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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C09K 5/04, 3/30, C08J 9/14

A1

(11) International Publication Number: WO 94/26837

(43) International Publication Date: 24 November 1994 (24.11.94)

(21) International Application Number: PCT/US94/05653

(22) International Filing Date: 19 May 1994 (19.05.94)

(30) Priority Data:

08/064,183	19 May 1993 (19.05.93)	US
08/242,511	13 May 1994 (13.05.94)	US

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(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: REFRIGERANT COMPOSITIONS INCLUDING AN ACYCLIC FLUOROETHER

(57) Abstract

Refrigerant compositions include mixtures of hexafluorodimethyl ether and cyclopropane, dimethylether or propylene; bis(difluoromethyl)ether and 2,2,3,4,4-pentafluorooxetane; fluoromethyl trifluoromethyl ether and 2,2,4,4,5,5-hexafluoro-1,3-dioxolane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, dimethylether or tris(trifluoromethyl)amine; trifluoromethyl methyl ether and perfluorooxetane, 2,2,4,4,5,5-hexafluoro-1,3-dioxolane, perfluoromethyl ethyl ether, perfluorodimethoxymethane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, dimethylether or tris(trifluoromethyl)amine; perfluoromethyl ethyl ether and dimethylether, propylene or 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane; perfluorodimethoxymethane and dimethylether or isobutane; 1-trifluoromethoxy-1,1,2,2-tetrafluoroethane and tris(trifluoromethyl)amine or dimethylether; difluoromethoxy pentafluoroethane and dimethylether, isobutane or tris(trifluoromethyl)amine; 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane and dimethylether or isobutane; 1-difluoromethoxy-1,1,2,2-tetrafluoroethane and $N(CHF_2)_2(CF_3)$; or 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)propane and 1,1,2,2,3-pentafluoropropane or 1,1,1,2,3-pentafluoropropane.

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TITLE
REFRIGERANT COMPOSITIONS INCLUDING AN ACYCLIC FLUOROETHER

FIELD OF THE INVENTION

This invention relates to refrigerant compositions that include at least one acyclic fluoroether. These compositions are useful as cleaning agents, expansion agents for polyolefins and polyurethanes, aerosol propellants, refrigerants, heat transfer media, gaseous dielectrics, fire extinguishing agents, power cycle working fluids, polymerization media, particulate removal fluids, carrier fluids, buffing abrasive agents, and displacement drying agents.

BACKGROUND OF THE INVENTION

Fluorinated hydrocarbons have many uses, one of which is as a refrigerant. Such refrigerants include trichlorofluoromethane (CFC-11) dichlorodifluoromethane (CFC-12) and chlorodifluoromethane (HCFC-22).

In recent years it has been pointed out that certain kinds of fluorinated hydrocarbon refrigerants released into the atmosphere may adversely affect the stratospheric ozone layer. Although this proposition has not yet been completely established, there is a movement toward the control of the use and the production of certain chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) under an international agreement.

Accordingly, there is a demand for the development of refrigerants that have a lower ozone depletion potential than existing refrigerants while still achieving an acceptable performance in refrigeration applications.

In refrigeration applications, a refrigerant is often lost during operation through leaks in shaft seals, hose connections, soldered joints and broken lines. In addition, the refrigerant may be released to the atmosphere during maintenance procedures on refrigeration equipment. If the refrigerant is not a pure component or an azeotropic or azeotrope-like composition, the refrigerant composition may change when leaked or discharged to the atmosphere from the refrigeration equipment, which may cause the refrigerant to become flammable or to have poor refrigeration performance.

Accordingly, it is desirable, if possible, to use as a refrigerant a single compound or an azeotropic or azeotrope-like composition of more than one

compound.

It is also desirable to find replacements for CFCs and HCFCs for use as a cleaning agent or solvent to clean, for example, electronic circuit boards. It is preferred that the cleaning agents be azeotropic or azeotrope-like because in vapor degreasing operations the cleaning agent is generally redistilled and reused for final rinse cleaning.

Replacements for CFCs and HCFCs may also useful as blowing agents in the manufacture of closed-cell polyurethane, phenolic and thermoplastic foams, as propellants in aerosols, as heat transfer media, gaseous dielectrics, fire extinguishing agents, power cycle working fluids such as for heat pumps, 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, as buffing abrasive agents to remove buffing abrasive compounds from polished surfaces such as metal, 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.

SUMMARY OF THE INVENTION

The present invention relates to the discovery of refrigerant compositions of hexafluorodimethyl ether and cyclopropane, dimethyl ether or propylene; bis(difluoromethyl) ether and 2,2,3,4,4-pentafluorooxetane; fluoromethyl trifluoromethyl ether and 2,2,4,4,5,5-hexafluoro-1,3-dioxolane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, dimethyl ether or tris(trifluoromethyl)amine; trifluoromethyl methyl ether and perfluorooxetane, 2,2,4,4,5,5-hexafluoro-1,3-dioxolane, perfluoromethyl ethyl ether, perfluorodimethoxymethane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, dimethyl ether or tris(trifluoromethyl)amine; perfluoromethyl ethyl ether and dimethyl ether or propylene; perfluorodimethoxymethane and dimethyl ether or isobutane; 1-trifluoromethoxy-1,1,2,2-tetrafluoroethane and tris(trifluoromethyl)amine or dimethyl ether; difluoromethoxy pentafluoroethane and dimethyl ether, isobutane or tris(trifluoromethyl)amine; 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane and dimethyl ether or isobutane; 1-difluoromethoxy-1,1,2,2-tetrafluoroethane and $N(CHF_2)_2(CF_3)$; or 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)propane and 1,1,2,2,3-pentafluoropropane or 1,1,1,2,3-pentafluoropropane. This invention

also relates to the discovery of effective amounts of the components of these compositions to form azeotropic or azeotrope-like compositions.

These compositions are also useful as cleaning agents, expansion agents for polyolefins and polyurethanes, aerosol propellants, heat transfer media, gaseous dielectrics, fire extinguishing agents, power cycle working fluids, polymerization media, particulate removal fluids, carrier fluids, buffing abrasive agents, and displacement drying agents.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph of the vapor/liquid equilibrium curve for mixtures of 116E and cyclopropane at 25°C;

Figure 2 is a graph of the vapor/liquid equilibrium curve for mixtures of 116E and DME at 25°C;

Figure 3 is a graph of the vapor/liquid equilibrium curve for mixtures of 116E and propylene at 25°C;

Figure 4 is a graph of the vapor/liquid equilibrium curve for mixtures of 134E and C-225eEαβ at 25°C;

Figure 5 is a graph of the vapor/liquid equilibrium curve for mixtures of 134aE and C-216E2 at 25°C;

Figure 6 is a graph of the vapor/liquid equilibrium curve for mixtures of 134aE and 227eaE at 25°C;

Figure 7 is a graph of the vapor/liquid equilibrium curve for mixtures of 134aE and DME at 25°C;

Figure 8 is a graph of the vapor/liquid equilibrium curve for mixtures of 134aE and $N(CF_3)_3$ at 25°C;

Figure 9 is a graph of the vapor/liquid equilibrium curve for mixtures of 143aE and C-216E at 25°C;

Figure 10 is a graph of the vapor/liquid equilibrium curve for mixtures of 143aE and C-216E2 at 25°C;

Figure 11 is a graph of the vapor/liquid equilibrium curve for mixtures of 143aE and 218E at 25°C;

Figure 12 is a graph of the vapor/liquid equilibrium curve for mixtures of 143aE and 218E2 at 25°C;

Figure 13 is a graph of the vapor/liquid equilibrium curve for mixtures of 143aE and 227eaE at 25°C;

Figure 14 is a graph of the vapor/liquid equilibrium curve for

mixtures of 143aE and DME at 25°C;

Figure 15 is a graph of the vapor/liquid equilibrium curve for mixtures of 143aE and $N(CF_3)_3$ at 25°C;

Figure 16 is a graph of the vapor/liquid equilibrium curve for mixtures of 218E and DME at 25°C;

Figure 17 is a graph of the vapor/liquid equilibrium curve for mixtures of 218E and propylene at 25°C;

Figure 18 is a graph of the vapor/liquid equilibrium curve for mixtures of 218E2 and DME at 25°C;

Figure 19 is a graph of the vapor/liquid equilibrium curve for mixtures of 218E2 and isobutane at 25°C;

Figure 20 is a graph of the vapor/liquid equilibrium curve for mixtures of 227caEαβ and $N(CF_3)_3$ at 25°C;

Figure 21 is a graph of the vapor/liquid equilibrium curve for mixtures of 227caEαβ and DME at 25°C;

Figure 22 is a graph of the vapor/liquid equilibrium curve for mixtures of 227caEβγ and DME at 25°C;

Figure 23 is a graph of the vapor/liquid equilibrium curve for mixtures of 227caEβγ and isobutane at 25°C;

Figure 24 is a graph of the vapor/liquid equilibrium curve for mixtures of 227caEβγ and $N(CF_3)_3$ at 25°C;

Figure 25 is a graph of the vapor/liquid equilibrium curve for mixtures of 227eaE and DME at 25°C;

Figure 26 is a graph of the vapor/liquid equilibrium curve for mixtures of 227eaE and isobutane at 25°C;

Figure 27 is a graph of the vapor/liquid equilibrium curve for mixtures of 236caE and $N(CHF_2)_2(CF_3)$ at 25°C;

Figure 28 is a graph of the vapor/liquid equilibrium curve for mixtures of E-42-11meEγδ and HFC-245ca at 19.05°C; and

Figure 29 is a graph of the vapor/liquid equilibrium curve for mixtures of E-42-11meEγδ and HFC-245eb at 14.14°C.

DETAILED DESCRIPTION

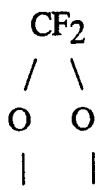
The present invention relates to the following compositions: hexafluorodimethyl ether and cyclopropane, dimethyl ether or propylene; bis(difluoromethyl) ether and 2,2,3,4,4-pentafluorooxetane; fluoromethyl

trifluoromethyl ether and 2,2,4,4,5,5-hexafluoro-1,3-dioxolane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, dimethyl ether or tris(trifluoromethyl)amine; trifluoromethyl methyl ether and perfluorooxetane, 2,2,4,4,5,5-hexafluoro-1,3-dioxolane, perfluoromethyl ethyl ether, perfluorodimethoxymethane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, dimethyl ether or tris(trifluoromethyl)amine; perfluoromethyl ethyl ether and dimethyl ether or propylene; perfluorodimethoxymethane and dimethyl ether or isobutane; 1-trifluoromethoxy-1,1,2,2-tetrafluoroethane and tris(trifluoromethyl)amine or dimethyl ether; difluoromethoxy pentafluoroethane and dimethyl ether, isobutane or tris(trifluoromethyl)amine; 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane and dimethyl ether or isobutane; 1-difluoromethoxy-1,1,2,2-tetrafluoroethane and $N(CHF_2)_2(CF_3)$; or 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)propane and 1,1,2,2,3-pentafluoropropane or 1,1,1,2,3-pentafluoropropane. This invention also relates to the discovery of effective amounts of the components of these compositions to form azeotropic or azeotrope-like compositions.

1-99 wt.% of each of the above components can be used as refrigerants.

The components of the refrigerants in this invention include the following.

1. Hexafluorodimethyl ether (116E, or CF_3OCF_3, boiling point = -59.0°C),
2. bis(difluoromethyl) ether (134E, or CHF_2OCHF_2, boiling point =5°C),
3. Fluoromethyl trifluoromethyl ether (134aE, or CH_2FOCF_3, boiling point = -20.0°C),
4. Trifluoromethyl methyl ether (143aE, or CH_3OCF_3, boiling point = -24.2°C),
5. Perfluorooxetane (C-216E or CF_2O | | CF_2CF_2, boiling point = -29.2°C),
6. 2,2,4,4,5,5-hexafluoro-1,3-dioxolane (C-216E2 or $C_3F_6O_2$, having a structure of



CF_2-CF_2

boiling point = -22.1°C),

7. Perfluoromethyl ethyl ether (218E, or $CF_3OCF_2CF_3$, boiling point = -23.3°C),
8. Perfluorodimethoxymethane (218E2, or $CF_3OCF_2OCF_3$, boiling point = -10.2°C),
9. 1-trifluoromethoxy-1,1,2,2-tetrafluoroethane (227caEαβ, or $CF_3OCF_2CHF_2$, boiling point = about -3°C),
10. Difluoromethoxy pentafluoroethane (227caEβγ, or $CHF_2OCF_2CF_3$, boiling point = -8.0°C),
11. 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane (227eaE, or $CF_3OCHFCF_3$, boiling point = -9.4°C),
12. 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)propane (E42-11meEγδ, or $CF_3CF_2CF_2OCHFCF_3$, boiling point = 40.8°C),
13. dimethyl ether (DME, or CH_3OCH_3)
14. 2,2,3,4,4-pentafluorooxetane (C-225eEαβ, or C_3HF_5O, having a structure of

$$\begin{array}{l} O\text{-}CF_2 \\ | \quad | \\ F_2C\text{-}CHF \end{array}$$

boiling point = 3.4°C)

15. tris(trifluoromethyl)amine, $(CF_3)_3N$, boiling point = -6.5°C),
16. 1-difluoromethoxy-1,1,2,2-tetrafluoroethane (236caE, or $CHF_2OCF_2CHF_2$, boiling point = 28.5°C),
17. 1,1,2,2,3-pentafluoropropane (HFC-245ca, or $CHF_2CF_2CH_2F$, boiling point = 25.13°C), and
18. 1,1,1,2,3-pentafluoropropane (HFC-245eb, or CF_3CHFCH_2F, boiling point = 22.46°C).

116E (CAS Reg. No. 1479-49-8) has been prepared by electrochemical fluorination of dimethyl ether as disclosed by Simons in U. S. Patent 2,519,983.

134aE (CAS Reg. No. 2261-01-0) has been made by the electrochemical fluorination of methyl 2-methoxypropionate as reported by Berenblit, et. al. Zh. Org. Khim., Vol. 12, pp. 767-770 (1976).

143aE (CAS Reg. No. 421-14-7) has been made by the reaction of

methyl fluoroformate with sulfur tetrafluoride as reported by Aldrich and Sheppard, J. Am. Chem. Soc., Vol. 29, 11-15 (1964).

C-216E (CAS Reg. No. 425-82-1) can be made by electrochemical fluorination of trimethylene oxide (oxetane) in anhydrous hydrogen fluoride as disclosed by Kauck and Simons in U. S. Patent 2,594,272.

C-216E2 (CAS Reg. No. 21297-65-4) has been prepared by UV irradiation of perfluoro-b-oxa-d-valerolactone in the vapor or liquid phase as reported by Throckmorton in J. Org. Chem., Vol. 34, pp. 3438-3440 (1969). The lactone was prepared by the reaction of KF with perfluorooxydiacetyl chloride.

218E (CAS Reg. No. 665-16-7) has been made by direct fluorination of $CF_3OCH_2CF_3$ (prepared by reaction of CF_3OF with vinylidene fluoride) as reported by Sekiya and Ueda in Chemistry Letters, pp. 609-612 (1990).

218E2 (CAS Reg. No. 53772-78-4) was made in the electrochemical fluorination of methyl 2-methoxypropionate as reported by Berenblit, et. al. Zh. Org. Khim., Vol. 12, pp. 767-770 (1976).

227caE$\alpha\beta$ (CAS Reg. No. 2356-61-8) has been prepared by reacting difluoroacetyl fluoride with cesium fluoride and carbonyl fluoride followed by treatment with sulfur tetrafluoride as disclosed by Eisemann in U. S. Patent 3,362,190.

227caE$\beta\gamma$ (CAS Reg. No. 53997-64-1) has been made by electrochemical fluorination of $CHCl_2OCF_2CHClF$ as reported by Okazaki, et. al. J. Fluorine Chem., Vol. 4, pp. 387-397 (1974).

227eaE (CAS Reg. No. 2356-62-9) was prepared by reacting 2-trifluoromethoxy-tetrafluoropropionyl fluoride ($CF_3CF(OCF_3)COF$) with aqueous potassium hydroxide at 230°C as disclosed by Eisemann in U. S. Patent 3,362,190.

236caE (CAS Reg. No. 32778-11-3) has been prepared by fluorination of $CHCl_2OCF_2CHF_2$ (prepared in turn by chlorination of $CH_3OCF_2CHF_2$) using anhydrous hydrogen fluoride with antimony pentachloride catalyst as reported by Terrell, et. al. in J. Medicinal Chem., Vol. 15, pp. 604-606 (1972).

E42-11meE$\gamma\delta$ (CAS Reg. No. 3330-15-2) has been prepared by heating $CF_3CF_2CF_2OCF(CF_3)CO_2$-Na+ in ethylene glycol as disclosed by Selman and Smith in French Patent No. 1,373,014 (Chemical Abstracts 62:13047g).

C-225eE$\alpha\beta$ (CAS Reg. No. 144109-03-5) may be prepared by direct fluorination of trimethylene oxide (cyclo-$CH_2CH_2CH_2O$-) using techniques described by Lagow and Margrave in Progress in Inorganic Chemistry, Vol. 26, pp. 161-210 (1979) or by Adcock and Cherry in Ind. Eng. Chem. Res., Vol. 26, pp. 208-

215 (1987). The direct fluorination is carried out to the desired level of fluorine incorporation into the starting material, and products recovered by fractional distillation.

$(CF_3)_3N$ (CAS Reg. No. 432-03-1) has been made by electrochemical fluorination of trimethyl amine in anhydrous hydrogen fluoride as disclosed by Kauck and Simons in U. S. Patent 2,616,927.

By "azeotropic" composition is meant a constant boiling liquid admixture of two or more substances that behaves as a single substance. 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.

By "azeotrope-like" composition is meant a constant boiling, or substantially constant boiling, liquid admixture of two or more substances that behaves as a single substance. One way to characterize an azeotrope-like composition is that the vapor produced by partial evaporation or distillation of the liquid has substantially the same composition as the liquid from which it was evaporated or distilled, that is, the admixture distills/refluxes without substantial composition change. Another way to characterize an azeotrope-like composition is that the bubble point vapor pressure and the dew point vapor pressure of the composition at a particular temperature are substantially the same.

It is recognized in the art that a composition is azeotrope-like if, after 50 weight percent of the composition is removed such as by evaporation or boiling off, the difference in vapor pressure between the original composition and the composition remaining after 50 weight percent of the original composition has been removed is less than 10 percent, when measured in absolute units. By absolute units, it is meant measurements of pressure and, for example, psia, atmospheres, bars, torr, dynes per square centimeter, millimeters of mercury, inches of water and other equivalent terms well known in the art. If an azeotrope is present, there is no difference in vapor pressure between the original composition and the composition remaining after 50 weight percent of the original composition has been removed.

Therefore, included in this invention are compositions of effective amounts of 116E and cyclopropane, DME or propylene; 134E and C-225eE$\alpha\beta$; 134aE and C-216E2, 227eaE, DME or $N(CF_3)_3$; 143aE and C-216E, C-216E2,

218E, 218E2, 227eaE, DME or $N(CF_3)_3$; 218E and DME or propylene; 218E2 and DME or isobutane; 227caEαβ and $N(CF_3)_3$ or DME; 227caEβγ and DME, isobutane or $N(CF_3)_3$; 227eaE and DME or isobutane; 236caE and $N(CHF_2)_2(CF_3)$; or E-42-11meEγδ and HFC-245ca or HFC-245eb, such that after 50 weight percent of an original composition is evaporated or boiled off to produce a remaining composition, the difference in the vapor pressure between the original composition and the remaining composition is 10 percent or less.

For compositions that are azeotropic, there is usually some range of compositions around the azeotrope point that, for a maximum boiling azeotrope, have boiling points at a particular pressure higher than the pure components of the composition at that pressure and have vapor pressures at a particular temperature lower than the pure components of the composition at that temperature, and that, for a minimum boiling azeotrope, have boiling points at a particular pressure lower than the pure components of the composition at that pressure and have vapor pressures at a particular temperature higher than the pure components of the composition at that temperature. Boiling temperatures and vapor pressures above or below that of the pure components are caused by unexpected intermolecular forces between and among the molecules of the compositions, which can be a combination of repulsive and attractive forces such as van der Waals forces and hydrogen bonding.

The range of compositions that have a maximum or minimum boiling point at a particular pressure, or a maximum or minimum vapor pressure at a particular temperature, may or may not be coextensive with the range of compositions that have a change in vapor pressure of less than about 10% when 50 weight percent of the composition is evaporated. In those cases where the range of compositions that have maximum or minimum boiling temperatures at a particular pressure, or maximum or minimum vapor pressures at a particular temperature, are broader than the range of compositions that have a change in vapor pressure of less than about 10% when 50 weight percent of the composition is evaporated, the unexpected intermolecular forces are nonetheless believed important in that the refrigerant compositions having those forces that are not substantially constant boiling may exhibit unexpected increases in the capacity or efficiency versus the components of the refrigerant composition.

The components of the compositions of this invention have the following vapor pressures at 25°C.

Components	Psia	kPa
116E	292.2	2015
134E	30.4	210
134aE	73.8	509
143aE	83.8	578
218E	83.8	578
218E2	52.3	361
227caEαβ	41.3	285
227caEβγ	48.7	336
227eaE	51.3	354
236caE	12.9	89
E-42-11meEγδ	8.1	56
Cyclopropane	105.0	724
DME	85.7	591
Propylene	165.9	1144
C-225eEαβ	31.1	214
C-216E2	76.7	529
$N(CF_3)_3$	45.8	316
C-216E	100.3	692
isobutane	50.5	348
$N(CHF_2)_2(CF_3)$	13.9	96
HFC-245ca	14.2	98
HFC-245eb	16.9	117

Substantially constant boiling, azeotropic or azeotrope-like compositions of this invention comprise the following (all compositions are measured at 25°C):

COMPONENTS	WEIGHT RANGES (wt.%/wt/%)	PREFERRED (wt.%/wt.%)
116E/cyclopropane	72-99/1-28	72-99/1-28
116E/DME	68-99/1-32	68-99/1-32
116E/propylene	60-99/1-40	60-99/1-40
134E/C-225eEαβ	1-99/1-99	1-80/20-99
134aE/C-216E2	1-99/1-99	20-99/1-80
134aE/227eaE	1-99/1-99	20-99/1-80
134aE/DME	1-99/1-99	20-99/1-80
134aE/$N(CF_3)_3$	20-99/1-80	40-99/1-60
143aE/C-216E	1-99/1-99	1-80/20-99
143aE/C-216E2	1-99/1-99	1-80/20-99
143aE/218E	1-99/1-99	1-80/20-99
143aE/218E2	1-99/1-99	1-99/1-99
143aE/227eaE	1-99/1-99	1-99/1-99

143aE/DME	1-99/1-99	10-90/10-90
143aE/$N(CF_3)_3$	27-99/1-73	27-99/1-73
218E/DME	50-92/8-50	50-92/8-50
218E/propylene	1-82/18-99	20-82/18-80
218E2/DME	1-86/14-99	30-86/14-70
218E2/isobutane	1-99/1-99	20-99/1-80
227caEαβ/$N(CF_3)_3$	1-99/1-99	1-80/20-99
227caEαβ/DME	1-80/20-99	10-80/20-90
227caEβγ/DME	1-83/17-99	20-83/17-80
227caEβγ/isobutane	1-99/1-99	20-99/1-80
227caEβγ/$N(CF_3)_3$	1-99/1-99	20-99/1-80
227eaE/DME	1-84/16-99	20-84/16-80
227eaE/isobutane	1-99/1-99	20-99/1-80
236caE/$N(CHF_2)_2(CF_3)$	1-99/1-99	1-80/20-99
E-42-11meEγδ/HFC-245ca	1-72/18-99	1-50/50-99
E-42-11meEγδ/HFC-245eb	98-99/1-2	---
E-42-11meEγδ/HFC-245eb	1-70/30-99	1-50/50-99

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.

For the purposes of this discussion, azeotropic or constant-boiling is intended to mean also essentially azeotropic or essentially-constant boiling. In other words, included within the meaning of these terms are not only the true azeotropes described above, but also other compositions containing the same components in different proportions, which are true azeotropes at other temperatures and pressures, as well as those equivalent compositions which are part of the same azeotropic system and are azeotrope-like in their properties. As is well recognized in this art, there is a range of compositions which contain the same components as the azeotrope, which will not only exhibit essentially equivalent properties for refrigeration and other applications, but which will also exhibit essentially

equivalent properties to the true azeotropic composition in terms of constant boiling characteristics or tendency not to segregate or fractionate on boiling.

It is possible to characterize, in effect, a constant boiling admixture which may appear under many guises, depending upon the conditions chosen, by any of several criteria:

* The composition can be defined as an azeotrope of A, B, C (and D...) since the very term "azeotrope" is at once both definitive and limitative, and requires that effective amounts of A, B, C (and D...) for this unique composition of matter which is a constant boiling composition.
* It is well known by those skilled in the art, that, at different pressures, the composition of a given azeotrope will vary at least to some degree, and changes in pressure will also change, at least to some degree, the boiling point temperature. Thus, an azeotrope of A, B, C (and D...) represents a unique type of relationship but with a variable composition which depends on temperature and/or pressure. Therefore, compositional ranges, rather than fixed compositions, are often used to define azeotropes.
* The composition can be defined as a particular weight percent relationship or mole percent relationship of A, B, C (and D...), while recognizing that such specific values point out only one particular relationship and that in actuality, a series of such relationships, represented by A, B, C (and D...) actually exist for a given azeotrope, varied by the influence of pressure.
* An azeotrope of A, B, C (and D...) can be characterized by defining the compositions as an azeotrope characterized by a boiling point at a given pressure, thus giving identifying characteristics without unduly limiting the scope of the invention by a specific numerical composition, which is limited by and is only as accurate as the analytical equipment available.

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.

Specific examples illustrating the invention are given below. Unless otherwise stated therein, all percentages are by weight. It is to be understood that

these examples are merely illustrative and in no way are to be interpreted as limiting the scope of the invention.

EXAMPLE 1

Phase Study

A phase study shows the following compositions are azeotropic, all at 25°C.

Composition No.	Weight percent of the components	Vapor Press. psia (kPa)	
116E/cyclopropane	96.9/3.1	295.1	2035
116E/DME	93.9/6.1	308.6	2128
116E/propylene	89.3/10.7	312.7	2156
134E/C-225eEαβ	35.6/64.4	31.8	219
134aE/C-216E2	27.8/72.2	77.9	537
134aE/227eaE	94.0/6.0	73.9	510
134aE/DME	36.7/63.3	86.7	598
134aE/$N(CF_3)_3$	71.8/28.2	76.9	530
143aE/C-216E	3.8/96.2	100.4	692
143aE/C-216E2	60.3/39.7	85.4	589
143aE/218E	39.3/60.7	105.6	728
143aE/218E2	73.8/26.2	85.7	591
143aE/227eaE	92.9/7.1	83.9	578
143aE/DME	51.4/48.6	92.6	638
143aE/$N(CF_3)_3$	71.0/29.0	87.6	604
218E/DME	75.5/24.5	126.6	873
218E/propylene	40.1/59.9	171.9	1185
218E2/DME	60.9/39.1	100.2	691
218E2/isobutane	83.6/16.4	53.5	369
227caEαβ/$N(CF_3)_3$	35.1/64.9	48.0	331
227caEαβ/DME	4.7/95.3	85.7	591
227caEβγ/DME	49.5/50.5	93.2	643
227caEβγ/isobutane	39.1/60.9	50.6	349
227caEβγ/$N(CF_3)_3$	80.0/20.0	48.9	337
227eaE/DME	52.9/47.1	95.1	656
227eaE/isobutane	80.9/19.1	51.8	357
236caE/$N(CHF_2)_2(CF_3)$	16.2/83.8	14.0	97
E-42-11meEγδ/HFC-245ca	26.0/74.0	15.2	105
E-42-11meEγδ/HFC-245eb	15.7/84.3	16.4	113

EXAMPLE 2

Impact of Vapor Leakage on Vapor Pressure at 25°C

A vessel is charged with an initial composition at 25°C, and the vapor pressure of the composition is measured. The composition is allowed to leak from the vessel, while the temperature is held constant at 25°C, until 50 weight percent of the initial composition is removed, at which time the vapor pressure of the composition remaining in the vessel is measured. The results are summarized below.

WT%A/WT%B	INITIAL		50% LEAK		
	PSIA	KPA	PSIA	KPA	DELTA %P
116E/cyclopropane					
96.9/3.1	295.1	2035	295.1	2035	0.0
99/1	293.9	2026	293.8	2026	0.0
60/40	255.9	1764	133.6	921	47.8
80/20	276.4	1906	262.7	1811	5.
75/25	270.6	1866	250.4	1726	7.5
72/28	267.4	1844	241.7	1666	9.6
71/29	266.4	1837	238.2	1642	10.6
116E/DME					
93.9/6.1	308.6	2128	308.6	2128	0.0
99/1	299.0	2062	296.8	2046	0.7
70/30	292.7	2018	275.8	1902	5.8
68/32	291.6	2011	267.6	1845	8.2
67/33	291.1	2007	257.7	1777	11.5
116E/propylene					
89.3/10.7	312.7	2156	312.7	2156	0.0
99/1	297.2	2049	295.9	2040	0.4
60/40	292.1	2014	263.3	1815	9.9
59/41	291.2	2008	259.5	1789	10.9
134E/C-225eEαβ					
35.6/64.4	31.8	219	31.8	219	0.0
20/80	31.6	218	31.6	218	0.0
1/99	31.1	214	31.1	214	0.0
80/20	31.1	214	31.1	214	0.0
99/1	30.5	210	30.5	210	0.0

	134aE/C-216E2					
	27.8/72.2	77.9	537	77.9	537	0.0
	15/85	77.7	536	77.7	536	0.0
	1/99	76.8	530	76.8	530	0.0
	60/40	76.9	530	76.8	530	0.1
	80/20	75.6	521	75.5	521	0.1
	99/1	73.9	510	73.9	510	0.0
	134aE/227eaE					
	94.0/6.0	73.9	510	73.9	510	0.0
	99/1	73.8	509	73.8	509	0.0
	60/40	71.9	496	71.3	492	0.8
	40/60	68.4	472	66.8	461	2.3
	20/80	62.3	430	59.6	411	4.3
	10/90	57.6	397	55.4	382	3.8
	1/99	52.	359	51.7	356	0.6
	134aE/DME					
	36.7/63.3	86.7	598	86.7	598	0.0
	20/80	86.5	596	86.5	596	0.0
	1/99	85.8	592	85.8	592	0.0
	60/40	86.0	593	85.8	592	0.2
	80/20	83.0	572	82.4	568	0.7
	99/1	74.6	514	74.4	513	0.3
	134aE/$N(CF_3)_3$					
	71.8/28.2	76.9	530	76.9	530	0.0
	85/15	76.3	526	76.1	525	0.3
	99/1	74.1	511	74.	510	0.1
	40/60	73.6	507	71.2	491	3.3
	20/80	65.9	454	59.3	409	10.
	19/81	65.3	450	58.6	404	10.3
	143aE/C-216E					
	3.8/96.2	100.4	692	100.4	692	0.0
	1/99	100.4	692	100.4	692	0.0
	20/80	99.5	686	99.4	685	0.1
	40/60	96.9	668	96.4	665	0.5
	60/40	93.3	643	92.3	636	1.1
	80/20	88.9	613	87.9	606	1.1
	90/10	86.4	596	85.8	592	0.7
	99/1	84.1	580	84.	579	0.1

	143aE/C-216E2					
	60.3/39.7	85.4	589	85.4	589	0.0
	80/20	85.	586	84.9	585	0.1
	99/1	83.9	578	83.9	578	0.0
	30/70	83.9	578	83.7	577	0.2
	1/99	77.1	532	77.1	532	0.0
	143aE/218E					
	39.3/60.7	105.6	728	105.6	728	0.0
	20/80	102.6	707	100.7	694	1.9
	10/90	96.7	667	93.1	642	3.7
	1/99	85.6	590	84.7	584	1.1
	60/40	103.6	714	101.7	701	1.8
	70/30	101.4	699	97.	669	4.3
	80/20	97.9	675	91.3	629	6.7
	90/10	92.5	638	86.5	596	6.5
	99/1	84.9	585	84.	579	1.1
	143aE/218E2					
	73.8/26.2	85.7	591	85.7	591	0.0
	85/15	85.4	589	85.3	588	0.1
	99/1	84.	579	83.9	578	0.1
	60/40	85.2	587	85.	586	0.2
	40/60	82.3	567	80.2	553	2.6
	20/80	74.4	513	68.5	472	7.9
	15/85	70.8	488	64.3	443	9.2
	13/87	69.2	477	62.5	431	9.7
	12/88	68.2	470	61.7	425	9.5
	10/90	66.3	457	59.9	413	9.7
	9/91	65.2	450	59.1	407	9.4
	5/95	60.2	415	55.8	385	7.3
	1/99	54.1	373	52.9	365	2.2
	143aE/227eaE					
	92.9/7.1	83.9	578	83.9	578	0.0
	99/1	83.9	578	83.9	578	0.0
	60/40	81.6	563	80.7	556	1.1
	40/60	77.3	533	74.4	513	3.8
	20/80	68.8	474	63.6	439	7.6
	15/85	65.5	452	60.4	416	7.8
	10/90	61.6	425	57.1	394	7.3
	1/99	52.5	362	51.8	357	1.3

143aE/DME						
58.9/41.1	88.2	608	88.2	608	0.0
80/20	87.5	603	87.4	603	0.1
99/1	84.1	580	84.1	580	0.0
40/60	87.9	606	87.8	605	0.1
20/80	86.9	599	86.9	599	0.0
1/99	85.8	592	85.8	592	0.0
143aE/$N(CF_3)_3$					
71.0/29.0	87.6	604	87.6	604	0.0
85/15	86.9	599	86.5	596	0.5
99/1	84.1	580	84.	579	0.1
40/60	84.2	581	80.9	558	3.9
20/80	74.9	516	64.4	444	14.
25/75	78.2	539	69.7	481	10.9
27/73	79.3	547	71.6	494	9.7
218E/DME					
75.5/24.5	126.6	873	126.6	873	0.0
90/10	121.7	839	114.0	786	6.3
92/8	119.0	820	108.3	747	9.0
93/7	117.2	808	105.0	724	10.4
50/50	124.1	856	111.8	771	9.9
49/51	124.0	855	109.3	754	11.9
218E/propylene					
40.1/59.9	171.9	1185	171.9	1185	0.0
20/80	170.4	1175	169.7	1170	0.4
1/99	166.2	1146	166.1	1145	0.1
60/40	169.9	1171	168.2	1160	1.
80/20	158.8	1095	146.2	1008	7.9
85/15	151.7	1046	133.5	920	12.
82/18	156.4	1078	141.6	976	9.5
218E2/DME					
60.9/39.1	100.2	691	100.2	691	0.0
80/20	97.7	674	93.8	647	4.0
86/14	94.3	650	85.1	587	9.8
87/13	93.4	644	83.1	573	11.0
40/60	99.0	683	96.3	664	2.7
30/70	97.5	672	92.0	634	5.6
15/85	93.5	645	87.2	601	6.7
1/99	86.4	596	85.8	592	0.7

218E2/isobutane						
83.6/16.4	53.5	369	53.5	369	0.0
90/10	53.3	367	53.3	367	0.0
99/1	52.5	362	52.5	362	0.0
60/40	52.8	364	52.8	364	0.0
40/60	52.	359	51.9	358	0.2
20/80	51.2	353	51.1	352	0.2
1/99	50.5	348	50.5	348	0.0
227caEαβ/$N(CF_3)_3$						
35.1/64.9	48.	331	48.	331	0.0
15/85	47.3	326	47.2	325	0.2
1/99	46.	317	45.9	316	0.2
60/40	47.1	325	46.9	323	0.4
80/20	45.1	311	44.5	307	1.3
99/1	41.6	287	41.5	286	0.2
227caEαβ/DME						
4.7/95.3	85.7	591	85.7	591	0.0
1/99	85.7	591	85.7	591	0.0
40/60	84.4	582	83.9	578	0.6
60/40	81.5	562	79.4	547	2.6
80/20	73.8	509	66.7	460	9.6
81/19	73.1	504	65.6	452	10.3
227caEβγ/DME						
49.5/50.5	93.2	643	93.2	643	0.0
80/20	87.9	606	81.7	563	7.1
83/17	86.0	593	77.8	536	9.5
84/16	85.3	588	76.3	526	10.6
20/80	90.8	626	89.1	614	1.9
1/99	86.1	594	85.8	592	0.3
227caEβγ/isobutane						
39.1/60.9	50.6	349	50.6	349	0.0
60/40	50.5	348	50.5	348	0.0
80/20	50.1	345	50.1	345	0.0
90/10	49.6	342	49.6	342	0.0
99/1	48.8	336	48.8	336	0.0
20/80	50.6	349	50.6	349	0.0
10/90	50.5	348	50.5	348	0.0
1/99	50.5	348	50.5	348	0.0

	227caEβγ/$N(CF_3)_3$					
	80.0/20.0	48.9	337	48.9	337	0.0
	90/10	48.8	336	48.8	336	0.0
	99/1	48.7	336	48.7	336	0.0
	60/40	48.7	336	48.7	336	0.0
	40/60	48.2	332	48.2	332	0.0
	20/80	47.3	326	47.2	325	0.2
	1/99	45.9	316	45.9	316	0.0
	227eaE/DME					
	52.9/47.1	95.1	656	95.1	656	0.0
	20/80	92.0	634	89.3	616	2.9
	1/99	86.2	594	85.8	592	0.5
	80/20	90.6	625	85.0	586	6.2
	84/16	88.1	607	79.8	550	9.4
	85/15	87.3	602	78.2	539	10.4
	227eaE/isobutane					
	80.9/19.1	51.8	357	51.8	357	0.0
	99/1	51.3	354	51.3	354	0.0
	60/40	51.5	355	51.5	355	0.0
	40/60	51.2	353	51.2	353	0.0
	20/80	50.8	350	50.8	350	0.0
	1/99	50.5	348	50.5	348	0.0
	236caE/$N(CHF_2)_2(CF_3)$					
	16.2/83.8	14.	97	14.	97	0.0
	1/99	13.9	96	13.9	96	0.0
	40/60	13.9	96	13.9	96	0.0
	70/30	13.5	93	13.5	93	0.0
	90/10	13.2	91	13.1	90	0.8
	99/1	13.	90	12.9	89	0.8
	E42-11meEγδ/HFC-245ca					
	1/99	14.7	101	14.7	101	0.2
	10/90	15.0	104	14.9	103	0.5
	20/80	15.2	105	15.2	105	0.1
	26.0/74.0	15.2	105	15.2	105	0.0
	30/70	15.2	105	15.2	105	0.1
	40/60	15.1	104	15.0	103	0.6
	50/50	14.9	102	14.6	100	2.0
	60/40	14.5	100	13.8	95	4.6
	70/30	13.8	95	12.6	87	8.6

E42-11meEγδ/HFC-245eb					
99/1	8.5	59	8.2	56	4.4
98/2	9.0	61.8	8.3	56.9	7.9
73/27	14.3	99	12.7	88	11.1
70/30	14.6	101	13.2	91	9.5
50/50	15.8	109	15.4	106	2.5
30/70	16.3	112	16.2	112	0.3
15.7/84.3	16.4	113	16.4	113	0
1/99	16.3	112	16.3	112	0

The results of this Example show that these compositions are azeotropic or azeotrope-like because when 50 wt.% of an original composition is removed, the vapor pressure of the remaining composition is within about 10% of the vapor pressure of the original composition, at a temperature of 25°C.

EXAMPLE 3

Impact of Vapor Leakage at 0°C

A leak test is performed on compositions of 218E2 and DME at the temperature of 0°C. The results are summarized below.

WT%A/WT%B	INITIAL		50% LEAK		
	PSIA	KPA	PSIA	KPA	DELTA %P
218E2/DME					
59.9/40.1	45.4	313	45.4	313	0.0
70/30	45.2	312	44.8	309	0.9
84/16	43.3	299	39.5	272	8.8
85/15	43.0	296	38.6	266	10.2
40/60	44.9	310	43.7	301	2.7
20/80	43.2	298	39.7	274	8.1
15/85	42.5	293	39.2	270	7.8
1/99	39.0	269	38.7	267	0.8

These results show that compositions of 218E2 and DME are azeotropic or azeotrope-like at different temperatures, but that the weight pecents of the components vary as the temperature is changed.

EXAMPLE 4

Refrigerant Performance

The following table shows the performance of various refrigerants. The data are based on the following conditions.

Evaporator temperature	48.0°F (8.9°C)
Condenser temperature	115.0°F (46.1°C)
Subcooled	12.0°F (6.7°C)
Return gas temperature	65.0°F (18.3°C)
Compressor efficiency is	75%.

The refrigeration capacity is based on a compressor with a fixed displacement of 3.5 cubic feet per minute and 75% volumetric efficiency. Capacity is intended to mean the change in enthalpy of the refrigerant in the evaporator per pound of refrigerant circulated, i.e. the heat removed by the refrigerant in the evaporator per time. Coefficient of performance (COP) is intended to mean the ratio of the capacity to compressor work. It is a measure of refrigerant energy efficiency.

Refrig. Comp.	Evap. Press. Psia (kPa)	Cond. Press. Psia (kPa)	Comp. Dis. Temp. °F (°C)	COP	Capacity BTU/min (kw)
HCFC-22	95 (655)	258 (1779)	183 (83.9)	4.60	397 (7.0)
116E/cyclopropane					
5.0/95.0	69 (476)	184 (1269)	173 (78.3)	4.92	302 (5.3)
96.9/3.1*	95 (655)	335 (2310)	122 (50)	2.78	277 (4.9)
99.0/1.0*	98 (676)	331 (2282)	117 (47.2)	2.88	284 (5)
*90/10/15/30/0.75					
116E/DME					
5.0/95.0	54 (372)	155 (1069)	166 (74.4)	4.99	256 (4.5)
93.9/6.1	166 (1145)	405 (2792)	138 (58.9)	3.60	436 (7.7)
99.0/1.0*	97 (669)	343 (2365)	121 (49.4)	2.68	271 (4.8)
*90/10/15/30/0.75					

116E/propylene						
5.0/95.0	112 (772)	283 (1951)	159 (70.6)	4.52	411 (7.2)
89.3/10.7*	101 (696)	344 (2372)	125 (51.7)	2.84	294 (5.2)
99.0/1.0*	101 (696)	352 (2427)	121 (49.4)	2.66	277 (4.9)

*90/10/15/30/0.75

134E/C-225eEαβ					
5.0/95.0	18 (124)	59 (407)	131 (55)	4.83	91 (1.6)
35.6/64.4	18 (124)	60 (414)	138 (58.9)	4.88	93 (1.6)
95.0/5.0	16 (110)	58 (400)	153 (67.2)	4.95	92 (1.6)
134aE/C-216E2					
5.0/95.0	47 (324)	138 (951)	121 (49.4)	4.36	186 (3.3)
27.8/72.2	46 (317)	138 (951)	126 (52.2)	4.47	193 (3.4)
95.0/5.0	44 (303)	136 (938)	143 (61.7)	4.67	201 (3.5)
134aE/227eaE					
5.0/95.0	31 (214)	102 (703)	125 (51.7)	4.48	141 (2.5)
94.0/6.0	44 (303)	135 (931)	143 (61.7)	4.66	200 (3.5)
99.0/1.0	44 (303)	135 (931)	144 (62.2)	4.68	201 (3.5)
134aE/DME					
5.0/95.0	51 (352)	149 (1027)	167 (75)	4.88	240 (4.2)
36.7/63.3	53 (365)	153 (1055)	161 (71.7)	4.82	242 (4.3)
95.0/5.0	46 (317)	141 (972)	146 (63.3)	4.7	211 (3.7)
134aE/$N(CF_3)_3$					
5.0/95.0	29 (200)	95 (655)	120 (48.9)	4.38	128 (2.3)
71.8/28.2	45 (310)	137 (945)	137 (58.3)	4.56	197 (3.5)
95.0/5.0	45 (310)	136 (938)	143 (61.7)	4.65	201 (3.5)
143aE/C-216E					
1.0/99.0	59 (407)	165 (1138)	124 (51.1)	4.18	211 (3.7)
3.8/96.2	60 (414)	168 (1158)	124 (51.1)	4.18	216 (3.8)
95.0/5.0	52 (359)	153 (1055)	145 (62.8)	4.69	230 (4)
143aE/C-216E2					
5.0/95.0	47 (324)	140 (965)	121 (49.4)	4.35	189 (3.3)
60.3/39.7	51 (352)	150 (1034)	137 (58.3)	4.6	218 (3.8)
95.0/5.0	51 (352)	150 (1034)	145 (62.8)	4.69	225 (4)

143aE/218E						
	5.0/95.0	54 (372)	161 (1110)	124 (51.1)	4.08	199 (3.5)
	39.3/60.7	62 (427)	179 (1234)	132 (55.6)	4.3	238 (4.2)
	95.0/5.0	52 (359)	153 (1055)	145 (62.8)	4.69	229 (4)
143aE/218E2						
	5.0/95.0	35 (241)	114 (786)	121 (49.4)	4.2	145 (2.6)
	73.8/26.2	50 (345)	149 (1027)	139 (59.4)	4.59	217 (3.8)
	95.0/5.0	51 (352)	150 (1034)	145 (62.8)	4.68	224 (3.9)
143aE/227eaE						
	5.0/95.0	32 (221)	104 (717)	126 (52.2)	4.48	144 (2.5)
	92.9/7.1	50 (345)	149 (1027)	145 (62.8)	4.68	223 (3.9)
	99.0/1.0	51 (352)	149 (1027)	146 (63.3)	4.7	225 (4)
143aE/DME						
	5.0/95.0	51 (352)	149 (1027)	167 (75)	4.87	240 (4.2)
	58.9/41.1	54 (372)	157 (1082)	157 (69.4)	4.80	245 (4.3)
	95.0/5.0	51 (352)	152 (1048)	148 (64.4)	4.71	230 (4)
143aE/$N(CF_3)_3$						
	5.0/95.0	30 (207)	98 (676)	120 (48.9)	4.41	133 (2.3)
	71.0/29.0	52 (359)	152 (1048)	139 (59.4)	4.57	221 (3.9)
	95.0/5.0	51 (352)	151 (1041)	145 (62.8)	4.67	225 (4)
218E/DME						
	5.0/95.0	54 (372)	154 (1062)	165 (73.9)	4.98	253 (4.5)
	75.5/24.5	80 (552)	219 (1510)	138 (58.9)	4.30	294 (5.2)
	95.0/5.0	63 (434)	184 (1269)	127 (52.8)	4.13	231 (4.1)
218E/propylene						
	5.0/95.0	109 (752)	277 (1910)	159 (70.6)	4.5	401 (7.1)
	40.1/59.9	107 (738)	275 (1896)	152 (66.7)	4.37	381 (6.7)
	95.0/5.0	63 (434)	185 (1276)	128 (53.3)	4.16	233 (4.1)
218E2/DME						
	5.0/95.0	52 (359)	151 (1041)	166 (74.4)	4.89	243 (4.3)
	60.9/39.1	61 (421)	174 (1200)	142 (61.1)	4.59	254 (4.5)
	95.0/5.0	41 (283)	133 (917)	121 (49.4)	4.31	173 (3)
218E2/isobutane						
	5.0/95.0	31 (214)	90 (621)	134 (56.7)	4.78	138 (2.4)
	5.09756	31 (214)	100 (689)	121 (49.4)	4.44	137 (2.4)
	95.0/5.0	32 (221)	104 (717)	117 (47.2)	4.26	135 (2.4)

227caEαβ/N(CF_3)$_3$					
5.0/95.0	27 (186)	88 (607)	118 (47.8)	4.33	116 (2)
35.1/64.9	26 (179)	85 (586)	118 (47.8)	4.37	114 (2)
95.0/5.0	24 (165)	80 (552)	119 (48.3)	4.45	110 (1.9)
227caEαβ/DME					
5.0/95.0	52 (359)	150 (1034)	166 (74.4)	4.88	241 (4.2)
4.7/95.3	52 (359)	150 (1034)	166 (74.4)	4.88	241 (4.2)
95.0/5.0	31 (214)	101 (696)	124 (51.1)	4.67	145 (2.6)
227caEβγ/DME					
5.0/95.0	52 (359)	150 (1034)	166 (74.4)	4.88	242 (4.3)
49.5/50.5	57 (393)	163 (1124)	152 (66.7)	4.72	250 (4.4)
95.0/5.0	36 (248)	115 (793)	129 (53.9)	4.61	164 (2.9)
227caEβγ/isobutane					
5.0/95.0	31 (214)	90 (621)	134 (56.7)	4.79	138 (2.4)
39.1/60.9	30 (207)	90 (621)	133 (56.1)	4.74	137 (2.4)
95.0/5.0	29 (200)	93 (641)	125 (51.7)	4.53	131 (2.3)
227caEβγ/N(CF_3)$_3$					
5.0/95.0	27 (186)	88 (607)	118 (47.8)	4.33	117 (2.1)
80.0/20.0	28 (193)	93 (641)	123 (50.6)	4.46	127 (2.2)
95.0/5.0	29 (200)	93 (641)	124 (51.1)	4.48	129 (2.3)
227eaE/DME					
5.0/95.0	52 (359)	150 (1034)	166 (74.4)	4.88	242 (4.3)
52.9/47.1	58 (400)	166 (1145)	150 (65.6)	4.7	251 (4.4)
95.0/5.0	38 (262)	119 (820)	129 (53.9)	4.59	170 (3)
227eaE/isobutane					
5.0/95.0	31 (214)	90 (621)	134 (56.7)	4.79	138 (2.4)
80.9/19.1	30 (207)	94 (648)	128 (533)	4.61	136 (2.4)
95.0/5.0	30 (207)	97 (669)	125 (51.7)	4.51	136 (2.4)
236caE/N(CHF_2)$_2$(CF_3)					
5.0/95.0	7 (48)	29 (200)	128 (53.3)	4.84	43 (0.8)
16.2/83.8	7 (48)	29 (200)	129 (53.9)	4.85	43 (0.8)
95.0/5.0	7 (48)	27 (186)	133 (56.1)	4.91	41 (0.7)

EXAMPLE 5

Refrigerant Performance

The following table shows the performance of a refrigerant mixture. The data are based on the following conditions.

Evaporator temperature 40.0°F (4.4°C)
Condenser temperature 100.0°F (37.8°C)
Return gas temperature 40.0°F (4.4°C)
Compressor efficiency is 75%.
No subcooling or superheat.

Refrig. Comp.	Evap. Press. Psia (kPa)	Cond. Press. Psia (kPa)	Comp. Dis. Temp. °F (°C)	COP	Capacity BTU/min (kw)
CFC-11	6.9 (48)	23.5 (162)	133 (56.1)	5.63	43.6 (0.8)
E42-11meEγδ/HFC-245ca					
26.0/74.0	6.4 (44)	24.3 (168)	102 (38.9)	5.32	40.4 (0.7)
5/95	6.2 (43)	23.7 (163)	108 (42.2)	5.38	40.0 (0.7)
E42-11meEγδ/HFC-245eb					
15.7/84.3	6.7 (46)	26.3 (181)	111 (43.9)	5.26	43.2 (0.8)
5/95	6.7 (46)	26.3 (181)	115 (46.1)	5.28	43.3 (0.8)

EXAMPLE 6

This Example is directed to measurements of the liquid/vapor equilibrium curves for the mixtures in Figures 1-27.

Turning to Figure 1, the upper curve represents the composition of the liquid, and the lower curve represents the composition of the vapor.

The data for the compositions of the liquid in Figure 1 are obtained as follows. A stainless steel cylinder is evacuated, and a weighed amount of 116E is added to the cylinder. The cylinder is cooled to reduce the vapor pressure of 116E, and then a weighed amount of cyclopropane is added to the cylinder. The cylinder is agitated to mix the 116E and cyclopropane, and then the cylinder is placed in a constant temperature bath until the temperature comes to equilibrium at 25°C, at which time the vapor pressure of the 116E and cyclopropane in the cylinder is measured. Additional samples of liquid are measured the same way, and the results

are plotted in Figure 1.

The curve which shows the composition of the vapor is calculated using an ideal gas equation of state.

Vapor/liquid equilibrium data are obtained in the same way for the mixtures shown in Figures 2-27.

The data in Figures 1-27 show that at 25°C, there are ranges of compositions that have vapor pressures higher than the vapor pressures of the pure components of the composition at that same temperature. As stated earlier, the higher than expected pressures of these compositions may result in an unexpected increase in the refrigeration capacity or efficiency of those compositions when compared to the pure components of the compositions.

EXAMPLE 7

This Example is directed to measurements of the liquid/vapor equilibrium curve for mixtures of E-42-11meEγδ and HFC-245ca and E-42-11meEγδ and HFC-245eb. The liquid/vapor equilibrium data for these mixtures are shown in Figures 28 and 29. The upper curve represents the liquid composition, and the lower curve represents the vapor composition.

The procedure for measuring the composition of the liquid for mixtures of E-42-11meEγδ/HFC-245ca in Figure 28 was as follows. A stainless steel cylinder was evacuated, and a weighed amount of E-42-11meEγδ was added to the cylinder. The cylinder was cooled to reduce the vapor pressure of E-42-11-meEγδ, and then a weighed amount of HFC-245ca was added to the cylinder. The cylinder was agitated to mix the E-42-11-meEγδ and HFC-245ca, and then the cylinder was placed in a constant temperature bath until the temperature came to equilibrium at 19.05°C, at which time the vapor pressure of the content of the cylinder was measured. Samples of the liquid in the cylinder were taken and analyzed, and the results are plotted in Figure 28 as asterisks, with a best fit curve having been drawn through the asterisks.

This procedure was repeated for various mixtures of E-42-11-meEγδ/HFC-245ca as indicated in Figure 28.

The curve which shows the composition of the vapor is calculated using an ideal gas equation of state.

The data in Figure 28 show that at 19.05°C, there are ranges of compositions that have vapor pressures higher than the vapor pressures of the pure components of the composition at that same temperature.

The procedure for measuring the vapor pressure of mixtures of E-42-11-meEγδ/HFC-245ca were carried out in the same way for mixtures of E-42-11-meEγδ/HFC-245eb, except that the measurements of the vapor pressure of mixtures of E-42-11-meEγδ/HFC-245eb were taken at 14.14°C.

The novel compositions of this invention, including the azeotropic or azeotrope-like compositions, may be used to produce refrigeration by condensing the compositions and thereafter evaporating the condensate in the vicinity of a body to be cooled. The novel compositions may also be used to produce heat by condensing the refrigerant in the vicinity of the body to be heated and thereafter evaporating the refrigerant.

The novel compositions of the invention are particularly suitable for replacing refrigerants that may affect the ozone layer, including R-11, R-12, R-22, R-114 and R-502.

In addition to refrigeration applications, the novel constant boiling or substantially constant boiling compositions of the invention are also useful as aerosol propellants, heat transfer media, gaseous dielectrics, fire extinguishing agents, expansion agents for polyolefins and polyurethanes and power cycle working fluids.

ADDITIONAL COMPOUNDS

Other components, such as aliphatic hydrocarbons having a boiling point of -60 to +60°C, hydrofluorocarbonalkanes having a boiling point of -60 to +60°C, hydrofluoropropanes having a boiling point of between -60 to +60°C, hydrocarbon esters having a boiling point between -60 to +60°C, hydrochlorofluorocarbons having a boiling point between -60 to +60°C, hydrofluorocarbons having a boiling point of -60 to +60°C, hydrochlorocarbons having a boiling point between -60 to +60°C, chlorocarbons and perfluorinated compounds, can be added to the azeotropic or azeotrope-like compositions described above without substantially changing the properties thereof, including the constant boiling behavior, of the compositions.

Additives such as lubricants, corrosion inhibitors, surfactants, stabilizers, dyes and other appropriate materials may be added to the novel compositions of the invention for a variety of purposes provides they do not have an adverse influence on the composition for its intended application. Preferred lubricants include esters having a molecular weight greater than 250.

CH-2358-A

CLAIMS

1. A composition of hexafluorodimethyl ether and cyclopropane, dimethylether or propylene; bis(difluoromethyl) ether and 2,2,3,4,4-pentafluorooxetane; fluoromethyl trifluoromethyl ether and 2,2,4,4,5,5-hexafluoro-1,3-dioxolane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, dimethylether or tris(trifluoromethyl)amine; trifluoromethyl methyl ether and perfluorooxetane, 2,2,4,4,5,5-hexafluoro-1,3-dioxolane, perfluoromethyl ethyl ether, perfluorodimethoxymethane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, dimethylether or tris(trifluoromethyl)amine; perfluoromethyl ethyl ether and dimethylether or propylene; perfluorodimethoxymethane and dimethylether or isobutane; 1-trifluoromethoxy-1,1,2,2-tetrafluoroethane and tris(trifluoromethyl)amine or dimethylether; difluoromethoxy pentafluoroethane and dimethylether, isobutane or tris(trifluoromethyl)amine; 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane and dimethylether or isobutane; 1-difluoromethoxy-1,1,2,2-tetrafluoroethane and $N(CHF_2)_2(CF_3)$ or 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)propane and 1,1,2,2,3-pentafluoropropane or 1,1,1,2,3-pentafluoropropane.

2. Effective amounts of the following compounds to form an azeotropic or azeotrope-like composition: hexafluorodimethyl ether and cyclopropane, dimethylether or propylene; bis(difluoromethyl) ether and 2,2,3,4,4-pentafluorooxetane; fluoromethyl trifluoromethyl ether and 2,2,4,4,5,5-hexafluoro-1,3-dioxolane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, dimethylether or tris(trifluoromethyl)amine; trifluoromethyl methyl ether and perfluorooxetane, 2,2,4,4,5,5-hexafluoro-1,3-dioxolane, perfluoromethyl ethyl ether, perfluorodimethoxymethane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, dimethylether or tris(trifluoromethyl)amine; perfluoromethyl ethyl ether and dimethylether or propylene; perfluorodimethoxymethane and dimethylether or isobutane; 1-trifluoromethoxy-1,1,2,2-tetrafluoroethane and tris(trifluoromethyl)amine or dimethylether; difluoromethoxy pentafluoroethane and dimethylether, isobutane or tris(trifluoromethyl)amine; 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane and dimethylether or isobutane; 1-difluoromethoxy-1,1,2,2-tetrafluoroethane and $N(CHF_2)_2(CF_3)$ or 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)propane and 1,1,2,2,3-pentafluoropropane or 1,1,1,2,3-

pentafluoropropane.

3. The azeotropic or azeotrope-like composition of Claim 2, said composition comprising: 72-99 weight percent hexafluorodimethyl ether and 1-28 weight percent cyclopropane; 68-99 weight percent hexafluorodimethyl ether and 1-32 weight perecent dimethylether; 60-99 weight percent hexafluorodimethyl ether and 1-40 weight percent propylene; 1-99 weight percent bis(difluoromethyl) ether and 1-99 weight percent 2,2,3,4,4-pentafluorooxetane; 1-99 weight percent fluoromethyl trifluoromethyl ether and 1-99 weight percent 2,2,4,4,5,5-hexafluoro-1,3-dioxolane; 1-99 weight percent fluoromethyl trifluoromethyl ether and 1-99 weight percent 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane; 1-99 weight percent fluoromethyl trifluoromethyl ether and 1-99 weight percent dimethylether; 20-99 weight percent fluoromethyl trifluoromethyl ether and 1-80 weight percent tris(trifluoromethyl)amine; 1-99 weight percent trifluoromethyl methyl ether and 1-99 weight percent perfluorooxetane; 1-99 weight percent trifluoromethyl methyl ether and 1-99 weight percent 2,2,4,4,5,5-hexafluoro-1,3-dioxolane; 1-99 weight percent trifluoromethyl methyl ether and 1-99 weight percent perfluoromethyl ethyl ether; 1-99 weight percent trifluoromethyl methyl ether and 1-99 weight percent perfluorodimethoxymethane; 1-99 weight percent trifluoromethyl methyl ether and 1-99 weight percent 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane; 1-99 weight percent trifluoromethyl methyl ether and 1-99 weight percent dimethylether; 27-99 weight percent trifluoromethyl methyl ether and 1-73 weight percent tris(trifluoromethyl)amine; 50-92 weight percent perfluoromethyl ethyl ether and 8-50 weight percent dimethylether; 1-82 weight percent perfluoromethyl ethyl ether and 18-99 weight percent propylene; 1-86 weight percent perfluorodimethoxymethane and 14-99 weight percent dimethylether; 1-99 weight percent perfluorodimethoxymethane and 1-99 weight percent isobutane; 1-99 weight percent 1-trifluoromethoxy-1,1,2,2-tetrafluoroethane and 1-99 weight percent tris(trifluoromethyl)amine; 1-80 weight percent 1-trifluoromethoxy-1,1,2,2-tetrafluoroethane and 20-99 weight percent dimethylether; 1-83 weight percent difluoromethoxy pentafluoroethane and 17-99 weight percent dimethylether; 1-99 weight percent difluoromethoxy pentafluoroethane and 1-99 weight percent isobutane; 1-99 weight percent difluoromethoxy pentafluoroethane and 1-99 weight percent tris(trifluoromethyl)amine; 1-84 weight percent 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane and 16-99 weight percent dimethylether; 1-99 weight percent 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane and 1-99 weight percent isobutane; 1-99

weight percent 1-difluoromethoxy-1,1,2,2-tetrafluoroethane and 1-99 weight percent $N(CHF_2)_2(CF_3)$; 1-72 weight percent 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)propane and 18-99 weight percent 1,1,2,2,3-pentafluoropropane; 98-99 weight percent 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)propane and 1-2 weight percent 1,1,1,2,3-pentafluoropropane; or 1-70 weight percent 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)propane and 30-99 weight percent 1,1,1,2,3-pentafluoropropane.

4. Effective amounts of hexafluorodimethyl ether and cyclopropane, dimethylether or propylene; bis(difluoromethyl) ether and 2,2,3,4,4-pentafluorooxetane; fluoromethyl trifluoromethyl ether and 2,2,4,4,5,5-hexafluoro-1,3-dioxolane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, dimethylether or tris(trifluoromethyl)amine; trifluoromethyl methyl ether and perfluorooxetane, 2,2,4,4,5,5-hexafluoro-1,3-dioxolane, perfluoromethyl ethyl ether, perfluorodimethoxymethane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, dimethylether or tris(trifluoromethyl)amine; perfluoromethyl ethyl ether and dimethylether or propylene; perfluorodimethoxymethane and dimethylether or isobutane; 1-trifluoromethoxy-1,1,2,2-tetrafluoroethane and tris(trifluoromethyl)amine or dimethylether; difluoromethoxy pentafluoroethane and dimethylether, isobutane or tris(trifluoromethyl)amine; 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane and dimethylether or isobutane; 1-difluoromethoxy-1,1,2,2-tetrafluoroethane and $N(CHF_2)_2(CF_3)$ or 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)propane and 1,1,2,2,3-pentafluoropropane or 1,1,1,2,3-pentafluoropropane to form binary compositions having a vapor pressure higher than that of both of the components of the binary composition.

5. A process for producing refrigeration, comprising condensing a composition of any of Claims 1 to 4 and thereafter evaporating said composition in the vicinity of the body to be cooled.

6. A process for producing heat comprising condensing a composition of any of Claims 1 to 4 in the vicinity of a body to be heated, and thereafter evaporating said composition.

FIG. 1

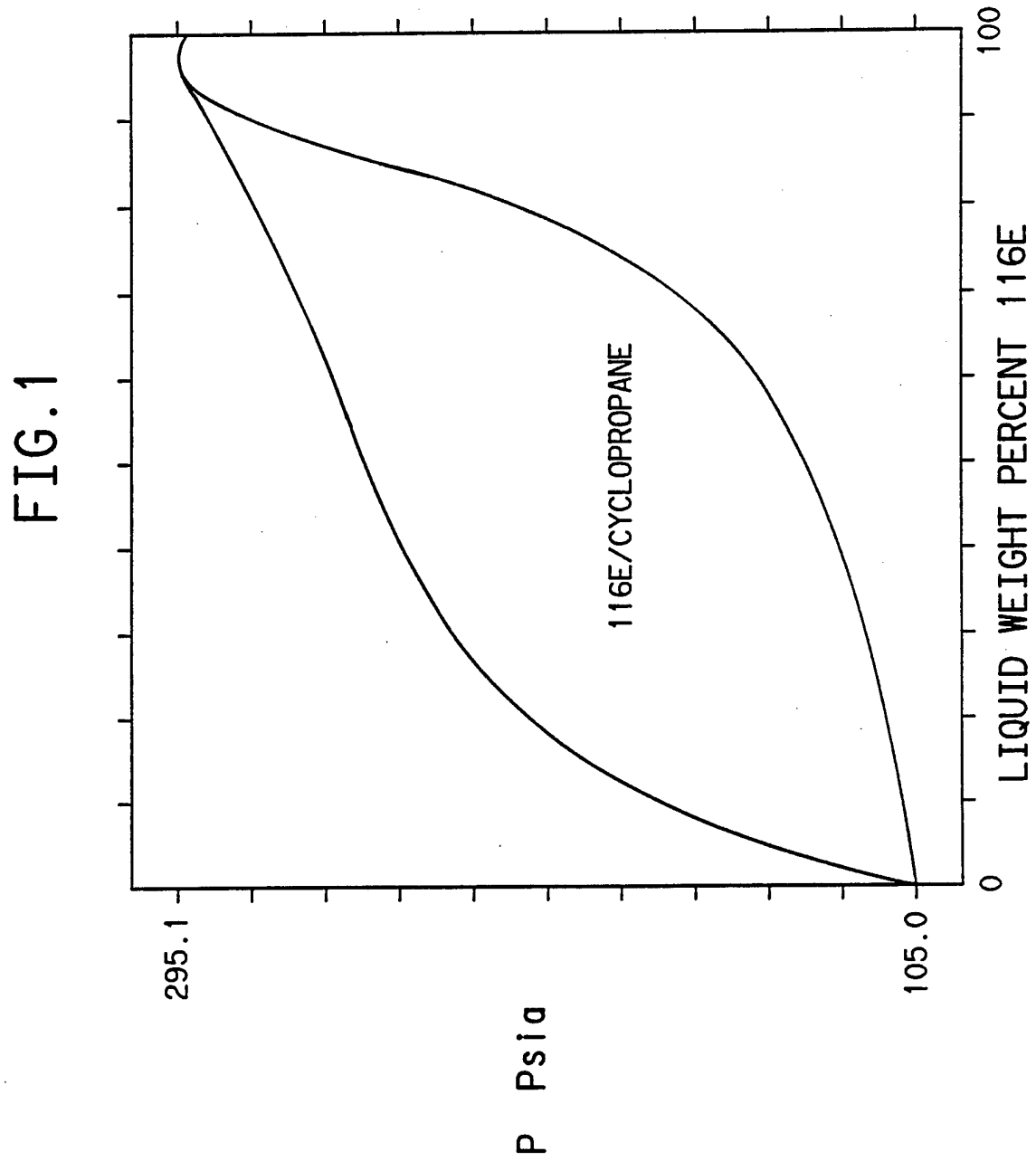

295.1
105.0
P Psia
0
100
LIQUID WEIGHT PERCENT 116E
116E/CYCLOPROPANE

FIG.2

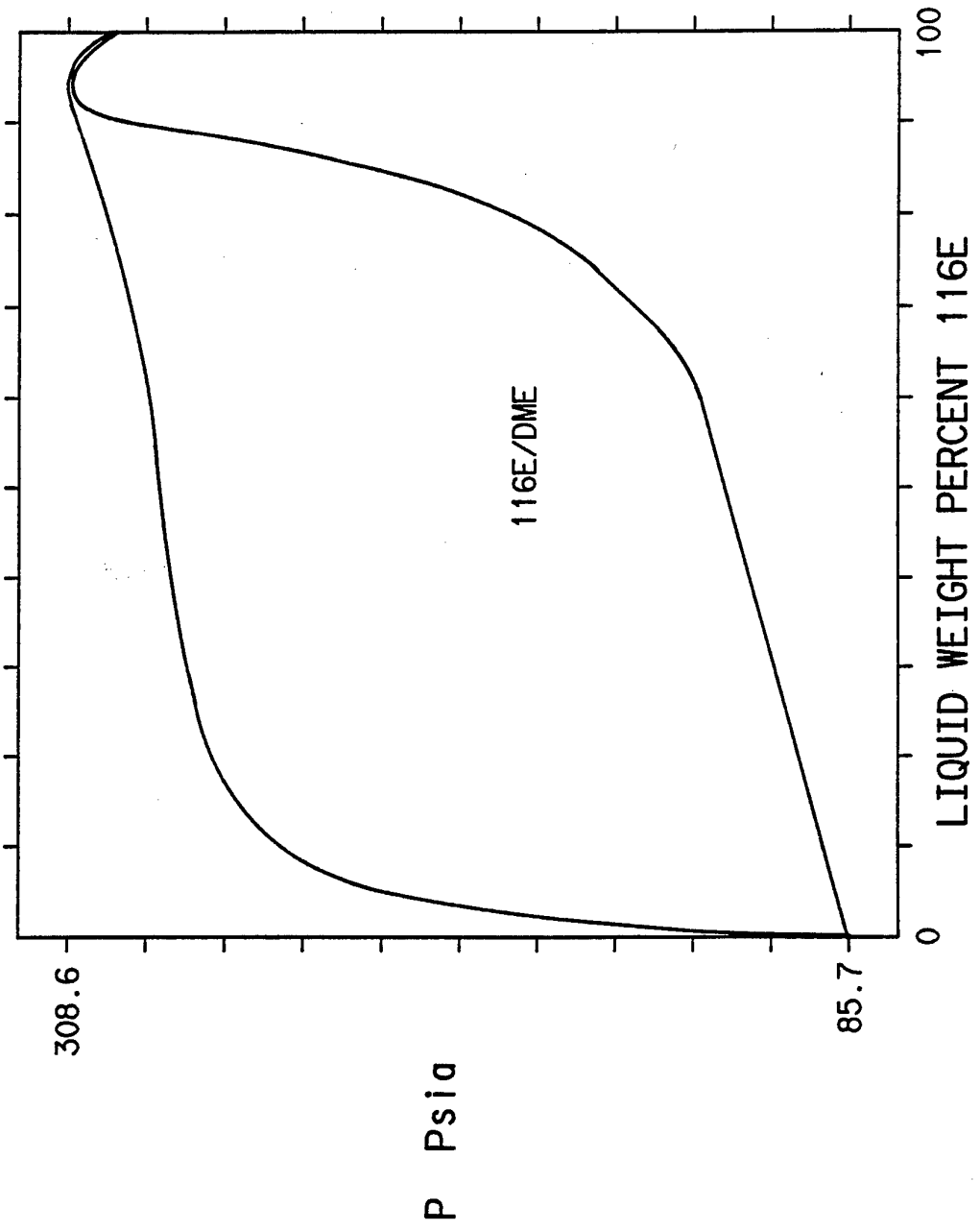


FIG.3

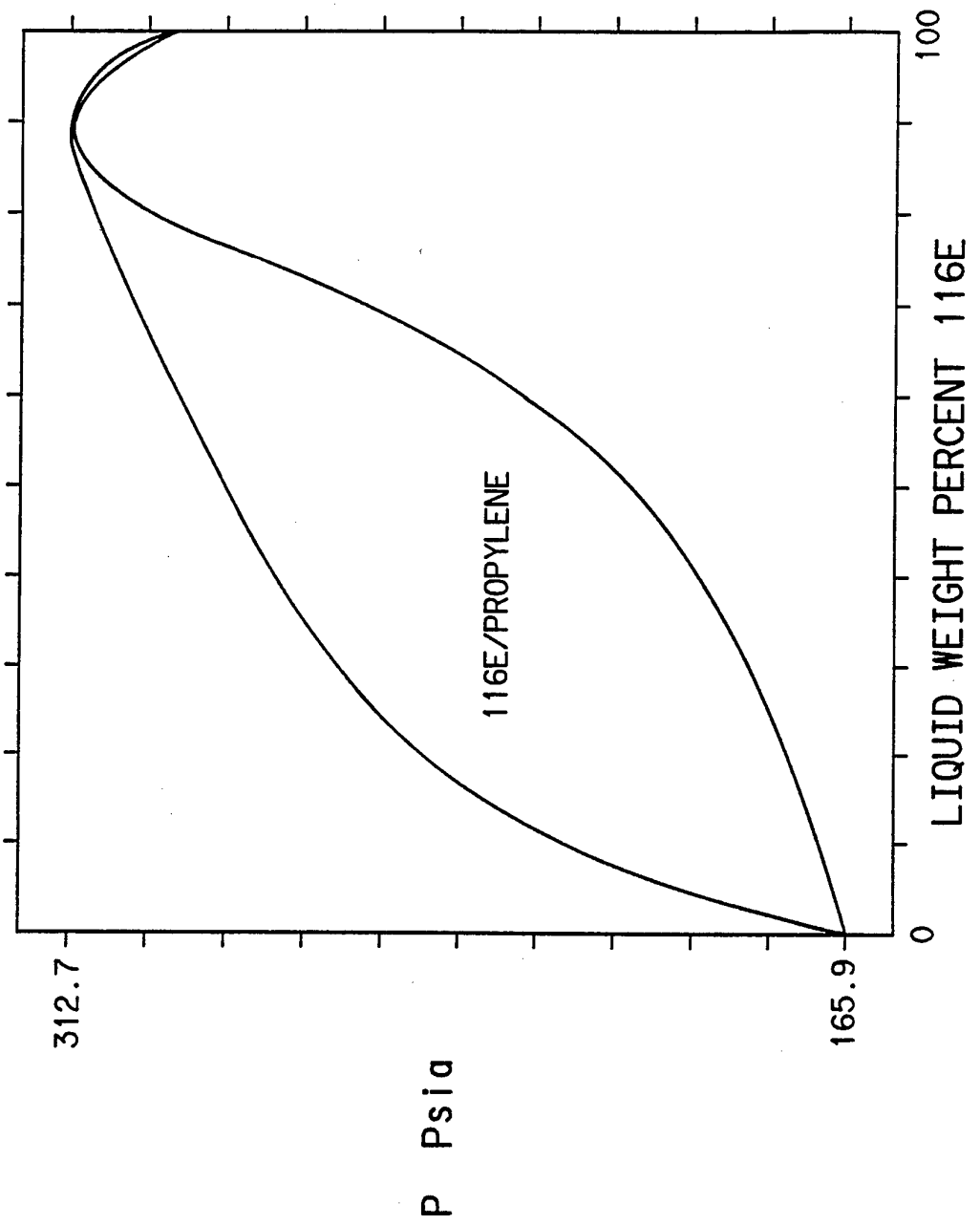

312.7
165.9
P Psia
0
100
LIQUID WEIGHT PERCENT 116E
116E/PROPYLENE

FIG.4

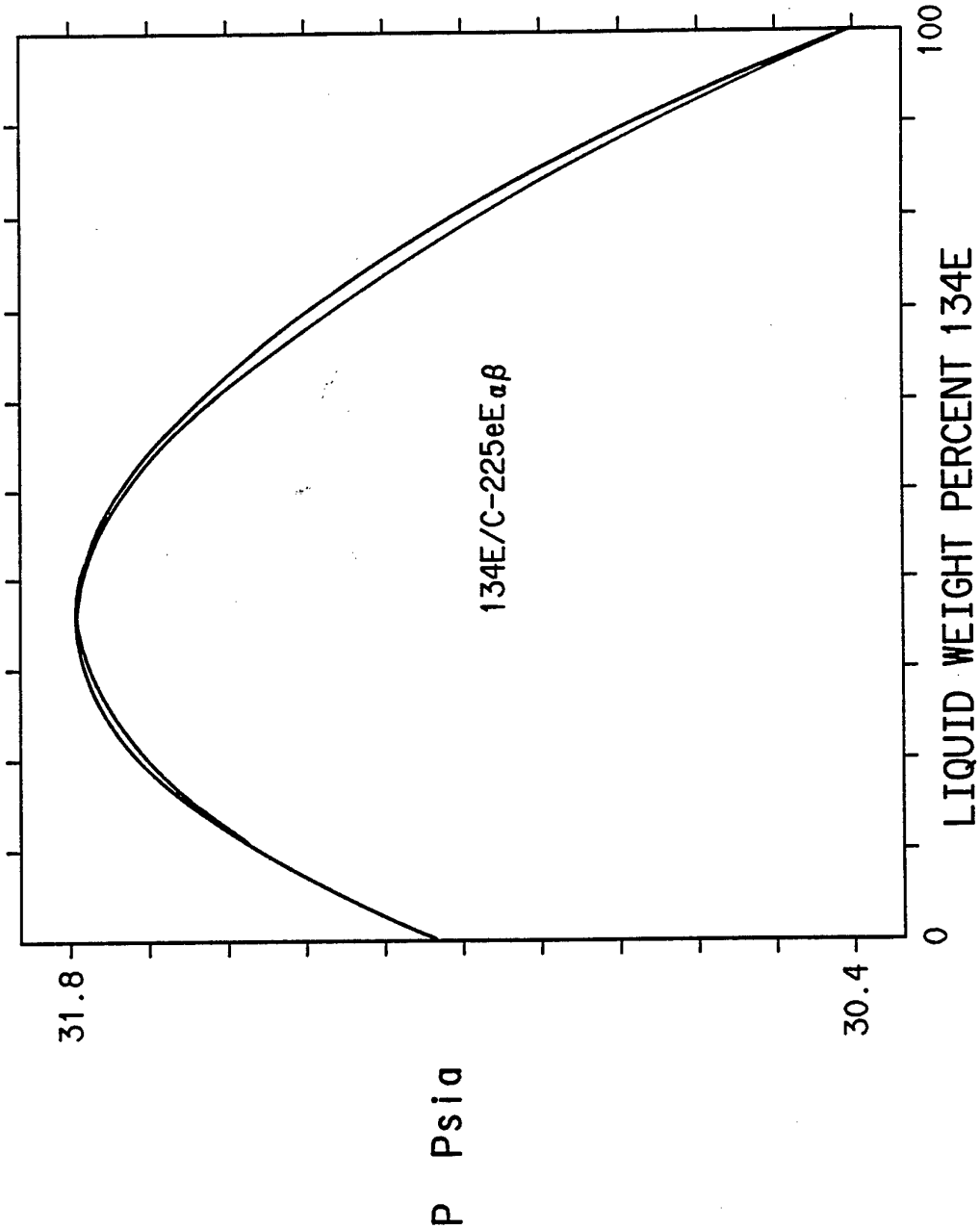

31.8
30.4
P Psia
0
100
LIQUID WEIGHT PERCENT 134E
134E/C-225eEαβ

FIG.5

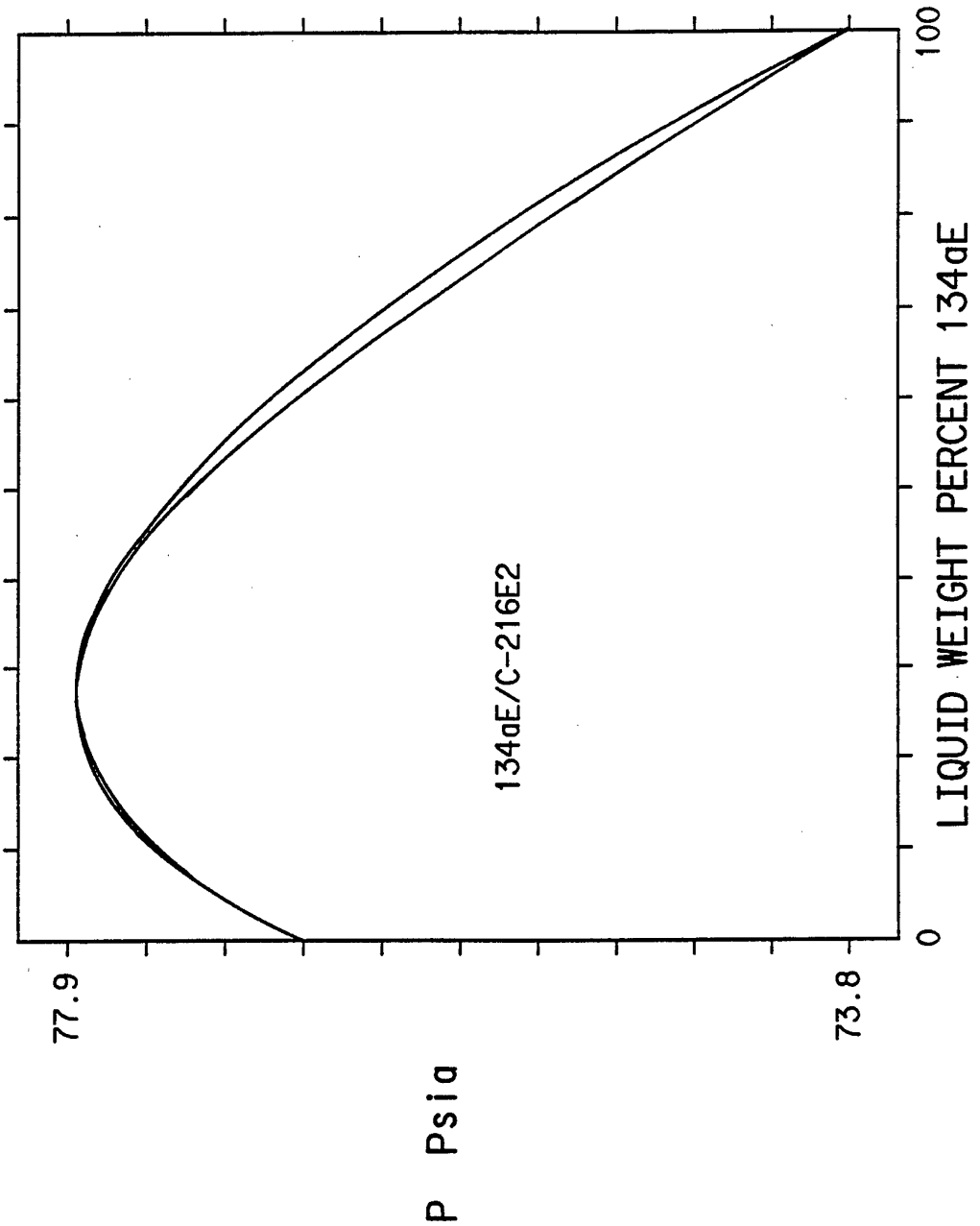

77.9
73.8
P Psia
0
100
LIQUID WEIGHT PERCENT 134aE
134aE/C-216E2

FIG.6

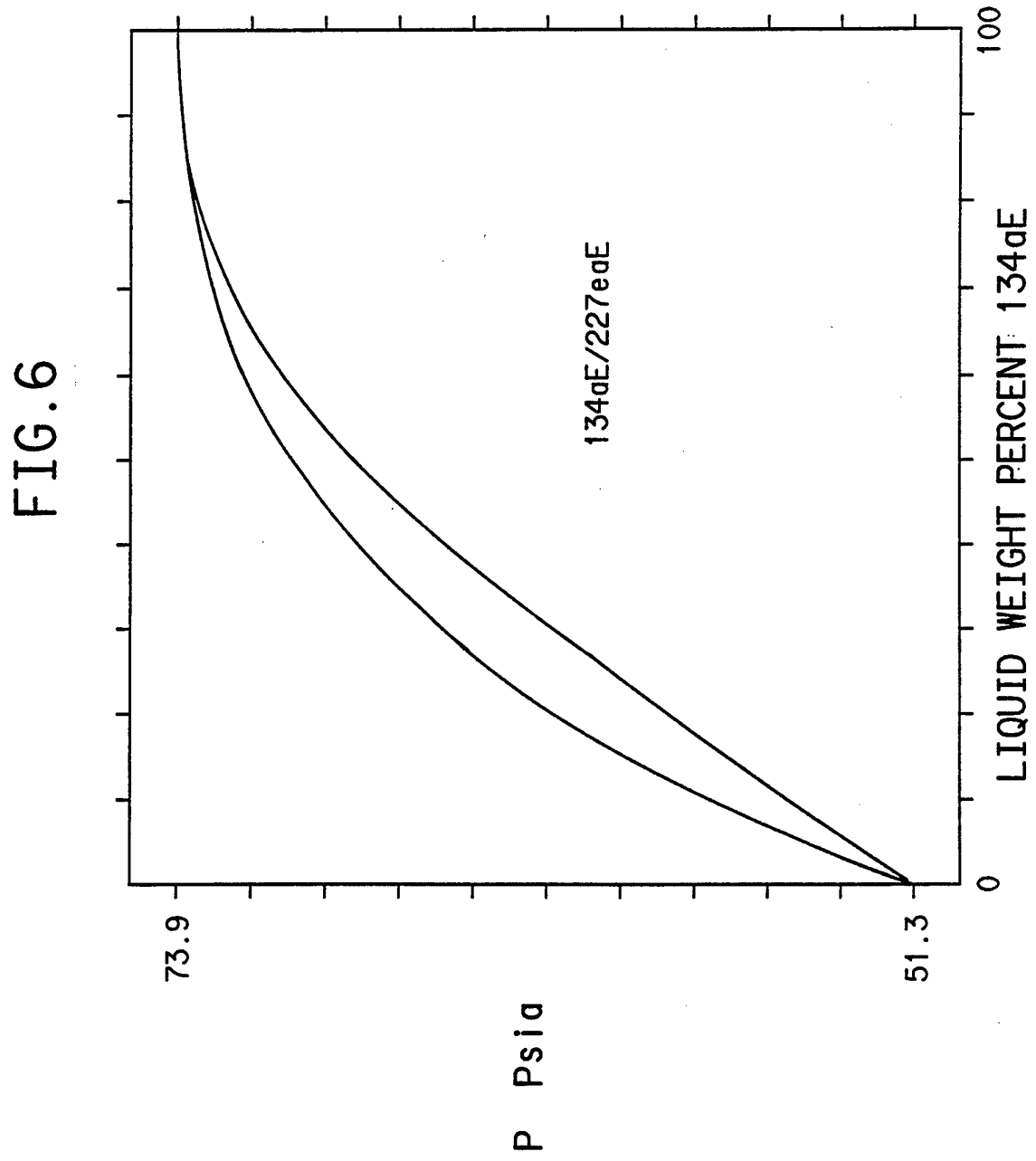

73.9
51.3
P Psia
0
100
LIQUID WEIGHT PERCENT 134aE
134aE/227eaE

FIG.7

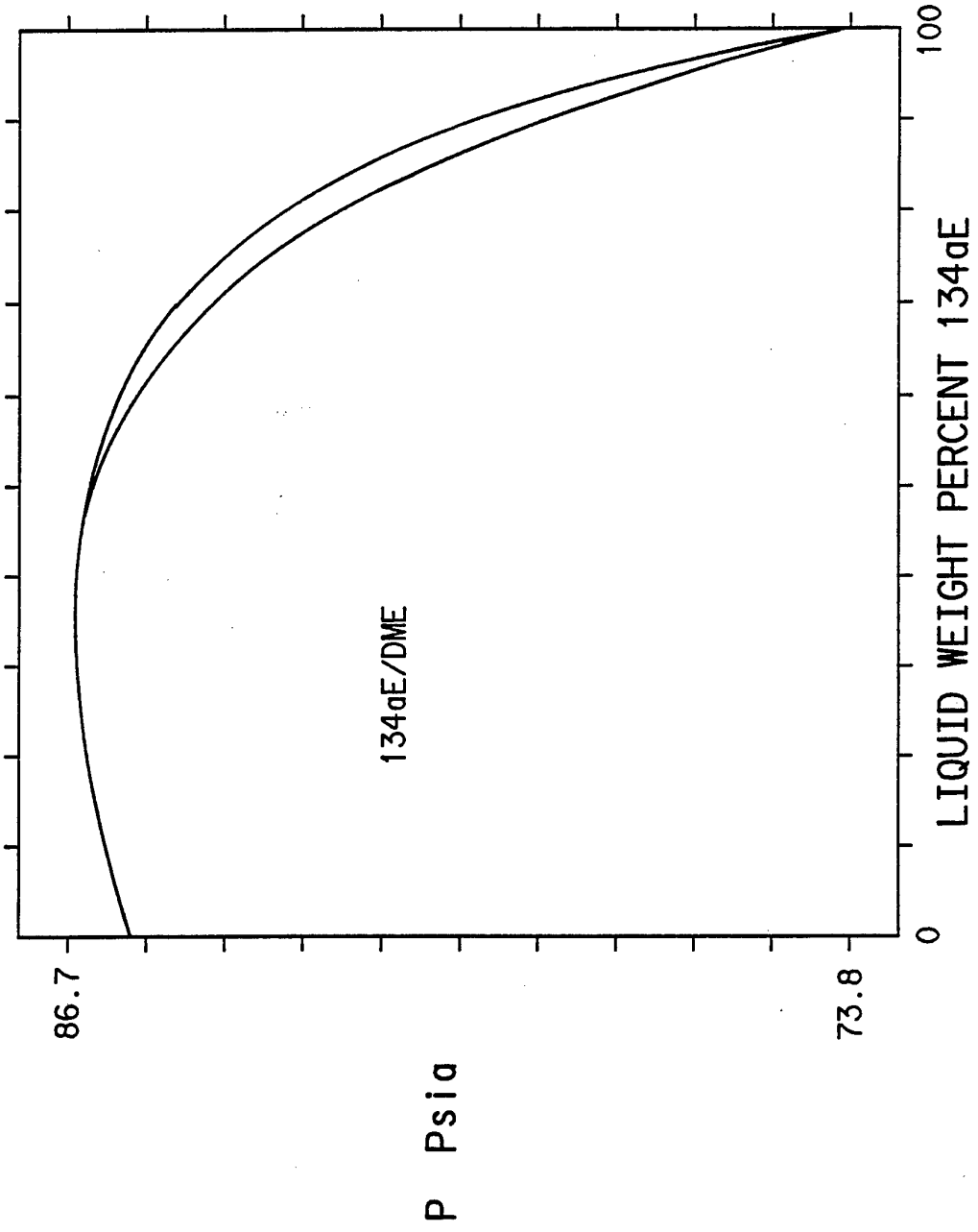


FIG.8

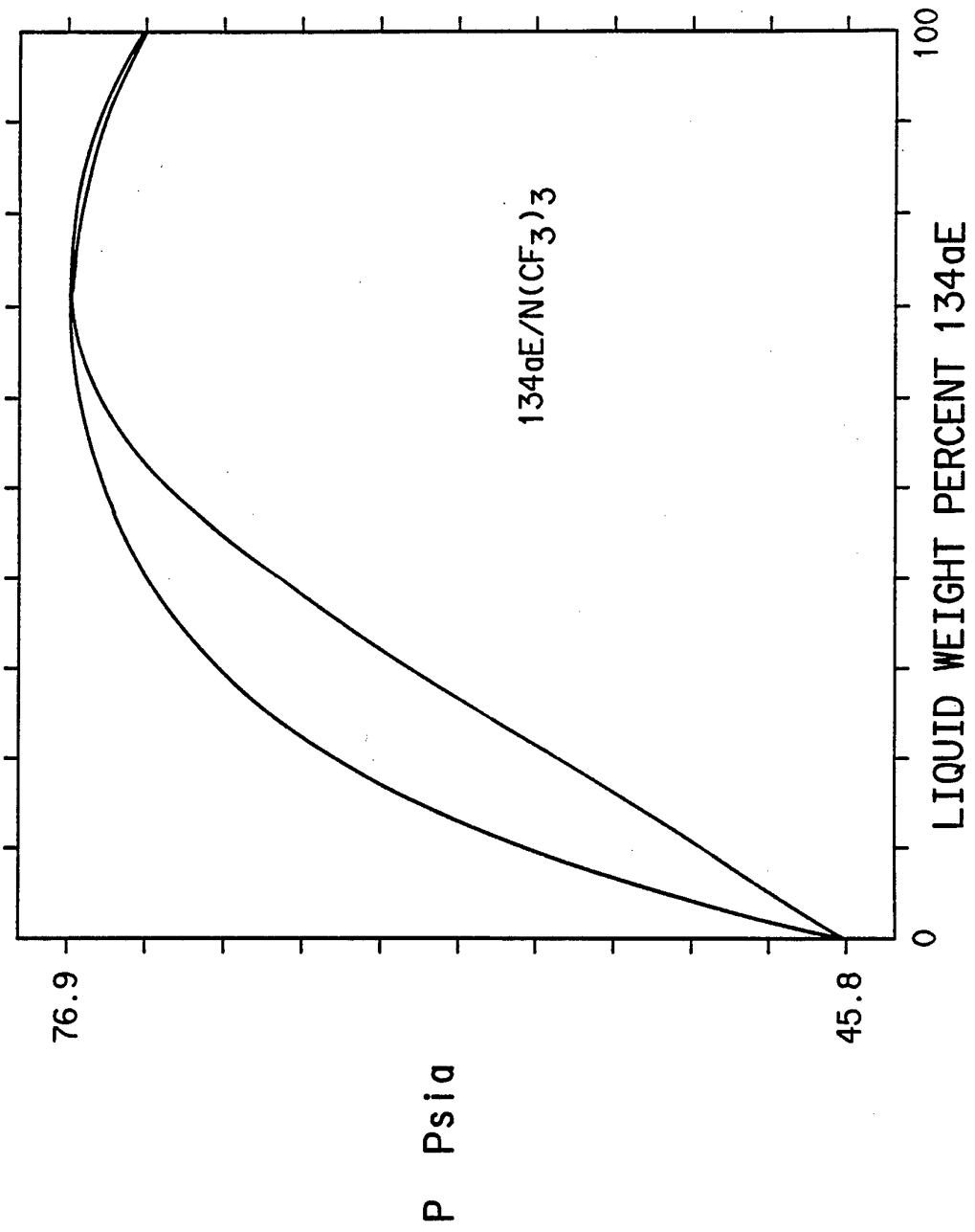


FIG.9

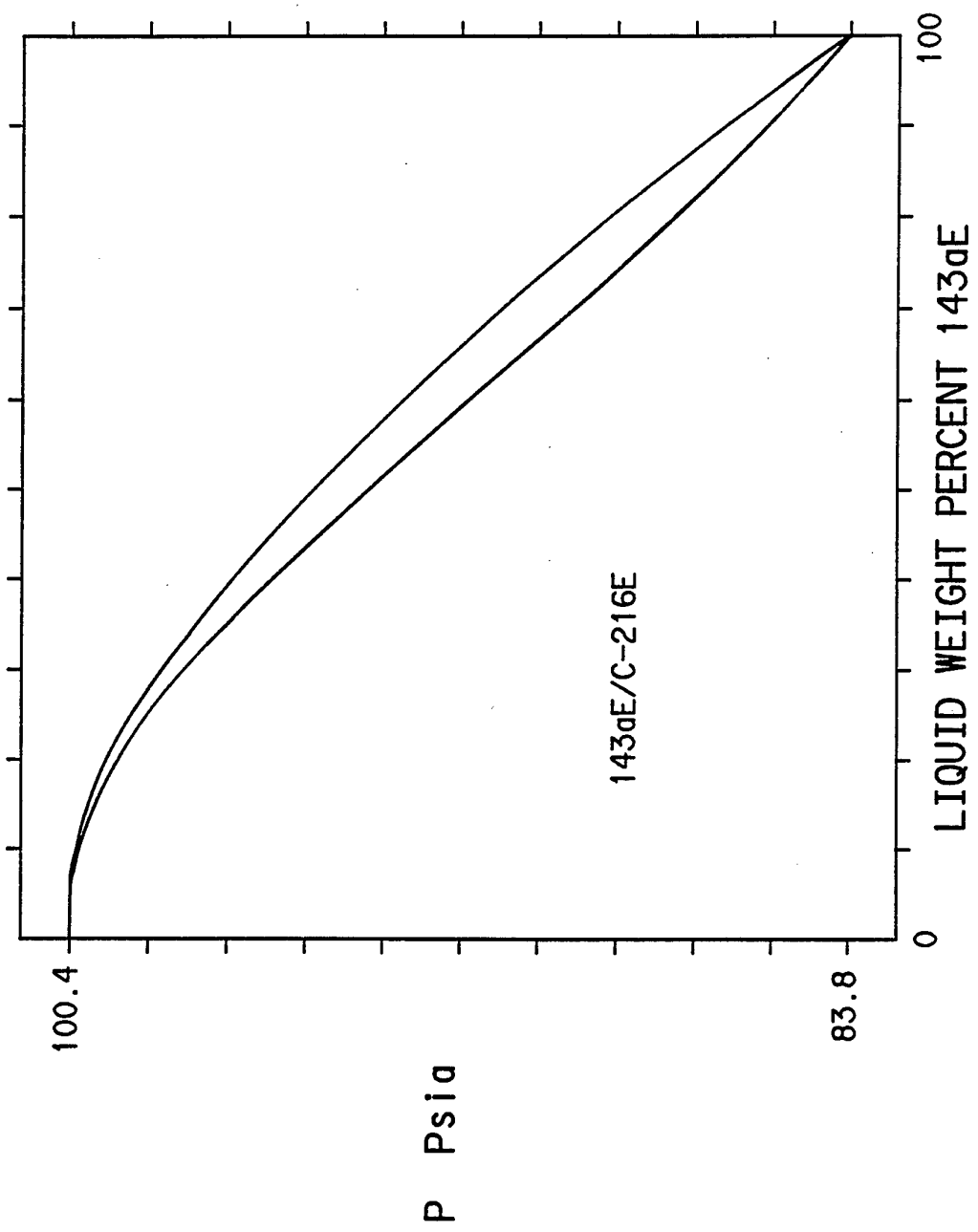

100.4
83.8
P Psia
0
100
LIQUID WEIGHT PERCENT 143aE
143aE/C-216E

FIG.10

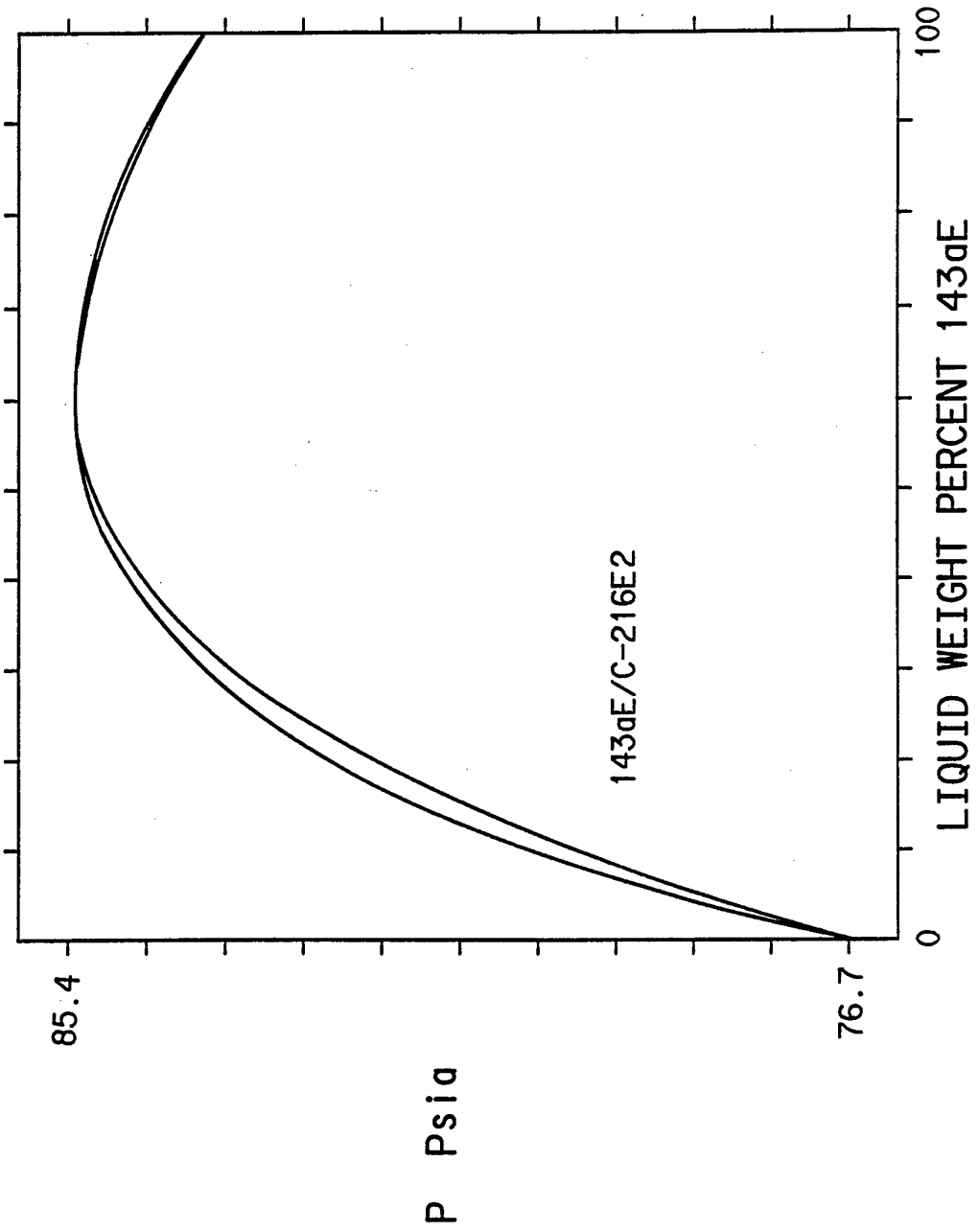

85.4
76.7
P Psia
0
100
LIQUID WEIGHT PERCENT 143aE
143aE/C-216E2

FIG. 11

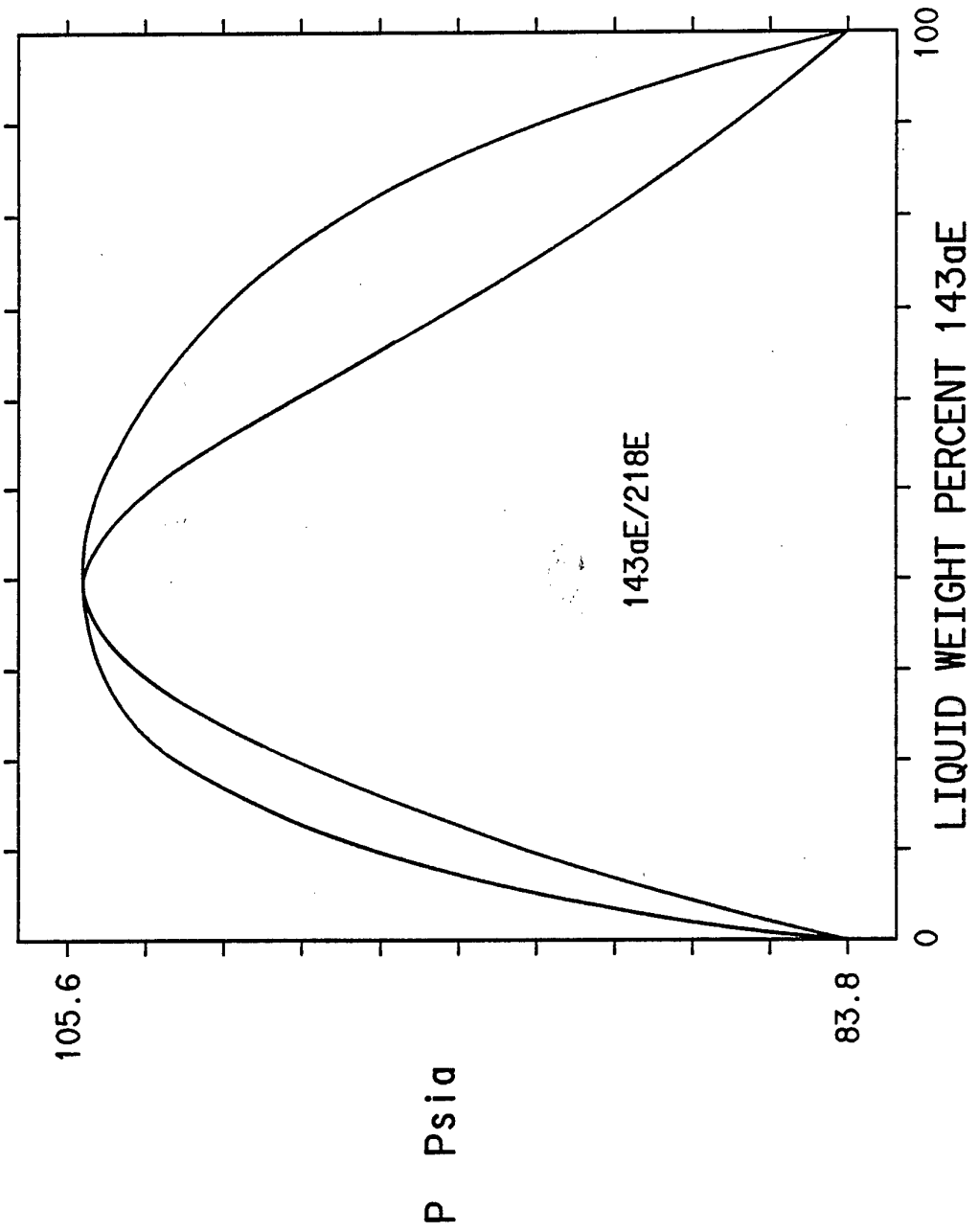


FIG.12

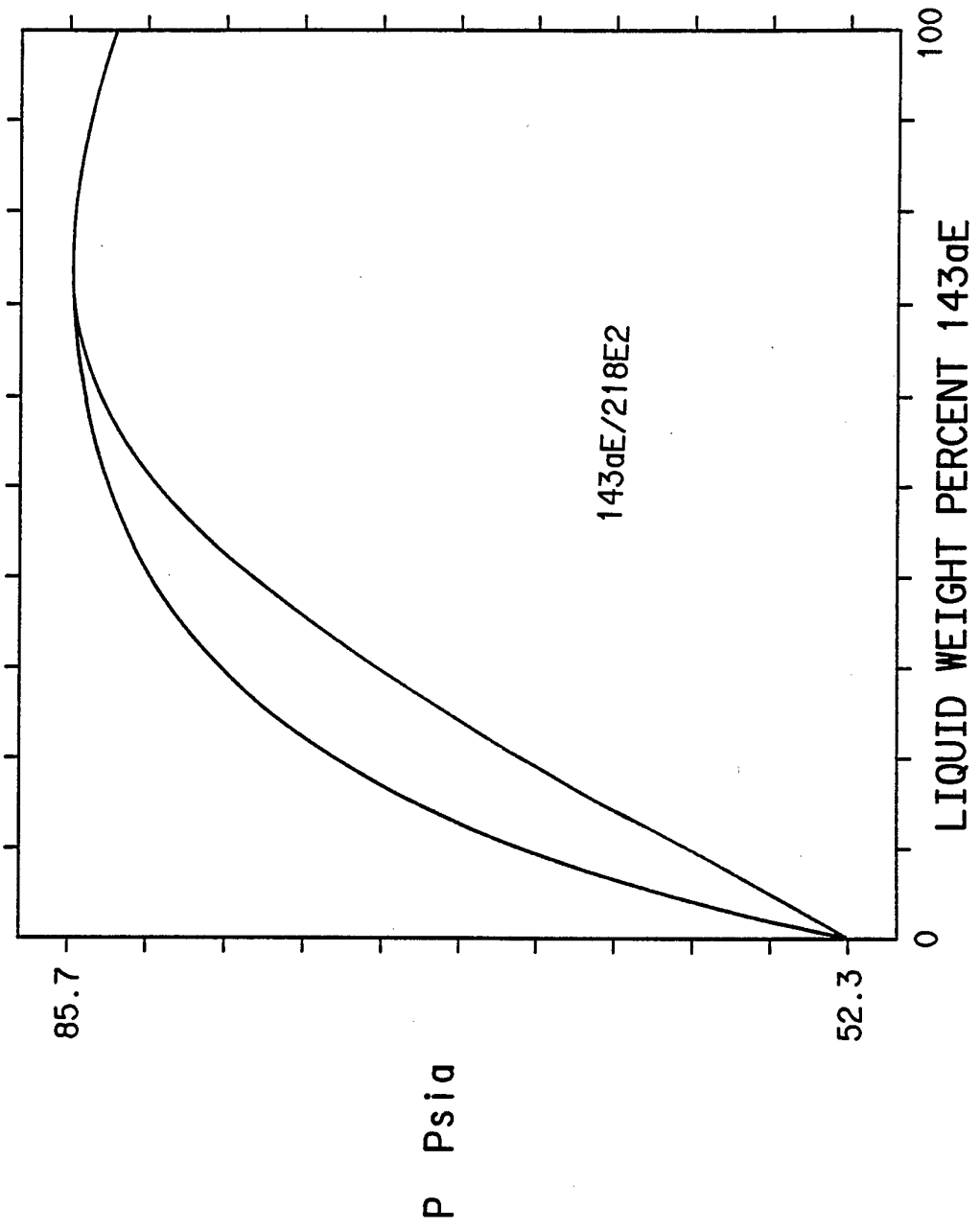


FIG. 13

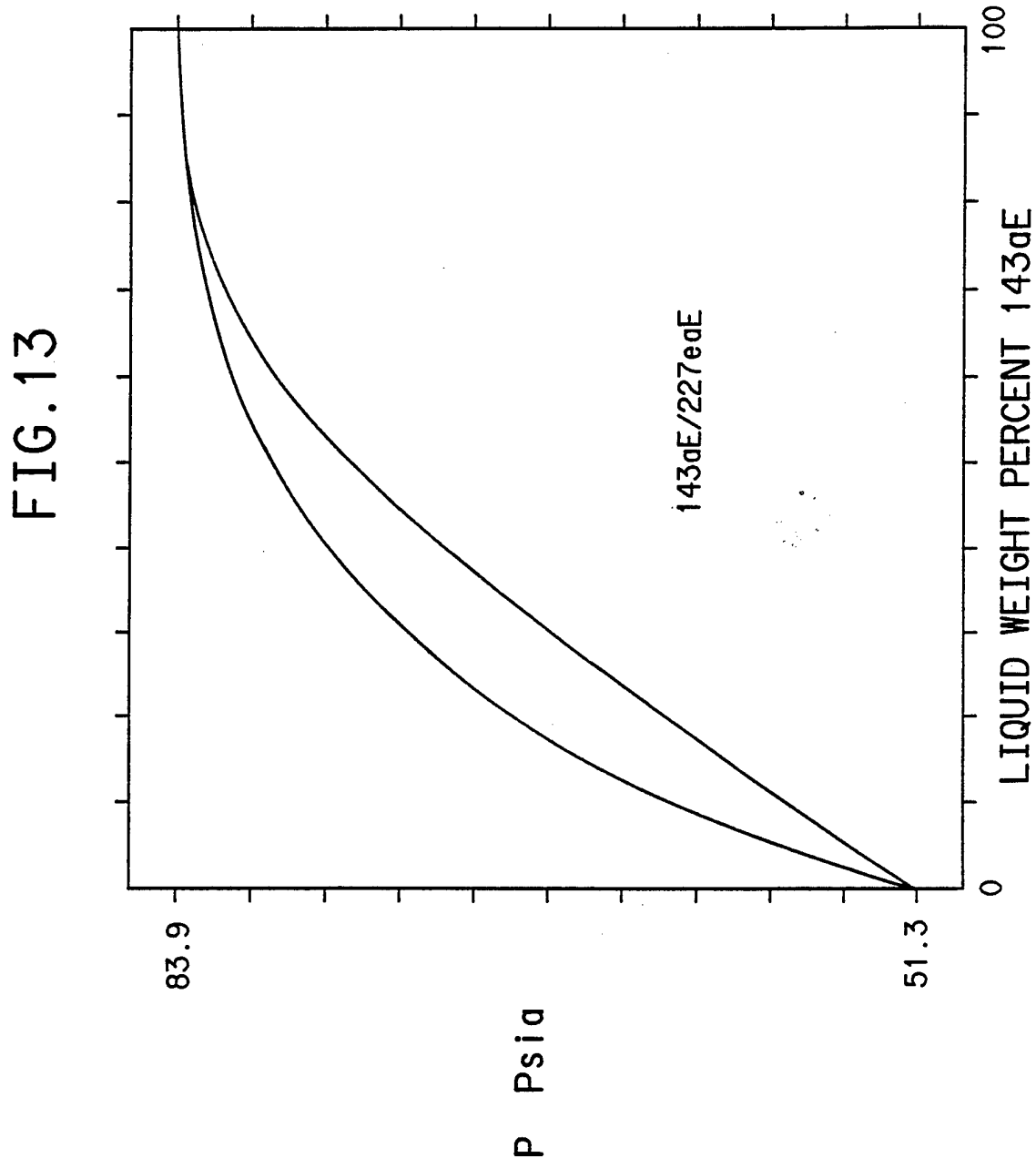

83.9
51.3
P Psia
0
100
LIQUID WEIGHT PERCENT 143aE
143aE/227eaE

FIG. 14

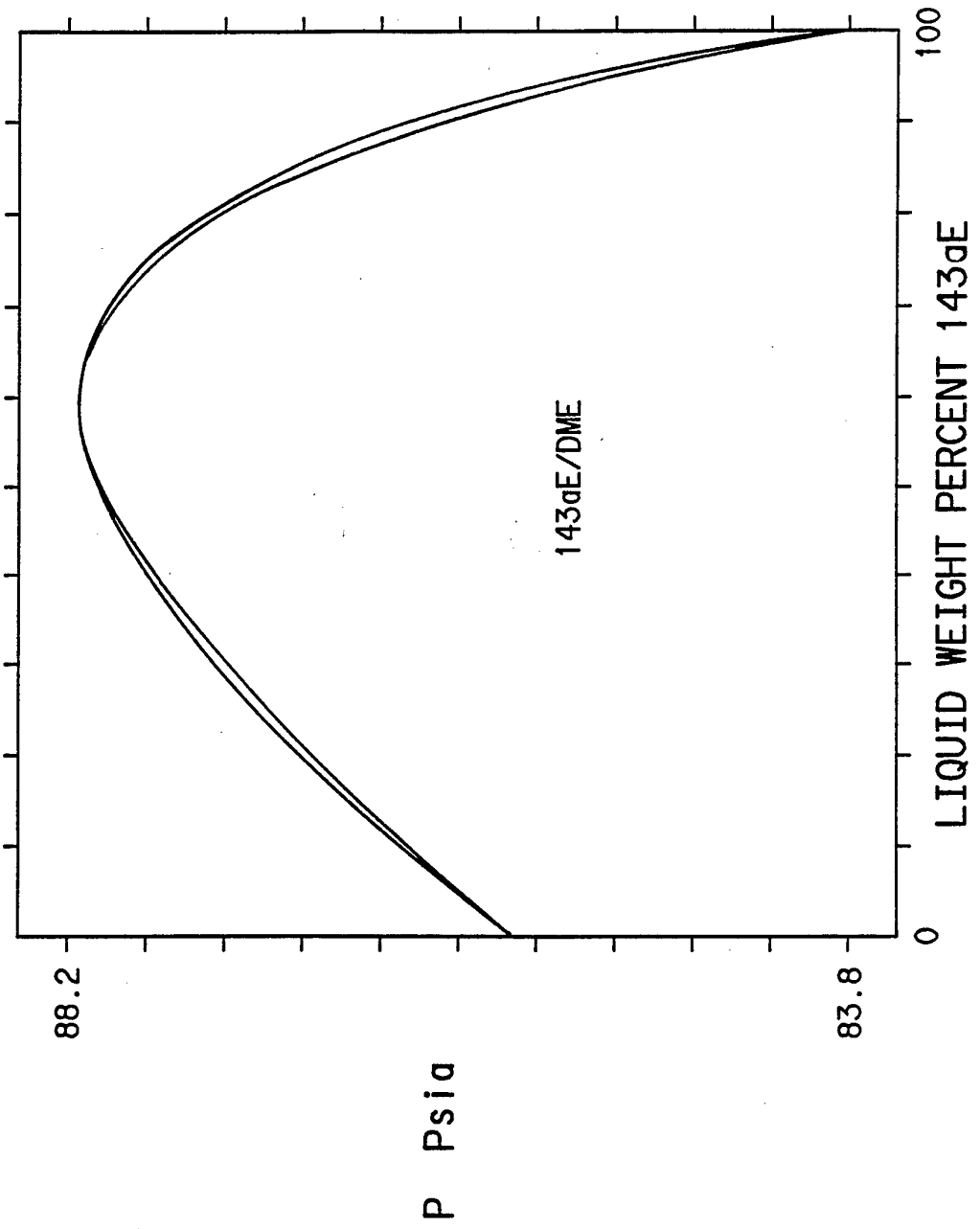


FIG.15

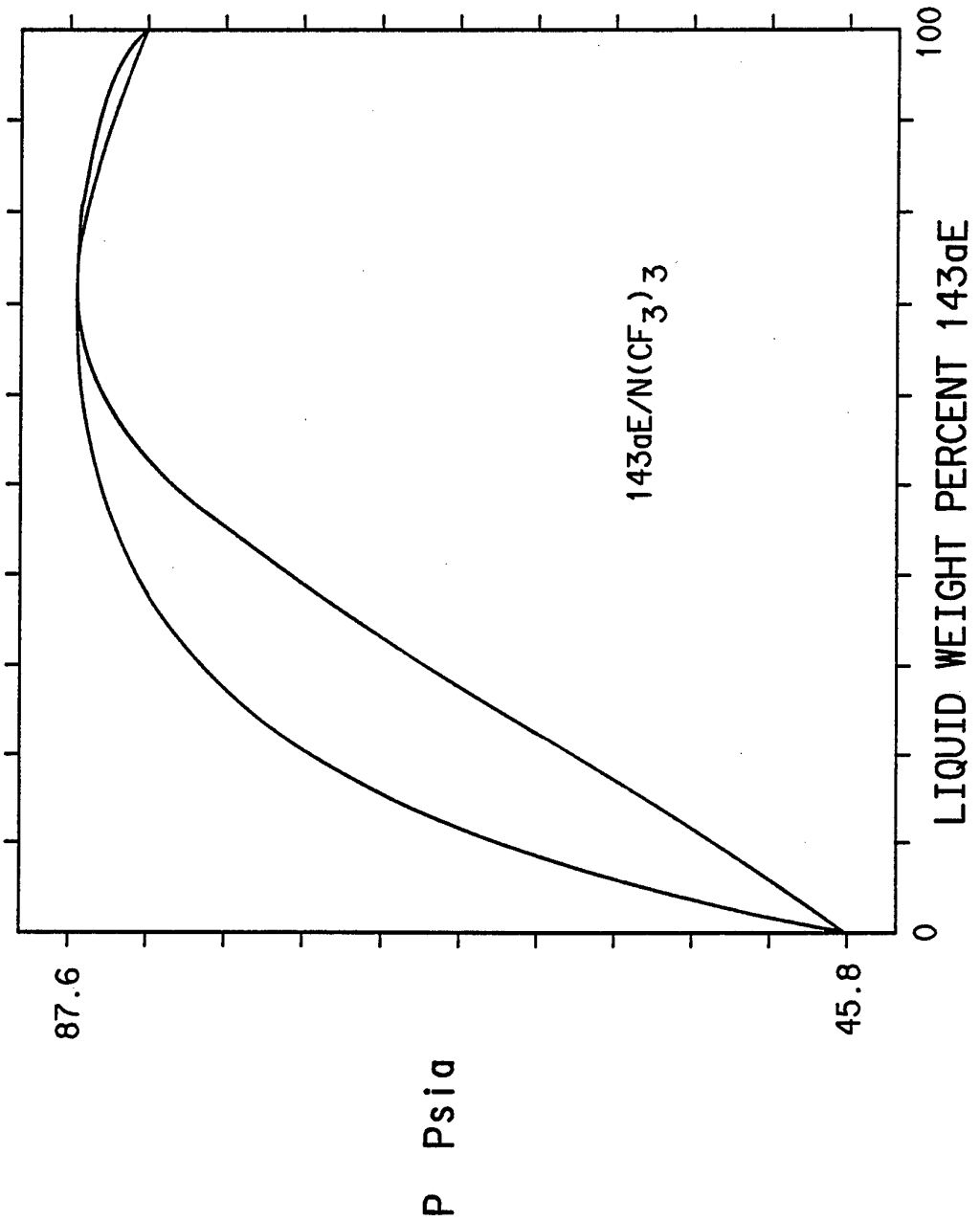


FIG.16

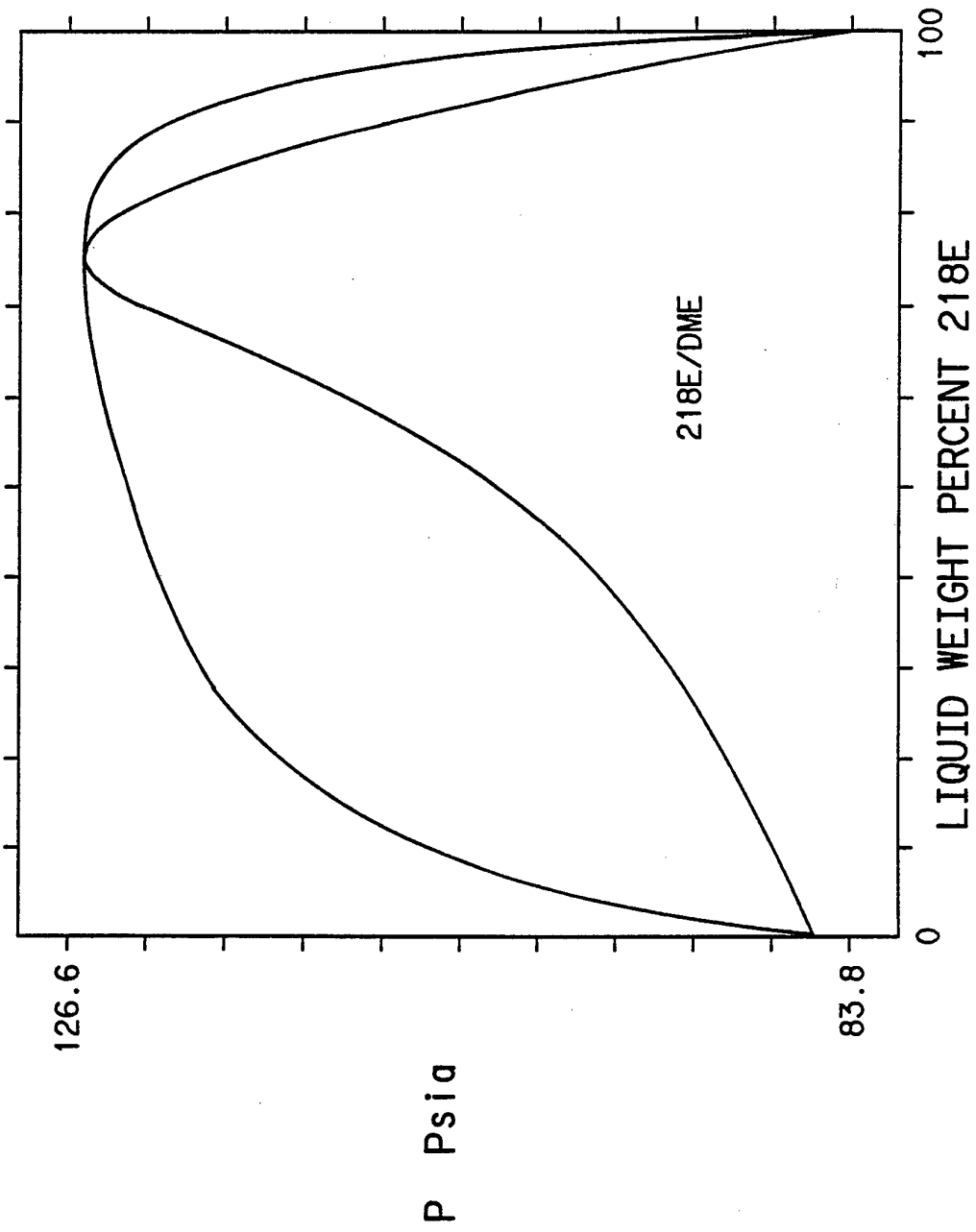


FIG.17

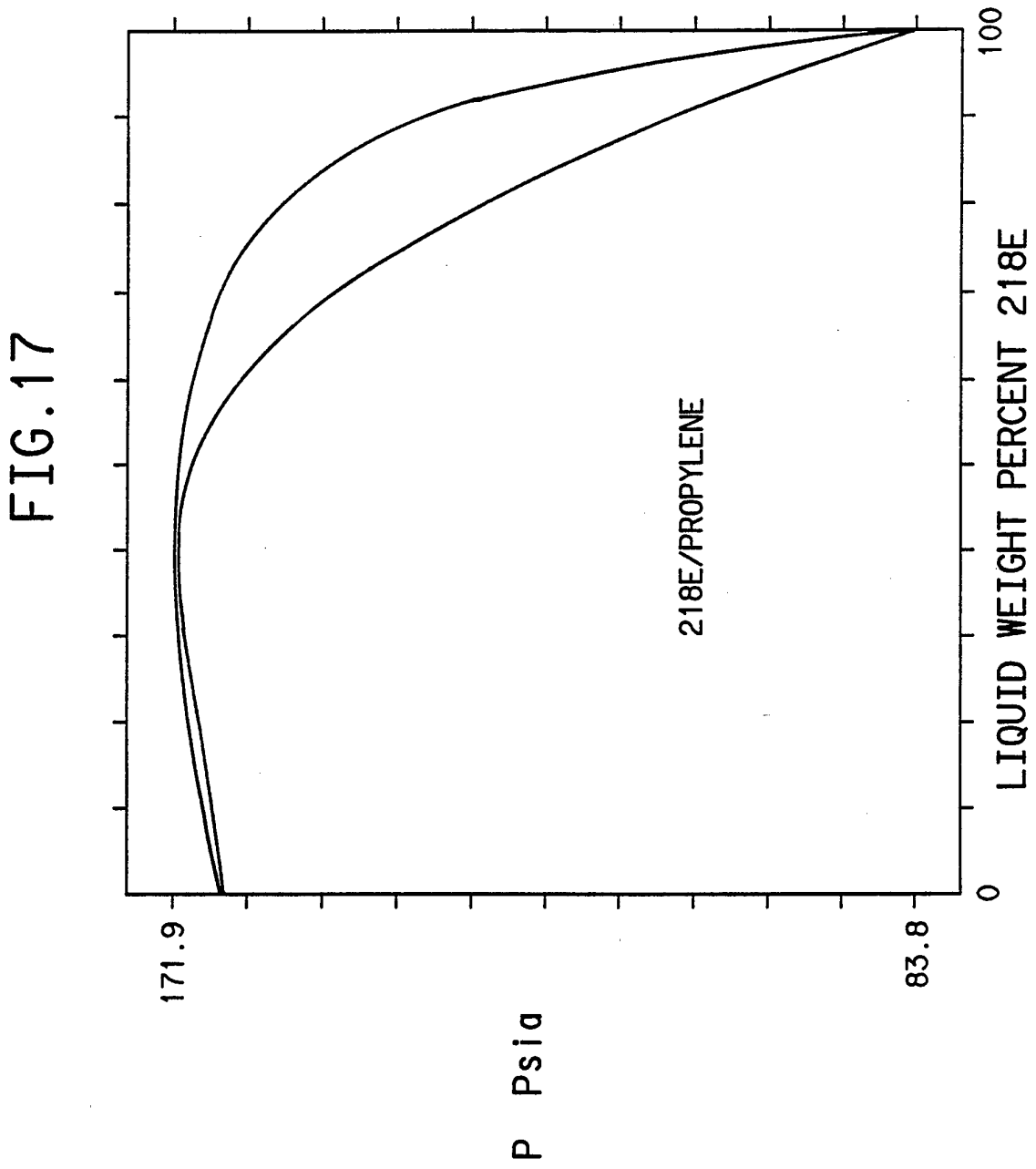

171.9
83.8
P Psia
0
100
LIQUID WEIGHT PERCENT 218E
218E/PROPYLENE

FIG. 18

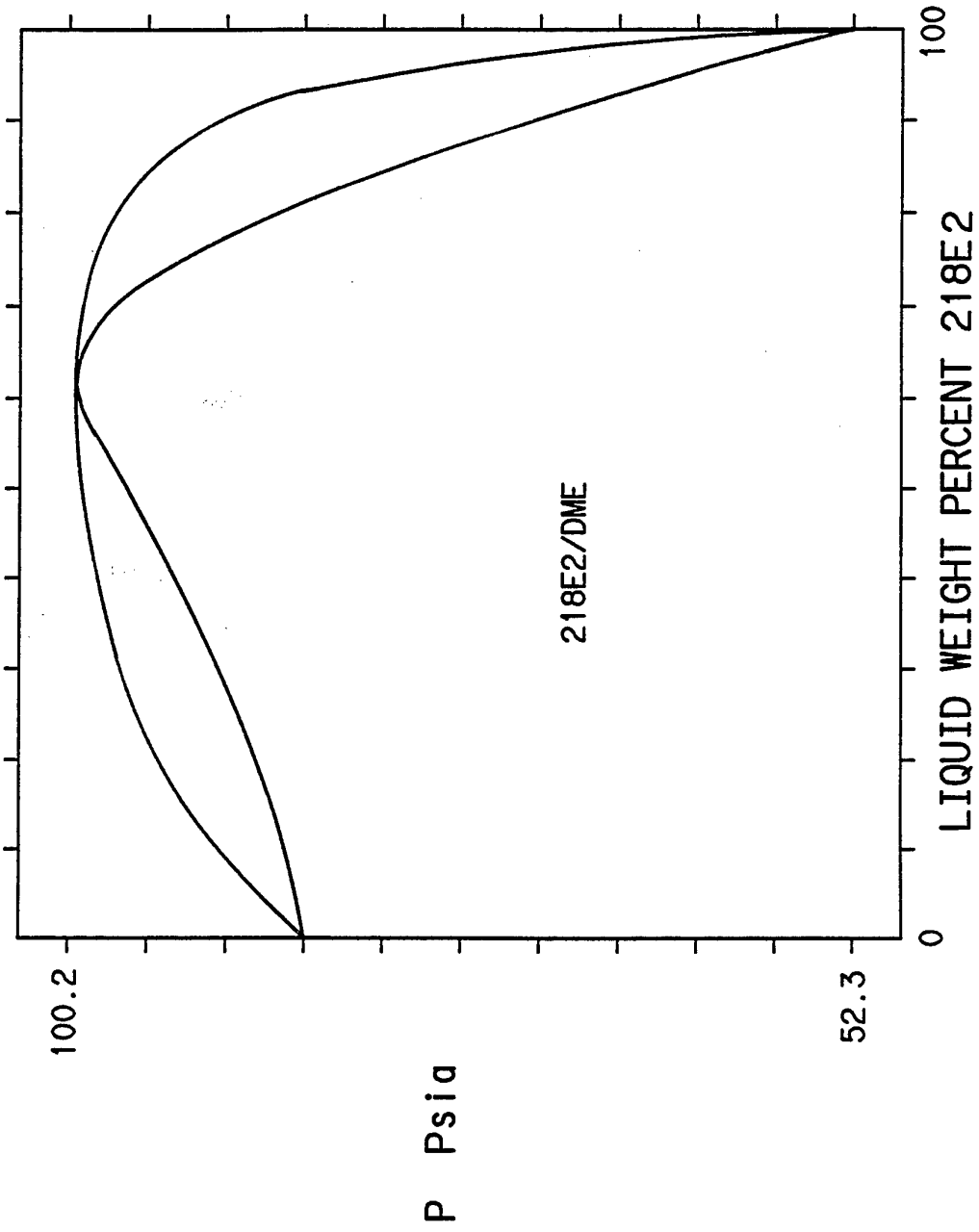


FIG.19

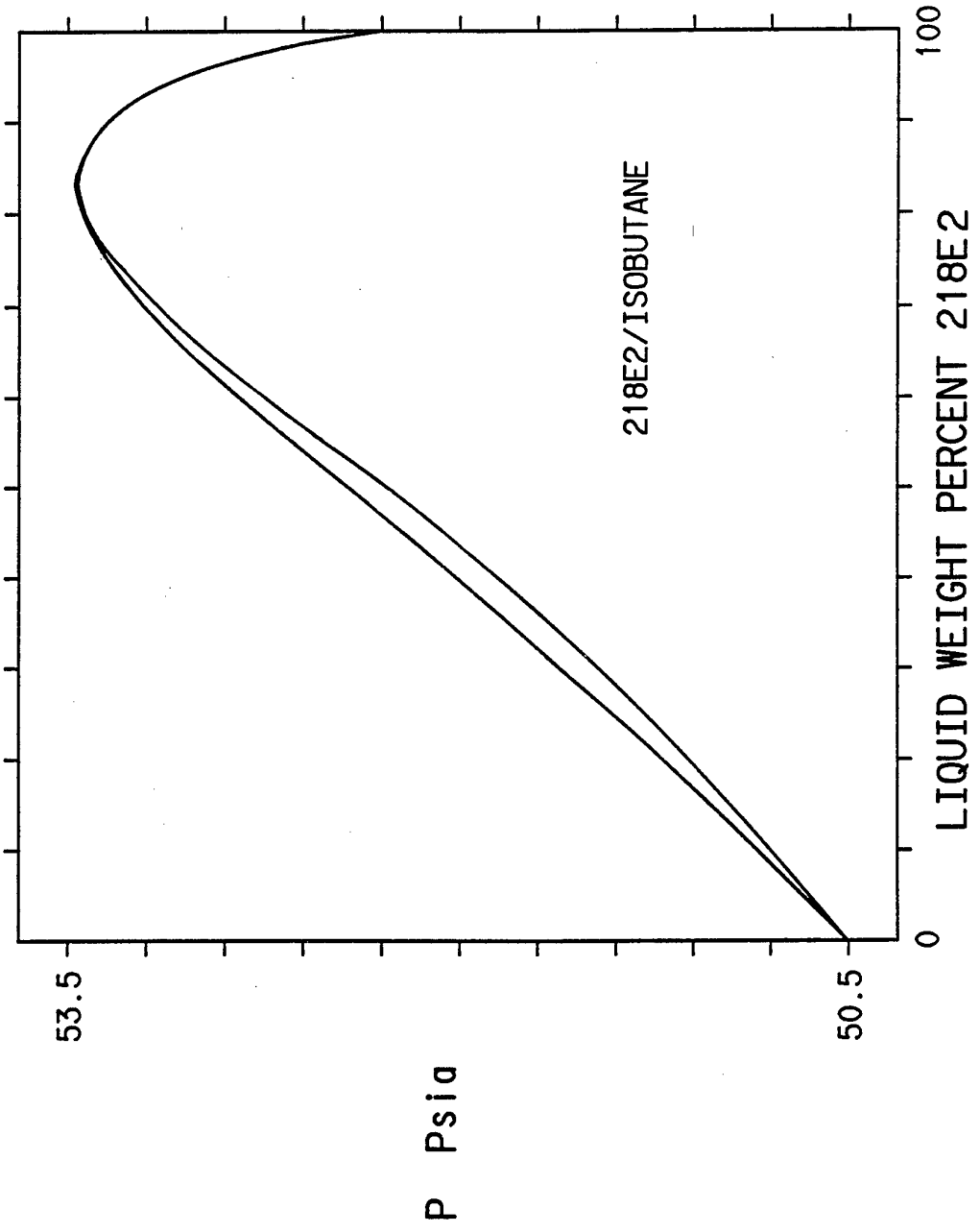

218E2/ISOBUTANE
53.5
50.5
P Psia
0
100
LIQUID WEIGHT PERCENT 218E2

FIG.20

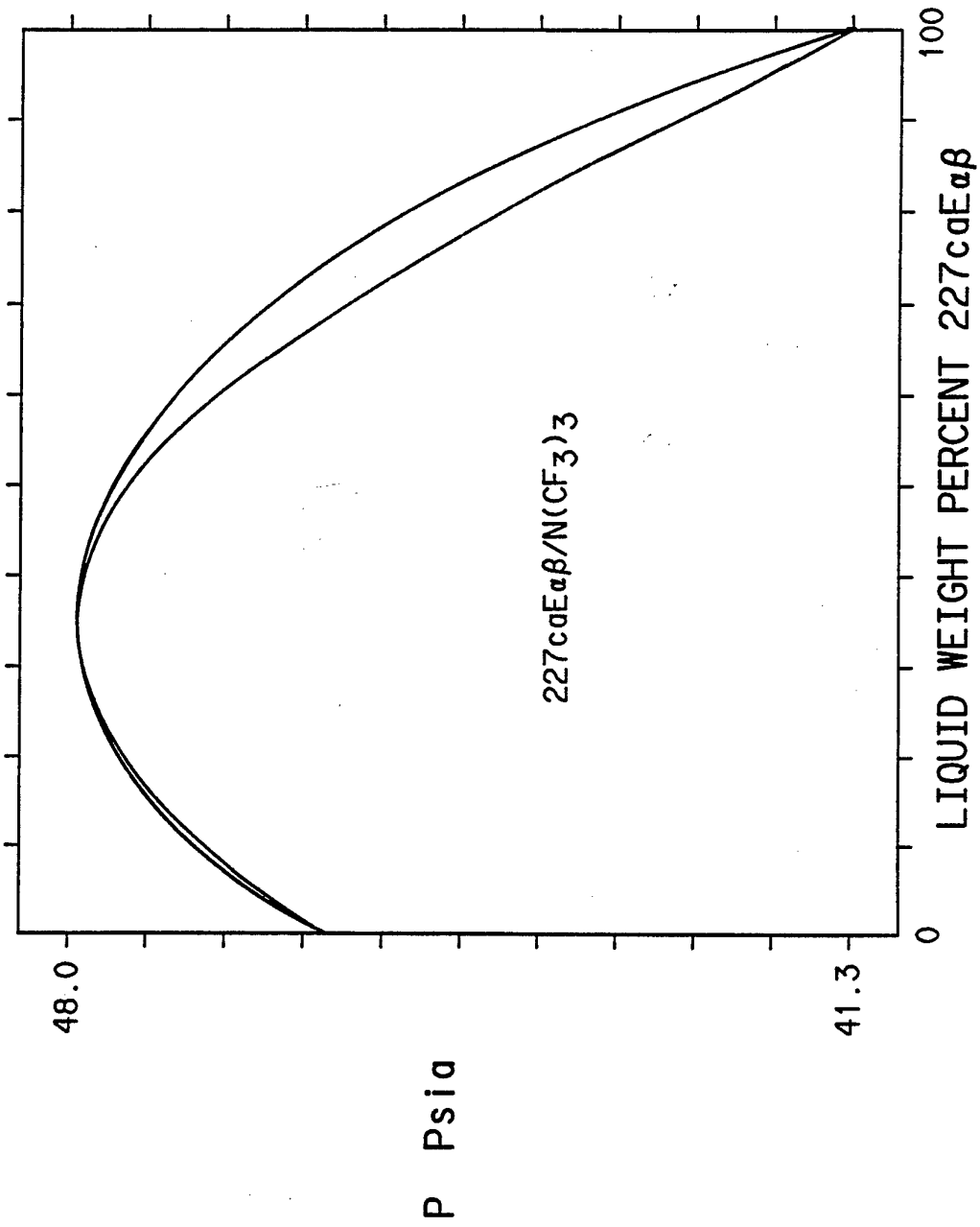

48.0
41.3
P Psia
0
100
LIQUID WEIGHT PERCENT 227caEαβ
227caEαβ/N(CF3)3

FIG.21

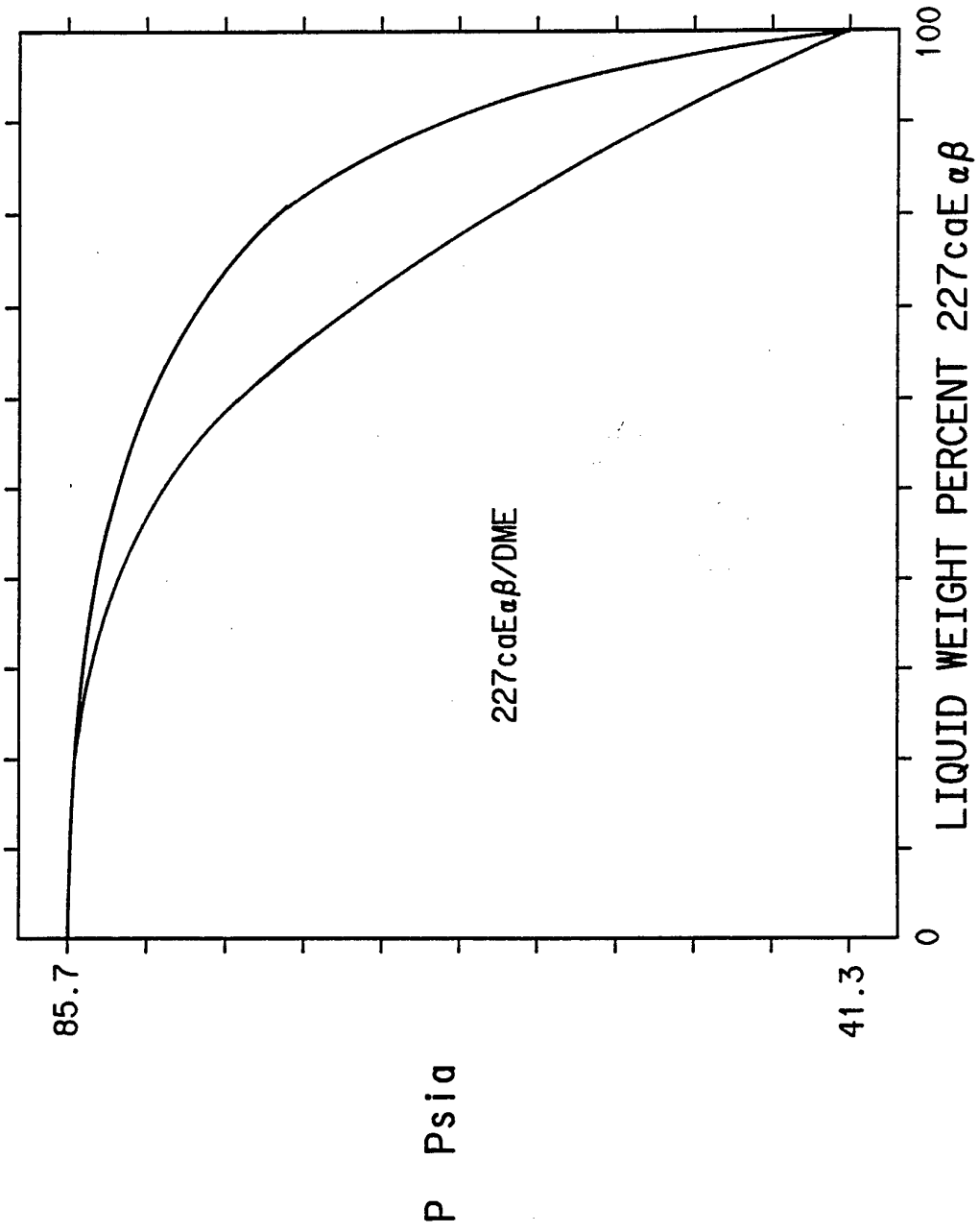

85.7
41.3
P Psia
0
100
LIQUID WEIGHT PERCENT 227caEαβ
227caEαβ/DME

FIG.22

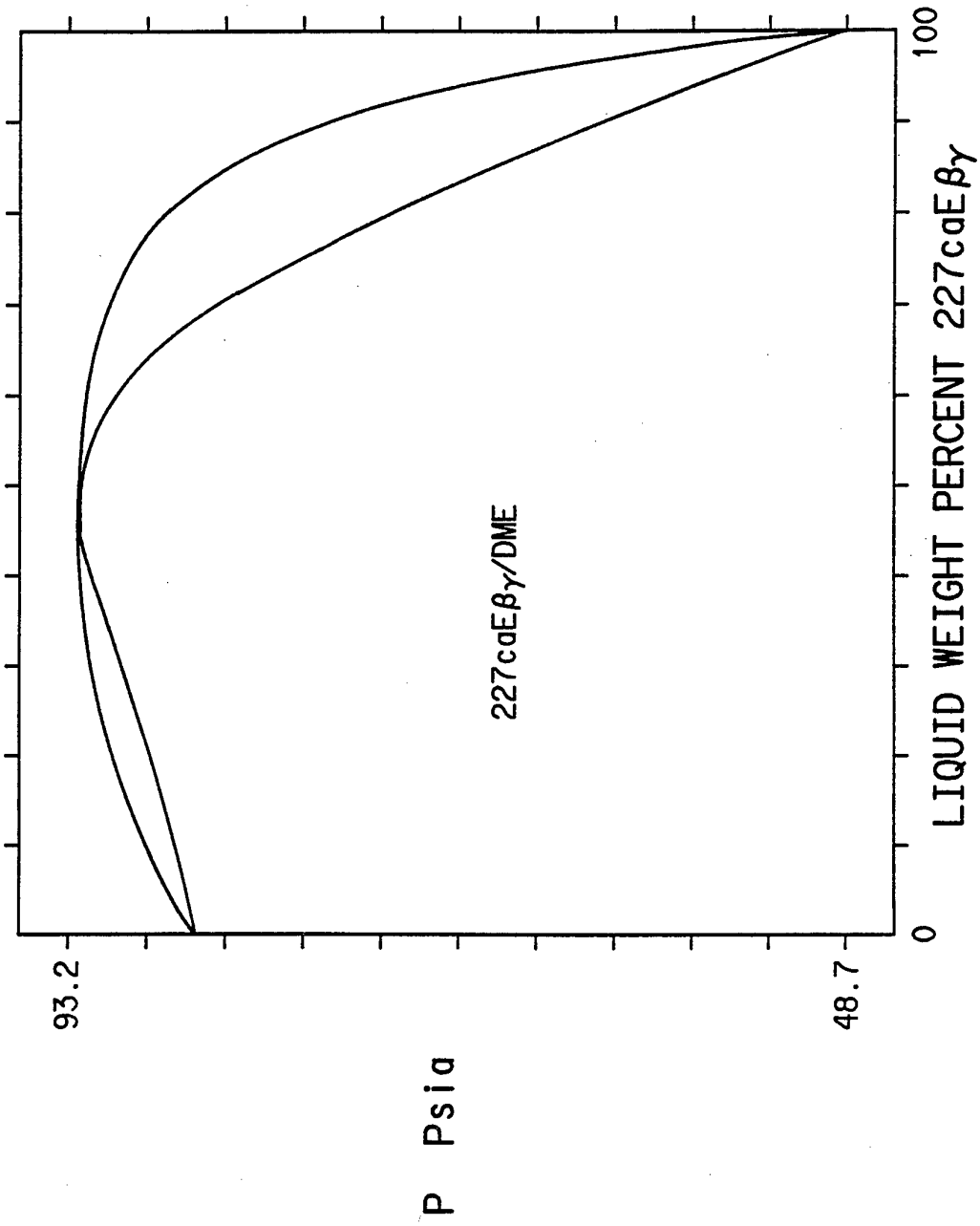

93.2
48.7
P Psia
0
100
LIQUID WEIGHT PERCENT 227caEβγ
227caEβγ/DME

FIG.23

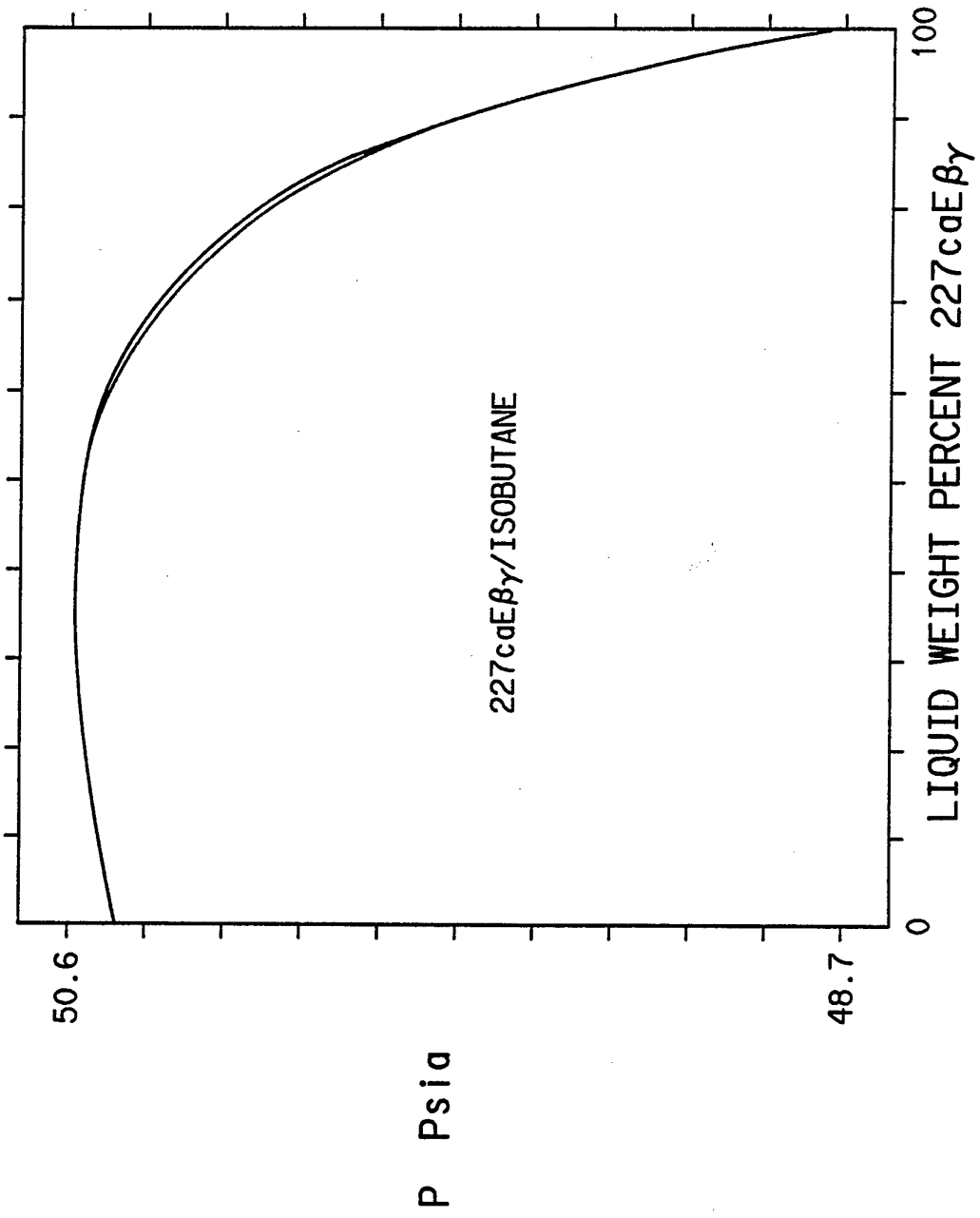

227caEβγ/ISOBUTANE
LIQUID WEIGHT PERCENT 227caEβγ
0
100
P Psia
50.6
48.7

FIG.24

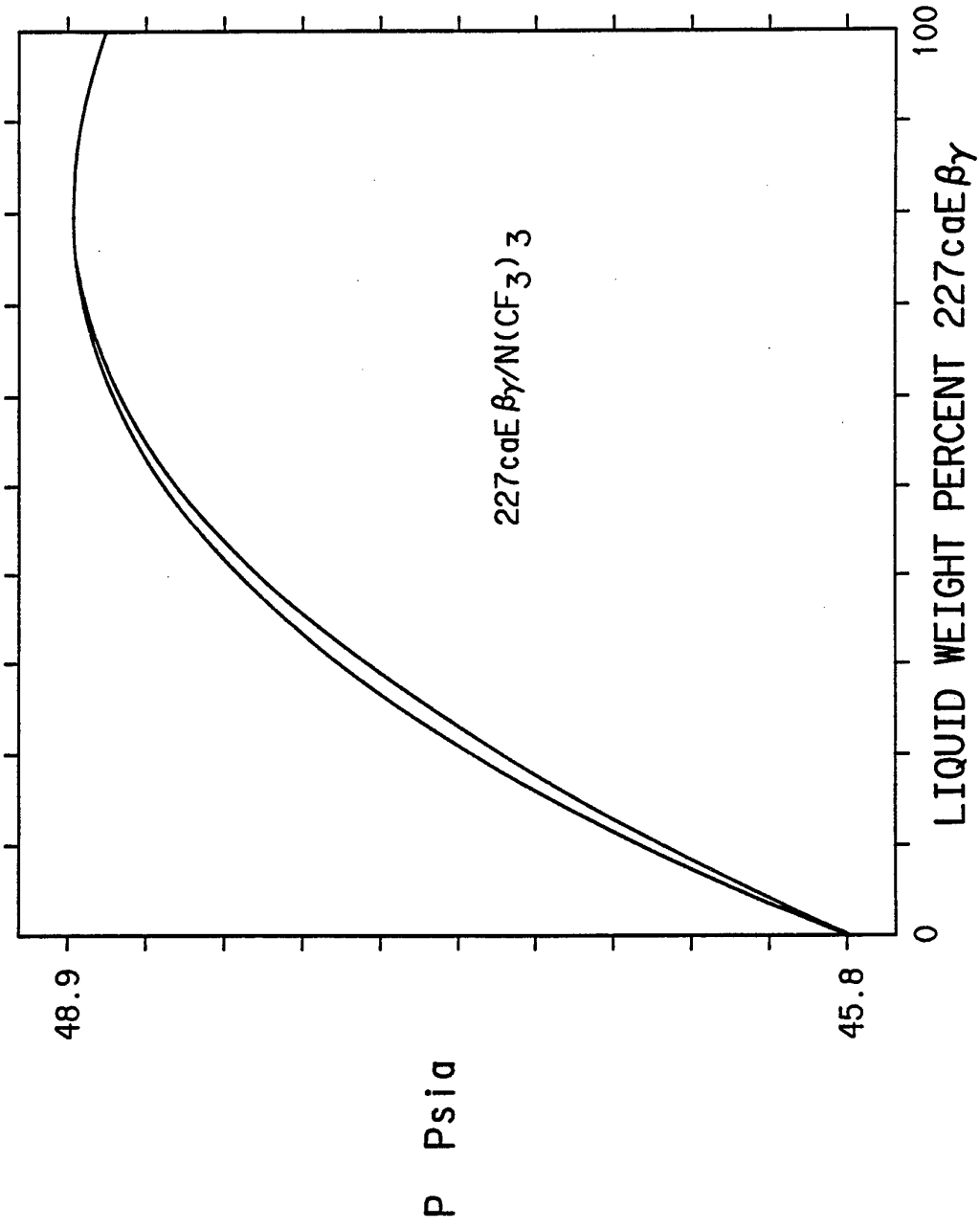

227caE βγ/N(CF3)3
P Psia
48.9
45.8
0
100
LIQUID WEIGHT PERCENT 227caE βγ

FIG.25

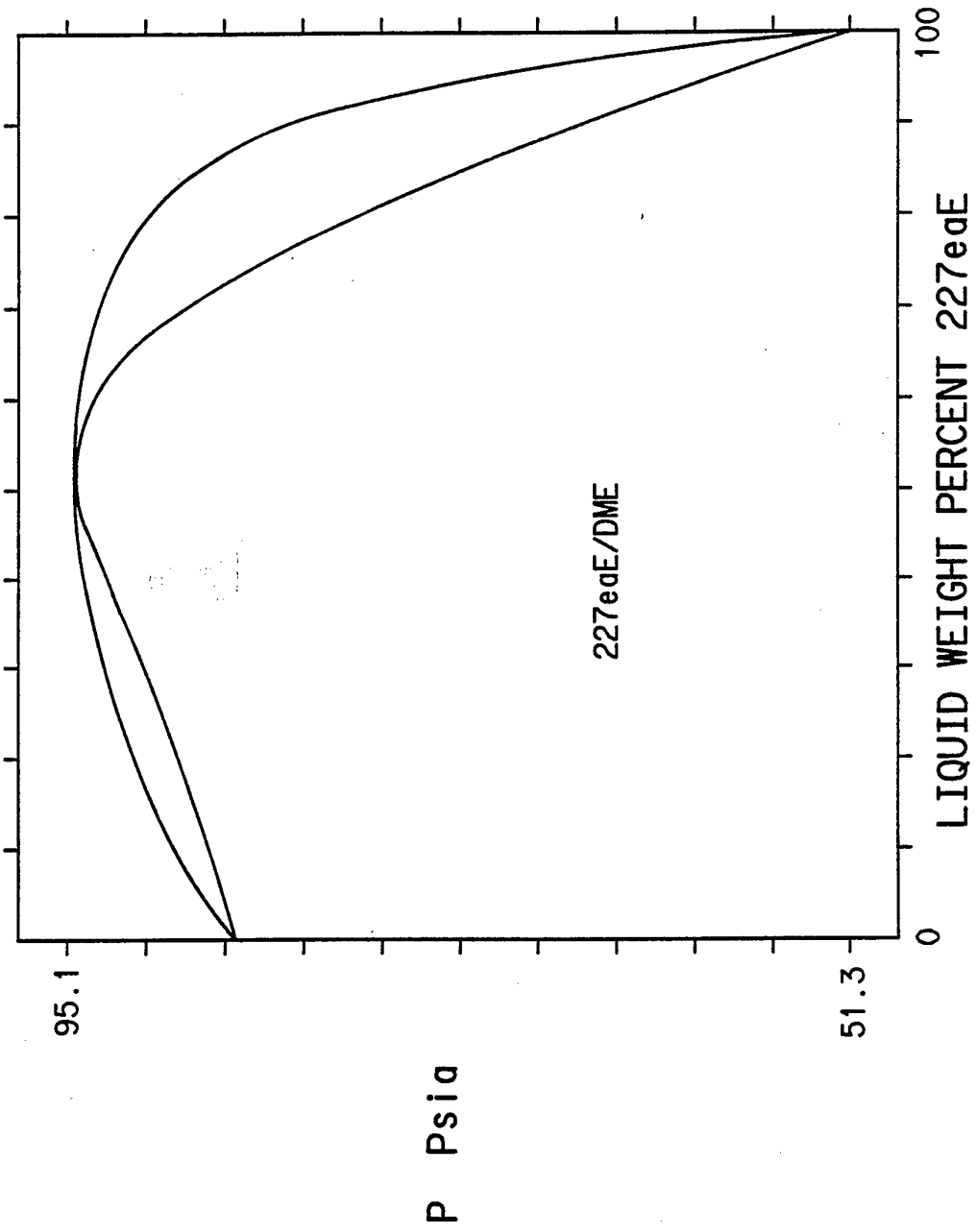


FIG.26

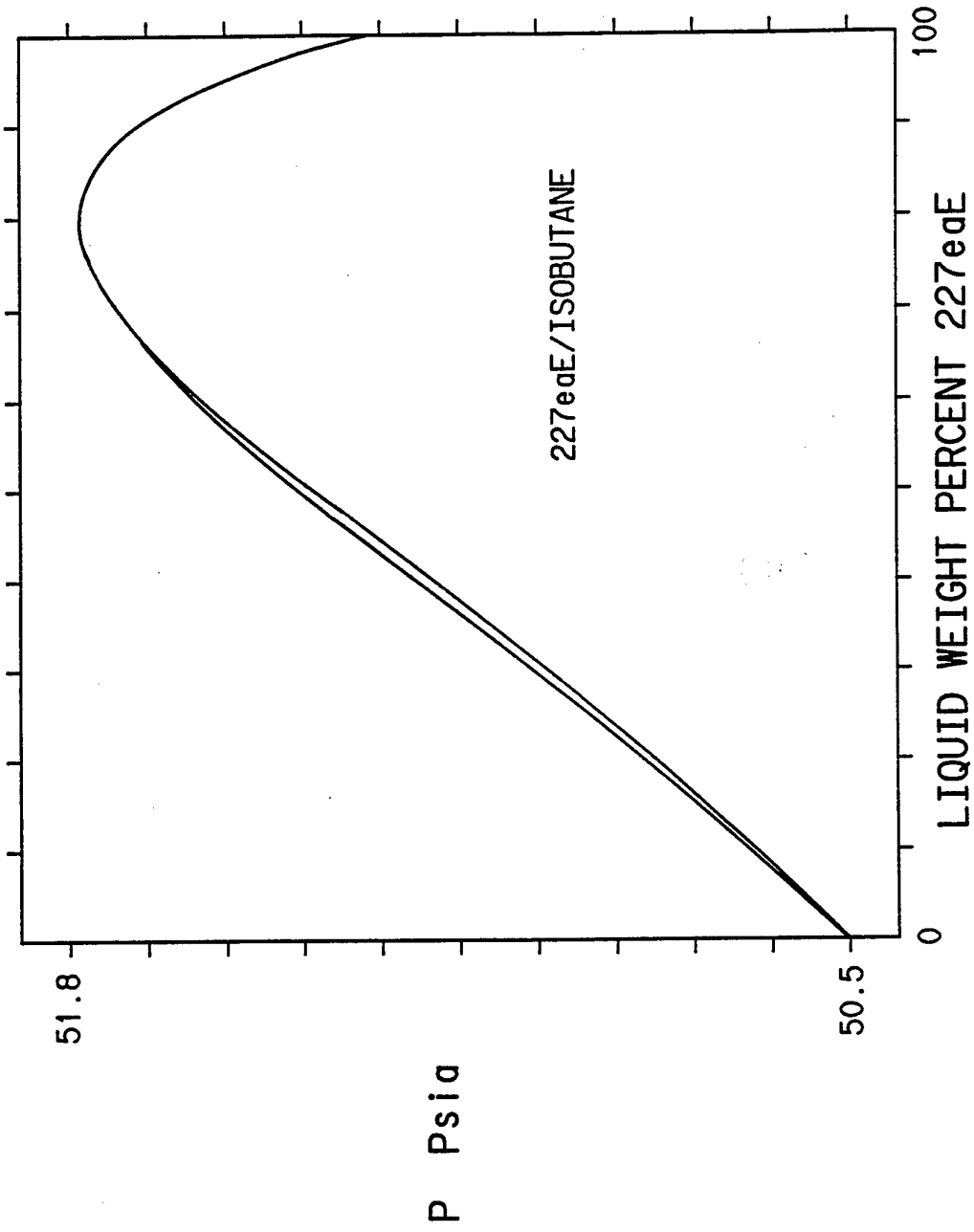

227eaE/ISOBUTANE
P Psia
51.8
50.5
0
100
LIQUID WEIGHT PERCENT 227eaE

FIG.27

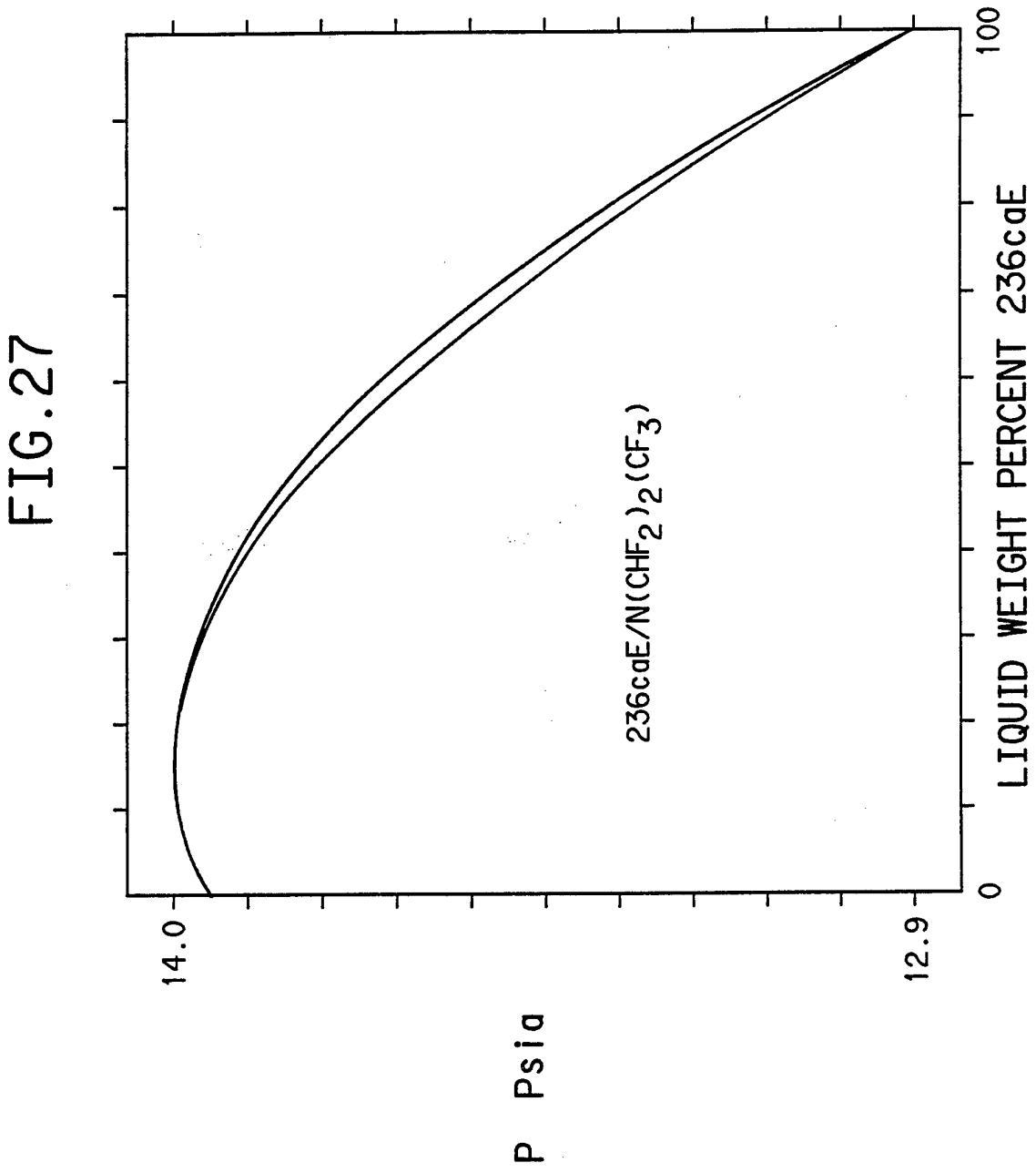

14.0
12.9
P Psia
0
100
LIQUID WEIGHT PERCENT 236caE
236caE/N(CHF2)2(CF3)

FIG.28

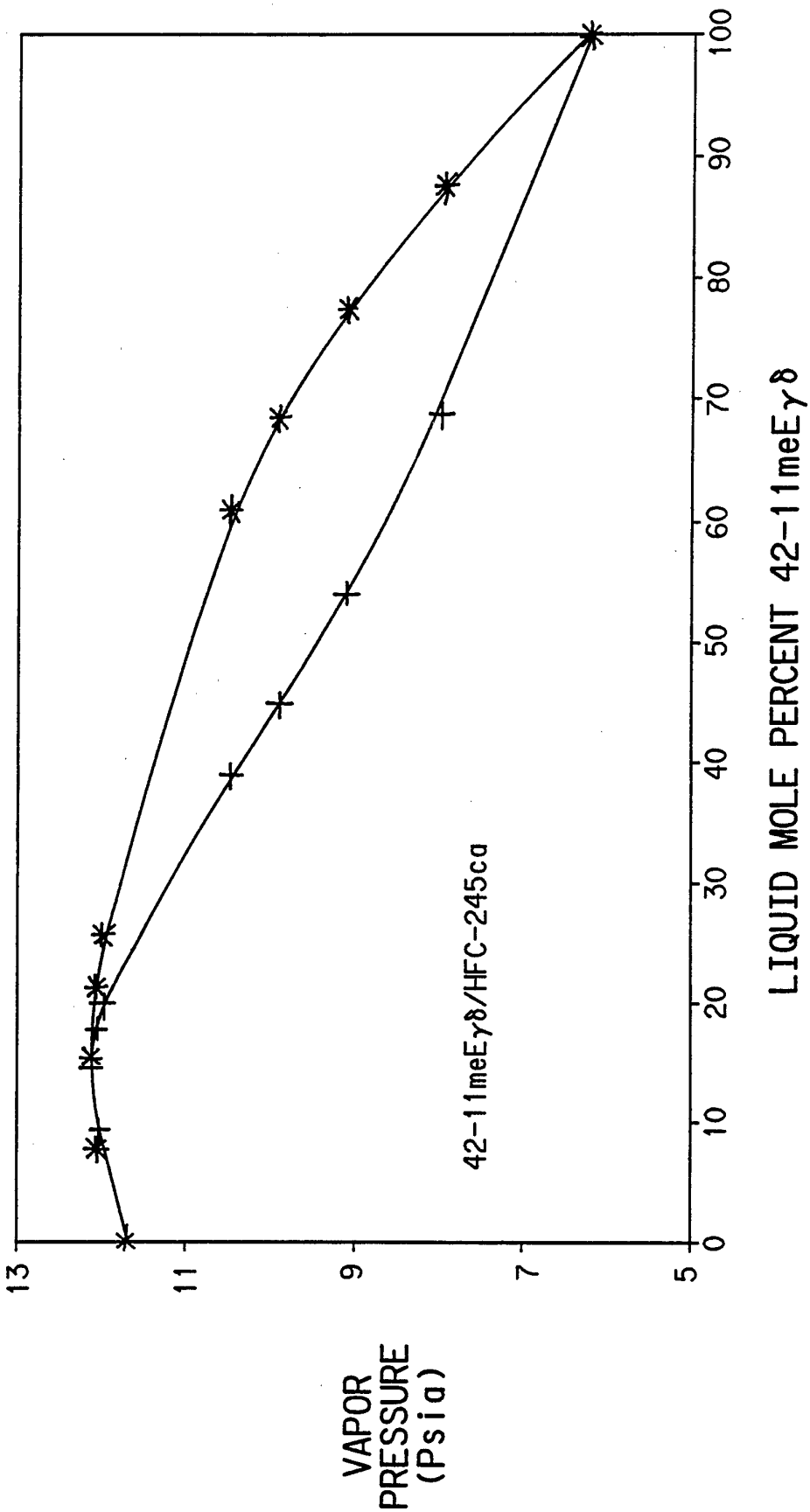
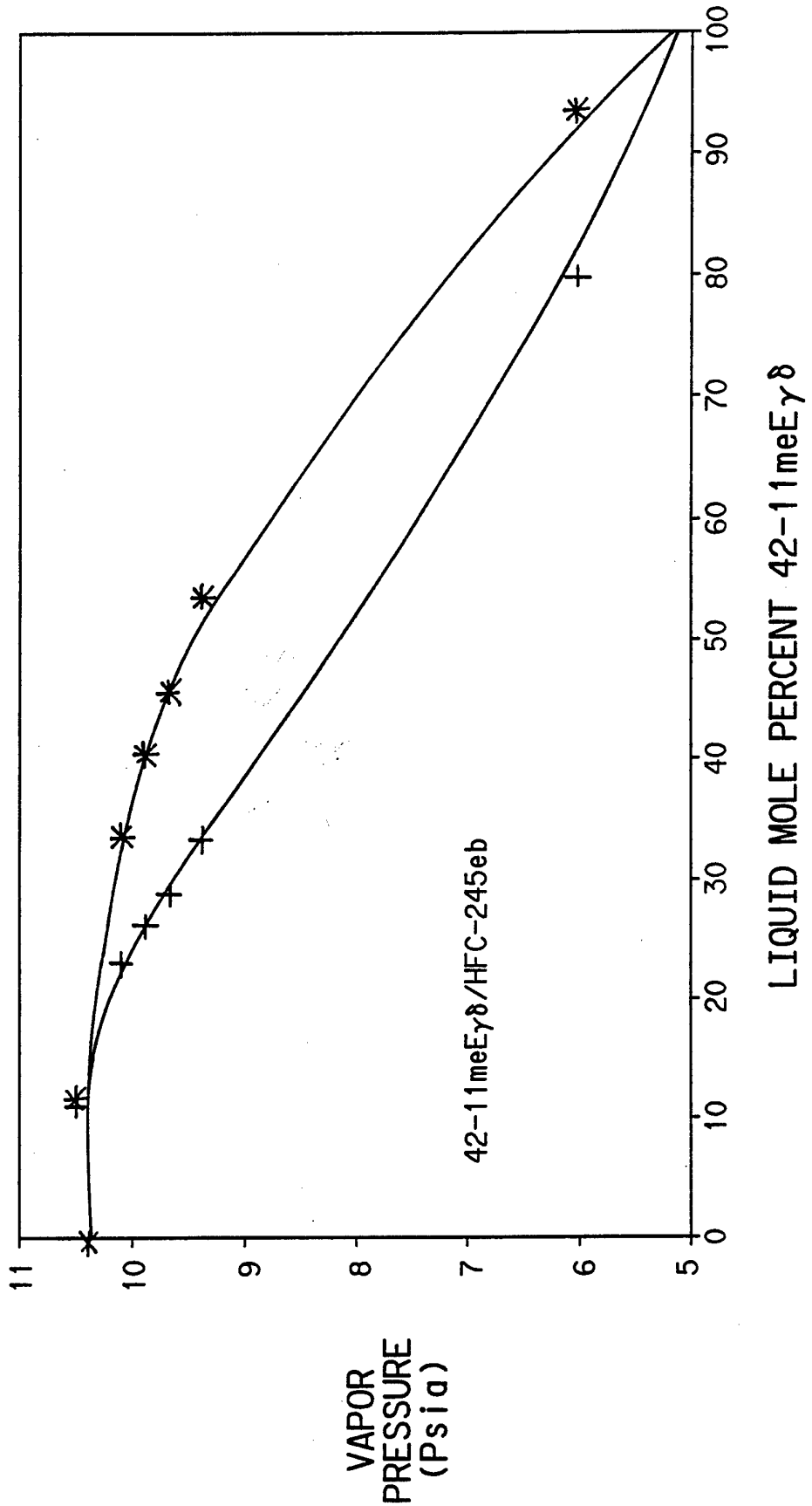

VAPOR PRESSURE (Psia)
13
11
9
7
5
0
10
20
30
40
50
60
70
80
90
100
LIQUID MOLE PERCENT 42-11meEγδ
42-11meEγδ/HFC-245ca

FIG.29


VAPOR PRESSURE (Psia)
11
10
9
8
7
6
5
0
10
20
30
40
50
60
70
80
90
100
LIQUID MOLE PERCENT 42-11meEγδ
42-11meEγδ/HFC-245eb

INTERNATIONAL SEARCH REPORT

Interna al Application No
PCT/US 94/05653

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C09K5/04 C09K3/30 C08J9/14

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)
IPC 5 C09K

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 385 737 (W.A. GRACE & CO.) 5 September 1990 see the whole document ---	1,2,5
A	EP,A,0 510 295 (HALOCARBON PRODUCTS CORPORATION) 28 October 1992 see the whole document ---	1,2,5
A	US,A,5 023 009 (A. N. MERCHANT) 11 June 1991 see the whole document ---	1,2,5
A	WO,A,93 04138 (DU PONT DE NEMOURS) 4 March 1993 see the whole document ---	1,2,5,6

-/--

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

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
20 September 1994	29. 09. 94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Puetz, C

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INTERNATIONAL SEARCH REPORT

Interna al Application No
PCT/US 94/05653

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 9318, Derwent Publications Ltd., London, GB; AN 93-149162 & JP,A,5 085 970 (DAIKIN KOGYO KK) 6 April 1993 see abstract ---	1,5
A	DATABASE WPI Week 9122, Derwent Publications Ltd., London, GB; AN 91-159422 & JP,A,3 093 883 (DAIKIN KOGYO KK) 18 April 1991 see abstract ---	1,2,5,6
A	DATABASE WPI Week 9122, Derwent Publications Ltd., London, GB; AN 91-159421 & JP,A,3 093 882 (DAIKIN KOGYO KK) 18 April 1991 see abstract ---	1,2,5,6
A	DATABASE WPI Week 9122, Derwent Publications Ltd., London, GB; AN 91-159425 & JP,A,3 093 886 (DAIKIN KOGYO KK) 18 April 1991 see abstract ---	1,2,5,6
A	DATABASE WPI Week 9221, Derwent Publications Ltd., London, GB; AN 92-172537 & JP,A,4 110 386 (DAIKIN KOGYO KK) 10 April 1992 see abstract -----	1,2,5,6

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Interna al Application No
PCT/US 94/05653

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0385737	05-09-90	US-A-	4961321	09-10-90
		AU-B-	614215	22-08-91
		AU-A-	4929990	06-09-90
		CA-A-	2008862	31-08-90
		JP-A-	2248490	04-10-90
EP-A-0510295	28-10-92	JP-A-	4359988	14-12-92
US-A-5023009	11-06-91	NONE		
WO-A-9304138	04-03-93	AU-A-	2503992	16-03-93
		EP-A-	0601070	15-06-94