CHILLER REFRIGERANTS

This invention relates to refrigerant compositions, particularly compositions which can be used for chillers. In particular, these are devices for producing chilled water or aqueous solutions at temperatures typically from 1 to 10 °C.

Chillers require large amounts of cooling. Recently R22 ($CHClF_2$) has been used for this purpose. However, there is the need for an alternative refrigerant, since R22 is an ozone depleter that will be phased out over the next decade, in accordance with the Montreal protocol.

Therefore, there is a requirement for a refrigerant that has similar properties to R22, but is not an ozone depleter. Of particular concern is that the temperature/vapour pressure relationship for such a refrigerant should be sufficiently similar to R22 that it can be used in R22 equipment without having to change the control systems which are usually programmed in the factory making the chiller.

This is of particular concern for systems that have sensitive control devices, which rely on both the inlet pressure to the expansion valve and the outlet pressure. These control systems are based on R22 properties. Therefore, if an R22 substitute does not have a temperature/vapour pressure behaviour similar to R22, the system will not operate correctly.

By similar we mean that the vapour pressure of the substitute should not differ by more than ±12% and preferably not more than ±6% at any given mean evaporating temperature between -40°C to +10°C.

It is also important that any such refrigerant has a similar capacity and efficiency as R22.

By similar capacity we mean a capacity that is no more than 20% lower than R22 and preferably not more than 10% lower than R22 at mean evaporating temperatures between -35°C to -28°C. By similar efficiency we mean not more

than 10% lower and preferably not more than 5% lower at mean evaporating temperatures between -35° to -28°C.

According to the present invention there is provided a refrigerant composition which comprises:

(a) pentafluoroethane, trifluoromethoxydifluoromethane or hexafluorocyclopropane, or a mixture of two or more thereof, in an amount of from 60 to 70% by weight based on the weight of the composition,

(b) 1,1,1,2- or 1,1,2,2-tetrafluoroethane, trifluoromethoxypentafluoroethane, 1,1,1,2,3,3-heptafluoropropane or a mixture of two or more thereof, in an amount of from 26 to 36% by weight based on the weight of the composition and

(c) an ethylenically unsaturated or saturated hydrocarbon, optionally containing one or more oxygen atoms, with a boiling point from -12°C to +10°C, or a mixture thereof, or a mixture of one or more said hydrocarbons with one or more other hydrocarbons, said mixture having a bubble point from -12°C to +10°C, in an amount from 1% to 4% by weight based on the weight of the composition. It has suprisingly been found that these particular formulations have the condition of properties which enable them to be used as a "drop in" replacement for R22.

The percentages quoted above refer, in particular, to the liquid phase. The corresponding ranges for the vapour phase are as follows:

(a) 75 to 87% (b) 10-28% and (c) 0.9 - 4.1%, all by weight based on the weight of the composition. These percentages preferably apply both in the liquid and vapor phases.

The present invention also provides a process for producing refrigeration which comprises condensing a composition of the present invention and thereafter evaporating the composition in the vicinity of a body to be cooled. The invention also provides a refrigeration apparatus containing, as refrigerant, a composition of the present invention.

Component (a) is present in an amount from 60 to 70% by weight based on

the weight of the composition. Preferably, the concentration is 62 to 67%, especially above 64% and up to 66%, by weight. Preferably, component (a) is R125 (pentafluorethane) or a mixture containing at least an half, especially at least three quarters (by mass) of R125. Most preferably component (a) is R125 (alone).

Component (b) is present in the composition in an amount from 26 to 36%, especially 28 to 32%, by weight based on the weight of the composition. Component (b) is preferably a mixture containing at least an half, especially at least three quarters (by mass) of R134a (1,1,1,2-tetrafluoroethane). Most preferably component (b) is R134a (alone).

The weight ratio of component (a): component (b) is desirably at least 1.5:1, preferably 1.5:1 to 3:1 and especially 1.8:1 to 2.2:1.

Component (c) is a saturated or ethylenically unsaturated hydrocarbon, optionally containing one or more oxygen atoms, in particular one oxygen atom, with a boiling point from -12°C to +10°C, especially -12°C to -5°C or a mixture thereof. Preferred hydrocarbons which can be used possess three to five carbon atoms. They can be acyclic or cyclic. Acyclic hydrocarbons which can be used include one or more of propane, n-butane, isobutane, and ethylmethyl ether. Cyclic hydrocarbons which can be used include methyl cyclo propane. Preferred hydrocarbons include n-butane and/or isobutane. Component (c) can also be a mixture of such a hydrocarbon with one or more other hydrocarbons, said mixture having a bubble point from -12°C to +10°C, especially -12°C to -5°C.. Other hydrocarbons which can be used in such mixtures include pentane and isopentane, propene, dimethyl ether, cyclobutane, cyclopropane and oxetan.

The presence of at least one further component in the composition is not excluded. Thus although, typically, the composition will comprise the three essential components, a fourth component, at least, can also be present. Typical further components include other fluorocarbons and, in particular, hydrofluorocarbons, such as those having a boiling point at atmospheric pressure of at most -40°C, preferably at most -49°C, especially those where the F/H ratio in the molecule is at least 1, preferably R23, trifluoromethane and, most preferably, R32, difluoromethane. In

general, the maximum concentration of these other ingredients does not exceed 10% and especially not exceeding 5% and more especially not exceeding 2%,by weight, based on the sum of the weights of components (a), (b) and (c). The presence of hydrofluorocarbons generally has a neutral effect on the desired properties of the formulation. Desirably one or more butanes, especially n-butane or iso-butane, represents at least 70%, preferably at least 80% and more preferably at least 90%, by weight of the total weight of hydrocarbons in the composition. It will be appreciated that it is preferable to avoid perhalocarbons so as to minimise any greenhouse effect and to avoid hydrohalogenocarbons with one or more halogens heavier than fluorine. The total amount of such halocarbons should advantageously not exceed 2%, especially 1% and more preferably 0.5%, by weight.

According to a preferred embodiment, the composition comprises, as component (a) 62to 67% based on the weight of the composition of pentafluoroethane, as component (b) 3 to 35% by weight based on the weight of the composition of 1,1,1,2-tetrafluoroethane and, as component (c), butane and/or isobutane or a said mixture of hydrocarbons comprising butane and/or isobutane. When component (c) is a mixture the concentration of butane and/or isobutane in the mixture is preferably at least 50% by weight especially at least 70% by weight, more preferably at least 80% by weight and even more preferably at least 90% by weight, based on the weight of the composition. The other component of the mixture is preferably pentane.

It has been found that the compositions of the present invention are highly compatible with the mineral oil lubricants which have been conventionally used with CFC refrigerants. Accordingly the compositions of the present invention can be used not only with fully synthetic lubricants such as polyol esters (POE), polyalkyleneglycols (PAG) and polyoxypropylene glycols or with fluorinated oil as disclosed in EP-A-399817 but also with mineral oil and alkyl benzene lubricants including naphthenic oils, paraffin oils and silicone oils and mixtures of such oils and lubricants with fully synthetic lubricants and fluorinated oil.

The usual additives can be used including "extreme pressure" and antiwear

additives, oxidation and thermal stability improvers, corrosion inhibitors, viscosity index improvers, pour point depressants, detergents, anti-foaming agents and viscosity adjusters. Examples of suitable additives are included in Table D in US-A-4755316.

The following Examples further illustrate the present invention.

Examples

The samples used for testing are detailed below:

Butane (3.5%) blend:	R125/134a/600 (65.0/31.5/3.5)
Isobutane (3.5%) blend:	R125/134a/600a (64.9/31.7/3.4)

Equipment and experimental

The samples, each approximately 600g, used for the determination of the vapour pressures were prepared in aluminium disposable cans (Drukenbehalter - product 3469), which were then fully submerged in a thermostatically controlled water bath. For each determination the can was charged with about 600g. A maximum of two samples could be processed at any one time. The bath temperature was measured using a calibrated platinum resistance thermometer (152777/1B) connected to a calibrated Isotech TTI1 indicator. Pressure readings were taken using the two calibrated Druck pressure transducers, DR1 and DR2.

The temperature of the bath was set to the lowest temperature required and it was then left until it had cooled. When the temperature and pressure had remained constant for at least a quarter of an hour they were then recorded. Further

temperature and pressure readings were taken in increments of 5°C to a maximum of 50°C, each time ensuring that they were steady for at least a quarter of an hour before recording them.

The data obtained does not give the dew point and as such does not give the glide. An approximate evaluation of the glide can be obtained by using the REFPROP 6 program. The relationship of the glide to the bubble point can be represented by a polynomial equation. This equation can now be used to give an approximate glide for the experimentally determined bubble points. This is effectively a normalisation of the calculated glide to the experimentally determined data. The dew point pressures can then be approximated by subtracting the temperature glide from the temperature in the bubble point equation.

These equations are then used to obtain vapour/pressure tables. The experimental equation derived for the bubble points and the glide equation from REFPROP 6 are shown in Table 1.

Notes:

1. In this equation x=1/T, where T is the bubble point in Kelvin: y= ln(p), where p is the saturated vapour pressure in psia. To convert psia to MPa absolute pressure, multiply by 0.006895.

2. In this equation x = t, where t is liquid temperature (bubble point) in degree C and y = glide in degree C at the bubble point temperature.

3. The vapour pressures for R22 were obtained from the Ashrae handbook by interpolation.

Determination of the performance of the refrigerants on the low temperature (LT) calorimeter.

Equipment and general operating conditions

The performance of the refrigerants was determined on the low temperature (LT) calorimeter. The LT calorimeter is fitted with a Bitzer semi-hermetic condensing unit containing Shell SD oil. The hot vapour passes out of the compressor, through an oil separator and into the condenser. The discharge pressure at the exit of the compressor is kept constant by the means of a packed gland shut-off valve. This inevitably has an effect on the condensing pressure/temperature – the system is actually condensing at a temperature below 40°C. The refrigerant then travels along the liquid line to the evaporator.

The evaporator is constructed from 15mm Cu tubing coiled around the edges of a well-insulated 32-litre SS bath. The bath is filled with 50:50 glycol:water solution and heat is supplied to it by 3x1kW heaters controlled by a PID controller. A stirrer with a large paddle ensures that the heat is evenly distributed. The evaporating pressure is controlled by an automatic expansion valve.

The refrigerant vapour returns to the compressor through a suction line heat exchanger.

Twelve temperature readings, five pressure readings, compressor power and heat input are all recorded automatically using Dasylab.

The tests were run at a condensing temperature of 40°C and an evaporator superheat of 8°C (±0.5°C).

For R22 the temperature at the end of the evaporator was maintained at 8°C above the

temperature equivalent to the evaporating pressure (bubble point).

For the other refrigerants the temperature at the end of the evaporator was maintained at 8°C above the temperature equivalent to the evaporating pressure (Dew point)

The mean evaporator temperature for these refrigerants was calculated by taking the temperature equivalent to the evaporator pressure from the bubble point table and adding to that half the glide at that temperature.

When running the calorimeter the evaporating and condensing pressures are initially set to an approximate value along with the temperature of the bath. The calorimeter is then allowed time for the conditions to stabilise. During this period coarse adjustments can be carried out and it must also be monitored in order to make sure that sufficient heat is being put into the bath to avoid any liquid getting back to the compressor. When the system is virtually steady fine adjustments of pressure and temperature are made until the calorimeter has stabilised at the required evaporating pressure with a condensing pressure equivalent to 40°C and an evaporator superheat of 8°C. (Note – the superheat is measured from the third evaporator outlet)

The run is then commenced and run for a period of one hour, during which time no adjustments are made to the system, except for possibly minor changes to the condensing pressure to compensate for fluctuations in the ambient temperature.

Specific experimental details for each refrigerant

R22: The calorimeter was charged with R22 (3.5kg into the liquid receiver). Ten data points were obtained between the evaporating temperatures of –38°C and –22°C.

Butane (3.5%) blend: Approximately 3.55kg were charged into the liquid receiver and five data points were obtained between the mean evaporating temperatures of -38°C and -22°C.

Isobutane (3.5%) blend: Approximately 3.48kg of the blend were charged into the liquid receiver of the LT-calorimeter. Five data points between the mean evaporating temperatures of -38°C and -22°C were obtained.

Results

The results obtained are summarised in Tables 2-4. Mean Ev. Temp = Mean evaporation temperature; Air on condenser = temperature of the air blowing over the condenser; Press = pressure.

Comments and discussion on the experimental results

The results obtained are shown graphically in Graphs 1 to 6. Graph 1 shows the saturated vapour pressures for the blends investigated along with that for R22. The graph shows that the vapour pressures of the blends are only slightly higher than that for R22.

Graph 2 shows a comparison of the capacities with respect to R22 at a mean evaporating temperature of -30°C – a typical temperature at which these blends would be expected to operate. At this temperature the butane blend is only 4% down on capacity against R22, whereas the capacity of isobutane blend is slightly inferior, being 5.5% down on R22.

The COP results obtained are shown in Graph 3. This graph shows that at a mean evaporating temperature of −30°C the COP values of both the hydrocarbon blends are less than 1% down on R22.

In Graph 4, the capacity is fixed to that of R22 at the evaporating temperature of −30°C. The COPs at this constant capacity for the different refrigerants can now be compared. The graph shows that both the butane blend (by 2.5%) and the isobutane blend (by 3.0%) are more efficient than R22 for this given capacity.

The capacity of the hydrocarbon blends relative to R22 is shown in Graph 5. The lines for the two blends are parallel to one another and the capacities are similar with that of the isobutane blend being slightly inferior.

Graph 6 shows the COP of the RX blends relative to R22. The COP of R22 and that of the two blends is shown to be similar. The lines of the hydrocarbons blends cross over one another (and R22) at a mean evaporating temperature of −32°C showing the increase in the relative COP of R22 and the decrease in the relative COP of the isobutane blend. As before though the differences are only minimal.

Table 1 Results of the experimental SVP measurements and the glide from REFPROP 6

Description	SVP Equation (see note 1)	Glide equation (see note 2)
Butane (3.5%) blend R125/134a/600 (65.0/31.5/3.5)	y = -2347.46820x + 12.96325 R2 = 0.99999	y = -0.02618x + 3.51740 R2 = 0.99790
Isobutane (3.5%) blend R125/134a/600a (64.9/31.7/3.4)	y = -2356.045324x + 12999729 R^2 = 0.999956	y = -000001x^3 - 0.000012x^2 - 0.028998x + 3.628716
R22	(see note 3)	Not applicable

TABLE 2 R22 CONDENSING AT 40°C IN LT-CALORIMETER

Mean Ev. Temp °C	Discharge Temp °C	Air On Condenser °C	Discharge absolute Press Mpa	Condensing Temp °C	Evaporator Inlet Press MPa	Evap Temp BUBBLE °C	Evap Temp DEW °C	Compressor Power kwh	Capacity Heat Input kwh	C.O.P.	Evap. Superheat °C
-37.6	149.9	20.8	1.439	40.1	0.016	-37.6	-37.6	1.161	0.614	0.53	8.3
-35.9	154.5	22.3	1.425	39.8	0.025	-35.9	-35.9	1.208	0.846	0.70	8.5
-34.0	156.1	22.2	1.433	40.0	0.036	-34.0	-34.0	1.283	1.031	0.80	8.3
-31.6	156.3	22.9	1.438	40.1	0.051	-31.6	-31.6	1.375	1.282	0.93	8.3
-29.5	155.7	23.4	1.450	40.4	0.065	-29.5	-29.5	1.388	1.412	1.02	7.8
-28.8	152.8	22.0	1.447	40.4	0.071	-28.8	-28.8	1.418	1.508	1.06	8.1
-28.1	154.7	23.9	1.430	39.9	0.076	-28.1	-28.1	1.457	1.586	1.09	8.4
-25.4	152.7	22.7	1.449	40.4	0.096	-25.4	-25.4	1.593	1.992	1.25	8.0
-24.0	152.8	23.8	1.446	40.3	0.108	-24.0	-24.0	1.646	2.167	1.32	8.6
-22.1	149.6	23.8	1.450	40.4	0.124	-22.1	-22.1	1.688	2.387	1.41	8.4

TABLE 3 BUTANE (3.5%) CONDENSING AT 40°C IN LT-CALORIMETER

Mean Ev. Temp °C	Discharge Temp °C	Air On Condenser °C	Discharge absolute Press MPa	Cond-ensing Temp °C	Evaporator Inlet absolute press MPa	Evap Temp BUBBLE °C	Evap Temp DEW °C	Compr-essor Power kwh	Capacity Heat Input kwh	C.O.P.	Evap. Superheat °C	Total Superheat °C
-37.4	*114.1*	*20.8*	*1.528*	*39.9*	*0.025*	*-39.7*	*-35.1*	*1.094*	*0.629*	*0.58*	*7.7*	*47.0*
-34.2	*115.8*	*21.6*	*1.529*	*39.9*	*0.044*	*-36.4*	*-31.9*	*1.237*	*0.976*	*0.79*	*7.9*	*43.5*
-30.4	*112.1*	*21.1*	*1.539*	*40.2*	*0.068*	*-32.6*	*-28.3*	*1.336*	*1.317*	*0.99*	*7.8*	*39.7*
-25.9	*108.9*	*21.4*	*1.540*	*40.2*	*0.102*	*-28.0*	*-23.8*	*1.459*	*1.729*	*1.18*	*8.0*	*36.7*
-22.5	*106.8*	*22.6*	*1.543*	*40.3*	*0.132*	*-24.6*	*-20.4*	*1.592*	*2.161*	*1.36*	*8.3*	*35.5*

TABLE 4 ISOBUTANE BLEND (3.5%) CONDENSING AT 40°C IN LT-CALORIMETER

Mean Ev. Temp °C	Discharge Temp °C	Air On Condenser °C	Discharge absolute Press Mpa	Condensing Temp °C	Evaporator Inlet absolute press. Mpa	Evap Temp BUBBLE °C	Evap Temp DEW °C	Compressor Power kwh	Capacity Heat Input kwh	C.O.P.	Evap. Superheat °C	Total Superheat °C
-37.7	114.6	23.1	1.544	40.0	0.023	-40.1	-35.3	1.033	0.596	0.58	8.0	49.0
-34.3	116.2	23.2	1.544	39.9	0.043	-36.6	-31.9	1.194	0.950	0.80	8.3	44.8
-29.8	113.1	22.2	1.544	40.0	0.072	-32.1	-27.5	1.353	1.361	1.01	8.5	40.1
-26.2	109.7	22.4	1.538	39.8	0.100	-28.4	-23.9	1.440	1.682	1.17	8.6	37.7
-21.5	106.4	24.2	1.562	40.4	0.140	-23.6	-19.3	1.622	2.252	1.39	8.2	35.4

CLAIMS

1. A refrigerant composition which comprises:

(a) pentafluorethane, trifluoromethoxydifluoromethane or hexafluorocyclopropane, or a mixture of two or more thereof, in an amount of from 62 to 67% by weight based on the weight of the composition,

(b) 1,1,1,2-or1,1,2,2-tetrafluoroethane, trifluoromethoxypentafluoroethane, 1,1,1,2,3,3,3-heptafluoropropane or a mixture of two more thereof, in an amount of from 28 to 32% by weight based on the weight of the composition and

(c) isobutane thereof in an amount from 3 to 4% by weight based on the weight of the composition.

(d) wherein the composition contains no more than 5% of another fluorocarbon component.

2. A composition according to claim 1 in which component (c) is present is an amount about 3.5% by weight based on the weight of the composition.

3. A composition according to claim 1 or 2 which further comprises another hydrocarbon.

4. A composition according to any one of the preceding claims in which component (a) is pentafluoroethane.

5. A composition according to claim 1 in which component (a) is present in an amount above 64 up to 66% weight based on the weight of the composition.

6. A composition according to any one of the preceding claims in which component (b) is or 1,1,1,2-tetrafluoroethane.

7. A composition according to any one of the preceding claims in which the weight ratio of component (a): component (b) is at least 1.5:1.

8. A composition according to claim 7 in which the said weight ratio is 1.5:1 to 3:1.

9. A composition according to any one of the preceding claims which comprises, as component (a), 62 to 67% pentafluoroethane as component (b), 26 to 35% by weight based on the weight of the composition 1,1,1,2-tetrafluoroethane and as component (c), n-butane, isobutane, or a said mixture of hydrocarbons comprising n-butane, isobutene, or a mixture thereof.

10. A composition according to claim 1 in which the further component is a hydrofluorocarbon.

11. A composition according to claim 10 in which the hydrofluorocarbon has a boiling point at atmospheric pressure of at most -40°C.

12. A composition according to claim 10 or 11 in which the F/H ratio in the hydrofluorocarbon is at least 1.

13. A composition according to claim 12 in which the hydrofluorocarbon is difluoromethane or trifluoromethane.

14. A composition according to claim 1 in which the further component is present in an amount not exceeding 2% by weight based on the weight of (a), (b) and (c).

15. Use of a composition as claimed in any one of the preceding claims as a refrigerant in a refrigeration apparatus.

16. A process for producing refrigeration which comprises condensing a composition as claimed in any one of claims 1 to 14 and thereafter evaporating the composition in the vicinity of a body to be cooled.

17. A refrigeration apparatus containing, as refrigerant, a composition as claimed in any one of claims 1 to 14.