



Señora

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E.

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Referencia: Solicitud de Patente de Invención denominada
“MEZCLAS REFRIGERANTES DE BAJO PCG”.

Asunto: Respuesta al Requerimiento No. 13819 del 31 de agosto de 2022

Expediente No. NC2020/0006343

Juan Carlos Cuesta Quintero, mayor de edad, identificado como aparece al pie de mi firma obrando en mi calidad de apoderado de **RPL Holdings Limited**, doy respuesta al Oficio No. 13819 del 31 de agosto de 2022 bajo los siguientes términos:

1. De la solicitud de patente

1.1. Reivindicaciones

1.1.1. Modificaciones

El examinador objeta la claridad de las reivindicaciones, argumentando lo siguiente:

“En las reivindicaciones 1, 2 y 15 la expresión: “seleccionado del grupo”, es imprecisa, por lo cual, no permite distinguir la invención del estado de la técnica.



Se sugiere sustituirlo por términos precisos o rangos concretos.

El capítulo reivindicatorio hace referencia a los compuestos refrigerantes por su sistema de identificación, dado que por claridad es adecuado dar el nombre por el que se conocen los compuestos químicos reclamados, se sugiere entonces reclamar por ejemplo como “2,3,3,3-tetrafluoropropano (R1234yf)”.

Con el fin de subsanar las objeciones presentadas por el examinador, el solicitante presenta un nuevo capítulo reivindicatorio en el cual se han hecho las siguientes correcciones:

La reivindicación 1 se ha modificado incluyendo los nombres de los compuestos químicos correspondientes a cada compuesto refrigerante. Soporte para esta modificación se puede encontrar en la Tabla 1 de la memoria descriptiva.

De igual forma, el solicitante presenta las siguientes aclaraciones:

Respecto a la objeción del examinador a las reivindicaciones 1, 2 y 15 debido a que considera que la expresión “seleccionado del grupo” es imprecisa.

El Solicitante respetuosamente discrepa ya que la expresión objetada no da lugar a impresión ya que se trata de una lista cerrada (“que consiste en”) de compuesto entre los que se pueden seleccionar y, tal y como se indica en las reivindicaciones, las cantidades se seleccionan de cualquier intervalo dado para un total del 100 %.

En relación con la objeción del examinador de que el capítulo reivindicatorio hace referencia a los compuestos refrigerantes por su sistema de identificación y solicita dar el nombre por el que se conocen los compuestos químicos reclamados. Por ejemplo, como “2,3,3,3-tetrafluoropropano (R1234yf)”.



Con el fin de solventar la presente solicitud se ha modificado la reivindicación 1 en línea con lo sugerido por el Examinador.

2. Examen de Patentabilidad

2.1. Novedad y Nivel Inventivo

El examinador objeta la novedad de las reivindicaciones 1 y 2 a la luz de las enseñanzas del documento US20150315446 (en adelante D1).

De igual forma, objeta el nivel inventivo de la reivindicación 3 a la luz de las enseñanzas combinadas de D1 y WO2016/156812 (en adelante D2), argumentando que:

“La diferencia entre la invención definida entre la reivindicación 3 y la composición divulgada en D2, consiste en que comprende CO₂ y una proporción mayor de R11234ze.

El efecto que se logra al incluir específicamente una proporción mayor de R11234ze y CO₂ es disminuir el potencial de calentamiento global de la composición.

Por lo tanto, el problema técnico objetivo que pretende resolver esta invención se puede formular así: ¿cómo modificar la composición divulgada en D2 para proporcionar una composición refrigerante con un potencial de calentamiento global disminuido?

Sin embargo, el incluir CO₂ y una mayor cantidad de un refrigerante derivado de hidrofluoroolefina como R1234yf, ya está divulgado en D1 que se refiere a una composición refrigerante caracterizada porque comprende CO₂, R32 y al menos



69.5% de R1234yf, esta composición tiene un PCG muy bajo (146). Por otro lado, es importante resaltar que en el estado de la técnica es ampliamente conocido el uso de refrigerantes derivados de hidrofluoroolefina como el R1234yf y R1234ze por su bajo PGC en mezclas refrigerantes, como lo muestra Nawaz K. et. al. 3 (Octubre de 2017).

En consecuencia, la persona normalmente versada en la materia estaría motivada a incluir el CO₂ y una mayor cantidad de un refrigerante derivado de hidrofluoroolefina del D1 en la composición de D2, para así llegar al objeto de la reivindicación 3. Por lo cual se considera obvia.

Adicionalmente, D1 y D2 muestran que la cantidad de los compuestos refrigerantes en la composición pueden variar, por lo que una persona normalmente versada en la materia está en la capacidad de realizar las modificaciones necesarias en su trabajo de rutina y encontrar cuales son los porcentajes más adecuados en una composición.”

Con el fin de subsanar las objeciones del examinador, el solicitante presenta un nuevo capítulo reivindicatorio. Así mismo, presenta las siguientes observaciones y aclaraciones:

Los documentos D1 y D2 fueron citados en el Informe de Búsqueda Internacional emitido por la EPO (como Administración Internacional de Búsqueda) para la correspondiente solicitud de patente internacional PCT/EP2018/082583 de la que deriva la presente solicitud. Dichos documentos fueron citados con categoría “A”, es decir, como no relevantes para la patentabilidad de las reivindicaciones. Además, en el Informe Preliminar Internacional sobre Patentabilidad emitido también por la EPO se reconoció la novedad o actividad inventiva de las reivindicaciones de la solicitud internacional, las cuales son equivalentes a las reivindicaciones de la presente solicitud en Colombia. Se adjunta el Informe de Búsqueda Internacional y el Informe Preliminar Internacional sobre Patentabilidad.



Además, se hace notar que se ha emitido (28/10/2022) la intención de concesión para la correspondiente solicitud europea **EP3704203A1**. Se adjunta el texto concedido en el que se puede comprobar que las reivindicaciones son equivalentes a las reivindicaciones de la presente solicitud en Colombia.

3. Conclusiones

En consecuencia, por todas las razones aquí expuestas, el Solicitante respetuosamente considera subsanadas las objeciones con el nuevo conjunto de reivindicaciones y los argumentos ahora presentados. Por lo tanto, le pedimos amablemente al examinador que considere su opinión y conceda la patente para la presente invención, por lo que queda evidenciado que la invención cumple con los requisitos de patentabilidad definidos en la Decisión 486 de 2000.

Cordialmente,

Juan Carlos Cuesta Quintero.

C.C. 79.339.809 de Bogotá

T.P. 43.273 del C.S. de la J.

Anexos: Comprobante de pago por modificación voluntaria de la solicitud.
Capítulo reivindicatorio modificado en control de cambios.
Capítulo reivindicatorio modificado en limpio.
Copia de la solicitud aprobada para concesión por la EPO

REIVINDICACIONES

1. Una composición refrigerante que consiste esencialmente en:

dióxido de carbono	1-35 %
un HFO seleccionado del grupo que consiste en:	
<u>2,3,3,3-tetrafluoropropano (R1234yf)</u> y <u>3-tetrafluoroprop-1-eno (R1234ez(E))</u> , y mezcla de los mismos,	30-92 %
R32	1-30 %
R125	1-30 %
<u>1,1,1,3,3,3-hexafluoropropano (R227ea)</u>	1-15 %
R134a	0-15 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

2. Una composición refrigerante de acuerdo con la reivindicación 1 que consiste esencialmente en:

dióxido de carbono	5-20 %
un HFO seleccionado del grupo que consiste en:	
R1234yf y R1234ez(E), y mezcla de los mismos,	30-92 %
R32	5-30 %
R125	5-30 %
R227ea	1-15 %
R134a	0-15 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

3. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en:

R125	6-23 %
dióxido de carbono	6-20 %
R1234ze	55-68 %
R227ea	2-15 %
R32	6-20 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

4. Una composición refrigerante, de acuerdo con la reivindicación 3, que consiste esencialmente en:

R125	6-20 %
dióxido de carbono	6-18 %
R1234ze	55-67 %
R227ea	3-15 %
R32	7-20 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

5. Una composición refrigerante, de acuerdo con la reivindicación 4, que consiste esencialmente en:

R125	9,5 %
dióxido de carbono	8 %
R1234ze	65 %
R227ea	8 %
R32	9,5 %

en donde los porcentajes son en masa.

6. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en una de las siguientes composiciones:

(a)

R125	9,5 %
dióxido de carbono	9 %
R1234ze	57 %
R227ea	15 %
R32	9,5 %

en donde los porcentajes son en masa, (b)

(b)

R125	9,5 %
dióxido de carbono	9 %
R1234ze	58 %
R227ea	14 %
R32	9,5 %
R227ea	14 %
R32	9,5 %

en donde los porcentajes son en masa.

(c)

R125	19 %
dióxido de carbono	16 %
R1234ze	41 %
R227ea	5 %
R32	19 %

en donde los porcentajes son en masa.

7. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en:

R125	12-23 %
dióxido de carbono	8-20 %
R1234ze	35-55 %
R227ea	3-10 %
R32	12-23 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

8. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en una de las siguientes composiciones:

(a)

R125	9,5 %
dióxido de carbono	9 %
R1234ze	58 %
R227ea	7 %
R32	9,5 %

R134a 7 %

en donde los porcentajes son en masa.

(b)

R125 11 %

dióxido de carbono 11 %

R1234ze 57 %

R227ea 7 %

R32 11 %

R134a 3 %

en donde los porcentajes son en masa.

(c)

R125 18 %

dióxido de carbono 11 %

R1234ze 44 %

R227ea 6 %

R32 17 %

R134a 4 %

en donde los porcentajes son en masa.

(d)

R125 11 %

dióxido de carbono 11 %

R1234ze 55 %

R227ea 7 %

R32 11 %

R134a 5 %

en donde los porcentajes son en masa.

(e)

R125 13 %

dióxido de carbono 11 %

R1234ze 53 %

R227ea 7 %

R32 13 %

R134a 3 %

en donde los porcentajes son en masa.

(f)

R125	13 %
dióxido de carbono	11 %
R1234ze	55 %
R227ea	7 %
R32	13 %
R134a	1 %

en donde los porcentajes son en masa.

(g)

R125	14 %
dióxido de carbono	11 %
R1234ze	51 %
R227ea	7 %
R32	14 %
R134a	3 %

en donde los porcentajes son en masa.

(h)

R125	14 %
dióxido de carbono	11 %
R1234ze	55 %
R227ea	7 %
R32	13 %

en donde los porcentajes son en masa.

(i)

R125	10,5 %
dióxido de carbono	11 %
R1234ze	57 %
R227ea	7 %
R32	10,5 %
R134a	4 %

en donde los porcentajes son en masa,

(j)

R125	10,5 %
dióxido de carbono	11 %
R1234ze	58 %
R227ea	7 %
R32	10,5 %

R134a	3 %
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en donde los porcentajes son en masa.

(k)

R125	11,5 %
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dióxido de carbono	10 %
--------------------	------

R1234ze	57 %
---------	------

R227ea	7 %
--------	-----

R32	11,5 %
-----	--------

R134a	3 %
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en donde los porcentajes son en masa.

(l)

R125	11,5 %
------	--------

dióxido de carbono	10 %
--------------------	------

R1234ze	56 %
---------	------

R227ea	8 %
--------	-----

R32	11,5 %
-----	--------

R134a	3 %
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en donde los porcentajes son en masa.

9. Una composición refrigerante, de acuerdo con la reivindicación 1, que

consiste esencialmente en una de las siguientes composiciones:

(a)

R125	19 %
------	------

dióxido de carbono	10 %
--------------------	------

R1234ze	44 %
---------	------

R227ea	3 %
--------	-----

R32	17 %
-----	------

R134a	7 %
-------	-----

en donde los porcentajes son en masa.

(b)

R125	18 %
------	------

dióxido de carbono	11 %
--------------------	------

R1234ze	44 %
---------	------

R227ea	7 %
--------	-----

R32	17 %
-----	------

R134a	3 %
-------	-----

en donde los porcentajes son en masa.

(c)

R125	18 %
------	------

dióxido de carbono	11 %
--------------------	------

R1234ze	44 %
---------	------

R227ea	6 %
--------	-----

R32	17 %
-----	------

R134a	4 %
-------	-----

10. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en una de las siguientes composiciones:

(a)

R125	1-30 %
------	--------

dióxido de carbono	1-30 %
--------------------	--------

R1234yf	35-70 %
---------	---------

R227ea	1-10 %
--------	--------

R32	1-30 %
-----	--------

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

(b)

R125	5-30 %
------	--------

dióxido de carbono	5-20 %
--------------------	--------

R1234yf	35-70 %
---------	---------

R227ea	4-10 %
--------	--------

R32	5-30 %
-----	--------

11. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en:

R125	7-25 %
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dióxido de carbono	7-20 %
--------------------	--------

R1234yf	58-69 %
---------	---------

R227ea	5-10 %
--------	--------

R32	7-25 %
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en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

12. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en:

R125	9,5 %
dióxido de carbono	8 %
R1234yf	65 %
R227ea	8 %
R32	9,5 %

en donde los porcentajes son en masa.

13. Una composición refrigerante, de acuerdo con la reivindicación 12, que consiste esencialmente en:

R125	19 %
dióxido de carbono	16 %
R1234yf	41 %
R227ea	5 %
R32	19 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

14. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en:

R125	19 %
dióxido de carbono	16 %
R1234ze	20 %
R1234yf	21 %
R227ea	5 %
R32	19 %

en donde los porcentajes son en masa.

15. Una composición refrigerante de acuerdo con la reivindicación 1 que

consiste esencialmente en:

dióxido de carbono	1-35 %
un HFO seleccionado del grupo que consiste en R1234yf, R1234ze(E) y mezclas de los mismos,	30-95 %
R32	1-30 %
R125	1-30 %
R134a	1-30 %
R227ea	1-15 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

REIVINDICACIONES

1. Una composición refrigerante que consiste esencialmente en:

dióxido de carbono	1-35 %
un HFO seleccionado del grupo que consiste en:	
2,3,3,3-tetrafluoropropano (R1234yf) y 3-tetrafluoroprop-1-eno (R1234ez(E)), y mezcla de los mismos,	30-92 %
R32	1-30 %
R125	1-30 %
1,1,1,3,3,3-hexafluoropropano (R227ea)	1-15 %
R134a	0-15 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

2. Una composición refrigerante de acuerdo con la reivindicación 1 que consiste esencialmente en:

dióxido de carbono	5-20 %
un HFO seleccionado del grupo que consiste en:	
R1234yf y R1234ez(E), y mezcla de los mismos,	30-92 %
R32	5-30 %
R125	5-30 %
R227ea	1-15 %
R134a	0-15 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

3. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en:

R125	6-23 %
dióxido de carbono	6-20 %
R1234ze	55-68 %
R227ea	2-15 %
R32	6-20 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

4. Una composición refrigerante, de acuerdo con la reivindicación 3, que consiste esencialmente en:

R125	6-20 %
dióxido de carbono	6-18 %
R1234ze	55-67 %
R227ea	3-15 %
R32	7-20 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

5. Una composición refrigerante, de acuerdo con la reivindicación 4, que consiste esencialmente en:

R125	9,5 %
dióxido de carbono	8 %
R1234ze	65 %
R227ea	8 %
R32	9,5 %

en donde los porcentajes son en masa.

6. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en una de las siguientes composiciones:

(a)

R125	9,5 %
dióxido de carbono	9 %
R1234ze	57 %
R227ea	15 %
R32	9,5 %

en donde los porcentajes son en masa, (b)

(b)

R125	9,5 %
dióxido de carbono	9 %
R1234ze	58 %
R227ea	14 %
R32	9,5 %
R227ea	14 %
R32	9,5 %

en donde los porcentajes son en masa.

(c)

R125	19 %
dióxido de carbono	16 %
R1234ze	41 %
R227ea	5 %
R32	19 %

en donde los porcentajes son en masa.

7. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en:

R125	12-23 %
dióxido de carbono	8-20 %
R1234ze	35-55 %
R227ea	3-10 %
R32	12-23 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

8. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en una de las siguientes composiciones:

(a)

R125	9,5 %
dióxido de carbono	9 %
R1234ze	58 %
R227ea	7 %
R32	9,5 %

R134a 7 %

en donde los porcentajes son en masa.

(b)

R125 11 %

dióxido de carbono 11 %

R1234ze 57 %

R227ea 7 %

R32 11 %

R134a 3 %

en donde los porcentajes son en masa.

(c)

R125 18 %

dióxido de carbono 11 %

R1234ze 44 %

R227ea 6 %

R32 17 %

R134a 4 %

en donde los porcentajes son en masa.

(d)

R125 11 %

dióxido de carbono 11 %

R1234ze 55 %

R227ea 7 %

R32 11 %

R134a 5 %

en donde los porcentajes son en masa.

(e)

R125 13 %

dióxido de carbono 11 %

R1234ze 53 %

R227ea 7 %

R32 13 %

R134a 3 %

en donde los porcentajes son en masa.

(f)

R125	13 %
dióxido de carbono	11 %
R1234ze	55 %
R227ea	7 %
R32	13 %
R134a	1 %

en donde los porcentajes son en masa.

(g)

R125	14 %
dióxido de carbono	11 %
R1234ze	51 %
R227ea	7 %
R32	14 %
R134a	3 %

en donde los porcentajes son en masa.

(h)

R125	14 %
dióxido de carbono	11 %
R1234ze	55 %
R227ea	7 %
R32	13 %

en donde los porcentajes son en masa.

(i)

R125	10,5 %
dióxido de carbono	11 %
R1234ze	57 %
R227ea	7 %
R32	10,5 %
R134a	4 %

en donde los porcentajes son en masa,

(j)

R125	10,5 %
dióxido de carbono	11 %
R1234ze	58 %
R227ea	7 %
R32	10,5 %

R134a	3 %
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en donde los porcentajes son en masa.

(k)

R125	11,5 %
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dióxido de carbono	10 %
--------------------	------

R1234ze	57 %
---------	------

R227ea	7 %
--------	-----

R32	11,5 %
-----	--------

R134a	3 %
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en donde los porcentajes son en masa.

(l)

R125	11,5 %
------	--------

dióxido de carbono	10 %
--------------------	------

R1234ze	56 %
---------	------

R227ea	8 %
--------	-----

R32	11,5 %
-----	--------

R134a	3 %
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en donde los porcentajes son en masa.

9. Una composición refrigerante, de acuerdo con la reivindicación 1, que

consiste esencialmente en una de las siguientes composiciones:

(a)

R125	19 %
------	------

dióxido de carbono	10 %
--------------------	------

R1234ze	44 %
---------	------

R227ea	3 %
--------	-----

R32	17 %
-----	------

R134a	7 %
-------	-----

en donde los porcentajes son en masa.

(b)

R125	18 %
------	------

dióxido de carbono	11 %
--------------------	------

R1234ze	44 %
---------	------

R227ea	7 %
--------	-----

R32	17 %
-----	------

R134a	3 %
-------	-----

en donde los porcentajes son en masa.

(c)

R125	18 %
------	------

dióxido de carbono	11 %
--------------------	------

R1234ze	44 %
---------	------

R227ea	6 %
--------	-----

R32	17 %
-----	------

R134a	4 %
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10. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en una de las siguientes composiciones:

(a)

R125	1-30 %
------	--------

dióxido de carbono	1-30 %
--------------------	--------

R1234yf	35-70 %
---------	---------

R227ea	1-10 %
--------	--------

R32	1-30 %
-----	--------

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

(b)

R125	5-30 %
------	--------

dióxido de carbono	5-20 %
--------------------	--------

R1234yf	35-70 %
---------	---------

R227ea	4-10 %
--------	--------

R32	5-30 %
-----	--------

11. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en:

R125	7-25 %
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dióxido de carbono	7-20 %
--------------------	--------

R1234yf	58-69 %
---------	---------

R227ea	5-10 %
--------	--------

R32	7-25 %
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en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

12. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en:

R125	9,5 %
dióxido de carbono	8 %
R1234yf	65 %
R227ea	8 %
R32	9,5 %

en donde los porcentajes son en masa.

13. Una composición refrigerante, de acuerdo con la reivindicación 12, que consiste esencialmente en:

R125	19 %
dióxido de carbono	16 %
R1234yf	41 %
R227ea	5 %
R32	19 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.

14. Una composición refrigerante, de acuerdo con la reivindicación 1, que consiste esencialmente en:

R125	19 %
dióxido de carbono	16 %
R1234ze	20 %
R1234yf	21 %
R227ea	5 %
R32	19 %

en donde los porcentajes son en masa.

15. Una composición refrigerante de acuerdo con la reivindicación 1 que

consiste esencialmente en:

dióxido de carbono	1-35 %
un HFO seleccionado del grupo que consiste en R1234yf, R1234ze(E) y mezclas de los mismos,	30-95 %
R32	1-30 %
R125	1-30 %
R134a	1-30 %
R227ea	1-15 %

en donde los porcentajes son en masa y se seleccionan entre los intervalos citados hasta un total del 100 %.



SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

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Patente PCT
MEZCLAS REFRIGERANTES DE BAJO PCG

Detalle del pago

Id.	Rentístico	Concepto y Servicio	Cant.	Val. Unit.	Subtotal
1	50005-01-03	Modificaciones / Correcciones al registro Patente PCT (DESCUENTO INTERNET)	1	\$ 176,000	\$ 176,000
TOTAL					\$ 176,000

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LOW GWP REFRIGERANT BLENDS

This invention relates to refrigerant compositions which can be used in thermal pumps to pump heat from a lower temperature to a higher temperature by the input of work. When such devices are used to generate lower temperatures, they are typically called refrigerators or air conditioners. Where they are used to produce higher temperatures, they are typically termed heat pumps. The same device may supply heating or cooling depending upon the user's requirement. This type of thermal pump may be called a reversible heat pump or reversible air conditioner.

Chlorofluorocarbons (CFCs) such as CFC-12 and R502 and hydrochlorofluorocarbons (HCFCs) such as HCFC-22 have been widely used as refrigerants, but migrate to the stratosphere where they are broken down by ultra violet light producing chlorine atoms that destroy the ozone layer. These Ozone Depleting Substances (ODS) are being replaced by non-ozone depleting alternatives such as hydrofluorocarbons (HFCs), which are non-flammable, efficient and of low toxicity. In certain applications, particularly but not specifically related to low temperature refrigeration systems often used in supermarkets, R502 was the main refrigerant of choice due largely to its lower discharge temperature compared to R22. As a consequence of the global environmental agreement to protect the Ozone Layer embodied in the Montreal Protocol, R502 was banned and was largely replaced by the HFC blends R404A and R507. However, R404A and R507, while being excellent refrigerants in terms of energy efficiency, non-flammability, low toxicity and thermodynamic properties, nevertheless have Global Warming Potentials (GWP)s which are at the high end of the commonly used HFCs.

In this specification the numerical value for a Global Warming Potential (GWP) refer to an Integrated Time Horizon (ITH) of 100 years as contained in the Inter-Governmental Panel on Climate Change Fourth Assessment Report (AR4).

Although R22, which has been widely used in air conditioning systems, has a much lower ability to destroy ozone compared to CFCs, it is being phased out under the Montreal Protocol. Non-ozone depleting R410A has proved an excellent replacement for R22 in new air conditioning equipment, including split systems, but it is also now being phased down because the comparatively high GWP (2088) means it is no longer environmentally acceptable.

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The EU and other territories have imposed GWP quotas and/or taxes to progressively reduce the availability of R404A, R507 and R410A. These actions have two key consequences. Firstly, there will be shortages of these refrigerants available to service existing equipment and charge new equipment which will disrupt the refrigeration and air conditioning industries. Secondly, the price of remaining refrigerant will rapidly increase as supply can no longer meet demand. Without replacement refrigerants, critical equipment, e.g. for preserving food in supermarkets and air conditioning in hospitals, may stop functioning with serious social repercussions.

The composition of R404A is:

R125 44%;

R143a 52%; and

R134a 4%

(GWP = 3922)

The composition of R507 is:

R125 50%; and

R143a 50%

(GWP = 3985)

The composition of R410A is:

R125 50%; and

R32 50%

(GWP = 2088)

WO2017/151488 discloses refrigerant compositions comprising HFC-32, HFC-125, HFO-1234yf, HFC-134a and CO₂.

WO2016/156812 discloses a composition comprising R125 20-35%, R32 20-35%, R1234ze(E) 25-50% and R227ea 1-10%.

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According to a first aspect of the present invention there is provided a refrigeration composition consisting essentially of:

carbon dioxide 1-35%

an HFO selected from the group consisting of: R1234yf and R1234ze(E) and mixtures

5 thereof 30-92%

R32 1-30%

R125 1-30%

R227ea 1-15%

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wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

In this specification percentages or other amounts are by mass unless indicated otherwise. Amounts are selected from any ranges given to total 100%.

5

The term “consisting of” is used in this specification to refer to compositions which include only the recited ingredients, disregarding trace amounts of any impurities.

10 The term “consisting essentially of” is used in this specification to refer to compositions which consist of the recited ingredients with the possible addition of minor amounts of any further ingredients which do not substantially alter the essential refrigerant properties of the composition. These compositions include compositions which consist of the recited ingredients. Compositions which consist of the recited ingredients may be particularly advantageous.

15

This invention relates to low GWP blends, which particularly, but not exclusively, are compositions that can replace R404A, R507 and R410A in existing, modified or new refrigeration and air conditioning systems. The continued operation of existing and modified systems is facilitated. The blends have zero Ozone Depletion Potentials, so that they have no adverse effect on stratospheric ozone. The invention also provides compositions which may continue to be used in the event of progressive tightening of GWP restrictions, while minimising the cost to the user.

20

25 This invention relates particularly to refrigerant compositions that have GWP values in the range 0.5 to 1050. The values in this range are significantly lower than those of R404A, R507 and R410A. Exemplary compositions may have ASHRAE safety classifications of A1 (low toxicity/non-flammable) or A2L (low toxicity/slightly flammable). The compositions may possess energy efficiencies and cooling capacities at least comparable to the fluids they are replacing. The compositions may have maximum operating pressures no greater than 3 bar preferably 2 bar greater at 45°C than the refrigerants they may replace. Compositions with relatively high GWPs tend to be non-flammable (A1) while compositions with lower GWPs tend to be slightly flammable (A2L). For existing equipment there may be little scope for carrying out physical modifications. Therefore, non-flammability (A1) is essential for use in existing equipment. Compositions with higher GWP values may be required. For existing

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equipment, where modifications are possible and especially for new installations designed to exploit their advantageous properties, then blends with lower GWPs are preferred, even if they have an A2L rating.

5 The term “glide” has been previously defined as the temperature difference between the bubble point and the dew point at the specified constant pressure. This may be referred to as the ‘intrinsic’ refrigerant glide. Defined in this way, “glide” is a purely thermodynamic property of a refrigerant and is independent of equipment and operating conditions.

10 In the condenser where the refrigerant moves from the dew point to the bubble point as it condenses, the observed glide is a combination of the intrinsic glide of the refrigerant plus the glide induced by the pressure drop necessary to maintain the refrigerant flow.

15 In an evaporator where a portion of the refrigerant has already vaporised in the expansion device for example a valve or capillary tube, a two phase mixture enters the evaporator. In this case the glide is the difference between the entry temperature and the dew point. This difference may depend on operating conditions. The observed glide will be the intrinsic glide of the refrigerant minus the glide caused by the pressure drop in the evaporator required to maintain the refrigerant flow. A measured or calculated evaporator glide under
20 specified conditions may be used.

In this specification temperature glides under the specified operating conditions for the equipment may be classified as follows:

- | | | | |
|----|---------------------|---|------------------------|
| 25 | 1. Negligible glide | - | less than 0.5K |
| | 2. Small glide | - | 0.5K to 2.0K |
| | 3. Medium glide | - | more than 2.0K to 5.0K |
| | 4. Wide glide | - | more than 5K to 10.0K |
| | 5. Very wide glide | - | more than 10.0K |

Compositions of the present invention may have a wide or very wide temperature glide.

30

Exemplary compositions may consist essentially of CO₂, an HFO with a normal boiling point less than -15°C, and one or more of R32, R227ea, R134a and R125. Exemplary HFOs are R1234yf and R1234ze(E). These fluids may provide a combination of appropriate vapour pressures for formulating R404A, R507 and R410A replacements with low flammability and

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low toxicity. They may provide compositions where the flammability of the HFOs and R32 can be partially or completely compensated for, by the presence of the non-flammable gases CO₂, R125 and R227ea. Furthermore, the relatively high GWPs of R125 and R227ea and the moderate GWP of R32 can be offset by the very low GWPs of CO₂ and the HFOs.

5

Exemplary embodiments of this invention provide refrigerant compositions that allow equipment to continue operating at pressures suitable for use with R404A, R507 or R410A. These embodiments provide replacement refrigerants for servicing existing equipment and charging new equipment. This object may be achieved with compositions having GWPs not exceeding 1050. Initially, a reduced EU GWP quota may provide adequate latitude for compositions in accordance with this invention having thermodynamic and flammability properties that enable them to be retrofitted into existing designs of R404A, R507 and R410A equipment with few or no modifications. This is advantageous because a retrofit composition minimises the cost to the equipment owner.

15

As GWP regulations further reduce the supply, it may become difficult to provide sufficient refrigerant to meet market demands using retrofit compositions. Surprisingly, we have found that compositions with GWPs of less than 800, which, in themselves, do not have the thermodynamic properties to be retrofit fluids, can be used, for example, at the annual service, to top up the refrigerant remaining in a unit containing R404A, R507 or R410A, thus enabling the equipment to continue operating, for example, for at least 5 years, despite small persistent leakage. Such compositions may be termed “extenders”. A further aspect of this invention is to provide an extender with GWP of less than 300, which may be used as a refrigerant to service existing equipment as GWP regulations become stricter. These compositions may enable the continued use of existing technology and equipment, thereby avoiding the high cost of replacing equipment that is still functioning or the cost of developing new technologies.

While hydrocarbons, ammonia and carbon dioxide (CO₂) are technically feasible refrigerants for refrigeration and air conditioning systems and have considerably lower GWPs than HFCs, they are not direct replacements for R507 and R410A, since they have inherent disadvantages which work against their general usage, particularly in public areas such as supermarkets. Highly flammable hydrocarbons can only be used safely in conjunction with a secondary refrigeration circuit, which reduces energy efficiency and increases costs, or with

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small charges, in turn severely limiting the maximum cooling duty for which they can be used. Even when such safety precautions have been taken, hydrocarbon refrigerants and ammonia have caused building damage, injury and death. CO₂ must be used in the transcritical state on the high-pressure side of the system to allow heat rejection to ambient air. Pressures are often in excess of 100 bar, again resulting in an energy penalty and also a significantly higher capital cost compared to conventional R404A, R507 and R410A systems. Ammonia is markedly toxic. Leaks from industrial refrigeration installations may cause death and injury. Because of these adverse properties, hydrocarbons, ammonia and CO₂ cannot be retrofitted into existing R404A, R507 or R410A units.

Exemplary compositions have direct GWP values which are less than about 1050. GWP values are widely recorded in the literature for example as published by the US Environmental Protection Agency (EPA) or IPCC Reports.

Advantageous embodiments of this invention consist essentially of blends of carbon dioxide and R1234ze(E) and/or R1234yf, R125, R134a R227ea and R32, in the presently claimed proportions, wherein the compositions have safety classifications of A1 or A2L, according to ASHRAE Standard 34, while providing similar or superior refrigerating effects and performances as the refrigerants they are intended to replace, but with maximum operating pressures that allow them to be used with equipment components pressured rated for R404A, R507 or R410A.

Compositions of this invention may be used to completely or partially replace a refrigerant, for example, R404A, R410A or R507. The compositions may be used for completely retrofitting existing equipment or for topping up existing equipment, for example, following a gradual leak. Alternatively, the compositions may be used as refrigerants in new or original (OEM) equipment.

In a first exemplary embodiment the composition may be used in air conditioning equipment operating at an evaporating temperature in the range of about 0°C to about 15°C, for example, from about 2°C to about 15°C, for example, the equipment designed for use with R410A.

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In a second exemplary embodiment, the composition may be used in low temperature refrigeration equipment operating at an evaporating temperature, for example, from about -15°C to about -20°C, for example, with equipment designed for use with R404A or R507.

5 Exemplary compositions of this invention are capable of retaining the properties of the existing refrigerant, when used in combination with the existing refrigerant or as a complete replacement for the existing refrigerant. The following properties may be achieved.

The GWP of the refrigerant should be lower than the GWP of the original refrigerant.

10

The cooling capacity of the refrigerant should be similar, for example, ($\pm 20\%$) to that of the original refrigerant. This is important to enable the equipment to function adequately in a hot environment.

15 The discharge pressure should not exceed the maximum pressure rating of the equipment.

The discharge temperature should not significantly exceed the discharge temperature that the equipment is designed for. If the discharge temperature is excessive then the working
20 life of the equipment may be reduced.

It is an advantage that the compositions in accordance with this invention may have discharge temperatures which are lower than may be expected following a standard calculation, for example, using the Nist Cycle D method. Exemplary compositions may have discharge
25 temperatures which are lower than the calculated values and for example about 5°C to 10°C above the measured values for R404A, R507 or R410A.

The power consumption of the equipment when using the replacement refrigerant should not be significantly higher, for example, not more than 20% higher in comparison to
30 the power consumption when using the original refrigerant.

Exemplary compositions may have the further advantage that they are not azeotropes or azeotrope-like. Preferred compositions boil over a temperature range greater than about 10°C, for example, greater than 20°C.

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It is a common belief that an azeotrope-like composition is necessary. The present inventors have unexpectedly discovered that azeotrope-like compositions are not necessary and may even be disadvantageous. This discovery is particularly useful when using a direct heat exchange (DX) exchanger in which a progressive increase in temperature is dependent on the glide of the refrigerant.

In condenser equipment using a refrigerant composition, in this invention, the pressure drop glide is in the same direction as the refrigerant glide so that the effects are additive.

In contrast, in an evaporator, the pressure drop glide is in the opposite direction to the refrigerant glide so that the two effects may partially, or completely, cancel out. An evaporator cools, for example, an air stream or a liquid stream over a range from a higher temperature to a lower temperature. If the temperature glide of the evaporating refrigerant is significantly greater than the required cooling range, then the efficiency on the unit may be compromised. Preferably glide should be equal to, or less than, the range. Pressure-induced evaporator glide may act in opposition to the intrinsic refrigerant glide to produce an observed glide that is acceptable for a required cooling range.

In the event that the availability of high GWP R404A, R507 and R410A may be constrained by the EU F-Gas regulations, and similar global legislation following the ratification of the Kigali Amendment to the Montreal Protocol, insufficient quantities of these refrigerants may be available to service existing equipment. Major modifications of existing R404A, R507 and R410A equipment may be prohibitively expensive. The EU is limiting availability by further reducing GWP quotas to suppliers from 2018. Exemplary embodiments of this invention may overcome the quota limitation by providing refrigerants comprising an HFO, CO₂ and R227ea that can be used to “top up” R404A, R507 and R410A units, allowing them to operate for at least a further five years. Typically, commercial refrigeration equipment loses 5 to 20% of its refrigerant charge each year and is topped up with new refrigerant at its annual service. Surprisingly, we have found that blends comprising carbon dioxide, R1234yf and/or R1234ze(E), R227ea, R32, R125 and, optionally R134a, may be added to the R404A, R507 or R410A, remaining in a thermal pump after a leak, to allow continued operation of the device. Such compositions are called “extenders”, i.e. they extend the working life of the units to which they are added. Because most existing installations are not designed to handle

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flammable (A2) refrigerants, extenders are non-flammable A1 refrigerants. To ensure effective operation, the compositions require suction capacities and maximum operating temperatures comparable to the refrigerants they are replacing. Preferably, the GWPs of extender compositions should be less than 800 and preferably less than 300, to maximise the quantity of refrigerants available for topping up within the constraints of government-imposed quotas.

According to a third aspect of this invention, there is provided a refrigerant extender composition in accordance with the first aspect of this invention.

R227ea has a relatively high GWP of 3220 but is non-flammable and tends to co-distil with R1234ze(E) and R1234yf, thus helping the formulation of non-flammable blends. Conversely, R32 has a lower GWP (675), but is flammable. Since non-flammable extender blends are required, then it may be advantageous to omit R32 to maximise the quantity of R227ea that can be added to ensure non-flammability. For blends with a GWP not exceeding a GWP of 800, then the maximum R227ea content may be about ~24.8%; for a GWP not exceeding 500, the maximum amount of R227ea may be about 15.5%; and for a GWP not exceeding 300, the maximum may be about 9.2%.

In embodiments the amount of R227ea may be in the range of 4% to 15%.

Generally, refrigerant leaks may be small (5 to 20% per annum) allowing topping up at an annual service. However, catastrophic refrigerant losses may occur when most of the charge is lost, essentially requiring a complete replacement of the original refrigerant. The compositions described above, as extenders, may be used for this purpose, if necessary, by modifying the units to enable them to be compatible with the specific physical properties of these blends. But the compositions may result in excessive discharge temperatures in the condensers and evaporators if systems cannot be modified. In these circumstances, compositions are preferred that have inherently acceptable discharge temperatures, suction specific volumes, an A1 safety rating and maximum operating pressures to allow them to be used in existing R404A, R507 or R410A equipment. Surprisingly, we have found that this preferred combination of properties can be achieved by compositions comprising R32, R125, R1234yf, R1234ze and R227ea, as claimed in this invention.

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The present invention may enable the replacement of R404A, R507 and R410A - the most commonly used refrigerants in refrigeration and air conditioning equipment - providing a substantial reduction in GWP exceeding 80%, with blends having a GWP between 1 and 800 without any reduction in performance, including energy efficiency and capacity.

5

An exemplary refrigerant composition may consist essentially of the following:

carbon dioxide 5-20%

an HFO selected from the group consisting of: R1234yf and R1234ze(E) and mixtures thereof
30-92%

10 R32 5-30%

R125 5-30%

R227ea 4-15%

R134a 0-15%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

15

An exemplary refrigerant composition which may be used to completely or partially replace R404A, R507 or R410A consists or consists essentially of:

R125 6-23%

20 carbon dioxide 6-20%

R1234ze 55-68%

R227ea 6-15%

R32 6-20%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

25

An exemplary refrigerant composition which may be used to completely, or partially, replace R404A, R507 or R410A, consists or consists essentially of:

R125 6-20%

30 carbon dioxide 6-18%

R1234ze 55-67%

R227ea 7-15%

R32 7-20%

wherein the percentages are by mass and are selected from the ranges quoted to total 100% .

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An exemplary refrigerant composition may consist essentially of the following:

R125	9.5%
carbon dioxide	8%
R1234ze	65%
5 R227ea	8%
R32	9.5%

wherein the percentages are by mass.

An exemplary refrigerant composition may consist or consist essentially of one of the

10 following:

(a)

R125	9.5%
carbon dioxide	9%
R1234ze	58%
15 R227ea	7%
R32	9.5%
R134a	7%

wherein the percentages are by mass.

20 (b)

R125	11%
carbon dioxide	11%
R1234ze	57%
R227ea	7%
25 R32	11%
R134a	3%

wherein the percentages are by mass.

(c)

30 R125	18%
carbon dioxide	11%
R1234ze	44%
R227ea	6%
R32	17%

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R134a 4%

wherein the percentages are by mass.

(d)

5 R125 11%

carbon dioxide 11%

R1234ze 55%

R227ea 7%

R32 11%

10 R134a 5%

wherein the percentages are by mass.

(e)

R125 13%

15 carbon dioxide 11%

R1234ze 53%

R227ea 7%

R32 13%

R134a 3%

20 wherein the percentages are by mass.

(f)

R125 13%

carbon dioxide 11%

25 R1234ze 55%

R227ea 7%

R32 13%

R134a 1%

wherein the percentages are by mass.

30

(g)

R125 14%

carbon dioxide 11%

R1234ze 51%

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R227ea 7%

R32 14%

R134a 3%

wherein the percentages are by mass.

5

(h)

R125 14%

carbon dioxide 11%

R1234ze 55%

10 R227ea 7%

R32 13%

R134a -

wherein the percentages are by mass.

15 (i)

R125 10.5%

carbon dioxide 11%

R1234ze 57%

R227ea 7%

20 R32 10.5%

R134a 4%

wherein the percentages are by mass.

(j)

25 R125 10.5%

carbon dioxide 11%

R1234ze 58%

R227ea 7%

R32 10.5%

30 R134a 3%

wherein the percentages are by mass.

(k)

R125 11.5%

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carbon dioxide 10%

R1234ze 57%

R227ea 7%

R134a 3%

5 R32 11.5%

(l)

R125 11.5%

carbon dioxide 10%

10 R1234ze 56%

R227ea 8%

R32 11.5%

R134a 3%

15

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A, R507 or R410A, may consist or consist essentially of one of the following:

20 (a)

R125 19%

carbon dioxide 10%

R1234ze 44%

R227ea 3%

25 R32 17%

R134a 7%

wherein the percentages are by mass.

(b)

30 R125 18%

carbon dioxide 11%

R1234ze 44%

R227ea 7%

R32 11%

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R134a 3%

wherein the percentages are by mass.

5 An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A, R507 or R410A, may consist or consist essentially of:

R125 1-30%

carbon dioxide 1-30%

R1234yf 35-70%

10 R227ea 1-10%

R32 1-30%

R134a 0-15%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

15 An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist or consist essentially of:

R125 5-30%

carbon dioxide 5-25%

20 R1234yf 50-70%

R227ea 2-10%

R32 5-30%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

25 An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist or consist essentially of:

R125 6-27%

carbon dioxide 6-20%

30 R1234yf 55-70%

R227ea 3-10%

R32 6-27%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

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An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist or consist essentially of:

R125	7-25%
5 carbon dioxide	7-20%
R1234yf	58-69%
R227ea	5-10%
R32	7-25%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

10

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist or consist essentially of:

R125	7-23%
15 carbon dioxide	7-20%
R1234yf	58-68%
R227ea	6-10%
R32	7-20%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

20

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist or consist essentially of:

R125	7-20%
25 carbon dioxide	7-18%
R1234yf	59-67%
R227ea	7-10%
R32	7-20%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

30

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist or consist essentially of:

R125	9.5%
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carbon dioxide	8%
R1234yf	65%
R227ea	8%
R32	9.5%

- 5 wherein the percentages are by mass.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist or consist essentially of:

10	R125	9-25%
	carbon dioxide	7-20%
	R1234yf	35-60%
	R227ea	2-10%
	R32	9-25%

- 15 wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist or consist essentially of:

20	R125	12-23%
	carbon dioxide	8-20%
	R1234yf	35-55%
	R227ea	3-10%
	R32	12-23%

- 25 wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist or consist essentially of:

30	R125	19%
	carbon dioxide	16%
	R1234yf	41%
	R227ea	5%
	R32	19%

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wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, which may be used to provide an extender or new equipment alternative for R404A, R507 or R410A, may consist or consist essentially of:

- 5 carbon dioxide 1-35%
 an HFO selected from the group consisting of R1234yf and HFO1234ze(E) or mixtures thereof,
 30-95%
 R32 1-30%
 R125 1-30%
 10 and R227ea 1-15%
 and mixtures thereof,

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

- 15 An exemplary refrigerant composition not presently claimed, which may be used to provide an extender or new equipment alternative for R404A, R507 or R410A. may consist or consist essentially of:

carbon dioxide 10-30%
 an HFO selected from R1234yf or R1234ze(E) or mixtures thereof 45-85%
 R227ea 5-15%

- 20 wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, not presently claimed which may be used to provide an extender or new equipment alternative for R404A, R507 or R410A. may consist or consist essentially of:

- 25 carbon dioxide 10-25%
 an HFO selected from R1234yf or R1234ze(E) and mixtures thereof 60-83%
 R227ea 5-12%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

- 30 An exemplary refrigerant composition, not presently claimed which may be used to provide an extender or new equipment alternative for R404A or R507, may consist or consist essentially of:

carbon dioxide 22%
 R227ea 9%

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and R1234ze(E) or R1234yf 69%

wherein the percentages are by mass.

An exemplary refrigerant composition, not presently claimed which may be used to provide an extender or new equipment alternative for R410A, may consist or consist essentially of:

carbon dioxide 21-30%

R1234ze(E) 60-71%

R227ea 7-10%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, not presently claimed which may be used to provide an extender or new equipment alternative for R410A, may consist or consist essentially of:

15 carbon dioxide 25%

R227ea 9%

and R1234ze(E) or R1234yf 66%

wherein the percentages are by mass.

20 An exemplary refrigerant composition, not presently claimed which may be suitable as a replacement for R404A or R507 in refrigeration equipment, may consist or consist essentially of:

carbon dioxide 10-20%

and an HFO selected from R1234yf and R1234ze(E) or mixtures thereof 90-80%

25 wherein the percentages are by mass and are selected from the ranges quoted to total 100%

An exemplary refrigerant composition, not presently claimed which is suitable as a replacement for R404A or R507 in refrigeration equipment, may consist or consist essentially of:

30 carbon dioxide 10-30%

R1234ze 70-90%

wherein the percentages are by mass.

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An exemplary refrigerant composition, not presently claimed which is suitable as a replacement for R404A or R507 in refrigeration equipment, may consist or consist essentially of:

carbon dioxide 15-25%

5 R1234ze 75-90%

wherein the percentages are by mass

10 An exemplary refrigerant composition, not presently claimed which is suitable as a replacement for R404A or R507 in refrigeration equipment, may consist or consist essentially of:

carbon dioxide 15%

R1234ze 85%

wherein the percentages are by mass

15 An exemplary refrigerant composition, not presently claimed which is suitable as a replacement for R404A or R507 in refrigeration equipment, may consist or consist essentially of:

carbon dioxide 20%

R1234ze 80%

20 wherein the percentages are by mass

An exemplary refrigerant composition, not presently claimed which is suitable as a replacement for R404A or R507 in refrigeration equipment, may consist or consist essentially of:

25 carbon dioxide 12-23%

R1234yf 77-88%

wherein the percentages are by mass.

30 An exemplary refrigerant composition, not presently claimed which is suitable as a replacement for R410A in air conditioning equipment, may consist or consist essentially of:

carbon dioxide 12-20%

and an HFO selected from R1234yf and R1234ze(E) or mixtures thereof 80-88%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

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An exemplary refrigerant composition, not presently claimed, which is suitable as a replacement for R410A in air conditioning equipment, may consist or consist essentially of:

carbon dioxide 15-23%

R1234yf 77-85%

5 wherein the percentages are by mass.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist or consist essentially of:

10 R125 6-23%

carbon dioxide 6-20%

R1234ze 55-68%

R227ea 6-15%

R32 6-20%

15 wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist or consist essentially of:

20 R125 6-20%

carbon dioxide 6-18%

R1234ze 55-67%

R227ea 7-15%

R32 7-20%

25 wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist or consist essentially of:

30 R125 14%

carbon dioxide 11%

R1234ze 55%

R227ea 7%

R32 13%

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wherein the percentages are by mass.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist or

5 consist essentially of:

R125 9.5%

carbon dioxide 8%

R1234ze 65%

R227ea 8%

10 R32 9.5%

wherein the percentages are by mass.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist or

15 consist essentially of:

R125 9.5%

carbon dioxide 9%

R1234ze 57%

R227ea 15%

20 R32 9.5%

wherein the percentages are by mass.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist or

25 consist essentially of:

R125 9.5%

carbon dioxide 9%

R1234ze 58%

R227ea 14%

30 R32 9.5%

wherein the percentages are by mass.

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An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist or consist essentially of:

R125	12-23%
5 carbon dioxide	8-20%
R1234ze	35-55%
R227ea	3-10%
R32	12-23%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

10

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist or consist essentially of:

R125	19%
15 carbon dioxide	16%
R1234ze	41%
R227ea	5%
R32	19%

wherein the percentages are by mass.

20

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A, R507 or R410A, may consist or consist essentially of:

carbon dioxide	1-35%
25 R1234yf	15-45%
R1234ze	15-50%

and optionally, R32, R125 and R227ea or mixtures thereof, wherein the percentages of the components, including any optional components, are by mass, and are selected from the ranges quoted to total 100%.

30

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A, R507 and R410A, may consist or consist essentially of:

R125	19%
------	-----

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carbon dioxide 16%

R1234ze 20%

R1234yf 21%

R227ea 5%

5 R32 19%

wherein the percentages are by mass.

An exemplary refrigerant composition may consist or consist essentially of:

carbon dioxide 1-35%

- 10 an HFO selected from R1234yf and HFO1234ze(E) or mixtures thereof, 30-95%
and optionally, R32, R125, R134a and R227ea or mixtures thereof, wherein the percentages of the components, are by mass, and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, not presently claimed, may consist essentially of:

15 carbon dioxide 1-35%

an HFO selected from R1234yf and HFO1234ze(E) or mixtures thereof, 30-95%

and optionally, R32 1-30%

R125 1-30%

R134a 1-30%

20 and R227ea 1-15%

or mixtures thereof,

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, not presently claimed, which may be used to

- 25 provide a retrofit replacement, extender or new equipment alternative for R404A, R507 or R410A, may consist essentially of:

R125 1-30%

carbon dioxide 1-30%

R1234yf 30-70%

30 R134a 2-30%

R32 1-30%

and optionally R227ea 1-10%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

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An exemplary refrigerant composition, not presently claimed, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist essentially of:

R125 12-23%

5 carbon dioxide 8-20%

R1234yf 30-55%

R134a 7-25%

R32 12-23%

and optionally R227ea 3-10%

10 wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist essentially of:

R125 18%

15 carbon dioxide 16%

R1234yf 31%

R134a 17%

R32 18%

wherein the percentages are by mass and total 100%.

20

An exemplary refrigerant composition, not presently claimed, which may be used to provide an extender or new equipment alternative for R404A, R507 or R410A, may consist essentially of:

carbon dioxide 1-35%

25 an HFO selected from R1234yf and R1234ze(E) or mixtures thereof, 30-95%

and optionally, R32 1-30%

R125 1-30%

R134a 1-30%

and optionally R227ea 1-10%

30 or mixtures thereof,

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

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An exemplary refrigerant composition, not presently claimed, which may be used to provide an extender or new equipment alternative for R404A, R507 or R410A, may consist essentially of:

carbon dioxide	10-30%
5 an HFO selected from R1234yf or R1234ze(E) or mixtures thereof	30-85%
R134a	3-25%
and optionally R227ea	5-15%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

- 10 An exemplary refrigerant composition, not presently claimed, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A, R507 or R410A, may consist essentially of:

R125	1-30%
carbon dioxide	1-30%
15 R1234ze	30-70%
R134a	1-30%
R227ea	1-15%
R32	1-30%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

20

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist essentially of:

R125	5-30%
25 carbon dioxide	5-25%
R1234ze	30-68%
R134a	2-15%
R227ea	2-15%
R32	5-30%

- 30 wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist essentially of:

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R125	13%
carbon dioxide	11%
R1234ze	53%
R227ea	3%
5 R134a	7%
R32	13%

wherein the percentages are by mass.

10 An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist essentially of:

R125	14%
carbon dioxide	11%
R1234ze	51%
15 R227ea	3%
R134a	7%
R32	14%

wherein the percentages are by mass.

20 An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist essentially of:

R125	6-20%
carbon dioxide	6-18%
25 R1234ze	30-63%
R134a	5-10%
R227ea	7-15%
R32	7-20%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

30

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist essentially of:

R125	9.5%
------	------

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carbon dioxide	9%
R1234ze	58%
R227ea	7%
R134a	7%
5 R32	9.5%

wherein the percentages are by mass.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist essentially of:

R125	10.5%
carbon dioxide	11%
R1234ze	57%
R227ea	7%
15 R134a	4%
R32	10.5%

wherein the percentages are by mass.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A and R507, may consist essentially of:

R125	10.5%
carbon dioxide	11%
R1234ze	58%
25 R227ea	7%
R134a	3%
R32	10.5%

wherein the percentages are by mass.

An exemplary refrigerant composition, not presently claimed, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist essentially of:

R125	9-25%
carbon dioxide	6-20%

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R1234ze 30-60%

R134a 2-30%

R227ea 2-10%

R32 9-25%

- 5 wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist essentially of:

R125 19%

- 10 carbon dioxide 10%

R1234ze 44%

R134a 7%

R227ea 3%

R32 17%

- 15 wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist essentially of:

R125 18%

- 20 carbon dioxide 11%

R1234ze 44%

R134a 3%

R227ea 7%

R32 17%

- 25 wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist essentially of:

R125 18%

- 30 carbon dioxide 11%

R1234ze 44%

R134a 4%

R227ea 6%

R32 17%

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wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, not presently claimed, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist

5 essentially of:

R125 12-23%

carbon dioxide 8-20%

R1234ze 30-55%

R134a 5-25%

10 R227ea 3-10%

R32 12-23%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, not presently claimed, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist

15 essentially of:

R125 12-23%

carbon dioxide 8-20%

R1234ze 30-55%

20 R134a 5-25%

R32 12-23%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

An exemplary refrigerant composition, not presently claimed, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist

25 essentially of:

R125 13-21%

carbon dioxide 10-18%

R1234ze 30-45%

30 R134a 8-20%

R32 13-20%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

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An exemplary refrigerant composition, not presently claimed, which may be used to provide a retrofit replacement, extender or new equipment alternative for R410A, may consist essentially of:

R125	18%
5 carbon dioxide	16%
HFO-1234ze	31%
R134a	17%
R32	18%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

10

An exemplary refrigerant composition, not presently claimed, which may be used to provide a retrofit replacement, extender or new equipment alternative for R404A, R507 or R410A, may consist essentially of:

carbon dioxide	1-35%
15 R1234yf	15-45%
HFO-1234ze	15-50%

and optionally, R32, R125, R134a and R227ea or mixtures thereof, wherein the percentages of the components, including any optional components, are by mass, and are selected from the ranges quoted to total 100%.

20

Although the above blends described as top-up blends for existing R404A, R507 and R410A units, they can also be used as complete replacements in some instances, if necessary by modifying the units to enable them to be compatible with the specific physical properties of these blends.

25

The present invention enables the replacement of R404A, R507 and R410A, the most commonly used refrigerants in refrigeration and air conditioning equipment, providing a substantial reduction in GWP exceeding 80% with blends having a GWP between 1 and 500, and without any reduction in performance including energy efficiency and capacity.

30

Each blend that is the subject of this invention may be used in a thermal pump lubricated by an oxygen containing oil, for example POE or PAG, or by such oils mixed with a hydrocarbon lubricant up to 50%, for example, a mineral oil, alkyl benzene or polyalpha olefin.

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The invention is further described by means of examples but not in any limitative sense.

Example 1

- 5 Refrigerant compositions shown in Table 1 were assessed as replacements for R410A both in existing and new equipment.

Table 1

Refrigerant #	Chemical name	R410A	Blend 1	Blend 2
R125	pentafluoroethane	50	18.7	18
R134a	1,1,1,2-tetrafluoroethane	0	7.4	4.2
R744	carbon dioxide	0	10.3	10.9
R1234yf	2,3,3,3-tetrafluoroprop-1-ene	0	0	0
R227ea	1,1,1,3,3,3-hexafluoropropane	0	3	5.8
R1234ze(E)	E-1,3,3,3-tetrafluoroprop-1-ene	0	43.3	43.8
R32	difluoromethane	50	17.2	17.4
GWP		2088		

- A Toshiba reversible, split air conditioning unit, Model RAS-137SAV-E3, containing 0.8 kg R410A was used to cool a room and was monitored using temperature and pressure sensors positioned with a current meter to record the compressor electric power consumption. Data collected is shown in Table 2a. I(A) is the current in amps consumed by the compressor. T1 is the sensor located in the airstream leaving the evaporator. T2 is the sensor located within in the room. T3 is the sensor located in the airstream at the condenser outlet. T4 is the sensor located in the airstream entering the condenser. T5 is the sensor located on the refrigerant discharge from the compressor. P1 is the suction pressure of the compressor.

Table Refrigerant:

2a R410A

Mode: Cooling

T1(°C)	T2(°C)	T3(°C)	T4(°C)	T5(°C)	P1(barg)	I(A)	Time(min)
31	28.2	27.1	26.3	45.7	14.39	0.18	0
16.4	27.2	34.6	26.9	49.1	8.5	3.22	5
14.5	26.4	34	27.6	50.5	8.8	3.29	10
12.8	25.9	35.2	28.7	49.8	8.5	3.35	15
11.9	25.6	34.6	28.5	48.5	8.3	3.37	20
11	25.3	34.6	28.6	48.4	8	3.39	25
10.5	25.1	34.4	28.8	48.7	7.9	3.34	30

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The R410A was replaced by 0.8 kg of Blend 1 with the composition shown in Table 1 and the device again run to cool the room. The data collected is shown in Table 2b.

Table Refrigerant:
2b Blend 1

Mode: Cooling

T1(°C)	T2(°C)	T3(°C)	T4(°C)	T5(°C)	P1(barg)	I (A)	Time(min)
27.7	27.9	28.6	26.5	27.6	11.85	0	0
20	26.9	29.1	27.3	41.5	3.66	4	5
14.9	25.9	32.4	29.2	52.6	5.72	2.95	10
13.9	25.5	31.6	28.8	53.7	5.72	2.9	15
13.5	25.3	31.6	28.6	53.5	5.61	2.87	20
13.1	25.2	32.3	28.9	53.4	5.55	2.9	25
12.8	25	32.1	29.3	53.2	5.46	2.98	30
12.5	24.9	31.9	29	53.1	5.41	2.93	35

- Blend 1 was then removed from the device which was then recharged with 0.8 kg of
5 Blend 2. The device was again to cool the room and the data collected is shown in Table 2c.

Table Refrigerant:
2c Blend 2

Mode Cooling

T1(°C)	T2(°C)	T3(°C)	T4(°C)	T5(°C)	P1(barg)	I(A)	Time(min)
30	29.8	31.3	29.6	39.2	13.58	0	0
17.6	28.2	32.5	30	55.2	5.6	4.4	5
14.7	27.3	34.3	30.2	57.6	5.33	4.43	10
13.8	26.9	34.6	30.6	57.5	5.15	4.42	15
13.1	26.5	34.6	30.5	57.9	4.97	4.39	20
12.3	26.2	34.5	30.8	58.1	4.86	4.36	25
12	26	34.8	31.8	58.7	4.81	4.43	30

- The data shows that both Blend 1 and Blend 2 are effective retrofit replacements for R410 in a typical split air conditioning unit. Blend 1 is especially preferred because it has a
10 lower current consumption and thus a lower power consumption than R410A. In other words, Blend 1 is more efficient than R410A.

Example 2

- 15 Refrigerant compositions containing R1234ze(E) and R1234yf, shown in Table 2, were assessed as potential replacements for R410A in air conditioning units by modelling their performances using cycle simulations based on thermodynamic data generated by NIST's REFPROP v10. The results demonstrated that Blends 3 to 6 are acceptable replacements for R410A. Flow rates were similar so that the capillary expansion tubes, commonly found in

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smaller split air conditioning units, will continue to operate properly, thus avoiding costly modifications. The maximum operating pressures, which occurred in the condenser, were not more than 2 bar greater than that of R410A under comparable conditions, which is within the typical rating of a split air conditioning unit. The discharge temperatures were 15°C, or less, above that of R410A, avoiding thermal decomposition of lubricants or damage to other components. The GWPs of the blends were all less than 1000, so 1 tonne of a blend can replace more than 2 tonnes of R410A and remain within the EU imposed GWP cap.

Table 3

		R410A	Blend 3	Blend 4	Blend 5	Blend 6
R125		0.5	19	18	17	17
R134a		0	7	4	10	14
R744		0	10	11	11	11
R1234yf		0	0	0	22	41
R227ea		0	3	6	3	0
R1234zeE		0	44	44	22	0
R32		0.5	17	17	17	17
		2088	980	998	952	912
Input Parameters						
Cooling duty	kW	1	1	1	1	1
Condenser						
Midpoint	C	45	51	51	51	50
Subcool	kJ/kg	5	5	5	5	5
External air temperature	C	35	35	35	35	35
Evaporator						
Midpoint	C	7	15	15	15	15
Superheat	C	5	5	5	5	5
Compressor						
Isentropic efficiency		0.7	0.7	0.7	0.7	0.7
Electric motor efficiency		0.9	0.9	0.9	0.9	0.9
Volumetric efficiency		0.9	0.9	0.9	0.9	0.9
Output Results						
Condenser						
Pressure	bara	27.30	26.33	27.02	28.31	29.30
Dew point	C	45.06	60.29	60.76	59.19	57.11
Bubble point	C	44.94	41.71	41.24	42.81	42.89
Mid point	C	45	51	51	51	50
Glide	K	0.1	18.6	19.5	16.4	14.2
Exit temperature	C	39.9	36.7	36.2	37.8	37.9

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Heat out	kW	1.30	1.34	1.34	1.35	1.34
Evaporator						
Pressure	bara	9.93	7.88	8.08	8.69	9.45
Entry temperature	C	6.96	1.46	0.97	2.40	3.38
Dew point	C	7.04	16.54	17.03	15.60	14.62
Mid point	C	7	9	9	9	9
Glide	K	0.1	15.1	16.1	13.2	11.2
Exit temperature	C	12.0	21.5	22.0	20.6	19.6
Heat in	kW	1	1	1	1	1
Compressor						
Entry temperature to casing	C	12.0	21.5	22.0	20.6	19.6
Entry temperature to compressor	C	25.7	38.3	38.9	36.6	34.5
Discharge temperature	C	82.4	96.5	97.3	94.2	90.6
Compression ratio		2.7	3.3	3.3	3.3	3.1
Total power input	kW	0.30	0.34	0.34	0.35	0.34
Swept volume	m ³ /h	0.65	0.78	0.77	0.74	0.70
System						
Suction specific volume	kJ/m ³	4960	4135	4224	4356	4622
COP cooling		3.32	2.95	2.94	2.89	2.95
Mass flow rate	kg/s	0.00613	0.00622	0.00622	0.00655	0.00673

Example 3

Refrigerant composition Blend 7, shown in Table 4, was assessed as a replacement for R404A in the existing unit.

5

Table 4

Refrigerant #	Chemical name	R404A	Blend 7	
R125	Pentafluoroethane	44	11.4	
R134a	1,1,1,2-tetrafluoroethane	4	3.3	
R143a	1,1,1-trifluoroethane	52	0	
R744	carbon dioxide	0	10.4	
R1234yf	2,3,3,3-tetrafluoroprop-1-ene	0	0	
R227ea	1,1,1,3,3,3-hexafluoropropane	0	7.4	
R1234ze(E)	E-1,3,3,3-tetrafluoroprop-1-ene	0	56.1	
R32	Difluoromethane	0	11.4	
GWP		2088	733	

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Testing a composition in an actual unit may take several days to assess its performance. Initial screening of candidates is therefore typically carried out by using a computer program to model the Rankine refrigeration cycle, using as input the thermodynamic properties of the composition and important operating parameters, to generate key performance criteria as output. This type of program is widely employed throughout the refrigeration industry. The performances of R404A and Blend 7 were modelled under similar conditions typical of a commercial refrigeration freezer cabinet, with a cycle model, using NIST's REFPROP v10 providing thermodynamic data. Since Blend 7 has very wide temperature glides in the evaporator and condenser, the midpoint temperatures of the glide ranges were selected to be representative of the evaporating and condensing temperatures. The input and output parameters are summarised in Table 5.

Table 5

Input		R404A	Blend 7	
Cooling duty	kW	1	1	
Condenser				
Midpoint	C	35	35	
Subcool	kJ/kg	5	5	
Evaporator				
Midpoint	C	-35	-35	
Superheat	C	10	10	
Compressor				
Isentropic efficiency		0.7	0.7	
Electric motor efficiency		0.9	0.9	
Output				
Condenser				
Pressure	bara	16.1	16.4	
Dew point	C	35.2	47.5	
Bubble point	C	34.8	22.5	
Midpoint	C	35	35	
Glide	K	0.4	25.1	
Exit temperature	C	29.8	17.5	
Evaporator				
Pressure	bara	1.65	1.19	
Entry temperature	C	-35.2	-41.8	
Dew point	C	-34.8	-28.2	
Midpoint	C	-35	-35	

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Glide	K	0.49	13.5	
Exit temperature	C	-24.8	-18.2	
Heat in	kW	1	1	
Compressor				
Entry temperature to casing	C	-24.8	-18.2	
Entry temperature to compressor	C	-15.0	-4.3	
Discharge temperature	C	83.0	121.4	38.4
Compression ratio		9.8	13.8	
Total power input	kW	0.73	0.70	
Swept volume	m ³ /h	4.10	4.53	
System				
Suction specific volume	kJ/m ³	790.7	715.5	90.5
COP cooling		1.4	1.4	
Mass flow rate	kg/s	0.00898	0.00615	68.4

Although Blend 7 has a much lower GWP than R404A, and its maximum (discharge) pressure is acceptable as a retrofit for R404A, the model results indicated that the performance of Blend 7 was inferior to R404A in certain key respects.

5 The compressor discharge temperature is 38.4°C higher for Blend 7 than for R404A which would seriously reduce reliability and operating life of the compressor. The mass flow rate of Blend 7 is 68.4% lower than for R404A, so for a freezer, or other refrigeration unit with a fixed capillary tube expansion device, the flow rate of Blend 7 would be too large, and would potentially flood the evaporator, which may result in too high an evaporation temperature and also flooding of the evaporator which in turn could result in liquid returning to the compressor,
10 which may cause damage.

The very wide evaporator glide of 13.5 K resulted in the evaporator refrigerant exit temperature (-18.4°C) being above the maximum temperature needed to maintain frozen food below -18°C.

15 The very wide condenser glide of Blend 7 (25.1 K) resulted in a condenser exit temperature of 17.5°C compared to 29.9°C for R404A. On the basis that the exit temperature needed to be at least approximately 5 K above the ambient air temperature to ensure for adequate heat transfer from the refrigerant to the air, then R404A may need to be cooled by ambient air at 25°C and below, while Blend 7 would only work if the ambient temperature was below 12°C - an unrealistic value for a commercial freezer cabinet in a supermarket.

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The calculated suction cooling capacity of Blend 7 was only 68.4%. This indicated that R404A would not be able to maintain food in the required temperature range of -23°C to -18°C, especially at high ambient. The calculations predicted that Blend 7 could not be a retrofit replacement for R404A. Surprisingly, we have found that Blend 7 is a good retrofit for R404A in a real unit, contrary to what was predicted using the conventional calculations.

An AHT freezer display cabinet, Model Paris 250(-) type LE228, containing 0.276 kg R404A, was loaded with 182 kg of ice contained in 50 x 1.5 L, 1 x 3 L and 13 x 8 L plastic bottles to simulate typical freezer contents. The freezer was run until it reached, and maintained, a steady temperature, as recorded by its in-built temperature sensor. The ambient air temperature, the compressor gas discharge temperature, the suction pressure, the discharge pressure, the suction gas temperature, just before the compressor, and the current draw by the unit were also measured. The results are recorded in Table 6 after the freezer had been operating for 29.7 hours.

The R404A was then replaced by a similar weight of Blend 7 and the results recorded after 29.8 hours of operation

Table 6

		R404A	Blend 7
Room temperature	°C	14.2	14.0
Refrigerant suction temperature	°C	16.8	17.0
Refrigerant discharge temperature	°C	68.9	71.1
Freezer temperature (unit thermostat)	°C	-25.5	-28.0
Temperature top of freezer	°C	-22.0	-21.2
Suction pressure	barg	-0.02	0.13
Discharge pressure	barg	11.8	14.1
Current draw	amp	2.39	2.66
Running time	hour	29.7	29.8

The results show that Blend 7 is able to maintain the freezer temperature at, or below, its design rating of -18 to -23°C achieved with R404A. The fact that Blend 7 maintained a lower temperature than R404A indicates that it has a better cooling capacity than R404A, and thus will be acceptable for high ambient temperatures.

Surprisingly, the discharge temperature of Blend 7 was only 2.2°C higher than that of R404A, in contrast to the much greater difference predicted from the model calculation.

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Although the current draw (a measure of the electrical power input) is about 11% higher for Blend 7, this is acceptable.

The operating period of 29.8 hours showed that Blend 7 had reached a steady state and there was no indication of malfunctioning that might be associated with a flooded evaporator problem.

Example 4

The performances of Blends 8 to 12, whose compositions are shown in Table 7, were modelled for a typical low temperature refrigeration system using a Rankine Cycle program with thermodynamic data generated by NIST's REFPROP v10. The performance of R404A is included for comparison. The results in Table 7 indicate that these novel blends are acceptable replacements for retrofitting in R404A equipment.

Table 7

		Blend 8	Blend 9	Blend 10	Blend 11	Blend 12	R404A
Component							
R125		0.11	0.13	0.12	0.14	0.14	0.44
R143a		0	0	0	0	0	0.52
R134a		0.03	0.03	0.05	0.03	0.05	0.04
carbon dioxide		0.11	0.11	0.09	0.11	0.11	0
R1234yf		0	0	0.3	0	0.48	0
R227ea		0.07	0.07	0.05	0.07	0.08	0
R1234ze		0.57	0.53	0.28	0.51	0	0
R32		0.11	0.13	0.11	0.14	0.14	0
GWP		701	777	690	816	872	3943
Results							
Input							
Cooling duty	kW	1	1	1	1	1	1
Condenser							
Midpoint	C	35	35	35	35	35	35
Subcool	K	5	5	5	5	5	5

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Evaporator							
Midpoint	C	-35	-35	-35	-35	-35	-35
Superheat	C	5	5	5	5	5	5
Compressor							
Isentropic efficiency		0.7	0.7	0.7	0.7	0.7	0.7
Electric motor efficiency		0.9	0.9	0.9	0.9	0.9	0.9
Volumetric efficiency		0.9	0.9	0.9	0.9	0.9	0.9
Output							
Condenser							
Pressure	bara	16.6	17.3	17.1	17.6	20.1	16.12
Dew point	C	47.9	47.4	45.3	47.1	44.5	35.2
Bubble point	C	22.1	22.6	24.7	22.9	25.5	34.8
Mid point	C	35	35	35	35	35	35.00
Glide	K	25.7	24.8	20.5	24.3	19.0	0.4
Exit temperature	C	17.1	17.6	19.7	17.9	20.5	29.8
Evaporator							
Pressure	bara	1.20	1.28	1.34	1.32	1.74	1.65
Entry temperature	C	-42.0	-42.1	-40.3	-42.1	-40.2	-35.2
Dew point	C	-28.0	-27.9	-29.7	-27.9	-29.8	-34.8
Mid point	C	-35	-35	-35	-35	-35	-35
Glide	K	13.93	14.20	10.63	14.26	10.48	0.5
Exit temperature	C	-23.0	-22.9	-24.7	-22.9	-24.8	-29.8
Compressor							
Entry temperature to casing	C	-23.0	-22.9	-24.7	-22.9	-24.8	-29.8
Entry temperature to compressor	C	-9.3	-9.0	-12.0	-8.9	-12.1	-20.2
Discharge temperature	C	116.2	117.8	106.2	118.5	107.5	77.4
Compression ratio		13.8	13.4	12.7	13.3	11.6	9.75
Total power input	kW	0.70	0.71	0.71	0.71	0.73	0.74
Swept volume	m ³ /h	4.49	4.26	4.27	4.16	3.49	4.15
System							
Suction specific volume	kJ/m ³	721	760	759	779	927	780
COP cooling		1.42	1.42	1.40	1.41	1.37	1.36
Mass flow rate	kg/s	0.00626	0.00623	0.00687	0.00622	0.00701	0.00933

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CLAIMS

1. A refrigerant composition consisting essentially of:

carbon dioxide 1-35%

5 an HFO selected from the group consisting of:

R1234yf and R1234ze(E) and mixtures thereof, 30-92%

R32 1-30%

R125 1-30%

R227ea 1-15%

10 R134a 0-15%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

2. A refrigerant composition, as claimed in claim 1, consisting essentially of:

carbon dioxide 5-20%

15 an HFO selected from the group consisting of:

R1234yf and R1234ze(E) and mixtures thereof, 30-92%

R32 5-30%

R125 5-30%

R227ea 1-15%

20 R134a 0-15%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

3. A refrigerant composition, as claimed in claim 1, consisting essentially of:

R125 6-23%

25 carbon dioxide 6-20%

R1234ze 55-68%

R227ea 2-15%

R32 6-20%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

30

4. A refrigerant composition, as claimed in claim 3, consisting essentially of:

R125 6-20%

carbon dioxide 6-18%

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R1234ze 55-67%

R227ea 3-15%

R32 7-20%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

5

5. A refrigerant composition, as claimed in claim 4, consisting essentially of:

R125 9.5%

carbon dioxide 8%

R1234ze 65%

10 R227ea 8%

R32 9.5%

wherein the percentages are by mass.

15 6. A refrigerant composition, as claimed in claim 1, consisting essentially of one of the following compositions:

(a)

R125 9.5%

carbon dioxide 9%

R1234ze 57%

20 R227ea 15%

R32 9.5%

wherein the percentages are by mass.

(b)

25 R125 9.5%

carbon dioxide 9%

R1234ze 58%

R227ea 14%

R32 9.5%

30 wherein the percentages are by mass.

(c)

R125 19%

carbon dioxide 16%

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R1234ze 41%

R227ea 5%

R32 19%

wherein the percentages are by mass.

5

7. A refrigerant composition, as claimed in claim 1, consisting essentially of:

R125 12-23%

carbon dioxide 8-20%

R1234ze 35-55%

10 R227ea 3-10%

R32 12-23%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

8. A refrigerant composition, as claimed in claim 1, consisting essentially of one of the following compositions:

15

(a)

R125 9.5%

carbon dioxide 9%

R1234ze 58%

20 R227ea 7%

R32 9.5%

R134a 7%

wherein the percentages are by mass.

25 (b)

R125 11%

carbon dioxide 11%

R1234ze 57%

R227ea 7%

30 R32 11%

R134a 3%

wherein the percentages are by mass.

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(c)

R125 18%

carbon dioxide 11%

R1234ze 44%

5 R227ea 6%

R32 17%

R134a 4%

wherein the percentages are by mass.

10 (d)

R125 11%

carbon dioxide 11%

R1234ze 55%

R227ea 7%

15 R32 11%

R134a 5%

wherein the percentages are by mass.

(e)

20 R125 13%

carbon dioxide 11%

R1234ze 53%

R227ea 7%

R32 13%

25 R134a 3%

wherein the percentages are by mass.

(f)

R125 13%

30 carbon dioxide 11%

R1234ze 55%

R227ea 7%

R32 13%

R134a 1%

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wherein the percentages are by mass.

(g)

R125 14%

5 carbon dioxide 11%

R1234ze 51%

R227ea 7%

R32 14%

R134a 3%

10 wherein the percentages are by mass.

(h)

R125 14%

carbon dioxide 11%

15 R1234ze 55%

R227ea 7%

R32 13%

wherein the percentages are by mass.

20 (i)

R125 10.5%

carbon dioxide 11%

R1234ze 57%

R227ea 7%

25 R32 10.5%

R134a 4%

wherein the percentages are by mass.

(j)

30 R125 10.5%

carbon dioxide 11%

R1234ze 58%

R227ea 7%

R32 10.5%

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R134a 3%

wherein the percentages are by mass.

(k)

5 R125 11.5%

carbon dioxide 10%

R1234ze 57%

R227ea 7%

R32 11.5%

10 R134a 3%

wherein the percentages are by mass.

(l)

R125 11.5%

15 carbon dioxide 10%

R1234ze 56%

R227ea 8%

R32 11.5%

R134a 3%

20 wherein the percentages are by mass.

9. A refrigerant composition, as claimed in claim 1, consisting essentially of one of the following compositions:

(a)

25 R125 19%

carbon dioxide 10%

R1234ze 44%

R227ea 3%

R32 17%

30 R134a 7%

wherein the percentages are by mass.

(b)

R125 18%

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carbon dioxide 11%

R1234ze 44%

R227ea 7%

R32 17%

5 R134a 3%

wherein the percentages are by mass.

(c)

R125 18%

carbon dioxide 11%

10 R1234ze 44%

R227ea 6%

R32 17%

R134a 4%

15 10. A refrigerant composition, as claimed in claim 1, consisting essentially of one of the following compositions:

(a)

R125 1-30%

carbon dioxide 1-30%

20 R1234yf 35-70%

R227ea 1-10%

R32 1-30%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

25 (b)

R125 5-30%

carbon dioxide 5-20%

R1234yf 35-70%

R227ea 4-10%

30 R32 5-30%

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11. A refrigerant composition, as claimed in claim 1, consisting essentially of:

R125	7-25%
carbon dioxide	7-20%
R1234yf	58-69%
5 R227ea	5-10%
R32	7-25%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

12. A refrigerant composition, as claimed in claim 1, consisting essentially of:

10 R125	9.5%
carbon dioxide	8%
R1234yf	65%
R227ea	8%
R32	9.5%

15 wherein the percentages are by mass.

13. A refrigerant composition, as claimed in claim 1, consisting essentially of:

R125	19%
carbon dioxide	16%
20 R1234yf	41%
R227ea	5%
R32	19%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

25 14. A refrigerant composition, as claimed in claim 1, consisting essentially of:

R125	19%
carbon dioxide	16%
R1234ze	20%
R1234yf	21%
30 R227ea	5%
R32	19%

wherein the percentages are by mass.

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15. A refrigerant composition consisting essentially of:

carbon dioxide 1-35%

an HFO selected from the group consisting of R1234yf, R1234ze(E) and

mixtures thereof, 30-95%

5 R32 1-30%

R125 1-30%

R134a 1-15%

R227ea 1-15%

wherein the percentages are by mass and are selected from the ranges quoted to total 100%.

10