The present invention comprises a refrigerant mixture consisting of a first mole fraction of 1,1,1,2-tetrafluoroethane (R134a) and a second mole fraction of a component selected from the group consisting of a mixture of CHClFCF_3 (R124) and CH_3CClF_2 (R142b); a mixture of CHF_2CH_3 (R152u) and CHClFCF_3 (R124); a mixture of CHF_2CH_3 (R152a) and CH_3CClF_2 (R142b); and a mixture of CHClFCF_3 (R124), CH_3CClF_2 (R142b) and CHF_2CH_3 (R152a).

4,810,403 3/1989 Bivens et al. ............................................. 252/67
4,983,312 1/1991 Tamura et al. ............................................. 252/67
5,262,077 11/1993 Bivens et al. ............................................. 252/67

FOREIGN PATENT DOCUMENTS

Primary Examiner—Christine Skane
Attorney, Agent, or Firm—Limbach & Limbach; W. Patrick Bengtsson; Patricia Coleman James

7 Claims, 6 Drawing Sheets
FIG. 3

- 42.47 PSI
- 100% R134a
- 41.05 PSI
- 41.67 PSI
- 90% R134a
- 39.7 PSI
- 41.95 PSI
- 41.4 PSI
- 10% R142b
- 10% R152a
- 80% R134a
FIG. 4
42.47 PSI

100% R134a

41.54 PSI

41.62 PSI

90% R134a

41.05 PSI

39.7 PSI

80% R134a

40.1 PSI

10% R142b

10% R12A

FIG. 5
FIG. 7

- 90% R134a, 10% R124
- 80% R134a, 20% R124
NEAR AZEOTROPIC MIXTURE SUBSTITUTE

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected to retain title.

This is a continuation of application Ser. No. 07/672,947 filed on Mar. 21, 1991, now abandoned, which is a continuation of Ser. No. 07/503,465 filed on Mar. 23, 1990, now abandoned.

TECHNICAL FIELD

This invention relates to the field of refrigerants for air conditioner systems and more particularly to a replacement for dichlorodifluoromethane.

BACKGROUND ART

Chlorofluorocarbons (CFCs) have been used in refrigerators and air conditioners for many years. Dichlorodifluoromethane or refrigerant 12 (R12) has been the refrigerant of choice for automotive air conditioning systems ever since it was developed in 1930. The history of this development is discussed in detail in "Development of Chlorofluorocarbon Refrigerants", by R. Downing, ASHRAE Transactions 90 pt. 2, pp. 481-91, 1984. R12 is widely used in automobiles because it is non-flammable, low in toxicity, and compatible with the lubricants used in automotive air conditioning systems. Moreover it has the right combination of physical properties, such as boiling point and vapor pressure, to permit efficient use in these systems. However, over the years, large amounts of R12 have been released into the atmosphere as a result of damaged, leaky, or abandoned air conditioners as well as routine maintenance on these devices.

In 1974, it was postulated that chlorofluoromethanes as well as other chlorofluorocarbons are damaging to the earth's ozone layer. This research was reported in "Stratospheric Sink for Chlorofluoromethanes: Chlorine atom catalyzed Destruction of Ozone" by M. J. Molina and F. S. Rowland, Nature, 249:810-12, 1974. This theory has been confirmed recently by the discovery of ozone "holes" over the Arctic and Antarctic. Richard A. Kerr reported in Research News, pp. 1489-92, Mar. 25, 1988, that the ozone layer over latitudes corresponding to the United States has reduced about 5%.

The ozone layer acts as a barrier to UV radiation from the sun. Since UV radiation damages living organisms, destruction of the ozone layer would have a serious impact on life on this planet. In fact there is strong evidence that human skin cancer rates are on the rise and that phytoplankton in the ocean have been reduced by 25%.

This has resulted in a world-wide effort to eliminate release of ozone depleting CFCs into the atmosphere, culminating in Montreal in 1987 in the signing of an international agreement. The "Montreal Protocol" sets up a worldwide process to reduce production and consumption of materials that can damage the ozone layer. In response to this agreement, the aerosol, industrial cleaning and foam insulation industries are starting to use alternatives to CFCs. There was report of a proposal to ban automotive air conditioners in the Los Angeles Times on Jul. 18, 1989.

STATEMENT OF THE INVENTION

The present invention is directed towards a refrigerant mixture comprising essentially two halocarbon components. The first halocarbon component and the second halocarbon component are present in essentially near azeotropic proportions which is approximately equal to the first halocarbon component being present in a mole fraction of about 0.5 to less than 1.0 while the second halocarbon component is present in a mole fraction of about more than 0.0 to about 0.5. In the most preferred embodiment, the first halocarbon component is present in a mole fraction of about 0.7 to less than 1.0 while the second halocarbon component is present in a mole fraction of about more than 0.0 to about 0.3. The first halocarbon component is CH,F,CF, (R134a). The second halocarbon component can be CHClFCF, (R124), CHCClF, (R142b), a mixture of CHClFCF, and CH,CCLF, a mixture of CHF,CH, (R152a) and CHClFCF, a mixture of CH,F,CH, and CH,CCLF, or a mixture of CHClFCF, CH,CCLF, and CH,F,CH,.

The resulting refrigerant has a vapor pressure close to that of CF,Cl, a nearly constant vapor pressure with evaporation, and is substantially less damaging to the earth's ozone layer than CF,Cl,.

The preferred embodiment of this invention comprises about 0.5 (more preferably about 0.7) to less than 1.0 mole fraction CH,F,CF, and more than 0.0 to about 0.5 (more preferably about 0.3) mole fraction of a mixture of CHClFCF, and CH,CCLF,.

The most preferred embodiment of this invention comprises about 0.5 (more preferably about 0.7) to less than 1.0 mole fraction CH,F,CF, and more than 0.0 to about 0.5 (more preferably about 0.3) mole fraction CH,F,CCl,F,.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows vapor pressure curves for the binary mixture of R134a and R124 at 0°C.
DESCRIPTION OF THE INVENTION

The present invention contains at least two halocarbons, one of which is R134a. This invention comprises the mixtures shown in Table 1.

### TABLE 1

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Component A</th>
<th>Component B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R134a</td>
<td>R124</td>
</tr>
<tr>
<td>2</td>
<td>R134a</td>
<td>R124b</td>
</tr>
<tr>
<td>3</td>
<td>R134a</td>
<td>R124 + R142b</td>
</tr>
<tr>
<td>4</td>
<td>R134a</td>
<td>R152a + R134</td>
</tr>
<tr>
<td>5</td>
<td>R134a</td>
<td>R152a + R142b</td>
</tr>
<tr>
<td>6</td>
<td>R134a</td>
<td>R124 + R142b + R152a</td>
</tr>
</tbody>
</table>

Component A is present in the mixtures in a mole fraction of from about 0.5 (more preferably about 0.7) to less than 1.0 while Component B is present in the mixtures in a mole fraction of from more than 0.0 to about 0.5 (more preferably about 0.3). These mixtures were developed by reviewing the available literature to select components that have a boiling point in the range of −82 degrees C. and −5 degrees C., low toxicity, low ozone damage potential and low flammability, and testing to confirm that they were in fact near-azeotropic. To ensure compatibility with compressor lubricants, each mixture was formulated to contain at least one chlorinated compound.

A summary of literature data for the components of these mixtures is shown in Table 2. For comparison purposes, the literature data for R12 is also shown in Table 2.

### TABLE 2

<table>
<thead>
<tr>
<th>Boiling point (degrees C.)</th>
<th>Vapor Pressure (psia)@ 0 deg. C.</th>
<th>Ozone damage potential*</th>
<th>Toxicity (In ppm)</th>
<th>Flammability (vol % in air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R134a</td>
<td>−26.5</td>
<td>42.47</td>
<td>0</td>
<td>1000</td>
</tr>
<tr>
<td>R124</td>
<td>−12</td>
<td>32.72</td>
<td>&lt;0.05</td>
<td>NA</td>
</tr>
<tr>
<td>R142b</td>
<td>−3.7</td>
<td>NA</td>
<td>&lt;0.05</td>
<td>1000</td>
</tr>
<tr>
<td>R152a</td>
<td>−3.5</td>
<td>NA</td>
<td>0</td>
<td>1000</td>
</tr>
<tr>
<td>R12</td>
<td>−29.8</td>
<td>44.7</td>
<td>1</td>
<td>1000</td>
</tr>
</tbody>
</table>

*compared to R12.

To test for azeotropic properties, various binary, ternary and quaternary mixtures were measured for vapor pressure at a constant temperature of 0 degrees C. The results of these tests are summarized in FIGS. 1 through 6. It can be seen from the Figures that the vapor pressure of each mixture averages around 40 psia, which is close to the vapor pressure of R12. Further the vapor pressure of each mixture varies little with composition.

All of the above data suggest that each embodiment shown in Table 1 is near-azeotropic, non-flammable, non-toxic, and compatible with air conditioner lubricants while being at least 67 times less damaging to the ozone layer than R12. Thus any of the mixtures of Table 1 can be used as a direct replacement for R12.

The research has shown that mixture 3 of Table 1 is the preferred embodiment of this invention and mixture 2 of Table 1 is the most preferred embodiment of this invention because R142b has the highest solubility in present refrigeration lubricating oils. The near-azeotropic leakage characteristics of a typical mixture (R134a and R124) are shown in FIG. 7.

Although the present invention has been described in detail with reference to particular preferred embodiments, persons possessing ordinary skill in the art to which this invention pertains will appreciate that various modifications and enhancements may be made without departing from the spirit and scope of the claims that follow.

### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Number</th>
<th>Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R12</td>
<td>CCl2F2, Dichlorodifluoromethane</td>
</tr>
<tr>
<td>2</td>
<td>R134a</td>
<td>CH2FCF3, 1,1,1,2-Tetrafluoroethane</td>
</tr>
<tr>
<td>3</td>
<td>R124</td>
<td>CHCIFCF3, 1,1,1,2-tetrafluoroethane</td>
</tr>
<tr>
<td>4</td>
<td>R142b</td>
<td>CH3CClF2, 1-Chloro-1,1-difluoroethane</td>
</tr>
<tr>
<td>5</td>
<td>R152a</td>
<td>CH3CIF2, 1,1-Difluoroethane</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
<td></td>
</tr>
<tr>
<td>psia</td>
<td>pounds per square inch, absolute</td>
<td></td>
</tr>
<tr>
<td>ASHRAE</td>
<td>American Society of Heating, Refrigerating and Air-Conditioning Engineers</td>
<td></td>
</tr>
</tbody>
</table>

I claim:

1. A refrigerant consisting of a mixture of a first mole fraction of about 0.8 to less than 1.0 of CH2FCF3 and a second mole fraction of more than 0.0 to about 0.2 of a halocarbon selected from the group consisting of: a mixture of CHCI2CF3 and CH2CClF3; a mixture of CHF2CH3 and CHCICF3; a mixture of CHF2CH3 and CH2CClF3; and a mixture of CHCI2CF3, CH2CClF3 and CHF2CH3.

2. A method of formulating a refrigerant comprising the steps of: providing a first mole fraction of about 0.8 to less than 1.0 of CH2FCF3, and adding a second mole fraction of more than 0.0 to about 0.2 of a halocarbon selected from the group consisting of: a mixture of CHCI2CF3 and CH2CClF3; a mixture of CHF2CH3 and CHCICF3; a mixture of CHF2CH3 and CH2CClF3; and a mixture of CHCI2CF3, CH2CClF3 and CHF2CH3.

3. A refrigerant consisting of the ternary mixture of CH2FCF3, CHF2CH3 and CH2CClF3 defined by the triangular diagram of FIG. 3 and having the vapor pressures at 0 degrees C. shown therein.

4. A refrigerant consisting of the ternary mixture of CH2FCF3, CHF2CH3 and CHCICF3 defined by the trian-
5. A refrigerant consisting of the ternary mixture of CH₂FCF₃, CHClFCF₃ and CH₃CClF₂ defined by the triangular diagram of FIG. 5 and having the vapor pressures at 0 degrees C. shown therein.

6. A refrigerant consisting of the quaternary mixture of CH₂FCF₃, CHClFCF₃, CH₃CClF₂ and CHF₂CH₃ defined by the triangular diagram of FIG. 6 and having the vapor pressures at 0 degrees C. shown therein, said diagram representing the case where CH₃FCH₃ is about 90 mole percent.

7. A refrigerant consisting of the quaternary mixture of CH₂FCF₃, CHClFCF₃, CH₃CClF₂ and CHF₂CH₃ defined by the triangular diagram of FIG. 6(b) and having the vapor pressures at 0 degrees C. shown therein, said diagram representing the case where CH₃FCH₃ is about 80 mole percent.