	0.903	0.160	0.097	2.7642	2.6244	5.06%
0.00	0.842	0.904	0.158	0.096	2.7664	2.6292	4.96%
0.00	0.900	0.937	0.100	0.063	2.8275	2.7578	2.47%
0.00	0.998	0.999	0.002	0.001	2.9205	2.9198	0.03%
	1.000	1.000	0.000	0.000	2.9223	2.9223	0.00%
20.00	0.000	0.000	1.000	1.000	3.4438	3.4438	0.00%
20.00	0.002	0.006	0.998	0.994	3.4566	3.4483	0.24%
20.00	0.046	0.118	0.954	0.882	3.7313	3.5510	4.83%
20.00	0.048	0.122	0.952	0.878	3.7435	3.5558	5.01%
20.00	0.100	0.231	0.900	0.769	4.0502	3.6850	9.02%
20.00	0.200	0.390	0.800	0.610	4.5899	3.9589	13.75%
20.00	0.300	0.509	0.700	0.491	5.0685	4.2709	15.74%
20.00	0.400	0.602	0.600	0.398	5.4915	4.6267	15.75%
20.00	0.500	0.679	0.500	0.321	5.8645	5.0306	14.22%
20.00	0.600	0.746	0.400	0.254	6.1930	5.4822	11.48%
20.00	0.700	0.807	0.300	0.193	6.4821	5.9684	7.92%
20.00	0.778	0.853	0.222	0.147	6.6828	6.3483	5.01%
20.00	0.780	0.854	0.220	0.146	6.6877	6.3578	4.93%
20.00	0.800	0.866	0.200	0.134	6.7357	6.4510	4.23%
20.00	0.900	0.929	0.100	0.071	6.9549	6.8612	1.35%
20.00	0.998	0.998	0.002	0.002	7.1306	7.1298	0.01%
20.00	1.000	1.000	0.000	0.000	7.1337	7.1337	0.00%
29.93	0.000	0.000	1.000	1.000	5.4729	5.4729	0.00%
29.93	0.002	0.005	0.998	0.995	5.4906	5.4798	0.20%
29.93	0.058	0.134	0.942	0.866	5.9708	5.6790	4.89%
29.93	0.060	0.138	0.940	0.862	5.9874	5.6863	5.03%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. 4310mee	Vapor mol. frac. 4310mee	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
29.93	0.100	0.215	0.900	0.785	6.3123	5.8371	7.53%
29.93	0.200	0.370	0.800	0.630	7.0635	6.2466	11.57%
29.93	0.300	0.488	0.700	0.512	7.7325	6.7078	13.25%
29.93	0.400	0.583	0.600	0.417	8.3253	7.2261	13.20%
29.93	0.500	0.663	0.500	0.337	8.8483	7.8042	11.80%
29.93	0.600	0.732	0.400	0.268	9.3081	8.4359	9.37%
29.93	0.700	0.797	0.300	0.203	9.7105	9.0969	6.32%
29.93	0.740	0.822	0.260	0.178	9.8563	9.3582	5.05%
29.93	0.742	0.823	0.258	0.177	9.8634	9.3711	4.99%
29.93	0.800	0.859	0.200	0.141	10.0595	9.7312	3.26%
29.93	0.900	0.925	0.100	0.075	10.3547	10.2520	0.99%
29.93	0.998	0.998	0.002	0.002	10.5816	10.5808	0.01%
29.93	1.000	1.000	0.000	0.000	10.5854	10.5854	
40.00	0.000	0.000	1.000	1.000	8.3654	8.3654	0.00%
40.00	0.002	0.005	0.998	0.995	8.3890	8.3754	0.16%
40.00	0.074	0.155	0.926	0.845	9.2100	8.7510	4.98%
40.00	0.076	0.159	0.924	0.841	9.2319	8.7618	5.09%
40.00	0.100	0.201	0.900	0.799	9.4917	8.8939	6.30%
40.00	0.200	0.352	0.800	0.648	10.5049	9.4827	9.73%
40.00	0.300	0.469	0.700	0.531	11.4106	10.1383	11.15%
40.00	0.400	0.566	0.600	0.434	12.2150	10.8649	11.05%
40.00	0.500	0.647	0.500	0.353	12.9251	11.6613	9.78%
40.00	0.600	0.720	0.400	0.280	13.5479	12.5129	7.64%
40.00	0.700	0.787	0.300	0.213	14.0897	13.3805	5.03%
40.00	0.702	0.788	0.298	0.212	14.0998	13.3976	4.98%
40.00	0.800	0.853	0.200	0.147	14.5541	14.1878	2.52%
40.00	0.900	0.922	0.100	0.078	14.9380	14.8296	0.73%
40.00	0.998	0.998	0.002	0.002	15.2195	15.2187	0.00%
40.00	1.000	1.000	0.000	0.000	15.2240	15.2240	0.00%
60.00	0.000	0.000	1.000	1.000	17.8054	17.8054	0.00%
60.00	0.002	0.004	0.998	0.996	17.8448	17.8248	0.11%
60.00	0.100	0.179	0.900	0.821	19.6882	18.8191	4.41%
60.00	0.118	0.207	0.882	0.793	20.0086	19.0115	4.98%
60.00	0.120	0.210	0.880	0.790	20.0438	19.0330	5.04%
60.00	0.200	0.321	0.800	0.679	21.3967	19.9276	6.87%
60.00	0.300	0.437	0.700	0.563	22.9338	21.1345	7.85%
60.00	0.400	0.535	0.600	0.465	24.3040	22.4363	7.68%
60.00	0.500	0.620	0.500	0.380	25.5135	23.8160	6.65%
60.00	0.600	0.697	0.400	0.303	26.5684	25.2322	5.03%
60.00	0.602	0.699	0.398	0.301	26.5880	25.2604	4.99%
60.00	0.700	0.770	0.300	0.230	27.4736	26.6056	3.16%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. 4310mee	Vapor mol. frac. 4310mee	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
60.00	0.800	0.841	0.200	0.159	28.2287	27.8133	1.47%
60.00	0.900	0.916	0.100	0.084	28.8212	28.7136	0.37%
60.00	0.998	0.998	0.002	0.002	29.2069	29.2064	0.00%
60.00	1.000	1.000	0.000	0.000	29.2123	29.2123	0.00%
80.00	0.000	0.000	1.000	1.000	34.1318	34.1318	0.00%
80.00	0.002	0.004	0.998	0.996	34.1923	34.1656	0.08%
80.00	0.100	0.162	0.900	0.838	37.0346	35.8870	3.10%
80.00	0.200	0.296	0.800	0.704	39.6869	37.7715	4.83%
80.00	0.216	0.315	0.784	0.685	40.0877	38.0847	5.00%
80.00	0.218	0.317	0.782	0.683	40.1374	38.1241	5.02%
80.00	0.300	0.409	0.700	0.591	42.0847	39.7786	5.48%
80.00	0.400	0.508	0.600	0.492	44.2265	41.8870	5.29%
80.00	0.442	0.546	0.558	0.454	45.0500	42.7930	5.01%
80.00	0.444	0.548	0.556	0.452	45.0881	42.8363	4.99%
80.00	0.500	0.596	0.500	0.404	46.1135	44.0512	4.47%
80.00	0.600	0.678	0.400	0.322	47.7468	46.1888	3.26%
80.00	0.700	0.755	0.300	0.245	49.1251	48.1693	1.95%
80.00	0.800	0.831	0.200	0.169	50.2384	49.8196	0.83%
80.00	0.900	0.911	0.100	0.089	51.0561	50.9657	0.18%
80.00	0.998	0.998	0.002	0.002	51.5019	51.5017	0.00%
	1.000	1.000	0.000	0.000	51.5065	51.5065	
100.00	0.000	0.000	1.000	1.000	60.1374	60.1374	0.00%
100.00	0.002	0.003	0.998	0.997	60.2250	60.1921	0.05%
100.00	0.100	0.148	0.900	0.852	64.3551	62.9516	2.18%
100.00	0.200	0.275	0.800	0.725	68.2291	65.9189	3.39%
100.00	0.300	0.386	0.700	0.614	71.7421	69.0116	3.81%
100.00	0.400	0.486	0.600	0.514	74.8807	72.1775	3.61%
100.00	0.500	0.576	0.500	0.424	77.6345	75.3279	2.97%
100.00	0.600	0.661	0.400	0.339	79.9938	78.3264	2.08%
100.00	0.700	0.742	0.300	0.258	81.9440	80.9846	1.17%
100.00	0.800	0.823	0.200	0.177	83.4575	83.0805	0.45%
100.00	0.900	0.907	0.100	0.093	84.4768	84.4146	0.07%
100.00	0.998	0.998	0.002	0.002	84.8843	84.8843	0.00%
100.00	1.000	1.000	0.000	0.000	84.8853	84.8853	0.00%
120.00	0.000	0.000	1.000	1.000	98.8993	98.8993	0.00%
120.00	0.002	0.003	0.998	0.997	99.0215	98.9831	0.04%
120.00	0.100	0.137	0.900	0.863	104.7995	103.1798	1.55%
120.00	0.200	0.258	0.800	0.742	110.2376	107.6130	2.38%
120.00	0.300	0.367	0.700	0.633	115.1747	112.1356	2.64%
120.00	0.400	0.467	0.600	0.533	119.5766	116.6474	2.45%
120.00	0.500	0.559	0.500	0.441	123.4131	121.0009	1.95%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. 4310mee	Vapor mol. frac. 4310mee	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
120.00	0.600	0.646	0.400	0.354	126.6546	124.9944	1.31%
120.00	0.700	0.731	0.300	0.269	129.2657	128.3788	0.69%
120.00	0.800	0.816	0.200	0.184	131.1928	130.8897	0.23%
120.00	0.900	0.904	0.100	0.096	132.3437	132.3115	0.02%
120.00	0.998	0.998	0.002	0.002	132.5570	132.5569	0.00%
	1.000	1.000	0.000	0.000	132.5503	132.5503	
140.00	0.000	0.000	1.000	1.000	153.6232	153.6232	0.00%
140.00	0.002	0.003	0.998	0.997	153.7917	153.7485	0.03%
140.00	0.100	0.128	0.900	0.872	161.7708	159.9762	1.11%
140.00	0.200	0.244	0.800	0.756	169.2911	166.4385	1.69%
140.00	0.300	0.351	0.700	0.649	176.1079	172.8860	1.83%
140.00	0.400	0.450	0.600	0.550	182.1522	179.1450	1.65%
140.00	0.500	0.544	0.500	0.456	187.3617	184.9877	1.27%
140.00	0.600	0.634	0.400	0.366	191.6773	190.1364	0.80%
140.00	0.700	0.722	0.300	0.278	195.0356	194.2849	0.38%
140.00	0.800	0.810	0.200	0.190	197.3537	197.1419	0.11%
140.00	0.900	0.902	0.100	0.098	198.5046	198.4955	0.00%
140.00	0.998	0.998	0.002	0.002	198.2953	198.2947	0.00%
	1.000	1.000	0.000	0.000	198.2752	198.2752	0.00%

The near-azeotropes of the Z-1233zd/HFC-43-10mee system at atmospheric pressure were also modeled. At each temperature, the model was run over the full range from 0 to 1 of Z-1233zd liquid molar composition in increments of 0.002. Among the combinations, some qualify as azeotropic or near-azeotropic, and it is these combinations that Applicant claims. For purposes of brevity, the listing of the combinations was edited to reflect increments of 0.1 Z-1233zd liquid molar composition, or the boundaries of near-azeotropic behavior. The resulting abridged listing is presented in Table 3.3.

Table 3.3. Predicted Near-Azeotropes of the Z-1233zd/HFC-43-10mee System at 1 Atm.

Pressure (atm)	Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. 4310mee	Vapor mol. frac. 4310mee	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
1.00	54.620	0.000	0.000	1.000	1.000	14.696	14.696	0.00%
1.00	54.555	0.002	0.004	0.998	0.996	14.696	14.678	0.12%
1.00	51.734	0.096	0.181	0.904	0.819	14.696	13.968	4.96%
1.00	51.678	0.098	0.184	0.902	0.816	14.696	13.955	5.04%
1.00	51.623	0.100	0.188	0.900	0.812	14.696	13.943	5.12%
1.00	49.075	0.200	0.337	0.800	0.663	14.696	13.475	8.31%
1.00	46.918	0.300	0.457	0.700	0.543	14.696	13.244	9.88%
1.00	45.096	0.400	0.557	0.600	0.443	14.696	13.214	10.08%
1.00	43.560	0.500	0.642	0.500	0.358	14.696	13.353	9.14%
1.00	42.266	0.600	0.717	0.400	0.283	14.696	13.624	7.29%
1.00	41.239	0.694	0.782	0.306	0.218	14.696	13.954	5.05%
1.00	41.219	0.696	0.783	0.304	0.217	14.696	13.961	5.00%
1.00	41.199	0.698	0.785	0.302	0.215	14.696	13.969	4.95%
1.00	41.179	0.700	0.786	0.300	0.214	14.696	13.976	4.90%
1.00	40.273	0.800	0.853	0.200	0.147	14.696	14.329	2.50%
1.00	39.539	0.900	0.922	0.100	0.078	14.696	14.588	0.74%
1.00	39.005	0.998	0.998	0.002	0.002	14.696	14.695	0.01%
1.00	38.996	1.000	1.000	0.000	0.000	14.696	14.696	0.00%

The data in Tables 3.2 and 3.3 are broadly summarized in Tables 3.4 and 3.5 below. The broad ranges of azeotrope-like compositions (based on [(BP-VP)/BP] x 100 ≤ 5) are summarized in Table 3.4, and compositions that meet the 3% near-azeotropic criterion ([(BP-VP)/BP] x 100 ≤ 3) are summarized in Table 3.5.

Table 3.4. Summarized Near-Azeotropes of the Z-1233zd/HFC-43-10mee System.

Components	T (°C)	Z-1233zd/HFC-43-10mee Liquid Mole Percentage Range
Z-1233zd / HFC-43-10mee	-40	94-99 / 6-1
Z-1233zd / HFC-43-10mee	-20	90-99 / 10-1
Z-1233zd / HFC-43-10mee	0	1-3/99-97 85-99 / 15-1
Z-1233zd / HFC-43-10mee	20	1-4 / 99-96 78-99 / 22-1
Z-1233zd / HFC-43-10mee	30.02	1-5 / 99-95 75-99 / 25-1
Z-1233zd / HFC-43-10mee	40	1-7 / 99-93 71-99 / 29-1
Z-1233zd / HFC-43-10mee	60	1-11 / 89-99 61-99 / 39-1
Z-1233zd / HFC-43-10mee	80	1-21 / 79-99 45-99 / 55-1
Z-1233zd / HFC-43-10mee	100	1-99 / 99-1
Z-1233zd / HFC-43-10mee	120	1-99 / 99-1
Z-1233zd / HFC-43-10mee	140	1-99 / 99-1

Table 3.5. Summarized 3% Near-Azeotropes of the Z-1233zd/HFC-43-10mee System.

Components	T (°C)	Z-1233zd/HFC-43-10mee Liquid Mole Percentage Range
Z-1233zd / HFC-4310mee	-40	96-99 / 4-1
Z-1233zd / HFC-4310mee	-20	93-99 / 7-1
Z-1233zd / HFC-4310mee	0	89-99 / 11-1
Z-1233zd / HFC-4310mee	20	84-99 / 16-1
Z-1233zd / HFC-4310mee	30.02	81-99 / 19-1
Z-1233zd / HFC-4310mee	40	1-4 / 99-96 78-99 / 22-1
Z-1233zd / HFC-4310mee	60	1-6 / 99-94 71-99 / 29-1
Z-1233zd / HFC-4310mee	80	1-9 / 99-91 62-99 / 38-1
Z-1233zd / HFC-4310mee	100	1-15 / 99-85 50-99
Z-1233zd / HFC-4310mee	120	1-99 / 99-1
Z-1233zd / HFC-4310mee	140	1-99 / 99-1

At atmospheric pressure , near azeotropic compositions were predicted at Z-1233zd/HFC-43-10mee mole percentage ratios of 1-9 / 99-91 and 70-99/30-1 . 3% near azeotropic compositions were predicted at Z-1233zd/HFC-43-10mee mole percentage ratios of 1-5 / 99-95 and 78-99 / 22-1

EXAMPLE 4: Z-1233zd/HFC-245fa

The binary system of Z-1233zd/HFC-245fa was explored for potential azeotropic and near-azeotropic behavior. To determine the relative volatility of this binary system, the PTx method described above was used. The pressure in a PTx cell of known volume was measured at constant temperature of 30 ºC for various binary compositions. The collected experimental data are displayed in Table 4.1 below.

Table 4.1. Experimental VLE Data for the Z-1233zd/HFC-245fa System at 30 deg. C.

X_2	Y_2	Pexp (psia)	Pcalc (psia)	Pcalc - Pexp (psia)
0.000	0.000	25.8120		
0.039	0.022	25.4290	25.3665	-0.0025
0.085	0.049	24.8830	24.8259	-0.0023
0.134	0.076	24.2920	24.2544	-0.0015
0.191	0.108	23.6040	23.5738	-0.0013
0.264	0.149	22.6980	22.6837	-0.0006
0.323	0.184	21.9630	21.9401	-0.0010
0.389	0.223	21.1220	21.0900	-0.0015
0.531	0.319	19.0760	19.1176	0.0022
0.597	0.371	18.1040	18.1387	0.0019
0.662	0.429	17.0830	17.1123	0.0017
0.731	0.501	15.9240	15.9384	0.0009
0.804	0.592	14.6430	14.6393	-0.0003
0.874	0.704	13.2870	13.2640	-0.0017
0.942	0.843	11.8760	11.8452	-0.0026
1.000	1.000	10.5540		

X_2 = liquid mole fraction of Z-1233zd.

Y_2 = vapor mole fraction of Z-1233zd.

P_{exp} = experimentally measured pressure.

The above vapor pressure v. Z-1233zd liquid mole fraction data are plotted in Figure 4. The experimental data points are shown in Figure 4 as solid points. The solid line represents bubble point predictions using the NRTL equation (see below). The dashed line represents predicted dew points.

Based on these VLE data, interaction coefficients were extracted. The NRTL model was run over a temperature range from -40 to 140 deg. C in 20 deg. Increments, as well as at 29.93 deg. C. At each temperature, the model was run over the full range from 0 to 1 of Z-1233zd liquid molar composition in increments of 0.002. Thus the model was run at a total of 5511 combinations of temperature and Z-1233zd liquid molar composition (11 temperatures x 501 compositions = 5511). Among those 5511 combinations, some qualify as near-azeotropic, and it is these combinations that Applicant claims. For purposes of brevity, the listing of the 5511 combinations was edited to reflect increments of 0.100 Z-1233zd liquid molar composition, or the boundaries of near-azeotropic behavior. The resulting abridged listing is presented in Table 4.2.

Table 4.2. Predicted Near-Azeotropes of the Z-1233zd/HFC-245fa System.

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. HFC-245fa	Vapor mol. frac. HFC-245fa	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
-40.00	0.000	0.000	1.000	1.000	0.8144	0.8144	0.00%
-40.00	0.002	0.001	0.998	0.999	0.8137	0.8131	0.07%
-40.00	0.100	0.053	0.900	0.947	0.7783	0.7421	4.65%
-40.00	0.104	0.055	0.896	0.945	0.7768	0.7389	4.88%
-40.00	0.106	0.056	0.894	0.944	0.7761	0.7373	5.00%
-40.00	0.108	0.057	0.892	0.943	0.7753	0.7357	5.12%
-40.00	0.200	0.101	0.800	0.899	0.7409	0.6585	11.13%
-40.00	0.300	0.149	0.700	0.851	0.7019	0.5775	17.73%
-40.00	0.400	0.198	0.600	0.802	0.6605	0.5073	23.19%
-40.00	0.500	0.252	0.500	0.748	0.6153	0.4493	26.98%
-40.00	0.600	0.316	0.400	0.684	0.5651	0.4017	28.92%
-40.00	0.700	0.398	0.300	0.602	0.5084	0.3625	28.69%
-40.00	0.800	0.512	0.200	0.488	0.4432	0.3299	25.56%
-40.00	0.900	0.686	0.100	0.314	0.3675	0.3024	17.71%
-40.00	0.978	0.911	0.022	0.089	0.2997	0.2839	5.29%
-40.00	0.980	0.918	0.020	0.082	0.2979	0.2834	4.85%
-40.00	0.998	0.991	0.002	0.009	0.2810	0.2795	0.53%
-40.00	1.000	1.000	0.000	0.000	0.2790	0.2790	0.00%
-20.00	0.000	0.000	1.000	1.000	2.7787	2.7787	0.00%
-20.00	0.002	0.001	0.998	0.999	2.7762	2.7744	0.07%
-20.00	0.100	0.054	0.900	0.946	2.6548	2.5384	4.39%
-20.00	0.110	0.059	0.890	0.941	2.6423	2.5123	4.92%
-20.00	0.112	0.060	0.888	0.940	2.6397	2.5070	5.03%
-20.00	0.200	0.104	0.800	0.896	2.5271	2.2707	10.14%
-20.00	0.300	0.154	0.700	0.846	2.3939	2.0119	15.96%
-20.00	0.400	0.207	0.600	0.793	2.2527	1.7840	20.81%
-20.00	0.500	0.265	0.500	0.735	2.1002	1.5918	24.21%
-20.00	0.600	0.333	0.400	0.667	1.9325	1.4317	25.92%
-20.00	0.700	0.419	0.300	0.581	1.7450	1.2980	25.61%
-20.00	0.800	0.535	0.200	0.465	1.5325	1.1857	22.63%
-20.00	0.900	0.707	0.100	0.293	1.2892	1.0903	15.43%
-20.00	0.974	0.905	0.026	0.095	1.0855	1.0286	5.24%
-20.00	0.976	0.912	0.024	0.088	1.0797	1.0271	4.87%
-20.00	0.998	0.992	0.002	0.008	1.0146	1.0101	0.44%
-20.00	1.000	1.000	0.000	0.000	1.0086	1.0086	0.00%
0.00	0.000	0.000	1.000	1.000	7.6333	7.6333	0.00%
0.00	0.100	0.055	0.900	0.945	7.2931	6.9946	4.09%
0.00	0.118	0.065	0.882	0.935	7.2309	6.8717	4.97%
0.00	0.120	0.066	0.880	0.934	7.2239	6.8579	5.07%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. HFC-245fa	Vapor mol. frac. HFC-245fa	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
0.00	0.200	0.108	0.800	0.892	6.9425	6.3028	9.21%
0.00	0.300	0.160	0.700	0.840	6.5774	5.6344	14.34%
0.00	0.400	0.216	0.600	0.784	6.1920	5.0379	18.64%
0.00	0.500	0.278	0.500	0.722	5.7784	4.5261	21.67%
0.00	0.600	0.350	0.400	0.650	5.3276	4.0934	23.17%
0.00	0.700	0.439	0.300	0.561	4.8291	3.7277	22.81%
0.00	0.800	0.557	0.200	0.443	4.2712	3.4172	19.99%
0.00	0.900	0.727	0.100	0.273	3.6405	3.1515	13.43%
0.00	0.970	0.901	0.030	0.099	3.1479	2.9876	5.09%
0.00	0.972	0.907	0.028	0.093	3.1331	2.9832	4.79%
0.00	0.998	0.993	0.002	0.007	2.9376	2.9266	0.38%
	1.000	1.000	0.000	0.000	2.9223	2.9223	0.00%
20.00	0.000	0.000	1.000	1.000	17.7440	17.7440	0.00%
20.00	0.002	0.001	0.998	0.999	17.7284	17.7172	0.06%
20.00	0.100	0.057	0.900	0.943	16.9549	16.3154	3.77%
20.00	0.200	0.112	0.800	0.888	16.1417	14.7991	8.32%
20.00	0.300	0.167	0.700	0.833	15.2965	13.3341	12.83%
20.00	0.400	0.226	0.600	0.774	14.4073	12.0106	16.64%
20.00	0.500	0.291	0.500	0.709	13.4592	10.8580	19.33%
20.00	0.600	0.367	0.400	0.633	12.4347	9.8696	20.63%
20.00	0.700	0.459	0.300	0.541	11.3136	9.0247	20.23%
20.00	0.800	0.578	0.200	0.422	10.0734	8.3003	17.60%
20.00	0.900	0.744	0.100	0.256	8.6893	7.6758	11.66%
20.00	0.964	0.893	0.036	0.107	7.7153	7.3203	5.12%
20.00	0.966	0.899	0.034	0.101	7.6836	7.3097	4.87%
20.00	0.998	0.994	0.002	0.006	7.1667	7.1438	0.32%
20.00	1.000	1.000	0.000	0.000	7.1337	7.1337	0.00%
29.93	0.000	0.000	1.000	1.000	25.7347	25.7347	0.00%
29.93	0.002	0.001	0.998	0.999	25.7122	25.6964	0.06%
29.93	0.100	0.058	0.900	0.942	24.5914	23.7058	3.60%
29.93	0.132	0.076	0.868	0.924	24.2187	23.0247	4.93%
29.93	0.134	0.077	0.866	0.923	24.1952	22.9819	5.01%
29.93	0.200	0.114	0.800	0.886	23.4135	21.5692	7.88%
29.93	0.300	0.171	0.700	0.829	22.1903	19.5038	12.11%
29.93	0.400	0.231	0.600	0.769	20.9059	17.6272	15.68%
29.93	0.500	0.298	0.500	0.702	19.5407	15.9815	18.21%
29.93	0.600	0.375	0.400	0.625	18.0715	14.5608	19.43%
29.93	0.700	0.469	0.300	0.531	16.4722	13.3397	19.02%
29.93	0.800	0.589	0.200	0.411	14.7134	12.2880	16.48%
29.93	0.900	0.753	0.100	0.247	12.7629	11.3779	10.85%
29.93	0.960	0.887	0.040	0.113	11.4861	10.8896	5.19%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. HFC-245fa	Vapor mol. frac. HFC-245fa	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
29.93	0.962	0.892	0.038	0.108	11.4420	10.8740	4.96%
29.93	0.998	0.994	0.002	0.006	10.6315	10.6003	0.29%
29.93	1.000	1.000	0.000	0.000	10.5854	10.5854	
40.00	0.000	0.000	1.000	1.000	36.2187	36.2187	0.00%
40.00	0.002	0.001	0.998	0.999	36.1870	36.1656	0.06%
40.00	0.100	0.059	0.900	0.941	34.6109	33.4249	3.43%
40.00	0.140	0.082	0.860	0.918	33.9549	32.2577	5.00%
40.00	0.142	0.083	0.858	0.917	33.9218	32.1991	5.08%
40.00	0.200	0.116	0.800	0.884	32.9548	30.5018	7.44%
40.00	0.300	0.175	0.700	0.825	31.2365	27.6736	11.41%
40.00	0.400	0.237	0.600	0.763	29.4360	25.0900	14.76%
40.00	0.500	0.305	0.500	0.695	27.5282	22.8091	17.14%
40.00	0.600	0.384	0.400	0.616	25.4838	20.8277	18.27%
40.00	0.700	0.479	0.300	0.521	23.2696	19.1153	17.85%
40.00	0.800	0.599	0.200	0.401	20.8490	17.6340	15.42%
40.00	0.900	0.761	0.100	0.239	18.1816	16.3474	10.09%
40.00	0.958	0.887	0.042	0.113	16.5045	15.6778	5.01%
40.00	0.960	0.892	0.040	0.108	16.4448	15.6556	4.80%
40.00	0.998	0.994	0.002	0.006	15.2863	15.2450	0.27%
40.00	1.000	1.000	0.000	0.000	15.2240	15.2240	0.00%
60.00	0.000	0.000	1.000	1.000	66.7688	66.7688	0.00%
60.00	0.002	0.001	0.998	0.999	66.7103	66.6745	0.05%
60.00	0.100	0.061	0.900	0.939	63.8046	61.8505	3.06%
60.00	0.154	0.094	0.846	0.906	62.1686	59.0973	4.94%
60.00	0.156	0.095	0.844	0.905	62.1075	58.9951	5.01%
60.00	0.200	0.122	0.800	0.878	60.7530	56.7525	6.58%
60.00	0.300	0.183	0.700	0.817	57.5940	51.8058	10.05%
60.00	0.400	0.249	0.600	0.751	54.2984	47.2405	13.00%
60.00	0.500	0.321	0.500	0.679	50.8292	43.1587	15.09%
60.00	0.600	0.402	0.400	0.598	47.1437	39.5701	16.07%
60.00	0.700	0.499	0.300	0.501	43.1938	36.4366	15.64%
60.00	0.800	0.619	0.200	0.381	38.9270	33.7028	13.42%
60.00	0.900	0.777	0.100	0.223	34.2865	31.3120	8.68%
60.00	0.948	0.874	0.052	0.126	31.9089	30.2707	5.13%
60.00	0.950	0.878	0.050	0.122	31.8075	30.2287	4.96%
60.00	0.998	0.995	0.002	0.005	29.3184	29.2517	0.23%
60.00	1.000	1.000	0.000	0.000	29.2123	29.2123	0.00%
80.00	0.000	0.000	1.000	1.000	113.6113	113.6113	0.00%
80.00	0.002	0.001	0.998	0.999	113.5114	113.4575	0.05%
80.00	0.100	0.064	0.900	0.936	108.5492	105.6388	2.68%
80.00	0.176	0.113	0.824	0.887	104.6058	99.3861	4.99%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. HFC-245fa	Vapor mol. frac. HFC-245fa	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
80.00	0.178	0.114	0.822	0.886	104.5008	99.2215	5.05%
80.00	0.200	0.128	0.800	0.872	103.3418	97.4158	5.73%
80.00	0.300	0.193	0.700	0.807	97.9667	89.4034	8.74%
80.00	0.400	0.262	0.600	0.738	92.3874	81.9355	11.31%
80.00	0.500	0.337	0.500	0.663	86.5569	75.1801	13.14%
80.00	0.600	0.422	0.400	0.578	80.4199	69.1746	13.98%
80.00	0.700	0.520	0.300	0.480	73.9150	63.8800	13.58%
80.00	0.800	0.640	0.200	0.360	66.9753	59.2239	11.57%
80.00	0.900	0.793	0.100	0.207	59.5304	55.1252	7.40%
80.00	0.938	0.864	0.062	0.136	56.5536	53.6975	5.05%
80.00	0.940	0.868	0.060	0.132	56.3946	53.6242	4.91%
80.00	0.998	0.995	0.002	0.005	51.6732	51.5747	0.19%
	1.000	1.000	0.000	0.000	51.5065	51.5065	
100.00	0.000	0.000	1.000	1.000	181.5097	181.5097	0.00%
100.00	0.002	0.001	0.998	0.999	181.3487	181.2754	0.04%
100.00	0.100	0.068	0.900	0.932	173.3471	169.3983	2.28%
100.00	0.200	0.136	0.800	0.864	164.9587	156.9132	4.88%
100.00	0.204	0.138	0.796	0.862	164.6184	156.4152	4.98%
100.00	0.206	0.140	0.794	0.860	164.4481	156.1664	5.04%
100.00	0.300	0.205	0.700	0.795	156.3322	144.6793	7.45%
100.00	0.400	0.277	0.600	0.723	147.4334	133.1677	9.68%
100.00	0.500	0.355	0.500	0.645	138.2123	122.6421	11.27%
100.00	0.600	0.442	0.400	0.558	128.6074	113.1890	11.99%
100.00	0.700	0.542	0.300	0.458	118.5491	104.7811	11.61%
100.00	0.800	0.661	0.200	0.339	107.9624	97.3327	9.85%
100.00	0.900	0.808	0.100	0.192	96.7681	90.7369	6.23%
100.00	0.924	0.849	0.076	0.151	93.9821	89.2685	5.02%
100.00	0.926	0.853	0.074	0.147	93.7481	89.1481	4.91%
100.00	0.998	0.996	0.002	0.004	85.1302	84.9957	0.16%
100.00	1.000	1.000	0.000	0.000	84.8853	84.8853	0.00%
120.00	0.000	0.000	1.000	1.000	276.0074	276.0074	0.00%
120.00	0.002	0.001	0.998	0.999	275.7583	275.6697	0.03%
120.00	0.100	0.073	0.900	0.927	263.3647	258.5244	1.84%
120.00	0.200	0.145	0.800	0.855	250.3842	240.4131	3.98%
120.00	0.246	0.179	0.754	0.821	244.3120	232.1144	4.99%
120.00	0.248	0.180	0.752	0.820	244.0466	231.7560	5.04%
120.00	0.300	0.218	0.700	0.782	237.1040	222.5367	6.14%
120.00	0.400	0.294	0.600	0.706	223.5188	205.5642	8.03%
120.00	0.500	0.376	0.500	0.624	209.5934	189.8986	9.40%
120.00	0.600	0.465	0.400	0.535	195.2721	175.7050	10.02%
120.00	0.700	0.565	0.300	0.435	180.4862	162.9836	9.70%

Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. HFC-245fa	Vapor mol. frac. HFC-245fa	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
120.00	0.800	0.682	0.200	0.318	165.1587	151.6417	8.18%
120.00	0.900	0.823	0.100	0.177	149.2079	141.5453	5.14%
120.00	0.902	0.826	0.098	0.174	148.8820	141.3551	5.06%
120.00	0.904	0.829	0.096	0.171	148.5557	141.1653	4.97%
120.00	0.998	0.996	0.002	0.004	132.8909	132.7203	0.13%
	1.000	1.000	0.000	0.000	132.5503	132.5503	
140.00	0.000	0.000	1.000	1.000	403.8797	403.8797	0.00%
140.00	0.002	0.002	0.998	0.998	403.5025	403.4156	0.02%
140.00	0.100	0.080	0.900	0.920	384.6271	379.5635	1.32%
140.00	0.200	0.158	0.800	0.842	364.8595	354.0001	2.98%
140.00	0.300	0.236	0.700	0.764	344.8410	328.5830	4.71%
140.00	0.316	0.248	0.684	0.752	341.6231	324.6035	4.98%
140.00	0.318	0.250	0.682	0.750	341.2206	324.1083	5.02%
140.00	0.400	0.316	0.600	0.684	324.6726	304.3234	6.27%
140.00	0.500	0.400	0.500	0.600	304.3601	281.8149	7.41%
140.00	0.600	0.491	0.400	0.509	283.8567	261.3120	7.94%
140.00	0.700	0.591	0.300	0.409	263.0876	242.8404	7.70%
140.00	0.800	0.705	0.200	0.295	241.9640	226.2934	6.48%
140.00	0.866	0.791	0.134	0.209	227.7826	216.3456	5.02%
140.00	0.868	0.793	0.132	0.207	227.3495	216.0555	4.97%
140.00	0.900	0.839	0.100	0.161	220.3917	211.5016	4.03%
140.00	0.998	0.996	0.002	0.004	198.7235	198.5256	0.10%
	1.000	1.000	0.000	0.000	198.2752	198.2752	0.00%

The model was run for the Z-1233zd/HFC-245fa system at atmospheric pressure over the range of liquid mole percents of Z=1233zd from 0 to 1 in increments of 0.002. The abridged results are presented in Table 4.3, wherein compositions that meet the near-azeotropic criterion ([(BP-VP)/BP] x 100 ≤ 5) are displayed. Results are given in liquid mole fractional increments of 0.100 up to the point of criterion failure.

Table 4.3. Near-Azeotropes of the Z-1233zd/HFC245fa System at 1 Atm.

Pressure (atm)	Temp. (deg. C)	Liquid mol. frac. Z-1233zd	Vapor mol. frac. Z-1233zd	Liquid mol. frac. HFC-245fa	Vapor mol. frac. HFC-245fa	Bubble Point Pressure (psia)	Dew Point Pressure (psia)	[(BP-DP)/ BP] x 100
1.00	15.222	0.000	0.000	1.000	1.000	14.6960	14.6960	0.00%
1.00	15.244	0.002	0.001	0.998	0.999	14.6960	14.6865	0.06%
1.00	16.358	0.100	0.056	0.900	0.944	14.6960	14.1328	3.83%
1.00	16.670	0.126	0.071	0.874	0.929	14.6960	13.9630	4.99%
1.00	16.694	0.128	0.072	0.872	0.928	14.6960	13.9496	5.08%
1.00	17.598	0.200	0.111	0.800	0.889	14.6960	13.4580	8.42%
1.00	18.969	0.300	0.167	0.700	0.833	14.6960	12.7996	12.90%
1.00	20.514	0.400	0.226	0.600	0.774	14.6960	12.2585	16.59%
1.00	22.289	0.500	0.293	0.500	0.707	14.6960	11.8936	19.07%
1.00	24.377	0.600	0.370	0.400	0.630	14.6960	11.7423	20.10%
1.00	26.890	0.700	0.466	0.300	0.534	14.6960	11.8462	19.39%
1.00	29.987	0.800	0.588	0.200	0.412	14.6960	12.2729	16.49%
1.00	33.905	0.900	0.756	0.100	0.244	14.6960	13.1456	10.55%
1.00	36.686	0.958	0.885	0.042	0.115	14.6960	13.9403	5.14%
1.00	36.790	0.960	0.890	0.040	0.110	14.6960	13.9725	4.92%
1.00	38.880	0.998	0.994	0.002	0.006	14.6960	14.6559	0.27%
1.00	38.996	1.000	1.000	0.000	0.000	14.6960	14.6960	0.00%

The data in Tables 4.2 and 4.3 are broadly summarized in Tables 4.4 and 4.5 below. The broad ranges of azeotrope-like compositions (based on [(BP-VP)/BP] x 100 ≤ 5) are summarized in Table 4.4, and compositions that meet the 3% near-azeotropic criterion ([(BP-VP)/BP] x 100 ≤ 3) are summarized in Table 4.5.

Table 4.4. Summarized Near-Azeotropes of the Z-1233zd/HFC-245fa System.

Components	T (°C)	Z-1233zd/HFC-245fa Liquid Mole Percentage Range
Z-1233zd / HFC-245fa	-40	1-10 / 99-90 98-99 /2-1
Z-1233zd / HFC-245fa	-20	1-11 / 99-89 98-99 / 2-1
Z-1233zd / HFC-245fa	0	1-11 / 99-89
Z-1233zd / HFC-245fa	20	1-12 / 99-88 97-99 / 3-1
Z-1233zd / HFC-245fa	30.02	1-13 / 99-87 97-99 / 3-1
Z-1233zd / HFC-245fa	40	1-14 / 99-86 96-99 /4-1
Z-1233zd / HFC-245fa	60	1-15 / 99-85 95-99 / 5-1
Z-1233zd / HFC-245fa	80	1-17 / 99-83 93-99 / 7-1
Z-1233zd / HFC-245fa	100	1-20 / 99-80 92-99 / 8-1
Z-1233zd / HFC-245fa	120	1-24 / 99-76 91-99 / 9-1
Z-1233zd / HFC-245fa	140	1-31 / 99-69 87-99 / 13-1

Table 4.5. Summarized 3% Near-Azeotropes of the Z-1233zd/HFC-245fa System.

Components	T (°C)	Z-1233zd/HFC-245fa Liquid Mole Percentage Range
Z-1233zd / HFC-245fa	-40	1-7 / 99-93
Z-1233zd / HFC-245fa	-20	1-7 / 99-93
Z-1233zd / HFC-245fa	0	1-7 / 99-93
Z-1233zd / HFC-245fa	20	1-8 / 99-92 98-99/2-1
Z-1233zd / HFC-245fa	30.02	1-8 / 99-92 98-99/2-1
Z-1233zd / HFC-245fa	40	1-8 / 99-92 98-99/2-1
Z-1233zd / HFC-245fa	60	1-9 / 99-91 98-99/2-1
Z-1233zd / HFC-245fa	80	1-11 / 99-89 97-99 / 3-1
Z-1233zd / HFC-245fa	100	1-12/ 99-88 96-99 / 4-1
Z-1233zd / HFC-245fa	120	1-15 / 99-85 95-99 / 5-1
Z-1233zd / HFC-245fa	140	1-20 / 99-80 94-99 / 6-1

At atmospheric pressure, near azeotropic compositions were predicted at Z-1233zd to HFC-245fa mole percentage ratios of 1-12 / 99-88 and 96-99 /4-1 Z-1233zd liquid mole percent. 3% near azeotropic compositions were predicted at 1-8 / 99-92 and 98-99 / 2-1.

All references cited herein are incorporated in their entirety.

Those of skill in the art will understand that the invention is not limited to the scope of only those specific embodiments described herein, but rather extends to all equivalents, variations and extensions thereof.

CLAIMS

What is claimed is the following:

1. A composition comprising Z-1233zd and a second component, wherein said second component is selected from the group consisting of:
   (a) Methyl formate;
   (b) Dimethoxymethane;
   (c) HFC-43-10-mee; and,
   (d) HFC-245fa,

   wherein the second component is present in an effective amount to form an azeotrope or azeotrope-like mixture with the Z-1233zd.

2. The azeotrope-like composition of claim 1, comprising from 1 to 99 mole % Z-1233zd and from 99 mole % to 1 mole percent methylformate at a temperature of from -40 C to 140 C.

3. The azeotropic or azeotrope-like composition of claim 1, comprising from 38.0 to 47.1 mole % Z-1233zd and from 53.9 mole % to 62.0 mole % dimethoxymethane.

4. The composition of claim 3, wherein the vapor pressure is from 0.18 psia to 174.86 psia, at a temperature of from -40 C to 140 C.

5. The azeotrope-like composition of claim 1, comprising 1 to 99 mole % 1233zd and from 99 mole % to 1 mole percent % dimethoxymethane at a temperature of from -40 C to 140 C.

6. The azeotropic or azeotrope-like composition of claim 1, comprising from 1 to 5 mole % and from 78 to 99 mole % 1233zd and from 99 to 95 mole percent and 1 to 22 mole percent HFC-43-10mee at a temperature of from -40 C to 140 C.

7. The azeotropic or azeotrope-like composition of claim 1, comprising from 1 to 12 mole % and from 96 to 99 mole % 1233zd and from 99 to 88 mole percent and 1 to 4 mole percent HFC-245fa at a temperature of from -40 C to 140 C.

8. The composition according to Claim 1 further comprising an additive selected from the group consisting of lubricants, pour point modifiers, anti-foam agents, viscosity improvers, emulsifiers dispersants,

oxidation inhibitors, extreme pressure agents, corrosion inhibitors, detergents, catalysts, surfactants, flame retardants, preservatives, colorants, antioxidants, reinforcing agents, fillers, antistatic agents, solubilizing agents, IR attenuating agents, nucleating agents, cell controlling agents, extrusion aids, stabilizing agents, thermally insulating agents, plasticizers, viscosity modifiers, impact modifiers, gas barrier resins, polymer modifiers, rheology modifiers, antibacterial agents, vapor pressure modifiers, UV absorbers, cross-linking agents, permeability modifiers, bitterants, propellants and acid catchers.

9. A process of forming a foam comprising:
   (a) adding a foamable composition to a blowing agent; and,
   (b) reacting said foamable composition under conditions effective to form a foam,

wherein said blowing agent comprises the composition according to Claim 1.

10. A foam formed by the process according to Claim 9.

11. A foam comprising a polymer and the composition according to Claim 1.

12. A pre-mix composition comprising a foamable component and a blowing agent, said blowing agent comprising the composition according to Claim 1.

13. A process for producing refrigeration comprising;
   (a) condensing the composition according to Claim 1; and,
   (b) evaporating said composition in the vicinity of a body to be cooled.

14. A heat transfer system comprising a heat transfer medium, wherein said heat transfer medium comprises the composition according to Claim 1.

15. A method of cleaning a surface comprising bringing the composition according to Claim 1 into contact with said surface.

16. An aerosol product comprising a component to be dispensed and a propellant, wherein said propellant comprises the composition according to Claim 1.

17. A method for extinguishing or suppressing a flame comprising dispensing the composition according to Claim 1 at said flame.

18. A system for preventing or suppressing a flame comprising a vessel containing the composition according to Claim 1 and a nozzle to dispense said composition toward an anticipated or actual location of said flame.

19. A process for dissolving a solute comprising contacting and mixing said solute with a sufficient quantity of the composition according to Claim 1.

20. A method for preventing or rapidly quenching an electric discharge in a space in a high voltage device comprising injecting a gaseous dielectric into said space, wherein said gaseous dielectric comprises the composition according to Claim 1.

21. A high voltage device comprising a gaseous dielectric, wherein said gaseous dielectric comprises the composition according to Claim 1.

22. The high voltage device according to Claim 21 selected from the group consisting of a transformer, a circuit breaker, a switch and a radar waveguide.

FIG. 1

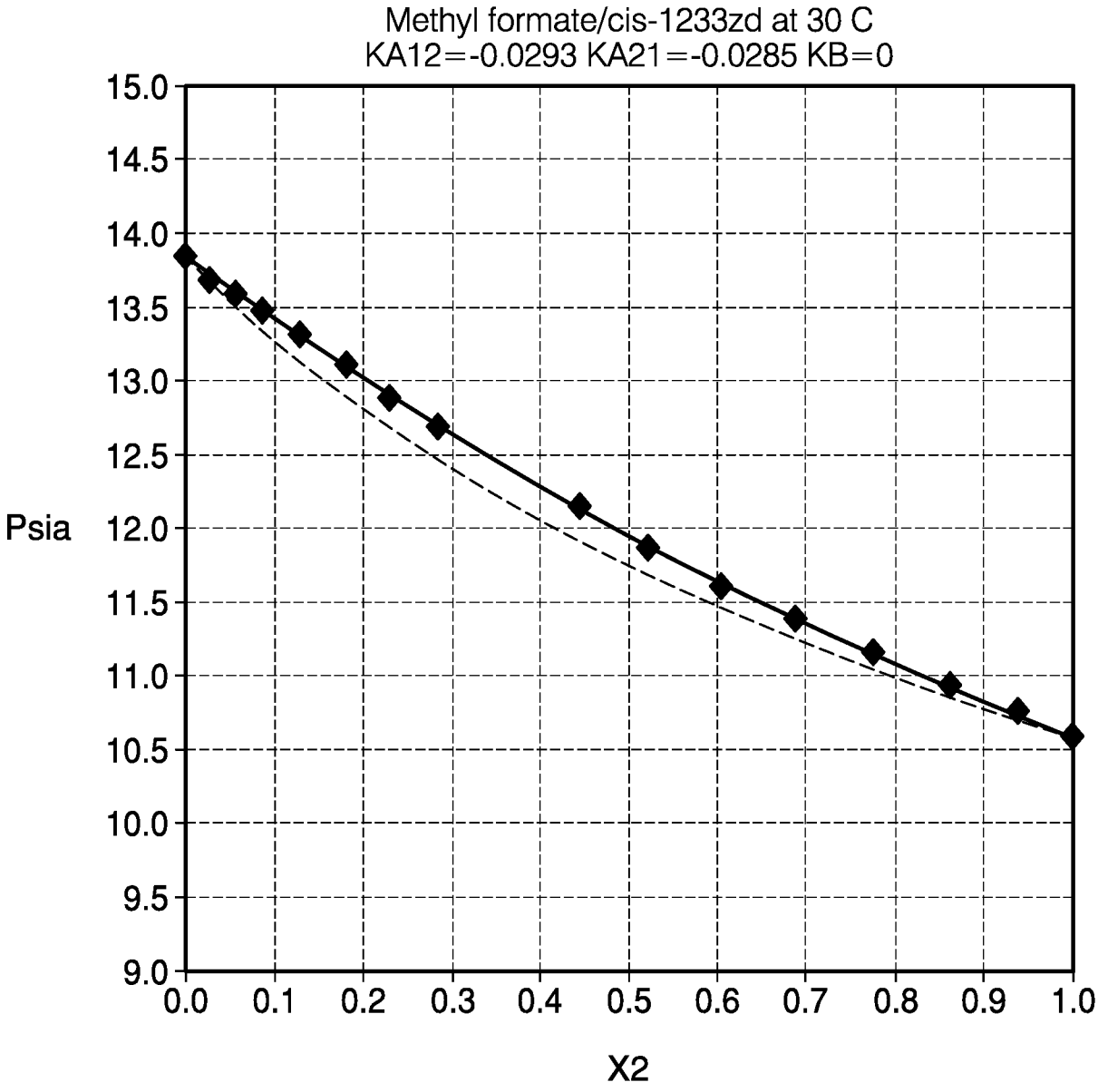

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12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
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0.4
0.5
0.6
0.7
0.8
0.9
1.0
X2

FIG. 2

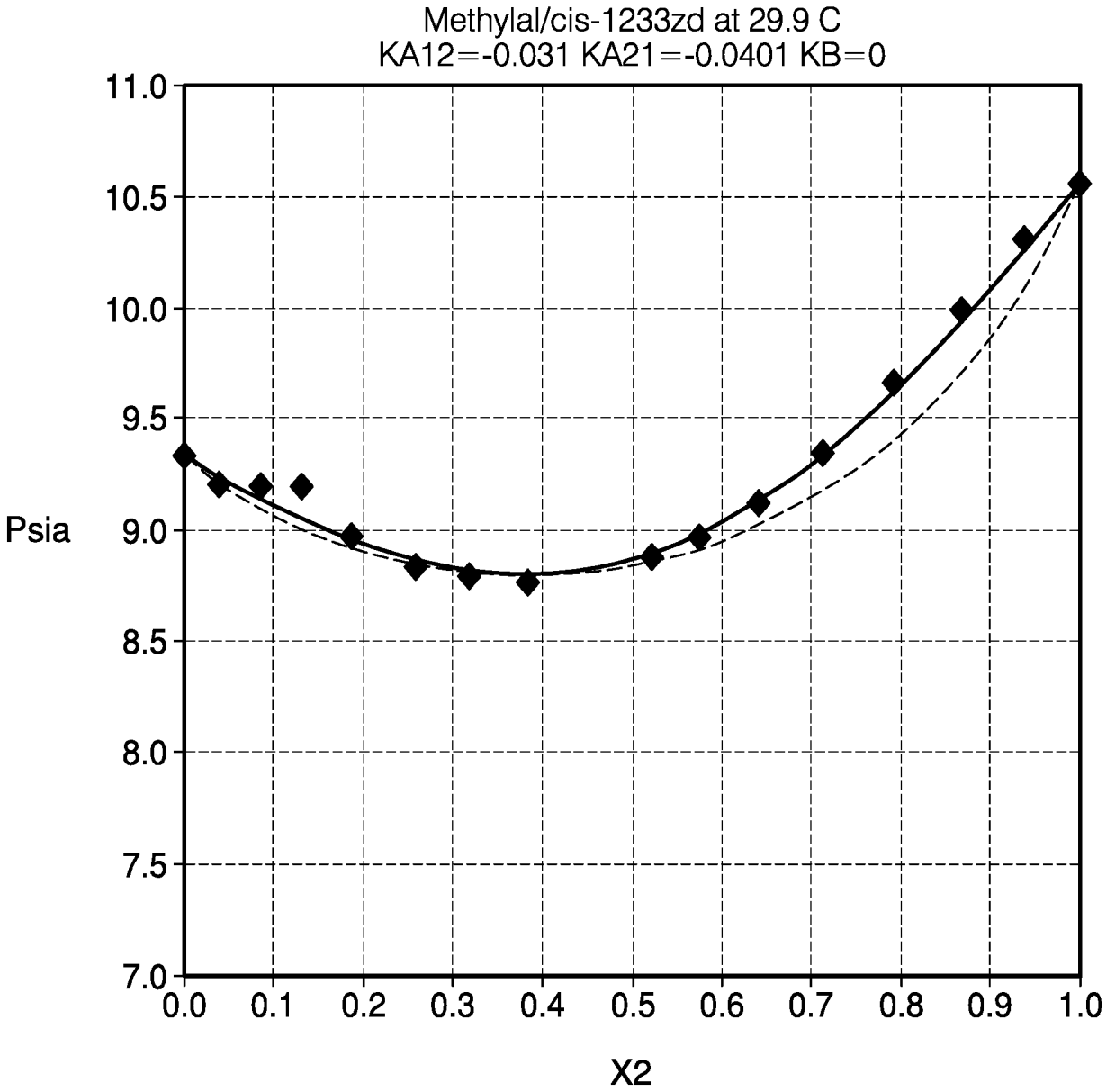

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0.6
0.7
0.8
0.9
1.0
X2

FIG. 3

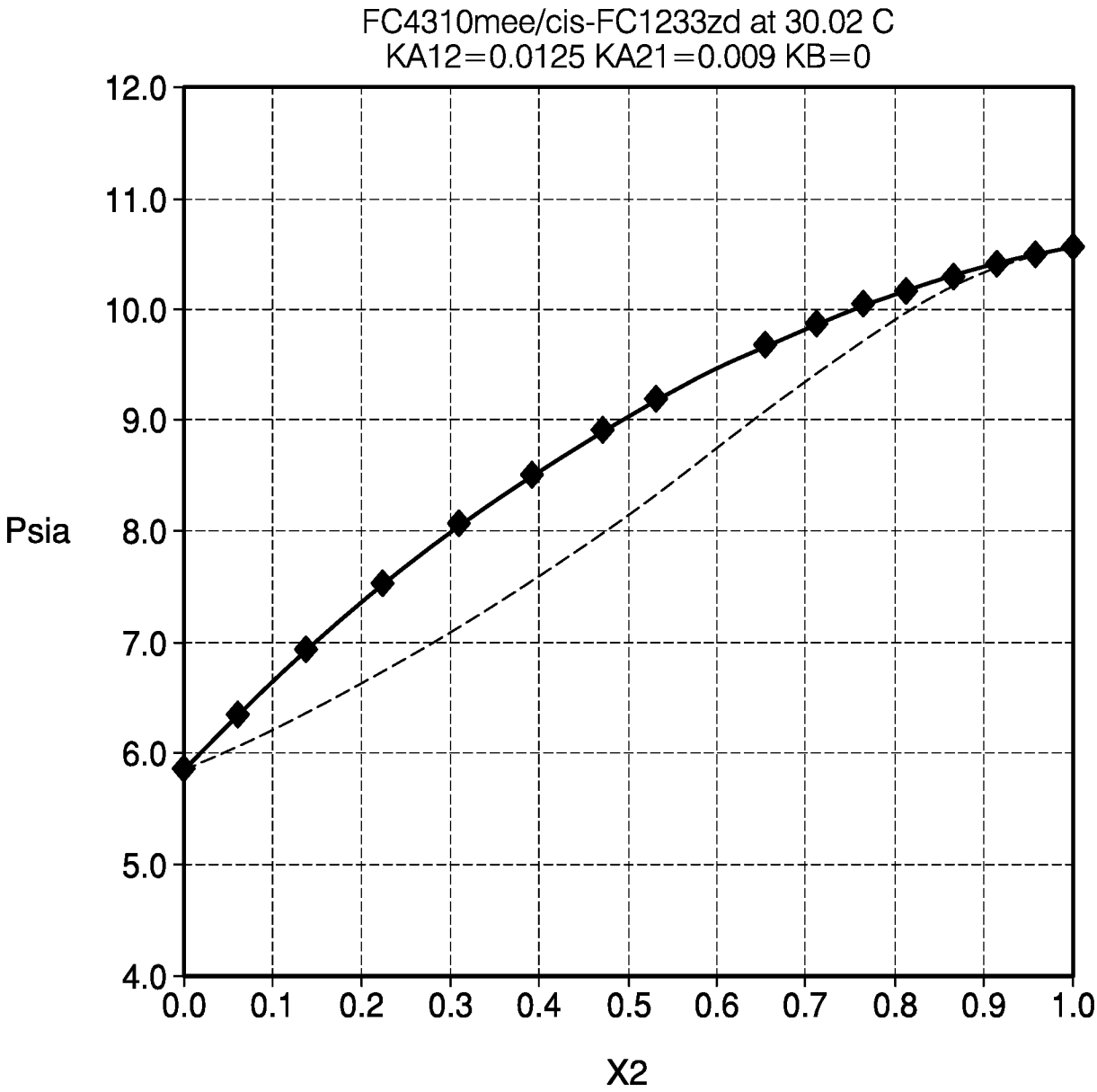
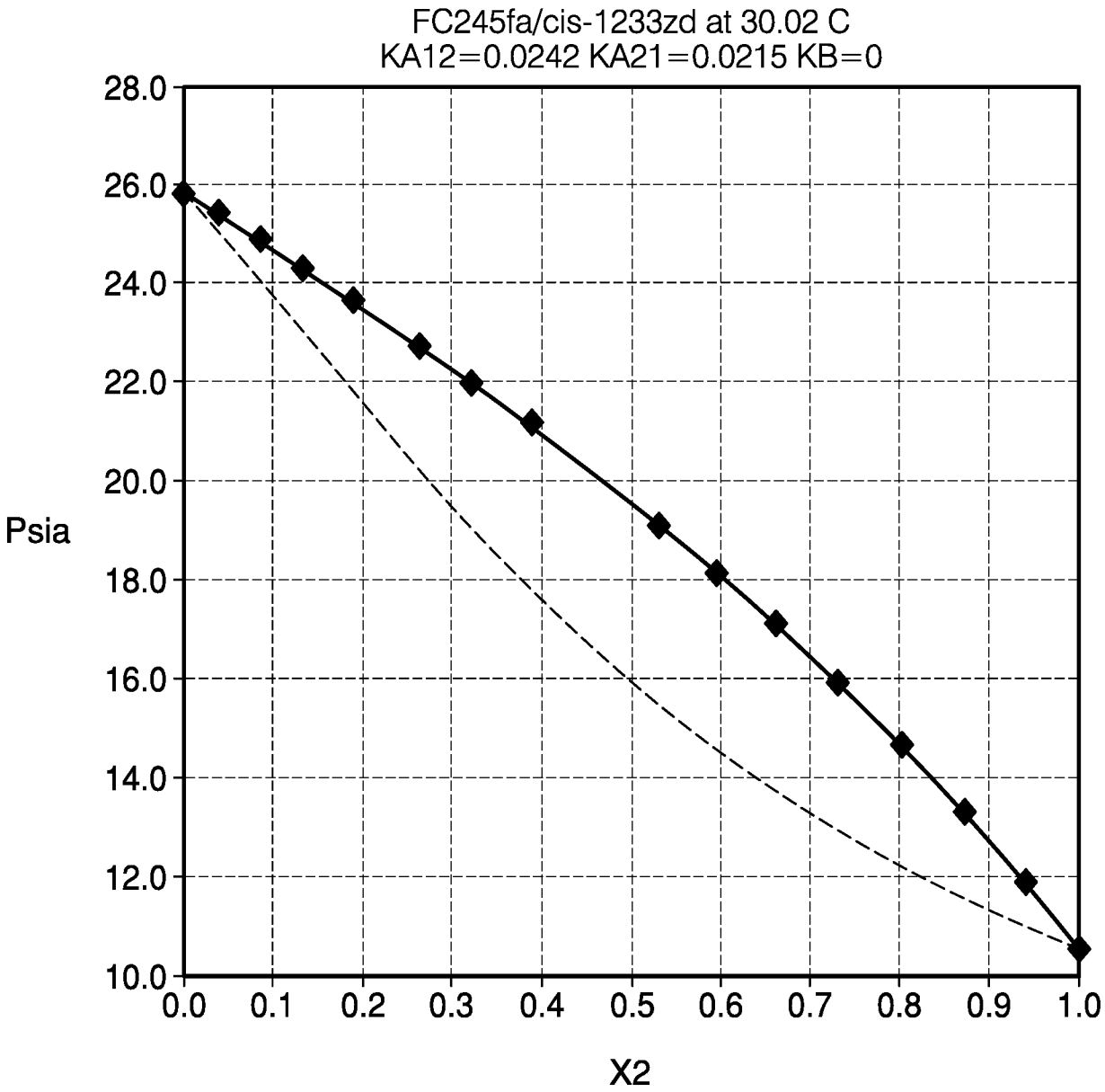

FC4310mee/cis-FC1233zd at 30.02 C
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0.9
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X2

FIG. 4


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0.8
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1.0
X2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/023001

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K3/30 A62D1/00 C09K5/04 C08J9/14 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)
C09K A62D C08J 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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2009/305876 A1 (SINGH RAJIV RATNA [US] ET AL) 10 December 2009 (2009-12-10) paragraphs [0052], [0068], [0076], [0079], [0103], [0104], [0205] - [0208], [0212], [0226] paragraphs [0249], [0255], [0271] - [0273] table on page 13 and 14 claims	1,2,6-19 20-22
X	US 7 438 825 B1 (CHEN BENJAMIN BIN [US] ET AL) 21 October 2008 (2008-10-21) the whole document	1,3-5, 8-16,19
X	WO 2009/061557 A1 (ARKEMA INC [US]; CHEN BENJAMIN B [US]; BONNET PHILIPPE [US]) 14 May 2009 (2009-05-14) the whole document	1,2, 8-16,19

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 June 2017	23/06/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Puetz, Christine

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/023001

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010/078585 A1 (ROBIN MARK [US]) 1 April 2010 (2010-04-01)	20-22
A	claims 21-36; tables 1-3,15-18	1-19

A	US 2011/232939 A1 (LULY MATTHEW H [US] ET AL) 29 September 2011 (2011-09-29) claims	1-22

A	US 2013/109771 A1 (HULSE RYAN [US] ET AL) 2 May 2013 (2013-05-02) the whole document	1-19

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/023001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009305876 A1	10-12-2009	BR PI0907370 A2	14-07-2015
		CA 2711861 A1	16-07-2009
		CN 102015050 A	13-04-2011
		CN 104045848 A	17-09-2014
		CN 104045849 A	17-09-2014
		CN 104045850 A	17-09-2014
		CN 104046332 A	17-09-2014
		EP 2234685 A2	06-10-2010
		EP 2712907 A1	02-04-2014
		EP 2719738 A1	16-04-2014
		EP 2719739 A1	16-04-2014
		EP 2727974 A1	07-05-2014
		JP 6074459 B2	01-02-2017
		JP 2011510119 A	31-03-2011
		JP 2014145081 A	14-08-2014
		JP 2015187279 A	29-10-2015
		JP 2016104873 A	09-06-2016
		KR 20110008156 A	26-01-2011
		KR 20160066559 A	10-06-2016
		MX 343610 B	14-11-2016
		RU 2010133493 A	20-02-2012
		TW 200940480 A	01-10-2009
		TW 201623202 A	01-07-2016
		US 2009305876 A1	10-12-2009
		US 2017158833 A1	08-06-2017
		WO 2009089511 A2	16-07-2009
		ZA 201004854 B	28-09-2011
US 7438825 B1	21-10-2008	CN 101959988 A	26-01-2011
		EP 2252671 A1	24-11-2010
		JP 4951124 B2	13-06-2012
		JP 2011513547 A	28-04-2011
		KR 20100134586 A	23-12-2010
		US 7438825 B1	21-10-2008
		WO 2009110925 A1	11-09-2009
WO 2009061557 A1	14-05-2009	CN 101848975 A	29-09-2010
		EP 2215174 A1	11-08-2010
		ES 2534231 T3	20-04-2015
		JP 4951123 B2	13-06-2012
		JP 2011503291 A	27-01-2011
		KR 20100084171 A	23-07-2010
		US 7479238 B1	20-01-2009
		WO 2009061557 A1	14-05-2009
US 2010078585 A1	01-04-2010	AU 2008246132 A1	06-11-2008
		BR PI0807301 A2	06-05-2014
		CA 2680166 A1	06-11-2008
		CN 101668566 A	10-03-2010
		CN 102604145 A	25-07-2012
		CO 6241139 A2	20-01-2011
		EP 2139568 A2	06-01-2010
		HK 1141748 A1	28-12-2012
		JP 5624882 B2	12-11-2014
		JP 5827673 B2	02-12-2015
		JP 2010526171 A	29-07-2010
		JP 2014088570 A	15-05-2014
		KR 20100017378 A	16-02-2010

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/023001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		KR 20150059799 A	02-06-2015
		SG 183037 A1	30-08-2012
		SG 183038 A1	30-08-2012
		SG 183039 A1	30-08-2012
		SG 183040 A1	30-08-2012
		SG 183041 A1	30-08-2012
		SG 183045 A1	30-08-2012
		SG 183047 A1	30-08-2012
		US 2010078585 A1	01-04-2010
		US 2011240903 A1	06-10-2011
		WO 2008134061 A2	06-11-2008
US 2011232939 A1	29-09-2011	US 2009095717 A1	16-04-2009
		US 2010171062 A1	08-07-2010
		US 2011232939 A1	29-09-2011
		WO 2009049144 A2	16-04-2009
US 2013109771 A1	02-05-2013	NONE	