

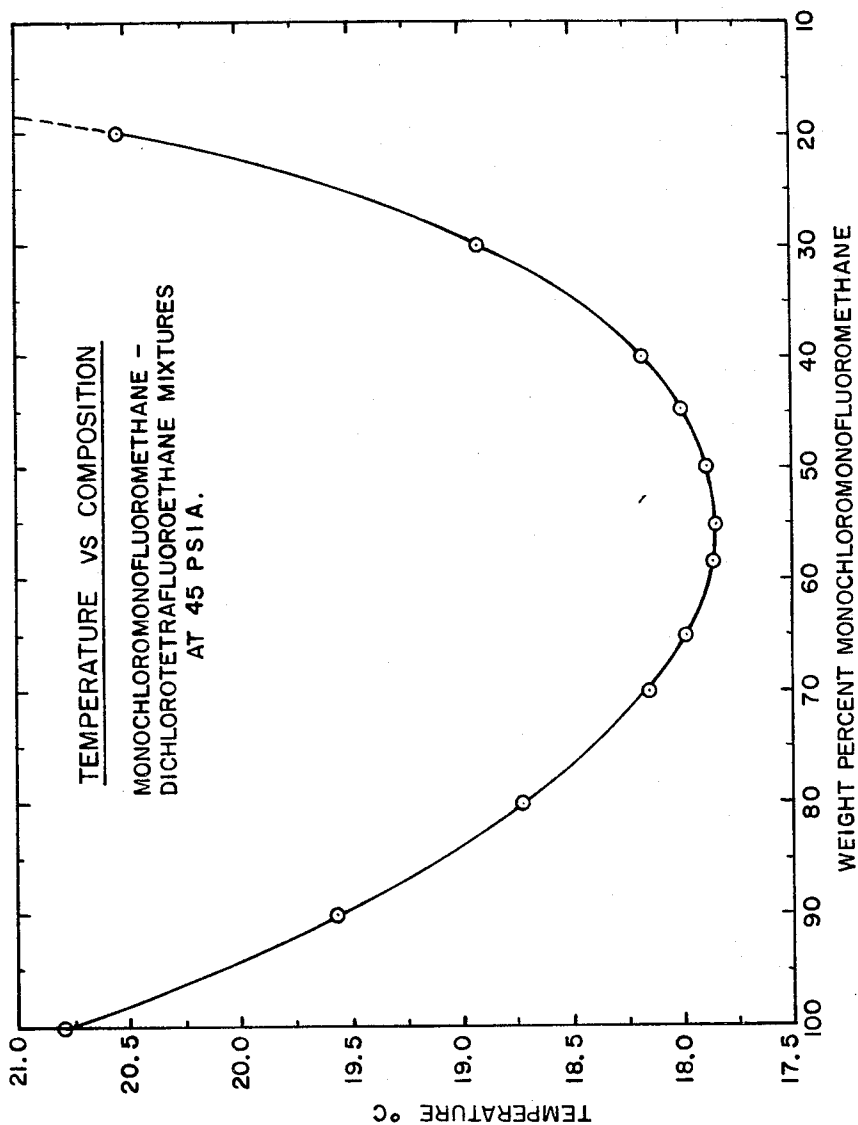
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K. P. MURPHY ET AL

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AZEOTROPIC MIXTURE

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INVENTORS

KEVIN P. MURPHY
SABATINO R. ORFEO

BY

Jonathan Plant
ATTORNEY

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AZEOTROPIC MIXTURE

Kevin Paul Murphy, Bernardsville, and Sabatino R. Orfeo, Morris Plains, N.J., assignors to Allied Chemical Corporation, New York, N.Y., a corporation of New York
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ABSTRACT OF THE DISCLOSURE

A low boiling azeotropic composition consisting essentially of a mixture of monochloromonofluoromethane and dichlorotetrafluoroethane, useful as a refrigerant, heat transfer medium, gaseous dielectric and as working fluid in a power cycle.

This invention relates to fluorinated hydrocarbons, and more particularly to constant boiling fluorocarbon mixtures, which comprise monochloromonofluoromethane and dichlorotetrafluoroethane and which are especially adapted for use as compression refrigerants particularly in system using centrifugal or rotary compressors.

The refrigerant capacity per volume pumped of a 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 related to boiling point of the refrigerant is minimum cooling temperature desired during the refrigeration cycle, the lower boiling refrigerants being used to achieve the lower refrigeration temperatures. For these reasons a large number of refrigerants of different boiling temperature and capacity are required to permit flexibility of design and the art is continually faced with the problem of providing new refrigerants as the need arises for new capacities and types of installations.

The lower aliphatic hydrocarbons when substituted by fluorine and chlorine are well-known to have potential as refrigerants. Many of these fluoro-chloro hydrocarbons exhibit certain desired properties including lower toxicity and nonflammability which have resulted in the extensive use of such components in a large number of refrigeration applications. Trichlorofluoromethane (CCl_3F) and dichlorodifluoromethane (CCl_2F_2) are two of the most commonly available chlorine-fluorine hydrocarbon refrigerants available today. There is a recognized need for a refrigerant with a boiling point temperature between the relatively high temperature of trichlorofluoromethane $+23.78^\circ\text{C}$. at atmospheric pressure, and the relatively low temperature of dichlorodifluoromethane, -29.8°C . at atmospheric pressure, in order to have available refrigerants of good performance and varying capacities.

Several fluoro-chloro hydrocarbons have boiling points in this range but suffer from other deficiencies such as flammability, poor stability or poor thermodynamic performance. Some examples of these types of refrigerants are tetrafluorodichloroethane, fluorodichloromethane, difluorochloroethane and fluorochloromethane.

It would also be possible to achieve the desired boiling point by mixing two refrigerants with boiling points above and below the desired one. In this case, for example, mixtures of trichlorofluoromethane and dichlorodifluoromethane could be used. It is well known, however, that simple mixtures create problems in design and operation because of segregation of the components in the liquid

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and vapor phases. This problem is particularly troublesome in systems using centrifugal compression because of the large quantities of liquid usually found in the evaporator.

An object of the present invention is to provide new mixtures with a boiling point between that of trichlorofluoromethane and dichlorodifluoroethane suitable for use as a refrigerant. More particularly it is an object of the present invention to provide a refrigerant system with a capacity between the refrigeration capacity of trichlorofluoromethane and dichlorodifluoroethane and which is useful as a compression refrigerant, particularly in systems using a centrifugal or rotary compressor. Another object is to provide a new low boiling azeotropic mixtures which are useful in producing refrigeration in those systems in which cooling is achieved by evaporation in the vicinity of the body to be cooled and in which because of the nature of the system, the problem of segregation is critical. A further object is to provide low boiling azeotropic mixtures in which the flammability is reduced to substantially negligible proportions.

The drawing shows boiling temperature of azeotropic mixtures according to the invention and will be discussed in more detail hereinafter.

In accordance with the invention it has been discovered that compositions consisting of dichlorotetrafluoroethane ($\text{C}_2\text{Cl}_2\text{F}_4$) with approximately 30 weight percent to 80 weight percent monochloromonofluoromethane (CH_2ClF) from azeotropic mixtures which have boiling points of about -12°C . at atmospheric pressure. Monochloromonofluoromethane has a boiling point temperature of -9.6°C . and dichlorotetrafluoroethane has a boiling point temperature of $+3.6^\circ\text{C}$., at atmospheric pressure. These monochloromonofluoromethane and dichlorotetrafluoroethane mixtures have a marked reduction in boiling point temperature as compared with the boiling temperature of the components. From the properties of the components alone the marked reduction in the boiling point temperature and the azeotropic characteristics of the mixtures are not expected.

The indicated monochloromonofluoromethane and dichlorotetrafluoroethane mixtures provide substantial increased refrigeration capacity over the components and represent new refrigeration mixtures useful especially in systems using centrifugal and rotary compressors. The use of the monochloromonofluoromethane and dichlorotetrafluoroethane mixtures eliminate the problem of segregation in handling and the operation of the system because azeotropic mixtures behave essentially as a single component as compared to simple mixtures. Furthermore, flammability of monochloromonofluoromethane is reduced by admixture with dichlorotetrafluoroethane such that all mixtures within the indicated range are substantially non-flammable.

An evaluation of the refrigeration properties of the monochloromonofluoromethane and dichlorotetrafluoroethane mixture and its components are shown in Table I, below.

TABLE I

	$\text{C}_2\text{Cl}_2\text{F}_4$	CH_2ClF	55 wt. percent CH_2ClF in $\text{CH}_2\text{ClF}/$ $\text{C}_2\text{Cl}_2\text{F}_4$
Evap. press., p.s.i.g.	0.5	10.6	13.7
Cond. press. p.s.i.g.	31.7	61.5	67.4
Comp. ratio	3.04	3.00	2.90
Compressor disp.	9.15	4.74	4.58
Discharge temp., $^\circ\text{F}$	100	145	112
H.P./ton	0.69	0.61	0.61
Mass flow	4.48	1.58	2.53

It is particularly pointed out in relation to the data of Table I that (1) the compression ratio of the azeotrope is lower than either component, and this property allows more efficient compressor and design, and (2) the compressor displacement shows the displacement of azeotrope to be lower than either component, which is of obvious advantage in a compressor. In addition, its H.P./ton value is much superior to that of dichlorotetrafluoroethane. When operated on similar cycles most refrigerants have very similar H.P./ton requirements. In centrifugal systems even small differences in H.P. per ton are quite important because of the large quantities of energy involved. Power cost is a major item in the operating costs of such systems. A favorably low power requirement is thus of particular benefit in refrigerants for centrifugal service. Furthermore, the mixture does not have the problem of flammability associated with pure monochloromonofluoromethane.

In addition, it is known that in the case of some refrigerants, such as dichlorotetrafluoroethane, on isentropic compression, such as occurs in the refrigeration cycle of a centrifugal or rotary compressor, the saturated vapor will partially condense. This is an undesirable situation as the liquid causes inefficiencies and erosion in the compressor. To overcome this "wet" compression the gas must be somewhat superheated before compression which requires heat exchange equipment. On the other hand, some refrigerants have a tendency to heat excessively on isentropic compression. This results in undesirable high temperature in the system (monochloromonofluoromethane and dichloromonofluoroethane are examples of this type of refrigerant). The monochloromonofluoromethane-dichlorotetrafluoroethane mixtures, however, heat only slightly on compression and thus substantially avoid "wet" compression as well as excessive heat on compression and thus are particularly useful as refrigerant liquids.

Boiling points of monochloromonofluoromethane and dichlorotetrafluoroethane mixtures were determined using monochloromonofluoromethane and dichlorotetrafluoroethane components of better than 99.9% purity. Monochloromonofluoromethane and dichlorotetrafluoroethane mixtures of various compositions were prepared and boiling points were measured at about 45 p.s.i.a. by thermostating the mixture and varying the temperature until the vapor pressure reached about 45 p.s.i.a. Temperatures were measured using a platinum resistance thermometer.

TABLE II

Boiling points of $\text{CH}_2\text{ClF}/\text{C}_2\text{Cl}_2\text{F}_4$ mixtures
At about 45 p.s.i.a.

Weight percent CH_2ClF in solution:	Boiling point ° C.
100.00 -----	20.80
90.00 -----	19.57
80.02 -----	18.73
70.04 -----	18.16
65.00 -----	17.99
58.60 -----	17.86
55.12 -----	17.84
50.00 -----	17.88
44.80 -----	18.00
39.96 -----	18.17
30.00 -----	18.92
20.00 -----	20.54

The data of Table II is plotted in the drawing. This data shows that mixtures at 45 p.s.i.a. of about 30 to 80 weight percent monochloromonofluoromethane have boiling points within about 1° C. and hence substantially similar vapor pressures. At 1 atmosphere the boiling points

of these compositions are about -12° C. The compositions within the range of 45 to 65 weight percent monochloromonofluoromethane have boiling points within about 0.2° C. at 45 p.s.i.a. Because the temperature and hence the vapor pressures are so similar between the weight percent limits set forth in the last sentence, those weight percent limits are especially preferable.

As shown in the drawing, it has been found that the most preferable percentage by weight monochloromonofluoromethane component in the monochloromonofluoromethane-dichlorotetrafluoroethane azeotropic mixture is about 55 percent.

Makeup of the azeotropic mixture of the invention requires no special procedures. The monochloromonofluoromethane-dichlorotetrafluoroethane components employed should be substantially pure, preferably at least about 99.0% pure, and contain no substances deleteriously affecting the boiling characteristics of the mixture or use as refrigerants.

The mixtures of the invention exhibit desired refrigeration properties, include non-flammability, boiling point substantially lower than either component, compression ratio lower than either component, lack of the presence of "wet" compression, and superior H.P./ton value. In addition to being used as new refrigerants providing refrigeration, especially in systems using centrifugal or rotary compressors, it will be noted that the mixtures disclosed herein may also be used for other purposes, including a heat transfer medium, gaseous dielectric, or as a working fluid in a power cycle.

It is intended that applicants' scope of protection only be limited by the claims that follow.

We claim:

1. A low boiling azeotropic composition consisting of a mixture of monochloromonofluoromethane and dichlorotetrafluoroethane in which the weight percent of monochloromonofluoromethane is within the range of about thirty to eighty.

2. A low boiling composition as recited in claim 1 said weight percent of monochloromonofluoromethane being within the range of about forty-five to sixty-five.

3. A low boiling composition as recited in claim 2, said weight percent of monochloromonofluoromethane being about fifty-five.

4. The process of producing refrigeration which comprises condensing an azeotropic mixture consisting of monochloromonofluoromethane and dichlorotetrafluoroethane in which the weight percent of monochloromonofluoromethane is within the range of thirty to eighty, and thereafter evaporating said mixture in the vicinity of a body to be cooled.

5. The process of producing refrigeration recited in claim 4, said weight percent of monochloromonofluoromethane being within the range of forty-five to sixty-five.

6. The process of producing refrigeration recited in claim 5, said weight percent of monochloromonofluoromethane being about fifty-five.

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LEON D. ROSDOL, Primary Examiner

S. D. SCHWARTZ, Assistant Examiner

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