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PROCESS OF TRANSFERRING HEAT

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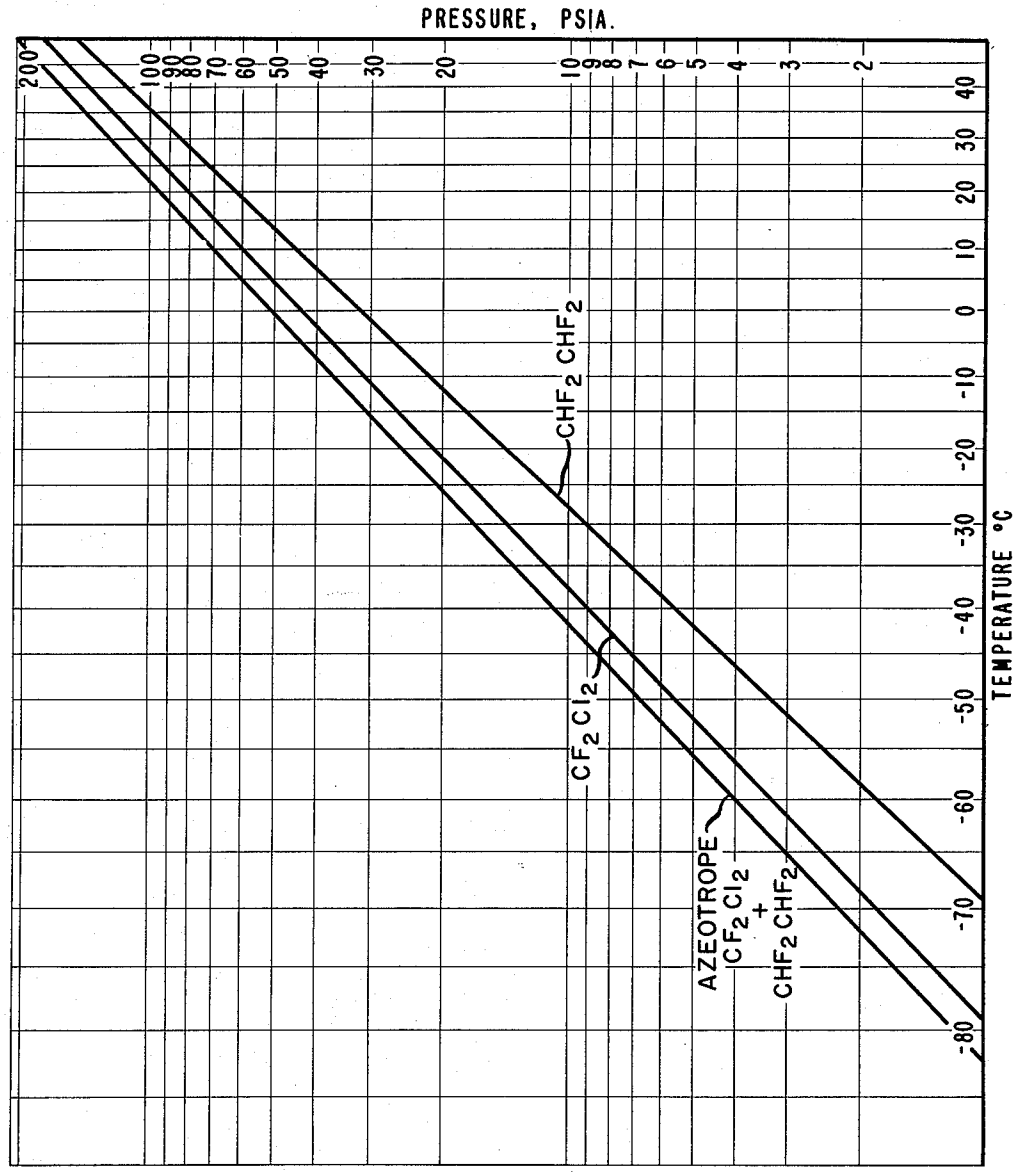

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PROCESS OF TRANSFERRING HEAT

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This invention relates to a refrigerant composition which is an azeotrope of dichlorodifluoromethane and 1,1,2,2-tetrafluoroethane and to a process for transferring heat in a refrigeration cycle by evaporating, compressing and condensing said azeotropic mixture.

The mixed fluorine and chlorine derivatives of methane and ethane have attained widespread use in the field of refrigeration as a result of their chemical inertness, their low specific volumes and the wide range of boiling points which is available in the various members of the series. Difluorodichloromethane (B.P. —29.8° C.), fluorotrichloromethane (B.P. 23.7° C.), fluorodichloromethane (B.P. 8.9° C.), monochlorodifluoromethane (B.P —40.8° C.), and tetrafluorodichloroethane (B.P. 3.5° C.) are among the most commonly used compounds of this type

When apparatus designed to employ a particular refrigerant has been installed, the need sometimes arises for greater refrigerating capacity. This may be obtained by the use of a refrigerant having a lower boiling point and consequently a higher vapor pressure at the temperature attained by the gas prior to its being compressed and liquefied. The capacity of any given refrigeration compressor is roughly proportional to the pressure of the gas at the suction side of the compressor. Since the compressor can handle a fixed volume of gas per unit of time, an increase in the suction pressure means an increase in the number of moles of gas put through the compressor in a given time. An increase in the number of moles means an increase in the total amount of heat required to vaporize the liquid in the evaporator, and an increase in the amount of heat that is removed from the refrigerated space. In general, other factors, such as variations in the latent heat of vaporization, play a relatively minor part in determining the change in capacity of a given refrigerating apparatus which will result from the substitution of one refrigerant for another.

In a given apparatus, it is not possible to use a refrigerant having a boiling point too much lower than that for which the apparatus has been designed, as the power input becomes undesirably high and the compressor motor becomes overloaded. In order to provide greater refrigerating capacity for installations designed for the use of dichlorodifluoromethane, it is therefore desirable to employ a gas which may be liquefied a few degrees below the boiling point of that material.

The use of azeotropic mixtures of pure materials as refrigerants is disclosed in U.S. Patent No. 2,101,993 and elsewhere in the art. Such mixtures have the advantage over other gas mixtures that the vapor composition of the azeotrope is the same as the liquid composition with which it is in equilibrium. With non-azeotropic mixtures, fractionation takes place during the refrigeration cycle, with consequent increase in condenser pressures and reduction in evaporator pressures and an overall loss of efficiency. Azeotropic gas mixtures are not subject to this defect.

U.S. Patent 2,479,259 and Reissue Patent 23,358 disclose that dichlorodifluoromethane and 1,1-difluoroethane form an azeotrope which is a useful refrigerant. It is impossible to predict that an azeotrope will form between any two compounds and so it is impossible to pick any two refrigerants and combine them to obtain an azeotrope boiling at some particular point by prediction. If an azeotrope occurs at all, its boiling point is a function of the system and is not under the control of the experimenter. The

mere existence of a large number of fluorinated hydrocarbons does not aid in predicting the formation of azeotropes by mixtures thereof.

It is an object of this invention to provide a novel azeotropic composition. Another object is to provide an azeotropic composition which is low boiling and which is effective to provide greater refrigerating capacity with apparatus designed for use with dichlorodifluoromethane. A further object is to provide an improved process of refrigeration by evaporating, compressing and condensing said novel azeotropic mixture in a refrigeration cycle. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished according to this invention which comprises a novel azeotropic composition which consists of a mixture of about 72% by weight of dichlorodifluoromethane and about 28% by weight of 1,1,2,2-tetrafluoroethane, and the process for transferring heat which comprises evaporating, compressing and condensing said azeotropic mixture in a refrigeration cycle.

It has been found that dichlorodifluoromethane and 1,1,2,2-tetrafluoroethane form an azeotrope having a boiling point of about —33.6° C. at 14.7 lbs./sq. in. absolute (p.s.i.a.). Said azeotrope consists of about 68.5 mole percent or about 72.0% by weight of dichlorodifluoromethane and about 31.5 mole percent or about 28.0% by weight of 1,1,2,2-tetrafluoroethane. Said azeotrope is a very desirable refrigerant. It has a normal boiling point about 3.8° C. below that of dichlorodifluoromethane, and is particularly valuable for use in a refrigeration system designed for dichlorodifluoromethane to provide about a 19.5% increase in the capacity of that refrigeration system.

The accompanying drawing shows the vapor pressure curve of the azeotropic mixture of this invention (the vapor pressure as a function of temperature), along with the vapor pressure curves of pure dichlorodifluoromethane and pure 1,1,2,2-tetrafluoroethane. It will be noted that the vapor pressure curve of the azeotrope is a straight line above and parallel to the vapor pressure curve for dichlorodifluoromethane. The vapor pressure curve also indicates the presence of the azeotrope, since the vapor pressure of a non-azeotropic mixture would be less than that of dichlorodifluoromethane. Furthermore, the curve indicates that the azeotrope is not affected by changes in temperature, which is very important for refrigeration use. If the mixture ceased to be an azeotrope at some temperature, the vapor pressure curve would drop to a point somewhere between the curves of the two components.

Dichlorodifluoromethane has a normal boiling point of —29.8° C. and 1,1,2,2-tetrafluoroethane has a normal boiling point of —19.7° C. When a mixture containing 89.9% by weight of dichlorodifluoromethane and 10.1% by weight of 1,1,2,2-tetrafluoroethane was subjected to careful fractionation, there was obtained, as the lowest boiling material, the azeotrope boiling at —33.1±0.5° C. containing 31.6 mole percent or 28.0 weight percent of 1,1,2,2-tetrafluoroethane (by vapor phase chromatography), the remainder being dichlorodifluoromethane. The azeotrope continued to distill until the tetrafluoroethane was exhausted from the mixture in the still, whereupon pure dichlorodifluoromethane distilled.

A mixture containing 50 mole percent of 1,1,2,2-tetrafluoroethane and 50 mole percent of dichlorodifluoromethane was also prepared and fractionally distilled. Again, the azeotrope distilled first and, when the dichlorodifluoromethane was exhausted, pure tetrafluoroethane distilled. The separation was very sharp. The composition of the azeotrope was again determined by a vapor

phase chromatography and was found to be 31.5±0.4 mole percent or 28.0 weight percent of 1,1,2,2-tetrafluoroethane and 68.5 mole percent or 72.0 weight percent of dichlorodifluoromethane. Thus, the two approaches to the azeotrope duplicate themselves extremely well.

The increase in efficiency, obtained by substituting one refrigerant for another, is due to the increased vapor pressure. In the present case, the increase in efficiency was determined at 0° C. (32° F.) by dividing the difference in vapor pressure between the azeotrope (52.6 p.s.i.a.) and dichlorodifluoromethane (44 p.s.i.a.) by the pressure of dichlorodifluoromethane, giving 0.195 or 19.5%.

Dichlorodifluoromethane is a readily available refrigerant which is manufactured on a very large scale. 1,1,2,2-tetrafluoroethane is a known compound which is readily prepared by several methods, e.g. from 1,1,2,2-tetrabromoethane or 1,1,2,2-tetrachloroethane (acetylene tetrachloride) as disclosed by Henne et al. in J.A.C.S., 58, 887 (1936), and by Cuculo et al. in J.A.C.S, 74, 710 (1952), or from 2,2,3,3-tetrafluoropropionaldehyde by decarbonylation in the presence of alkali. Tetrafluoropropionaldehyde is readily available from the corresponding alcohol as disclosed by Brace in U.S. Patent 2,842,601, which alcohol is commercially available.

From the preceding description, it will be apparent that this invention provides a novel azeotropic composition which is useful as a refrigerant and is particularly valuable for use in place of dichlorodifluoromethane to give greater refrigerating capacity in refrigerating systems designed for use with dichlorodifluoromethane. Therefore, it is apparent that this invention constitutes a valuable advance in and contribution to the art.

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

The process for transferring heat in a refrigeration cycle which comprises evaporating, compressing and condensing in said cycle an azeotropic mixture of about 72% by weight of dichlorodifluoromethane and about 28% by weight of 1,1,2,2-tetrafluoroethane.

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