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B. J. EISEMAN, JR
AZEOTROPIC COMPOSITION

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FIG. 3

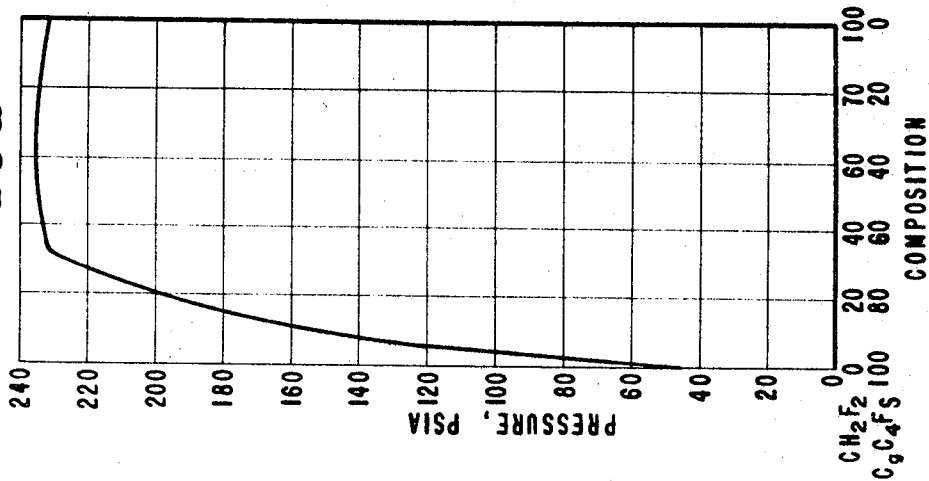


FIG. 2

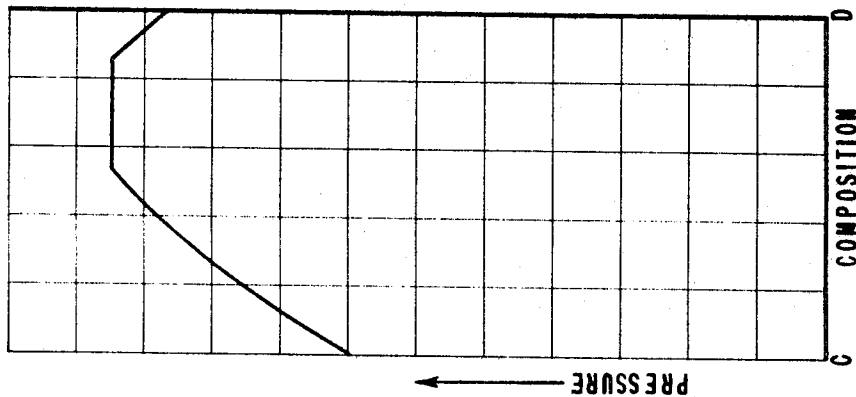
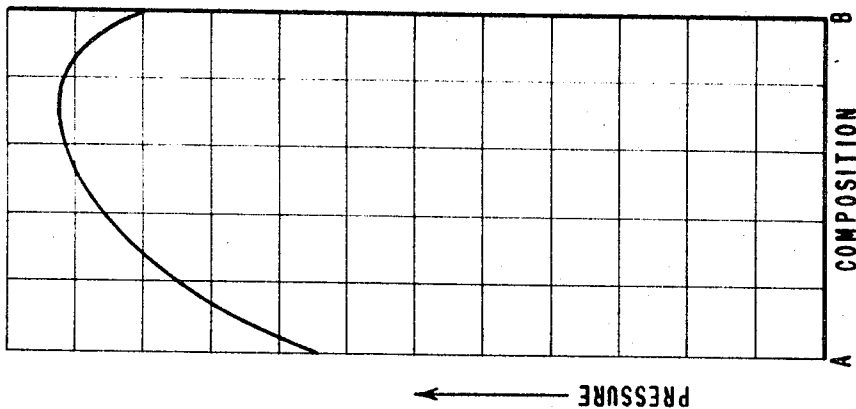


FIG. 1



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AZEOTROPIC COMPOSITION

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1 Claim

ABSTRACT OF THE DISCLOSURE

An essentially constant boiling composition of 30% to 90% by weight CH_2F_2 and 70% to about 10% by weight perfluorocyclobutane; and the process of transferring heat in a refrigeration cycle by evaporating, compressing and condensing the composition.

The present invention is directed to novel refrigerant compositions.

A continuing problem in refrigeration is that there exists only a limited number of properly low-boiling, liquefied gases having properties suitable for refrigeration purposes. In addition to being low boiling, other important properties which a useful refrigerant must possess are low toxicity, nonflammability, freedom from odor, high chemical and thermal stability. In view of the stringent physical property requirements, only a limited number of the halogenated hydrocarbons are useful as refrigerants. These hydrocarbons are widely spaced in boiling points. Consequently, there are gaps in the range of the normal boiling points of refrigerants where no single refrigerant is available. Since the design of refrigeration units is dependent to a large extent upon the boiling point of the refrigerant used, it is desirable to have refrigerants of varying boiling points to gain flexibility in design specifications.

The requirements for refrigerants of different boiling points can sometimes be met through the discovery of an azeotrope which fills the gap in the range of existing refrigerants. For example, the azeotrope of 48.8% by weight chlorodifluoromethane and 51.2% by weight of chloropentafluoromethane is a useful refrigerant having a normal boiling point of -50.1°F . This azeotrope lies in the gap between bromotrifluoromethane, having a boiling point of -72°F ., and chlorodifluoromethane, with a boiling point of -41.4°F . However, a gap of more than 20°F . still exists between the boiling point of the above-mentioned azeotrope and bromotrifluoromethane.

There exists, therefore, a need for a useful refrigerant with a normal boiling point between -50°F . and -72°F . It is to this need that the present invention is directed.

More specifically, the present invention is directed to a novel azeotrope-like composition consisting of from about 30% to about 90% by weight of difluoromethane and from about 70% to about 10% by weight of perfluorocyclobutane. The present invention is also directed to a novel process of transferring heat in a refrigeration cycle which comprises evaporating, compressing, and condensing a mixture consisting of 30% to 90% by weight of difluoromethane and 70% to 10% by weight of perfluorocyclobutane.

An azeotrope is a mixture of compounds having a minimum boiling point and yielding a distillate of the same composition as the original mixture. Ordinarily, azeotrope formation results from a vapor pressure composition relation similar to that shown graphically in the drawing. In the drawing, FIGURE 1 represents a typical homogeneous azeotrope, and FIGURE 2 represents a heterogeneous azeotrope. In the homogeneous system, represented by FIGURE 1, only one liquid phase exists and the so-called

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azeotropic point is at the highest pressure. In the heterogeneous system, represented by FIGURE 2, the compositions having the constant vapor pressure are shown by the flat, horizontal section of the curve. Over this range of compositions, the mixture comprises two liquid phases.

The azeotrope-like compositions of the present invention, however, are different from either of the general types and, hence, are unusual and unexpected. The compositions of the present invention result from the relation shown in FIGURE 3. In this system, the vapor pressure for an extended composition range is nearly constant and only slightly higher than that of difluoromethane, one of the components of the compositions. In this respect, it is similar to the heterogeneous azeotrope shown in FIGURE 2. However, unexpectedly there is only one liquid phase. Hence, the azeotrope is homogeneous. With such a system it follows that one may prepare a series of mixtures of different compositions having practically the same boiling point as difluoromethane and undergoing essentially no fractionation upon evaporation in the sense that the composition of the vapor will not change appreciably. In these respects, the compositions are equivalent in behavior to a refrigerant which is a single chemical compound.

The novel azeotrope-like compositions of difluoromethane and perfluorocyclobutane of the invention have a normal boiling point range between -61°F . and -62°F . and fill the gap between the refrigerant azeotrope of chlorodifluoromethane and chloropentafluoroethane (B.P. -50.1°F .) and the refrigerant bromotrifluoromethane (B.P. -72°F .). In addition, the azeotrope-like compositions of the present invention exhibit unexpected properties which well adapt them for use as refrigerants. The difluoromethane component of the azeotrope-like compositions has a high latent heat of vaporization and a low molecular weight, properties which, together with its low boiling point (-61°F .), are advantageous for the use of difluoromethane as a refrigerant. The flammability in air of the compound, however, precludes its general use as a refrigerant. The high rise in temperature on compression which it exhibits is also disadvantageous.

These deficiencies of difluoromethane are corrected by mixing it with perfluorocyclobutane. Mixtures containing 40% and above by weight of perfluorocyclobutane are nonflammable in air. Nonflammability of mixtures of difluoromethane and perfluorocyclobutane were demonstrated by the following test. Various mixtures of difluoromethane/perfluorocyclobutane were mixed with air. The total pressure of the mixture was one atmosphere. The mixtures were then put into an enclosed one-quart glass container at atmospheric pressure and a strike-anywhere match head was ignited by means of an electrical spark. If the mixture supported combustion, it was deemed flammable. The range of the partial pressures of difluoromethane was from 90 to 230 millimeters of mercury. The range of the partial pressures of perfluorocyclobutane was from 0 to 28 millimeters of mercury. The rest of the total pressure of about 760 millimeters of mercury was made up of air. Mixtures in which the molar proportion of C_4F_8 to CH_2F_2 was 15 to 85 or greater were essentially nonflammable.

There are, of course, refrigerant needs in areas, such as petroleum refineries, where flammability is of no consequence. Hence, flammable mixtures containing less than 40% by weight of perfluorocyclobutane are part of this invention.

Perfluorocyclobutane also tends to alleviate the problem of the high rise of temperature on compression exhibited by difluoromethane. The addition of a significant amount of perfluorocyclobutane, i.e., 10% by weight or greater, markedly lowers the compressor discharge temperature of difluoromethane. The magnitude of this effect is shown in Table I below. A refrigeration system wherein

the refrigerant compositions listed below are evaporated, compressed, and condensed in a refrigeration cycle is operated at an evaporator temperature of -10°F . and a condenser temperature of 100°F . The superheat of the suction gas is maintained in each case at 60°F . The approximate lowering of the compressor discharge temperature for each test is given below.

TABLE I.—COMPRESSOR DISCHARGE TEMPERATURE LOWERING IN DIFLUOROMETHANE/PERFLUOROCYCLOBUTANE MIXTURES

Composition of mixture, percent by weight		Approximate lowering of compressor discharge temp. of CH_2F_2 , in $^{\circ}\text{F}$.
CH_2F_2	cy- C_4F_8	
90	10	10
60	40	50
30	70	85

In a refrigeration cycle, it is economical to reach a low evaporator temperature with a single stage of compression, if the ratio of compression will not become too high as is known to those skilled in the art. To this end, it will be possible and desirable to use a high proportion of perfluorocyclobutane in a mixture with difluoromethane, in spite of the higher cost of the perfluoro compound. As already indicated, about 70% by weight of perfluorocyclobutane can be included without inherently changing the normal boiling point of the mixture. This is one of the significant advantages derived from the unusual vapor pressure/composition relation exhibited by the azeotropic-like mixtures of the present invention.

In the invention compositions, while perfluorocyclobutane provides improvement over difluoromethane in rendering mixtures containing 40% or more by weight of the perfluoro compound nonflammable in air and is significantly effective in lowering the compressor discharge temperature, the difluoromethane contributes its advantageous properties and provides improvement over the perfluoro compound. The difluoromethane component serves to raise the latent heat of evaporation of the mixture, lower its molecular weight, and lower its freezing point.

For low temperature refrigerant applications, a low freezing point of the refrigerant is needed. Pure perfluorocyclobutane freezes at -42.5°F . which limits its use in refrigeration. With the addition of difluoromethane to perfluorocyclobutane, the freezing point is so lowered that the mixture containing 30% by weight difluoromethane reaches -85°F . before freezing.

The invention compositions are thus seen to possess advantageous properties not exhibited by one or the other of the components taken separately. The components are of mutual benefit to each other. Part of the combined ad-

vantages exist over a composition range from about 30% to about 90% by weight of difluoromethane and from about 70% to about 10% by weight of perfluorocyclobutane. Throughout this composition range the compositions have the same boiling range between -61°F . to -62°F . and are azeotrope-like. The preferred composition range extends from about 30% to 60% by weight of difluoromethane and from about 70% to 40% by weight of perfluorocyclobutane.

The invention compositions are well adapted for use as refrigerants to effect cooling for refrigeration or freezing. The cooling is accomplished by a process for transferring heat in a repeated cycle of evaporating, compressing, and condensing a mixture of difluoromethane and perfluorocyclobutane.

Difluoromethane may be prepared by heating at about 130°C . a mixture of dichloromethane and anhydrous hydrogen fluoride in the presence of antimony trichloride and pentachloride as described in U.S. Patent 2,749,374. Perfluorocyclobutane may be produced by heating tetrafluoroethylene as described in U.S. Patent 2,404,374. The compositions of the present invention are prepared by simply mixing the components in the desired concentration.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claim.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An essentially constant boiling composition consisting of from about 30% to about 60% by weight difluoromethane and from about 70% to about 40% by weight perfluorocyclobutane, said composition having a normal boiling point range between -61°F . and -62°F .

References Cited

UNITED STATES PATENTS

3,173,872 3/1965 Broadley et al. 252—67

OTHER REFERENCES

Chemical Abstracts, vol. 51, col. 4601d (1957).

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U.S. Cl. X.R.

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