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PATENT

NOTICE OF ENTITLEMENT

We, E.I. DU PONT DE NEMOURS AND COMPANY, of 1007 Market Street, Wilmington, Delaware 19898, United States of America, being the applicant and the person nominated for grant of patent in respect of the Application for an invention entitled SUBSTANTIALLY CONSTANT BOILING COMPOSITIONS OF DIFLUOROMETHANE AND TRIFLUOROETHANE OR PERFLUOROETHANE

state the following:-

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Miriam D. McConahay

Signature

March 17, 1994

Date

Assistant Secretary to the Patent Board

Executive Position



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(57) Claim

1. A substantially constant boiling composition of fluorinated compounds comprising a binary mixture of 1-37 weight percent difluoromethane and 63-99 weight percent perfluoroethane, wherein when the temperature is adjusted to 25°C the composition has an initial vapor pressure of 488-564 psia, and wherein the initial vapor pressure of the composition at 25°C does not change by more than 10 percent after half the initial composition has been allowed to evaporate.

5. A process for cooling which comprises condensing a composition according to any one of claims 1 to 4 and thereafter evaporating said composition in the vicinity of a body to be cooled.

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(54) Title: SUBSTANTIALLY CONSTANT BOILING COMPOSITIONS OF DIFLUOROMETHANE AND TRIFLUOROETHANE OR PERFLUOROETHANE

(57) Abstract

Substantially constant boiling mixtures of difluoromethane and 1,1,1-trifluoroethane or perfluoroethane are useful as refrigerants, aerosol propellants, heat transfer media, gaseous dielectrics, fire extinguishing agents, and expansion agents for polymers.

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TITLESUBSTANTIALLY CONSTANT BOILING COMPOSITIONS
OF DIFLUOROMETHANE AND TRIFLUOROETHANE
OR PERFLUOROETHANE

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BACKGROUND OF THE INVENTION

This invention relates to compositions that are mixtures of fluorinated compounds and, more specifically, to mixtures that are substantially constant boiling compositions of difluoromethane and 1,1,1-trifluoroethane or perfluoroethane.

10 Recently the long-term environmental effects of chlorofluorocarbons have come under substantial scientific scrutiny, because it has been postulated that these materials decompose in the stratosphere under the influence of ultraviolet radiation to release chlorine atoms. Chlorine atoms are theorized to undergo chemical reaction in the stratosphere, which could deplete the stratospheric ozone layer which shields the
15 earth from harmful ultraviolet radiation. A substantial reduction of stratospheric ozone could have a serious deleterious impact on the quality of life on earth. In view of the potential environmental problem associated with stratospheric ozone depletion, there is a need for new materials possessing properties which make them useful substitutes for applications in which chlorofluorocarbons have been used and which are also potentially
20 environmentally safe.

There is a limit to the number of single fluorinated hydrocarbon substances which can be candidates as environmentally safe materials. Mixtures of known materials, however, might be used if the desired combination of properties could be found in a given mixture. Simple mixtures, however, create problems in design and
25 operation of refrigeration and other equipment because of component segregation in both the vapor and liquid phases. To avoid component segregation problems, it is particularly desirable to discover new substantially constant boiling fluorocarbon blends. Such blends would not suffer from component segregation problems. Unfortunately, it is not possible to predict the formation of constant boiling compositions, e.g.,
30 azeotropes, thus complicating the search for compositions which possess the desired combination of properties. Accordingly, there is an urgent need for substantially constant boiling compositions that have properties which make them particularly useful as power cycle working fluids, e.g., refrigerants, aerosol propellants, heat transfer media, gaseous dielectrics, fire extinguishing agents, and expansion agents for polymers, such as
35 polyolefins and polyurethanes, that are potentially environmentally safe.

SUMMARY OF THE INVENTION

The present invention is directed to substantially constant boiling compositions of fluorinated compounds comprising difluoromethane (HFC-32) and a

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fluorinated hydrocarbon selected from the group consisting of 1,1,1-trifluoroethane (HFC-143a) and perfluoroethane (FC-116). The compositions of the present invention that contain 1,1,1-trifluoroethane have a weight ratio of difluoromethane to 1,1,1-trifluoroethane of from about 1:99 to 99:1, usually from about 10:90 to 90:10, preferably 5 73:27 to 99:1 or 73:27 to 90:10. The compositions that contain perfluoroethane have a weight ratio of difluoromethane to perfluoroethane of from about 1:99 to 37:63, preferably from about 9:91 to 18:82. Especially preferred azeotropic compositions comprise about 78 weight percent difluoromethane and about 22 weight percent 1,1,1-trifluoroethane having a boiling point of about -17.2°C at about 3448 torr or an 10 azeotrope comprising about 11 weight percent difluoromethane to 89 weight percent perfluoroethane having a boiling point of about -19.6°C at about 9299 torr.

The compositions of the present invention exhibit a higher vapor pressure than either of its two fluorocarbon components. Substantially constant boiling compositions as used in the present invention means their initial vapor pressure at 25°C 15 does not change by more than 10% after half of the initial mixture has been allowed to evaporate. Thus, the compositions described herein resist component segregation which would seriously diminish their usefulness in the contemplated applications. These substantially constant boiling compositions of this invention that are mixtures of fluorinated compounds are especially useful as power cycle working fluids, e.g., 20 refrigerants, aerosol propellants, heat transfer media, gaseous dielectrics, fire extinguishing agents, and expansion agents for polymers such as polyolefins and polyurethanes.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

25 The fluorinated compounds used in the compositions of the present invention are mixtures identified in the industry as HFC-32 (difluoromethane) and the fluorinated hydrocarbon HFC-143a (1,1,1-trifluoroethane) or FC-116 (perfluoroethane) in nomenclature conventional in halocarbon technology.

A phase study of various mixtures of difluoromethane and 1,1,1-trifluoroethane or perfluoroethane containing widely different amounts of the 30 fluorocarbons indicates that at constant temperature an azeotrope is formed over the temperature range studied. Further studies for the evaluation of substantially constant boiling compositions containing a wide range of proportions of the fluorocarbon components result in resistance to component fractionation of the mixture so that the 35 compositions are substantially constant boiling at constant temperature. Utilizing the particular fluorocarbon components in the amounts disclosed, quite unexpectedly, illustrates that at a constant temperature of 25°C the change in vapor pressure of the composition even after 50% of the initial composition has been allowed to evaporate does not change more than 10%. The small change in vapor pressure at constant

temperature illustrates that the amount of separation and loss of one fluorocarbon component in excess amount that would substantially change the boiling point of the mixture does not occur which makes the compositions especially suitable for the contemplated uses, e.g., refrigerants, aerosol propellants, foaming agents, etc.

5 In addition, studies have indicated that the novel substantially constant boiling compositions of the present invention exhibit dew and bubble point pressures with small pressure differentials. As is well known in the art, the difference between dew point and bubble point pressures at the same temperature is an indication of the constant boiling or azeotrope-like behavior of mixtures. The pressure differentials
10 demonstrated by the substantially constant boiling fluorocarbon compositions of the present invention are very small when compared with those of several known non-azeotropic compositions.

 As is well recognized in this field of technology, there is a range of compositions which contain the same components as the true azeotrope, which not only
15 will exhibit substantially equivalent properties as the true azeotrope for refrigeration and other applications, but which will also exhibit substantially equivalent properties to the true azeotropic compositions in terms of constant boiling characteristics and tendency not to segregate or fractionate on boiling at other temperatures and pressures.

 Other fluorohydrocarbons can be added to the substantially constant
20 boiling mixtures of HFC-32 and HFC-143a or FC-116 without changing the azeotrope-like properties of the compositions. Representative fluorohydrocarbons that can be added to the constant boiling mixtures of the present invention include chlorodifluoromethane (HCFC-22), pentafluoro-ethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1-chloro-1,1,2,2-tetrafluoroethane (HCFC-124a), 1-
25 chloro-1,2,2,2-tetrafluoroethane (HCFC-124), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,2,2,3,3-heptafluoropropane (HFC-227ca), perfluoropropane (FC-218), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1-difluoroethane (HFC-152a) and fluoroethane (HFC-161). For example, the substantially constant boiling compositions of difluoromethane and 1,1,1-trifluoroethane can contain up to 90 weight percent
30 pentafluoroethane based on the total weight of the composition.

 Additives that are frequently incorporated in the fluorocarbon compositions of the present invention when used, for example, as refrigerants, include conventional lubricants, corrosion inhibitors, stabilizers and dyes used for such purposes.

 The fluorocarbon compositions described herein can be used to provide
35 refrigeration by condensing the constant boiling compositions and thereafter evaporating the compositions, e.g., condensate, in the vicinity of a body to be cooled. Further, these compositions can also be used to provide heat, for example, in a heat pump, by evaporating the fluorocarbon composition and thereafter condensing the constant boiling fluorocarbon compositions in the vicinity of a body to be heated.

In addition to refrigeration and heating applications, the novel constant boiling fluorocarbon compositions are useful as aerosol propellants, gaseous dielectrics, fire extinguishing agents, expansion agents for polymers, e.g., polyolefins and polyurethanes, and as power cycle working fluids.

5 The use of substantially constant boiling compositions of this invention eliminates the problem of component fractionation and handling in system operations, because these fluorocarbon compositions behave substantially as a single substance.

 The invention will be more clearly understood by referring to the following Examples illustrating preferred embodiments of the invention where parts are
10 by weight unless otherwise indicated.

EXAMPLE 1

 A phase study was made on mixtures of difluoromethane (HFC-32) and 1,1,1-trifluoroethane (HFC-143a) wherein the composition was varied and the vapor
15 pressures measured at a constant temperature of -17.2°C . An azeotropic composition was obtained, as evidenced by the maximum pressure observed, and was identified as follows:

 Difluoromethane = about 78 weight percent
 1,1,1-Trifluoroethane = about 22 weight percent
20 Vapor pressure = about 3448 torr at -17.2°C .

 A phase study shows that at other temperatures the azeotropic composition changes as follows:

(a) Difluoromethane = about 94 weight percent
 1,1,1-Trifluoroethane = about 6 weight percent
25 Vapor pressure = about 12768 torr at 25°C
(b) Difluoromethane = about 99 weight percent
 1,1,1-Trifluoroethane = about 1 weight percent
 Vapor pressure = about 16588 torr at 35°C
(c) Difluoromethane = about 73 weight percent
30 1,1,1-Trifluoroethane = about 27 weight percent
 Vapor pressure = about 901 torr at -50°C .

EXAMPLE 2

 A phase study was made on mixtures of difluoromethane (HFC-32) and
35 perfluoroethane (FC-116) wherein the composition was varied and the vapor pressures measured at a constant temperature of -19.6°C . An azeotropic composition was obtained, as evidenced by the maximum vapor pressure observed, and was identified as follows:

 Difluoromethane = about 11 weight percent

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Perfluoroethane = about 89 weight percent

Vapor pressure = about 9299 torr at -19.6°C .

A phase study shows that at other temperatures the azeotropic composition changes as follows:

- 5 (a) Difluoromethane = about 15 weight percent
 Perfluoroethane = about 85 weight percent
 Vapor pressure = about 29202 torr at 25°C
- (b) Difluoromethane = about 18 weight percent
 Perfluoroethane = about 82 weight percent
 10 Vapor pressure = about 48231 torr at 50°C
- (c) Difluoromethane = about 9 weight percent
 Perfluoroethane = about 91 weight percent
 Vapor pressure = about 3230 torr at -50°C .

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EXAMPLE 3

Phase studies were made on the constant boiling fluorocarbon compositions of (a) difluoromethane (HFC-32) and 1,1,1-trifluoroethane (HFC-143a) and (b) difluoromethane (HFC-32) and perfluoroethane (FC-116) to verify minimal fractionation and change in vapor pressure and composition during a vapor phase loss at 20 25°C , about room temperature. Initial liquid (IQ), final liquid (FQ), initial vapor (0), final vapor (1), vapor pressure and change in vapor pressure from initial vapor pressure were all studied to determine the effects of vapor leakage on both the compositions and the vapor pressure as illustrated below in Tables 1 and 2.

25

TABLE 1

| Sample | Percent Loss of Mixture | Composition (wt%) | | Vapor Pressure (psia) | Vapor Pressure Change (%) |
|--------|-------------------------|-------------------|----------|-----------------------|---------------------------|
| | | HFC-32 | HFC-143a | | |
| 30 IQ | 0 | 1.0 | 99.0 | 182.0 | 0 |
| 0 | 0 | 1.5 | 98.5 | 182.0 | 0 |
| 1 | 50 | 1.1 | 98.9 | 181.6 | 0.2 |
| FQ | 50 | 1.1 | 98.9 | 181.6 | 0.2 |
| 35 IQ | 0 | 20.0 | 80.0 | 204.6 | 0 |
| 0 | 0 | 26.6 | 73.4 | 204.6 | 0 |
| 1 | 50 | 21.5 | 78.5 | 200.1 | 2.2 |
| FQ | 50 | 15.9 | 84.1 | 200.1 | 2.2 |

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|----|----|----|------|------|-------|-----|
| | IQ | 0 | 40.0 | 60.0 | 221.8 | 0 |
| | 0 | 0 | 48.2 | 51.8 | 221.8 | 0 |
| | 1 | 50 | 42.6 | 57.4 | 217.6 | 1.9 |
| | FQ | 50 | 34.5 | 65.5 | 217.6 | 1.9 |
| 5 | IQ | 0 | 60.0 | 40.0 | 233.9 | 0 |
| | 0 | 0 | 66.6 | 33.4 | 233.9 | 0 |
| | 1 | 50 | 62.5 | 37.5 | 231.5 | 1.0 |
| | FQ | 50 | 55.3 | 44.7 | 231.5 | 1.0 |
| 10 | IQ | 0 | 80.0 | 20.0 | 241.9 | 0 |
| | 0 | 0 | 83.1 | 16.9 | 241.9 | 0 |
| | 1 | 50 | 81.3 | 18.7 | 241.2 | 0.3 |
| | FQ | 50 | 77.7 | 22.3 | 241.2 | 0.3 |
| 15 | IQ | 0 | 99.0 | 1.0 | 246.5 | 0 |
| | 0 | 0 | 99.1 | 0.9 | 246.5 | 0 |
| | 1 | 50 | 99.0 | 1.0 | 246.5 | 0 |
| | FQ | 50 | 98.9 | 1.1 | 246.5 | 0 |

TABLE 2

| 25 | Sample | Percent Loss of Mixture | Composition (wt%) | | Vapor Pressure (psia) | Vapor Pressure Change (%) |
|----|--------|-------------------------|-------------------|--------|-----------------------|---------------------------|
| | | | HFC-32 | FC-116 | | |
| | IQ | 0 | 1.0 | 99.0 | 488.3 | 0 |
| | 0 | 0 | 3.7 | 96.3 | 488.3 | 0 |
| | 1 | 50 | 0.5 | 99.5 | 458.7 | 6.07 |
| | FQ | 50 | 0.1 | 99.9 | 458.7 | 6.07 |
| 30 | IQ | 0 | 10.0 | 90.9 | 561.9 | 0 |
| | 0 | 0 | 13.7 | 86.3 | 561.9 | 0 |
| | 1 | 50 | 12.3 | 87.7 | 555.4 | 1.16 |
| | FQ | 50 | 7.0 | 93.0 | 555.4 | 1.16 |

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|----|----|----|------|------|-------|------|
| | IQ | 0 | 20.0 | 80.0 | 563.6 | 0 |
| | 0 | 0 | 16.1 | 83.9 | 563.6 | 0 |
| | 1 | 50 | 16.7 | 83.3 | 561.6 | 0.35 |
| | FQ | 50 | 24.1 | 75.9 | 561.6 | 0.35 |
| 5 | IQ | 0 | 30.0 | 70.0 | 557.8 | 0 |
| | 0 | 0 | 17.4 | 82.6 | 557.8 | 0 |
| | 1 | 50 | 19.3 | 80.7 | 540.0 | 3.19 |
| | FQ | 50 | 46.5 | 53.5 | 540.0 | 3.19 |
| 10 | IQ | 0 | 37.0 | 63.0 | 551.7 | 0 |
| | 0 | 0 | 18.1 | 81.9 | 551.7 | 0 |
| | 1 | 50 | 22.9 | 77.1 | 499.3 | 9.49 |
| | FQ | 50 | 64.8 | 35.2 | 499.3 | 9.49 |

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The data in the above Tables indicate that the mixtures of difluoromethane and 1,1,1-trifluoroethane and the mixtures of difluoromethane and perfluoroethane are substantially constant boiling with only a maximum change of 2.2% in the vapor pressure for difluoromethane and 1,1,1-trifluoroethane and only a maximum change of 9.49% for difluoromethane and perfluoroethane, with 50% of the initial mixture evaporated. A mixture can be considered substantially constant boiling if its vapor pressure at 25°C does not change by more than 10% after 50% of the initial mixture has been lost by, for example, evaporation.

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EXAMPLE 4

A phase study was made on the constant boiling fluorocarbon composition of difluoromethane (HFC-32) and 1,1,1-trifluoroethane (HFC-143a) containing varying amounts of pentafluoroethane (HFC-125) to verify minimal fractionation and change in the vapor pressure and composition during vapor phase loss at 25°C, about room temperature. Initial liquid (IQ), final liquid (FQ), initial vapor (0), final vapor (1), vapor pressure and change in vapor pressure from initial vapor pressure were all studied to determine the effects of vapor leakage on both the compositions and the vapor pressure, as illustrated below in Table 3.

30

TABLE 3

| | Sample | Percent Loss of Mixture | Composition (wt%) | | | Vapor Pressure (psia) | Vapor Pressure Change (%) |
|----|--------|-------------------------|-------------------|---------|----------|-----------------------|---------------------------|
| | | | HFC-32 | HFC-125 | HFC-143a | | |
| 5 | IQ | 0 | 5.0 | 5.0 | 90.0 | 187.6 | 0 |
| | 0 | 0 | 7.2 | 5.0 | 87.8 | 187.6 | 0 |
| | 1 | 50 | 5.3 | 5.0 | 89.7 | 185.9 | 0.9 |
| | FQ | 50 | 3.7 | 4.9 | 91.4 | 185.9 | 0.9 |
| 10 | IQ | 0 | 10.0 | 5.0 | 85.0 | 193.8 | 0 |
| | 0 | 0 | 13.9 | 4.9 | 81.2 | 193.8 | 0 |
| | 1 | 50 | 10.7 | 5.0 | 84.3 | 190.9 | 1.5 |
| | FQ | 50 | 7.6 | 5.0 | 87.4 | 190.9 | 1.5 |
| 15 | IQ | 0 | 10.0 | 10.0 | 80.0 | 194.2 | 0 |
| | 0 | 0 | 13.9 | 9.9 | 76.2 | 194.2 | 0 |
| | 1 | 50 | 10.7 | 10.1 | 79.2 | 191.3 | 1.5 |
| | FQ | 50 | 7.6 | 10.0 | 82.4 | 191.3 | 1.5 |
| 20 | IQ | 0 | 10.0 | 40.0 | 50.0 | 197.6 | 0 |
| | 0 | 0 | 13.3 | 40.1 | 46.6 | 197.6 | 0 |
| | 1 | 50 | 10.7 | 40.3 | 49.0 | 195.0 | 1.3 |
| | FQ | 50 | 7.9 | 39.8 | 52.3 | 195.0 | 1.3 |
| 25 | IQ | 0 | 10.0 | 70.0 | 20.0 | 204.3 | 0 |
| | 0 | 0 | 12.7 | 69.7 | 17.6 | 204.3 | 0 |
| | 1 | 50 | 10.6 | 70.2 | 19.2 | 202.0 | 1.1 |
| | FQ | 50 | 8.2 | 70.1 | 21.7 | 202.0 | 1.1 |
| 30 | IQ | 0 | 10.0 | 85.0 | 5.0 | 209.5 | 0 |
| | 0 | 0 | 12.6 | 83.2 | 4.2 | 209.5 | 0 |
| | 1 | 50 | 10.6 | 84.7 | 4.7 | 207.5 | 1.0 |
| | FQ | 50 | 8.3 | 86.1 | 5.6 | 207.5 | 1.0 |
| 35 | | | | | | | |

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|----|----|----|------|------|------|-------|-----|
| | IQ | 0 | 5.0 | 90.0 | 5.0 | 203.9 | 0 |
| | 0 | 0 | 6.4 | 89.3 | 4.3 | 203.9 | 0 |
| | 1 | 50 | 5.3 | 89.9 | 4.8 | 202.7 | 0.6 |
| | FQ | 50 | 4.1 | 90.4 | 5.5 | 202.7 | 0.6 |
| 5 | IQ | 0 | 30.0 | 5.0 | 65.0 | 214.3 | 0 |
| | 0 | 0 | 37.8 | 4.5 | 57.7 | 214.3 | 0 |
| | 1 | 50 | 32.2 | 4.9 | 62.9 | 209.7 | 2.1 |
| | FQ | 50 | 24.9 | 5.3 | 69.8 | 209.7 | 2.1 |
| 10 | IQ | 0 | 30.0 | 25.0 | 45.0 | 216.3 | 0 |
| | 0 | 0 | 37.3 | 23.0 | 39.7 | 216.3 | 0 |
| | 1 | 50 | 32.1 | 24.5 | 43.4 | 212.1 | 1.9 |
| | FQ | 50 | 25.3 | 26.2 | 48.5 | 212.1 | 1.9 |
| 15 | IQ | 0 | 30.0 | 45.0 | 25.0 | 219.8 | 0 |
| | 0 | 0 | 36.5 | 42.2 | 21.3 | 219.8 | 0 |
| | 1 | 50 | 31.9 | 44.4 | 23.7 | 216.1 | 1.7 |
| | FQ | 50 | 25.8 | 46.8 | 27.4 | 216.1 | 1.7 |
| 20 | IQ | 0 | 30.0 | 65.0 | 5.0 | 226.2 | 0 |
| | 0 | 0 | 35.6 | 60.5 | 3.9 | 226.2 | 0 |
| | 1 | 50 | 31.7 | 63.8 | 4.5 | 223.4 | 1.2 |
| | FQ | 50 | 26.3 | 67.9 | 5.8 | 223.4 | 1.2 |
| 25 | IQ | 0 | 50.0 | 5.0 | 45.0 | 228.8 | 0 |
| | 0 | 0 | 57.7 | 4.2 | 38.1 | 228.8 | 0 |
| | 1 | 50 | 52.7 | 4.7 | 42.6 | 225.5 | 1.4 |
| | FQ | 50 | 44.7 | 5.5 | 49.8 | 225.5 | 1.4 |
| 30 | IQ | 0 | 50.0 | 25.0 | 25.0 | 231.2 | 0 |
| | 0 | 0 | 56.1 | 23.1 | 20.8 | 231.2 | 0 |
| | 1 | 50 | 52.5 | 24.0 | 23.5 | 228.3 | 1.3 |
| | FQ | 50 | 45.1 | 27.0 | 27.9 | 228.3 | 1.3 |
| 35 | | | | | | | |

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| | | | | | | | |
|----|----|----|------|------|------|-------|-----|
| | IQ | 0 | 50.0 | 45.0 | 5.0 | 236.4 | 0 |
| | 0 | 0 | 55.6 | 40.6 | 3.8 | 236.4 | 0 |
| | 1 | 50 | 52.0 | 43.5 | 4.5 | 234.5 | 0.8 |
| | FQ | 50 | 46.1 | 48.0 | 5.9 | 234.5 | 0.8 |
| 5 | IQ | 0 | 70.0 | 5.0 | 25.0 | 238.8 | 0 |
| | 0 | 0 | 74.9 | 4.3 | 20.8 | 238.8 | 0 |
| | 1 | 50 | 72.0 | 4.7 | 23.3 | 237.3 | 0.6 |
| | FQ | 50 | 66.4 | 5.6 | 28.0 | 237.3 | 0.6 |
| 10 | IQ | 0 | 70.0 | 25.0 | 5.0 | 242.3 | 0 |
| | 0 | 0 | 73.7 | 22.4 | 3.9 | 242.3 | 0 |
| | 1 | 50 | 71.4 | 24.0 | 4.6 | 241.5 | 0.3 |
| | FQ | 50 | 67.4 | 26.8 | 5.8 | 241.5 | 0.3 |
| 15 | IQ | 0 | 90.0 | 5.0 | 5.0 | 245.4 | 0 |
| | 0 | 0 | 91.2 | 4.6 | 4.2 | 245.4 | 0 |
| | 1 | 50 | 90.4 | 4.9 | 4.7 | 245.2 | 0.1 |
| | FQ | 50 | 89.2 | 5.3 | 5.5 | 245.2 | 0.1 |

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The data in Table 3 indicate that mixtures of difluoromethane and 1,1,1-trifluoroethane containing widely varying amounts of pentafluoroethane (up to 90 weight percent) are substantially constant boiling with only a maximum change of 2.1% in the vapor pressure with 50% of the initial mixtures evaporated.

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EXAMPLE 5

A phase study was made on the constant boiling fluorocarbon composition of difluoromethane (HFC-32) and 1,1,1-trifluoroethane (HFC-143a) containing varying amounts of 1,2,2,2-tetrafluoroethane (HFC-134a) to verify minimal fractionation and change in vapor pressure and composition during vapor phase loss at 25°C, about room temperature. Initial liquid (IQ), final liquid (FQ), initial vapor (0), final vapor (1), vapor pressure and change in vapor pressure from initial vapor pressure were all studied to determine the effects of vapor leakage on both the compositions and the vapor pressure, as illustrated below in Table 4.

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TABLE 4

| 5 | Sample | Percent Loss of Mixture | Composition (wt%) | | | Vapor Pressure (psia) | Vapor Pressure Change (%) |
|----|--------|-------------------------------|----------------------|----------|----------|-----------------------------|------------------------------------|
| | | | HFC-32 | HFC-143a | HFC-134a | | |
| | IQ | 0 | 90.0 | 5.0 | 5.0 | 241.5 | 0 |
| | 0 | 0 | 93.8 | 4.4 | 1.8 | 241.5 | 0 |
| | 1 | 50 | 92.4 | 4.8 | 2.8 | 238.9 | 1.0 |
| | FQ | 50 | 86.9 | 5.4 | 7.7 | 238.9 | 1.0 |
| 10 | IQ | 0 | 5.0 | 90.0 | 5.0 | 183.7 | 0 |
| | 0 | 0 | 7.2 | 90.2 | 2.6 | 183.7 | 0 |
| | 1 | 50 | 5.3 | 91.0 | 3.7 | 180.7 | 1.6 |
| | FQ | 50 | 3.7 | 89.4 | 6.9 | 180.7 | 1.6 |
| 15 | IQ | 0 | 47.5 | 47.5 | 5.0 | 223.3 | 0 |
| | 0 | 0 | 56.6 | 41.6 | 1.8 | 223.3 | 0 |
| | 1 | 50 | 51.0 | 46.2 | 2.9 | 217.0 | 2.8 |
| | FQ | 50 | 41.2 | 51.2 | 7.6 | 217.0 | 2.8 |
| 20 | IQ | 0 | 80.0 | 5.0 | 15.0 | 232.0 | 0 |
| | 0 | 0 | 89.6 | 4.5 | 5.9 | 232.0 | 0 |
| | 1 | 50 | 85.7 | 4.9 | 9.4 | 224.5 | 3.2 |
| | FQ | 50 | 72.6 | 5.3 | 22.1 | 224.5 | 3.2 |
| 25 | IQ | 0 | 5.0 | 80.0 | 15.0 | 176.3 | 0 |
| | 0 | 0 | 7.2 | 84.6 | 8.2 | 176.3 | 0 |
| | 1 | 50 | 5.4 | 83.0 | 11.6 | 170.8 | 3.1 |
| | FQ | 50 | 3.7 | 76.1 | 20.2 | 170.8 | 3.1 |
| 30 | IQ | 0 | 42.5 | 42.5 | 15.0 | 212.4 | 0 |
| | 0 | 0 | 54.0 | 39.8 | 6.2 | 212.4 | 0 |
| | 1 | 50 | 46.8 | 43.2 | 10.0 | 201.2 | 5.3 |
| | FQ | 50 | 34.8 | 43.5 | 21.7 | 201.2 | 5.3 |
| 35 | | | | | | | |

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| | | | | | | | |
|----|----|----|------|------|------|-------|-----|
| | IQ | 0 | 55.0 | 5.0 | 40.0 | 203.2 | 0 |
| | 0 | 0 | 74.6 | 4.9 | 20.5 | 203.2 | 0 |
| | 1 | 50 | 63.7 | 5.3 | 31.0 | 185.0 | 9.1 |
| | FQ | 50 | 42.2 | 4.9 | 52.9 | 185.0 | 9.1 |
| 5 | IQ | 0 | 5.0 | 55.0 | 40.0 | 156.7 | 0 |
| | 0 | 0 | 7.7 | 66.7 | 25.6 | 156.7 | 0 |
| | 1 | 50 | 5.5 | 60.0 | 34.5 | 146.7 | 6.4 |
| | FQ | 50 | 3.4 | 46.5 | 50.1 | 146.7 | 6.4 |
| 10 | IQ | 0 | 30.0 | 30.0 | 40.0 | 182.7 | 0 |
| | 0 | 0 | 22.4 | 33.1 | 44.5 | 182.7 | 0 |
| | 1 | 50 | 34.2 | 32.8 | 33.0 | 165.1 | 9.6 |
| | FQ | 50 | 21.3 | 27.2 | 51.5 | 165.1 | 9.6 |

The data in Table 4 indicate that mixtures of difluoromethane and 1,1,1-trifluoroethane containing widely varying amounts of 1,2,2,2-tetrafluoroethane, up to 40 weight percent, are substantially constant boiling with only a maximum change of 9.6% in vapor pressure with 50% of the initial mixture evaporated.

EXAMPLE 6

Evaluation of the refrigeration properties of substantially constant boiling mixtures of difluoromethane (HFC-32) and 1,1,1-trifluoroethane (HCFC-143a) containing pentafluoroethane (HFC-125) are shown in Table 5 and compared with refrigerants (R-502), chlorodifluoromethane (HCFC-22) and pentafluoroethane (HFC-125).

TABLE 5

HFC-32/HCFC-143a/HFC-125

| | <u>(20/20/60)</u> | <u>(10/40/50)</u> | <u>(40/10/50)</u> |
|------------------------|-------------------|-------------------|-------------------|
| | <u>(wt%)</u> | <u>(wt%)</u> | <u>(wt%)</u> |
| Evaporator Temp., °F | -30.0 | -30.0 | -30.0 |
| Evaporator Pres., psia | 30.4 | 28.9 | 32.6 |
| Condenser Temp., °F | 115.0 | 115.0 | 115.0 |
| Condenser Pres., psia | 357.5 | 335.0 | 386.1 |

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| | | | | |
|----|--------------------------------|-------|-------|-------|
| | Return Gas Temp., °F | 65.0 | 65.0 | 65.0 |
| | Subcooling Temp., °F | 0 | 0 | 0 |
| 5 | Compressor Discharge Temp., °F | 254.0 | 240.0 | 283.0 |
| | Coefficient of Performance | 1.80 | 1.83 | 1.80 |
| 10 | Capacity (BTU/min) | 98.0 | 92.6 | 108.7 |

Commercial Refrigerants

| | <u>R-502</u> | <u>HCFC-22</u> | <u>HFC-125</u> |
|----|--------------------------------|----------------|----------------|
| 15 | Evaporator Temp., °F | -30.0 | -30.0 |
| | Evaporator Pres., psia | 24.0 | 26.7 |
| 20 | Condenser Temp., °F | 115.0 | 115.0 |
| | Condenser Pres., psia | 282.0 | 327.5 |
| | Return Gas Temp., °F | 65.0 | 65.0 |
| 25 | Subcooling Temp., °F | 0 | 0 |
| | Compressor Discharge Temp., °F | 238.8 | 304.4 |
| 30 | Coefficient of Performance | 1.89 | 1.97 |
| | Capacity (BTU/min) | 80.0 | 76.6 |

Capacity means the change in enthalpy of the refrigerant in the evaporator per round of refrigerant circulated, i.e., the heat removed by the refrigerant in the evaporator per time.

5 Coefficient of Performance (C.O.P.) is the ratio of net refrigeration effect to the compressor work. It is a measure of refrigeration energy efficiency.

10 The substantially constant boiling mixtures illustrated in Table 4 are based on a compressor with a 3.5 cubic foot displacement at 100% isentropic efficiency. As shown in Table 5, the compositions containing a mixture of difluoromethane, 1,1,1-trifluoroethane and pentafluoroethane offer an increase in capacity compared with pentafluoroethane; the discharge temperatures of the mixtures are lower than chlorodifluoromethane which results in potentially longer compressor lifetimes.

15 Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.



The claims defining the invention are as follows:

- 5 1. A substantially constant boiling composition of fluorinated compounds comprising a binary mixture of 1-37 weight percent difluoromethane and 63-99 weight percent perfluoroethane, wherein when the temperature is adjusted to 25°C the composition has an initial vapor pressure of 488-564 psia, and wherein the initial vapor pressure of the composition at 25°C does not change by more than 10 percent after half the initial composition has been allowed to evaporate.
- 10 2. A composition according to claim 1 comprising 9-18 weight percent difluoromethane and 82-91 weight percent perfluoroethane.
3. A composition according to claim 1 comprising 11 weight percent difluoromethane and 89 weight percent perfluoroethane.
4. A composition according to any one of claims 1 to 3 having a boiling point of about -19.6°C at 9299 torr.
- 15 5. A process for cooling which comprises condensing a composition according to any one of claims 1 to 4 and thereafter evaporating said composition in the vicinity of a body to be cooled.
6. A composition according to claim 1 or a process according to claim 5 substantially as hereinbefore described with reference to any one of the examples.

DATED this 17th day of August, 1995.



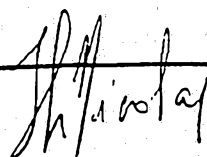
E I DU PONT DE NEMOURS AND COMPANY
By Their Patent Attorneys:
CALLINAN LAWRIE



INTERNATIONAL SEARCH REPORT

PCT/US 92/08141

International Application No

| | | |
|---|--|---|
| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ | | |
| According to International Patent Classification (IPC) or to both National Classification and IPC | | |
| Int.Cl. 5 C09K5/04; | C09K3/30; | C08J9/16; A62D1/00 |
| II. FIELDS SEARCHED | | |
| Minimum Documentation Searched ⁷ | | |
| Classification System | Classification Symbols | |
| Int.Cl. 5 | C09K | |
| Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶ | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ | | |
| Category ⁸ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
| E | WO,A,9 216 597 (ALLIED-SIGNAL) 1 October 1992 see claims 1,2,4,7 see page 6, line 3 see example 2 see page 9, line 21 - line 29 --- | 1,2,12, 13-19 |
| X | DATABASE WPIL Derwent Publications Ltd., London, GB; AN 91-262357 & JP,A,3 170 586 (MATSUSHITA) 24 July 1991 see abstract & PATENT ABSTRACTS OF JAPAN 22 October 1991 see abstract --- | 1,2, 13-19 |
| | --- | -/-- |
| <p>⁸ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> | | |
| IV. CERTIFICATION | | |
| Date of the Actual Completion of the International Search | Date of Mailing of this International Search Report | |
| 12 NOVEMBER 1992 | 19. 11. 92 | |
| International Searching Authority | Signature of Authorized Officer | |
| EUROPEAN PATENT OFFICE | NICOLAS H.J.F. |  |

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| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) | | |
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| Category ° | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No. |
| X | DATABASE WPIL Derwent Publications Ltd., London, GB; AN 91-262362 & JP,A,3 170 592 (MATSUSHITA) 24 July 1991 see abstract & PATENT ABSTRACTS OF JAPAN 22 October 1991 see abstract ----- | 1,2, 13-19 |

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9208141
SA 65268**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 12/11/92

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| WO-A-9216597 | 01-10-92 | None | |
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