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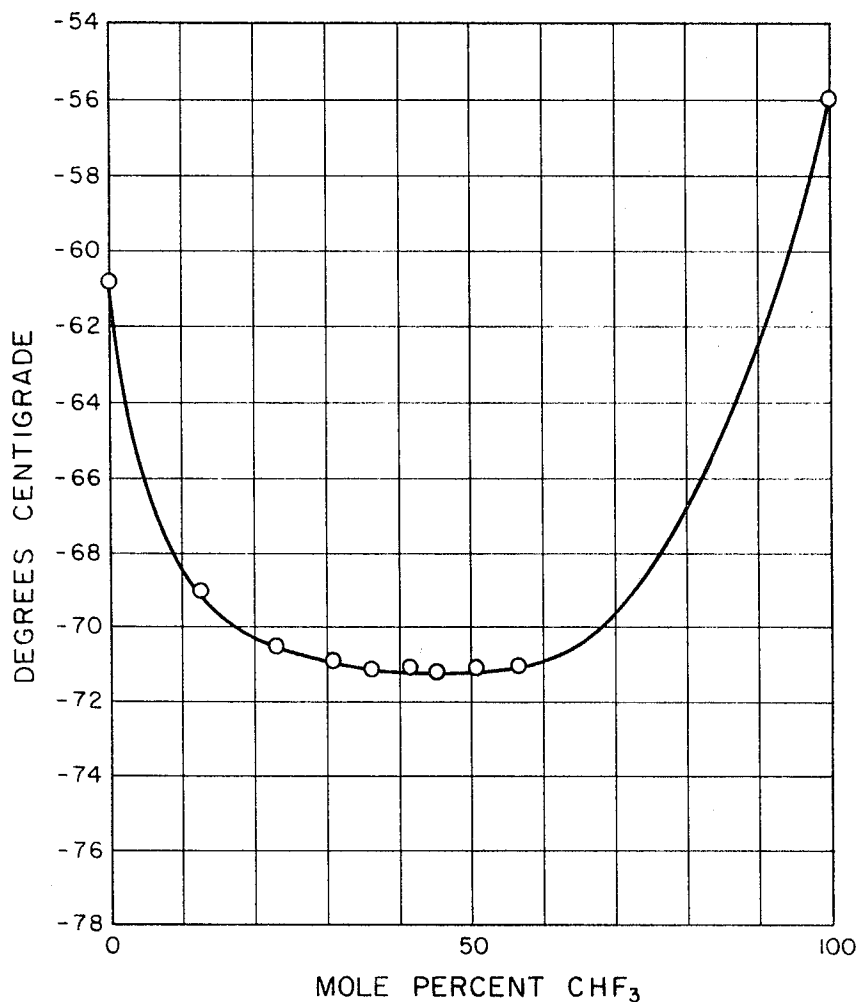
K. P. MURPHY ET AL

3,597,183

TRIFLUOROMETHANE-ETHANE AZEOTROPIC COMPOSITION

Filed May 15, 1967

2 Sheets-Sheet 1



BOILING POINT OF CHF₃/ETHANE
at 53.89 p.s.i.a.

FIG. 1.

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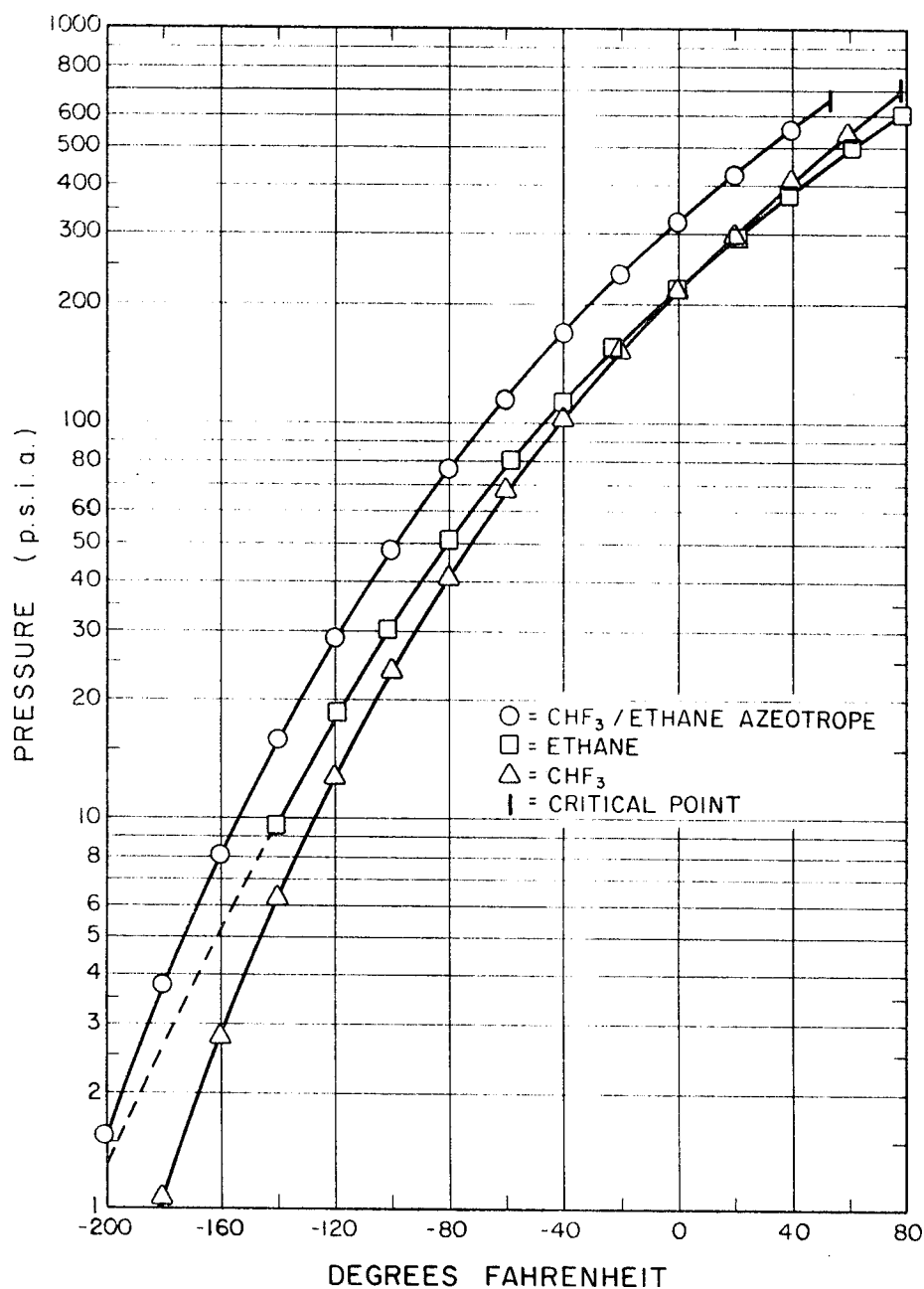
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VAPOR PRESSURE VS. TEMPERATURE CURVES

FIG. 2.

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TRIFLUOROMETHANE-ETHANE AZEOTROPIC COMPOSITION

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3 Claims

ABSTRACT OF THE DISCLOSURE

A low boiling azeotropic mixture, and equivalent mixtures, consisting of trifluoromethane and ethane, useful as refrigerants.

This invention relates to azeotropic mixtures including a fluorinated hydrocarbon. More particularly this invention relates to azeotropic mixtures including fluorocarbon-hydrocarbon mixtures which comprise trifluoromethane and ethane and which are especially adapted for use as high capacity, low temperature refrigeration compositions.

The refrigeration capacity of a given amount of refrigerant is largely a function of boiling point, the lower boiling refrigerants generally offering the greater capacity at a given evaporator temperature. This factor to a great extent influences the design of refrigeration equipment and affects capacity, power requirements, size and cost of the unit. Another important factor directly relating to boiling point of the refrigerant is minimum cooling temperature obtained in the evaporator during the refrigeration cycle, a refrigerant boiling at least as low and lower than the desired refrigeration temperature being preferred. For these reasons a large number of refrigerants of different boiling temperatures and capacities are required to permit flexibility in design, and the art is presently faced with the problem of providing new refrigerants as the need arises for new capacities and types of installations.

One of the major problems in the design and operation of very low temperature refrigeration systems is oil circulation, since at these very low temperatures the oil tends to remain in the cold evaporator section. One factor which influences the oil circulation is the solubility of the refrigerant gas in the oil. The greater the solubility, the better the oil circulation. Hydrocarbons, particularly ethane (C_2H_6 with a normal boiling point at $+86^\circ C.$), have found wide usage as a low temperature refrigerant. On the other hand the use of ethylene (C_2H_4), a hydrocarbon with very low boiling point (normal boiling point $-104^\circ C.$) is not wide spread because of its instability. There exists, therefore, a need for a refrigerant which would offer higher capacity than ethane while retaining its high oil solubility and stability.

The lower aliphatic hydrocarbons when substituted for by chlorine and fluorine are known to have potential as refrigerants. Many of these chlorofluorohydrocarbons exhibit certain desired properties including non-flammability and chemical inertness which have resulted in the extensive use of such compounds in a large number of refrigeration applications. Examples of such compounds include difluorodichloromethane (boiling point $-29.8^\circ C.$), chlorodifluoromethane (boiling point $-40.8^\circ C.$), fluorodichloromethane (boiling point $8.9^\circ C.$), fluorotrichloromethane (boiling point $23.8^\circ C.$) and tetrafluorodichloroethane (boiling point 3.50°). While these chlorine-fluorine derivatives provide an adequate range of refrigerants for many purposes, only a very few boil sufficiently low to offer any potential as low temperature refrigerants.

One commonly employed commercial method for producing low temperatures, say below about $-40^\circ C.$, is the so-called cascade refrigeration system in which a

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series of refrigerant liquids of progressively lower boiling points are condensed under pressure at the temperature produced by the evaporation of the next higher boiling refrigerant liquid. Because of its low boiling point and other desirable properties, such systems commonly use chlorotrifluoromethane (B.P. $-81.4^\circ C.$) in the second of two stages. Trifluoromethane is a good substitute for chlorotrifluoromethane, having about the same boiling point ($-82.0^\circ C.$). Ethane provides temperature capacity somewhat lower than trifluoromethane or chlorotrifluoromethane, but there is a need to reach even lower temperatures. In order to reach temperatures below the range of these refrigerants, however, tetrafluoromethane (B.P. $-128^\circ C.$), or equivalent, must be used and a third refrigeration stage added to the system.

It is well known that mixtures of substances having different boiling point results in a range of mixture compositions having boiling points intermediate of the two components. On this basis it would be possible to mix two refrigerants having different boiling points and obtain a complete series of compositions boiling at temperatures between those of the components. However, it is known that such normal mixtures may exhibit fractionation. Mixture compositions which are more desirable for use in refrigeration are those which are azeotropic and hence do not exhibit substantial fractionation. Unfortunately, as is well known in this field, there has not yet been found by anyone a basis for the predictability of the formation of azeotropes between any two compounds having a boiling point below the boiling point of any of the components contained therein.

Accordingly, it is a major object of the present invention to provide new azeotropic mixtures especially suitable for use as low temperature refrigerants.

More particularly, it is an object of the present invention to provide new refrigerants boiling lower and having greater capacity than the lower boiling ethane.

Another object of the invention is to provide low boiling compositions which offer higher capacity than ethane while retaining its relatively high oil solubility and stability.

Another object of the invention is to provide low boiling compositions comprising trifluoromethane (CF_3H), with a boiling point of about $-82^\circ C.$ and ethane (C_2H_6) mixtures, which boil at substantially constant temperature and function as a single substance and therefore are useable in producing refrigeration substantially without fractionation, including in those systems in which cooling is achieved by evaporation in the vicinity of the body to be cooled.

Another object of the invention is to provide a novel azeotropic composition boiling at temperatures lower than about $-88^\circ C.$, which compositions retain high oil solubility and relative stability and are particularly suited for use in cascade refrigeration type systems.

FIG. 1 of the drawing shows boiling point data.

FIG. 2 of the drawing shows various vapor pressure curves.

In accordance with the invention, it has been discovered that mixtures consisting of trifluoromethane and ethane containing approximately 35 to 50 mol percent trifluoromethane form an azeotrope boiling at a temperature of about $-71.18^\circ C. \pm .04^\circ C.$ at 53.39 p.s.i.a. (unless otherwise indicated, percentages indicated hereinafter are in terms of mol percent). It has also been found that mixtures comprising trifluoromethane and ethane substantially in the range of about 20 percent trifluoromethane to about 65 percent trifluoromethane have boiling temperatures within about $1^\circ C.$ of the azeotropic boiling point and exhibit only negligible fractionation on boiling under refrigeration conditions.

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In addition the azeotropic composition exhibits a number of advantages over the use of trifluoromethane alone, such as permitting lower temperatures to be reached and higher solubility of the refrigerant gas in the oil, producing better oil circulation.

To determine the azeotropic composition, the temperature-composition curve was experimentally measured at 53.39 p.s.i.a. Boiling points of $\text{CF}_3\text{H}/\text{C}_2\text{H}_6$ mixtures were determined using trifluoromethane better than 99.8 percent pure and commercial ethane having a purity of 99 percent and better. The static method was used to measure the boiling points of the mixtures. Weighed amounts of the components were distilled into a steel bomb and thermostated at constant temperature to better than $\pm 0.1^\circ \text{C}$. (bath temperature was adjusted until the vapor pressure of the mixture was 53.39 p.s.i.a.). The data at 53.39 p.s.i.a. are represented graphically by the curve of FIG. 1 and are summarized in Table I.

TABLE I.—TEMPERATURE—COMPOSITION FOR $\text{CF}_3\text{H}/\text{ETHANE}$

Pressure=53.39 p.s.i.a.

Mol percent CF_3H :	Temperature
0.0 -----	-60.83
12.8 -----	-69.04
23.0 -----	-70.50
31.0 -----	-70.89
36.6 -----	-71.13
41.5 -----	-71.16
45.2 -----	-71.22
50.3 -----	-71.15
56.8 -----	-71.02
100.0 -----	-56.00

Vapor pressures were read from a Bourdon Tube Pressure Gauge connected to said bomb. The bath temperature was controlled to better than 0.05°C . and was measured by an L & N platinum resistance thermometer which was calibrated against a N.B.S. certified platinum resistance thermometer. The accuracy of the temperature measurements was 0.02°C .

Table II shows the temperature-pressure relationship for the $\text{CF}_3\text{H}/\text{C}_2\text{H}_6$ azeotrope formed at about 45 mol percent trifluoromethane (the minimum point on the curve of FIG. 1).

TABLE II.—VAPOR PRESSURE OF $\text{CF}_3\text{H}/\text{C}_2\text{H}_6$ AZEOTROPE

Temperature $^\circ \text{C}$..	Pressure p.s.i.a.
-81.79 -----	32.58
-71.20 -----	53.39
-60.04 -----	83.70
-44.70 -----	145.60
-26.16 -----	258.70
-0.00 -----	506.70

The curves in FIG. 2 of the drawing compare graphically to the vapor pressure of the azeotrope to the vapor pressure of the trifluoromethane and ethane components. The vapor pressures (p.s.i.a.) are plotted as a function of temperature in $^\circ \text{F}$. It will be noted that the vapor pressure of the azeotrope remains higher than the respective vapor pressures of the components over a wide range of temperatures, thus indicating that the system remains azeotropic over this range.

The data of Table II and figure shows the normal boiling point of the azeotrope to be -97°C ., as compared to -88°C . for ethane, the lower boiling compound.

The boiling point data set forth in Table I and shown in FIG. 1 demonstrates that compositions consisting of ethane and about 35 to 50% trifluoromethane form a minimum boiling azeotrope. The data found shows that compositions consisting of ethane and 20 to 65 mol percent of trifluoromethane define a range of mixture compositions having boiling points which vary only slightly from that of the minimum boiling -71.22°C . at 53.39 p.s.i.a.,

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45.2 weight percent trifluoromethane composition. As compositions between about 20 to 65 mol percent trifluoromethane all boil within a variation of less than about 1°C . (at 53.39 p.s.i.a.), a substantially equivalent capacity would be obtainable from any compositions within this range and all such compositions are suited for use as refrigerants.

For the most advantageous refrigerant use it is desirable and preferred to employ mixtures at substantially about 35 to 50 percent trifluoromethane azeotropic compositions. However, since there is no significant boiling point difference in the CHF_3 composition range of about 20 to 65 weight percent; for general first-class operation, these compositions are preferred. In cases where operating requirements are less rigid, compositions in the range of about the 18 to 70 percent CHF_3 , all boil at about or below -70°C . at 53.39 p.s.i.a., are eminently suitable, since all such compositions boil within a variance of substantially 1.2°C .

Apart from the use of the indicated amounts of trifluoromethane and ethane, each of which is commercially available, makeup of the compositions of the invention requires no specific procedure. The CHF_3 and C_2H_6 employed should be substantially pure, preferably at least about 99 percent pure, and should contain no substances deleteriously affecting the boiling characteristics of the mixture composition or their use as refrigerants.

The trifluoromethane-ethane azeotrope has excellent oil solubility compared to fluorocarbons and thus it is easier to affect oil return in these systems. In addition it has desirable thermodynamic properties.

The azeotropic compositions of the invention represent a marked increase in refrigeration capacity as compared with the boiling temperature of the lower boiling ethane component, while offering significant advantages over the ethane component used alone.

C_2H_6 replacing CF_3H as the low stage refrigerant in a cascade refrigeration machine produces 1.32 tons of cooling at -130°F ., compared to 1.0 ton of refrigeration (12,000 B.t.u./hour) produced by CF_3H at -130°F . (the condensing temperature for the low stage being -40°F .). Replacing CF_3H with $\text{CF}_3\text{H}/\text{C}_2\text{H}_6$ azeotrope (about 45% trifluoromethane) produces 1.92 tons of refrigeration at -130°F . under the same conditions.

By way of summary, the compositions of the present invention exhibit the excellent refrigerant properties, the mixtures indicated boiling at temperatures substantially lower than either component and, therefore, represent new refrigerants offering lower refrigeration temperatures than either of these components. The essentially azeotropic properties of mixtures containing between about 20 to 65 percent trifluoromethane provide a substantial range of compositions suitable for use in the many types of refrigeration in which cooling is affected by condensing and thereafter evaporating the refrigerant in the vicinity of a body to be cooled. As refrigerants, these compositions are particularly useful in the specific situation known in the art to provide additional capacity where needed in equipment designed for cascade type cooling. It will be further noted that the azeotropic compositions disclosed herein may also be used for other purposes, including use as heat transfer media and as low temperature solvents.

We claim:

1. The process of producing refrigeration which comprises condensing a substantially constant boiling mixture consisting of trifluoromethane and ethane, in which mixture the mol percent of trifluoromethane is in the range of about 20 to 65, and thereafter evaporating said mixture in the vicinity of a body to be cooled.

2. The process of producing refrigeration as recited in claim 1, the mol percent of trifluoromethane being in the range of 35 to 50.

3. The process of producing refrigeration as recited in claim 1 in which the substantially constant boiling mixture which is condensed and evaporated is an azeotrope

of trifluoromethane and ethane containing about 45 mol percent trifluoromethane, which azeotrope has a boiling point of about -71.18°C . at 53.39 p.s.i.a.

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