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REFERENCIA: Expediente No. 06 – 96.953
TÍTULO: “COMPOSICION REFRIGERANTE”
SOLICITANTE: RPL HOLDINGS LIMITED
TRÁMITE: Respuesta a Concepto Técnico notificado mediante Oficio No. 17668 del 11 de noviembre de 2011.

JAIME EDUARDO DELGADO VILLEGAS, en mi condición de apoderado de la sociedad **RPL HOLDINGS LIMITED**, dentro del término legal, presento respuesta a Concepto Técnico notificado mediante Oficio No. 17668 del 11 de noviembre de 2011 y del cual se solicito prórroga.

1. DE LA SOLICITUD DE PATENTE.

- Título

El Examinador Técnico de Patentes objeto el título de la solicitud porque:

“El título no corresponde con el objeto de la solicitud porque el término composición refrigerante es ambiguo y amplio y no determina adecuadamente las mezclas o combinaciones de refrigerantes utilizados en la solicitud. Se sugiere al solicitante incluir en el título los nombres de los refrigerantes utilizados y los componentes de los hidrocarburos que componen las combinaciones refrigerantes definidas en la solicitud.”

R/: Nuestro poderdante se permite modificar el título de la invención de acuerdo a lo sugerido por el Examinador, como sigue:

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**Nuevo Título: COMPOSICION REFRIGERANTE DE UN
HIDROFLUOROCARBURU SELECCIONADO ENTRE
R134a, R125, R143a y R227ea Y UN HIDROCARBURU
SELECCIONADO DE UNA MEZCLA DE ISOPENTANO,
BUTANO E ISOBUTANO.**

**Non flamable
- Reivindicaciones**

El Examinador Técnico de Patentes objeto el Capítulo Reivindicatorio porque:

“El capítulo reivindicatorio presenta características esenciales de las composiciones de refrigerantes e hidrocarburos presentes en la invención que pueden ser determinados en una sola reivindicación por medio del uso de rangos y/o valores específicos que determinen el campo de la invención y las características fundamentales del proceso definido en la solicitud. Se sugiere al solicitante definir dichos rangos para determinar claramente los rangos de composición de hidrocarburos, composiciones formuladas en el equilibrio para mezclas líquido vapor y mezclas de vapor, composiciones de refrigerantes y de hidrocarburos en las composiciones refrigerantes deseadas por la invención.

“Se sugiere al solicitante hacer las aclaraciones correspondientes”.

R/: De acuerdo a las sugerencias del Examinador Técnico de Patentes nuestro poderdante procedió a modificar el capítulo reivindicatorio, además, teniendo en cuenta el análisis de novedad y nivel inventivo que más adelante se describe.

Por lo tanto, pone a consideración de su Despacho el **NUEVO CAPITULO REIVINDICATORIO** (ver **ANEXO 1**) de la invención, el cual comprende doce (12) reivindicaciones en dos folios, que cumplen con el requisito de claridad exigido por el art. 30 de la Decisión 486 del Acuerdo de la Comisión de la Comunidad Andina.

2. DEL ANÁLISIS DE PATENTABILIDAD.

Novedad.

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De acuerdo al análisis del examen técnico, el Examinador concluye que la novedad se ve afectada por el documento **D1 (US 6629419)**, donde expresa:

*“Tales composiciones refrigerantes evaluadas en el contenido de la reivindicación 1, carecen de novedad ya que habían sido divulgadas en el documento **D1** y en combinación con los hidrocarburos seleccionados del grupo en mención carecen de novedad y no pueden hacer parte de dicha reivindicación”.*

*“En consecuencia, la reivindicación 1 no tiene novedad, según lo divulgado en el documento **D1**.”*

Las reivindicaciones dependientes, 32 a 37 y 40 a 43 no mencionan alguna característica que hagan nueva a la composición refrigerante de la reivindicación 1.”

Nivel Inventivo.

El Examinador objeta el nivel inventivo para las reivindicaciones 1 a 44 con el documento **D1 (US 6629419)** y el documento **D2 (EP 0779352)** porque:

“Sin embargo, la utilización del refrigerante R-227 es para disminuir la inflamabilidad de la composición refrigerante y la afectación de la misma a la capa de ozono ya está divulgada en el documento D2 (página 9, renglón 43, página 10, renglones 1-32), que se refiere a una composición de refrigerante terciaria producida por las combinaciones entre los compuestos R-134^a, R-227ea, R-125 y entre materiales de hidrocarburos seleccionados de la familia que comprende butano, metano, Butil – butano, isopentano, n-Pentano y ciclopentano (Columna 2, renglones 64 a 67)”.

“En consecuencia, la persona normalmente versada en la materia, incluiría el refrigerante R-227ea de D2 en la composición de D1 para llegar así al objeto de la reivindicación 1 de la solicitud. Por lo cual se considera obvia”.

R/: Con relación a las objeciones del Examinador de Patentes con respecto a la **novedad y nivel inventivo** de la invención, el solicitante desea resaltar lo siguiente:



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Es un requisito para una **composición refrigerante que sea segura** para su uso en la práctica, **que no sea inflamable**. Esto no es una prueba sencilla, sino que requiere llevar a cabo experimentos complejos. La composición debe ser no inflamable bajo todas las condiciones. Éstas incluyen la fuga de vapor desde el aparato de refrigeración y también el líquido o el vapor que permanecen en la parte de atrás del aparato después de producirse una fuga. Además del requisito de no inflamabilidad, **debe estar presente una cantidad suficiente de hidrocarburo para permitir que el aceite lubricante se disuelva y circule** alrededor del sistema de refrigeración.

Aunque existen muchas publicaciones anteriores que intentan proporcionar refrigerantes adecuados, muy pocos de ellos cumplirán los requisitos de no inflamabilidad y solubilidad en aceite. Además, las propiedades termodinámicas de la mezcla deben ser satisfactorias. Si se usa un refrigerante nuevo para reemplazar una composición refrigerante de **CFC**, entonces las propiedades termodinámicas del reemplazo deben ser similares a las del refrigerante que se está reemplazando. Los requisitos se describen en las **normas de ASHRAE (ver ANEXO 2)**.

La **Reivindicación 1 modificada** cubre composiciones adecuadas para su uso para reemplazar **R22** en un equipo de refrigeración.

La composición de la **Reivindicación 2** ha recibido la aprobación por la norma y nuestro cliente la denomina **RS44**.

Los requisitos para una composición refrigerante exitosa son complejos. Las **normas de ASHRAE imponen estándares** muy estrictos sobre el **requisito de no inflamabilidad**.

Los requisitos generales para un refrigerante son que la mezcla gaseosa debe tener un punto de ebullición por debajo de 0 °C dentro de un intervalo de trabajo

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adecuado. Los requisitos de presión del aparato dependen del punto de ebullición del refrigerante: Un refrigerante de reemplazo, por ejemplo, para reemplazar un **CFC**, debe tener un punto de ebullición o un intervalo de ebullición que concuerde con el del compuesto que se va a reemplazar.

Preferentemente, un **refrigerante es no tóxico y debe ser no corrosivo**. El **compuesto también debe ser estable durante la vida útil del equipo**.

Un refrigerante de reemplazo debe tener una capacidad calorífica similar a la capacidad calorífica del compuesto tal como un **CFC** que se va a reemplazar. Un refrigerante de reemplazo exitoso debe ser compatible con el lubricante usado en el equipo existente.

El requisito de resistencia a la inflamabilidad lo establecen las normas de **ASHRAE**. En EE. UU., las normas de construcción requieren un nivel A1 de **ASHRAE** de resistencia a la llama. Esto establece el estándar internacional para composiciones refrigerantes aceptables.

La información sobre la inflamabilidad de **RS44** se describe en la sección 5.1 al final del informe. Las pruebas de inflamabilidad se realizan sobre las composiciones fabricadas y con los peores fraccionamientos de la mezcla refrigerante original. Se hace énfasis en la identificación del desplazamiento del intervalo de inflamabilidad del peor refrigerante fabricado debido a cualquier cambio en la composición general posterior a una fuga isotérmica (fraccionamiento) desde el sistema de refrigeración. Se realizan una serie de pruebas de inflamabilidad en las mezclas peor fabricadas y con peor fraccionamiento. Los procedimientos se describen en el informe.

Las tolerancias de la formulación se describen en la sección 4.1 del informe. Inicialmente, podría pensarse que la selección de una formulación

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comercialmente exitosa es un asunto evidente. No obstante, existen muchos factores que deben tenerse en cuenta y no es cierto, en modo alguno, que pudiera lograrse una formulación exitosa.

La identificación de una formulación adecuada no es un asunto sencillo, como parece sugerir el Examinador.

Las **variaciones en las proporciones de HFA** afectan a las propiedades termodinámicas de toda la composición. Las proporciones de los **HFA** se seleccionan para que cumplan los requisitos particulares de las aplicaciones específicas, por ejemplo, el tipo de unidad de refrigeración o de aire acondicionado. La selección de la mezcla de **HFA** no tiene un efecto principal en la inflamabilidad. El **HFA 134a** es esencialmente no inflamable. Sin embargo, el **HFA 125** es un retardante del fuego inherente y se vende por separado como un retardante del fuego. El **HFA 125** también se usa para contribuir a las propiedades termodinámicas de la mezcla refrigerante.

Los hidrocarburos son inflamables.

Los hidrocarburos con puntos de ebullición mayores contribuyen a la inflamabilidad en la fase líquida, en la que pueden acumularse durante la fuga. Por ejemplo, el isopentano tiene un punto de ebullición de 28 °C. Los hidrocarburos con puntos de ebullición mayores también tienen mejores propiedades de solubilidad en lubricantes tradicionales tales como aceites minerales y alquilbenceno. Sin embargo, el uso de proporciones mayores de hidrocarburos con mayor punto de ebullición incrementa el riesgo de incendio de la fase líquida.

Los hidrocarburos de menor punto de ebullición, por ejemplo, butano con un punto de ebullición de -5 °C o isopentano con un punto de ebullición de -11 °C,



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contribuyen al riesgo de incendio en la fase vapor. Los hidrocarburos con menor punto de ebullición tienen menos propiedades de buena solubilidad para lubricantes. En consecuencia, existía la necesidad de producir una composición equilibrada. No es evidente en ninguna situación particular que pueda lograrse que una composición para el reemplazo de un refrigerante de **CFC** particular cumpla los estrictos requisitos de las normas de **ASHRAE**. En otras palabras, una persona que quisiera desarrollar una formulación aceptable no sabría que existiera una formulación tal. Tampoco sabría por dónde empezar o qué cambios serían necesarios para alcanzar una formulación aceptable.

El simple reemplazo de un hidrocarburo con otro no proporcionaría la no inflamabilidad. El desarrollo de la composición **RS44** por el solicitante fue difícil. Tuvo que usarse un hidrocarburo de menor punto de ebullición, isobutano, para permitir el uso de una cantidad menor de pentano.

El solicitante llevó a cabo pruebas para determinar la inflamabilidad de diversas composiciones.

La composición de la tabla 9, mezcla 3 de nuestra patente de **US 6629419 (D1)**, es inflamable.

Mezcla A	%
R134a	92
R125	5
Isopentano	1
Butano	2

Esta composición se denomina mezcla A.

La mezcla siguiente se sometió a una prueba de inflamabilidad de acuerdo con el estándar 34 ASTM681 de **ASHRAE**.

Mezcla B	%
R134a	93,75

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R125	4
Isopentano	0,75
Butano	1,50

La cantidad y el tipo de los **HFC (R125 y R134a)** eran muy similares en las mezclas A y B, pero las cantidades de cada hidrocarburo en la mezcla B eran menores que en la mezcla A. Se descubrió que el límite inflamable más bajo de la mezcla B era del 11 % con ignición y se detectó una llama azul. Por lo tanto, dado que la mezcla A tiene un nivel más alto de hidrocarburos presentes pero una cantidad prácticamente igual de **HFC**, entonces cabría esperar que la mezcla A fuera inflamable de acuerdo con el estándar 34 de **ASHRAE**. En caso necesario, está disponible el informe de la prueba.

Debería reconocerse la presencia de una **actividad inventiva**. Cuando el solicitante decidió solicitar a **ASHRAE** un número de refrigerante y una clasificación de seguridad, su composición inicial para **RS-44** (un reemplazo de R22) era:

%	
R134a	50
R125	47
Isopentano	0,5
Butano	2,5

Nuestro cliente contrató los servicios de un laboratorio bien conocido en EE. UU. (y aceptado por **ASHRAE**), llamado **Safety Consulting Engineers Inc (SCE)**, ubicado en Illinois, para realizar las series de pruebas de inflamabilidad requeridas para cumplir el estándar 34 ATM 681 con el fin de obtener una clasificación de seguridad para la composición. Después de la realización inicial de algunas pruebas, el **SCE** descubrió que ésta composición estaba en el límite

de la inflamabilidad. Se adjunta el informe de actualización de **SCE** con fecha del 23 de octubre de 2001 para United Suppliers of America Inc. (el distribuidor del solicitante en EE. UU., en ese momento para nuestros refrigerantes) (ver **ANEXO 3**). Como resultado de éste trabajo se cambió la composición de esta formulación inicial de RS-44 con el fin de lograr una categoría de no inflamable de **ASHRAE** de 1.

La cantidad de isopentano se redujo desde el 0,5 % hasta el 0,3 % y el contenido en butano se incrementó desde el 2,5 % hasta el 2,7 %, permaneciendo inalterada la cantidad total de hidrocarburo en el 3 %. En junio de 2003, se realizó una solicitud de un número de **ASHRAE** con una clasificación de A1 (baja toxicidad y no inflamable) a **ASHRAE** para la composición siguiente:

	%
R134a	50
R125	48
Isopentano	0,3
Butano	2,70

El **SCE** llevó a cabo la gama completa de pruebas de inflamabilidad para esta mezcla de acuerdo con el estándar 34 ASTM 681 de **ASHRAE**, y se descubrió que esta mezcla era no inflamable bajo todas las condiciones de fraccionamiento de acuerdo con el estándar 34. Sin embargo, el comité de **ASHRAE** en junio de 2003 en Kansas City, **ASHRAE**, introdujo la modificación (e) en el estándar 34, que estipulaba que la cantidad de cualquier componente de una mezcla refrigerante no podía ser inferior a un mínimo del 0,6 % como se formula. Se conminó al solicitante a reformular la mezcla.

El incremento de la cantidad de isopentano en la mezcla hasta el 0,6 % incrementaría significativamente el porcentaje presente al final de la prueba de eliminación, es decir, cuando se haya retirado por una fuga la cantidad total de la



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composición refrigerante del cilindro hasta que esté casi vacío. Esto se debe a que el isopentano hierve a más temperatura (con un punto de ebullición de 28 °C) que el **R125** (PE - 48,1 °C) y el isobutano (-11,6 °C) y se forma en la fase líquida a medida que se vacía el cilindro. Sin embargo, el isopentano tiene un índice de solubilidad que es cuatro veces el del butano, de forma que puede obtenerse un grado de miscibilidad mayor de la composición refrigerante con aceite mineral que con butano o isobutano, es decir, puede usarse un porcentaje menor de isopentano en comparación con butano o isobutano para lograr el mismo grado de solubilidad con el lubricante. Esta posición puede ilustrarse como sigue:

%	Mezcla C	Mezcla D
R134a	47	47
R125	50	50
Isopentano	0,30	0,6
Butano	2,70	1,5
Índice de solubilidad del hidrocarburo	3,90	3,9

La mezcla C es, por supuesto, la mezcla que se presentó ante **ASHRAE** para un número de refrigerante en junio de 2003. La mezcla D tiene la misma solubilidad teórica con aceite mineral que la mezcla C, pero tiene un contenido en hidrocarburos considerablemente menor.

A partir de las pruebas de **SCE**, se concluyó que simplemente incrementando la cantidad de isopentano de la mezcla hasta el 0,6 %, pero sin alterar la cantidad y el tipo de otro hidrocarburo presente (butano), la composición resultante sería inflamable bajo el estándar 34. También se concluyó que, añadiendo isobutano a la mezcla, pasaría rápidamente a la fase vapor, dejando una cantidad menor de hidrocarburo presente total. Esto es esencial para lograr la no inflamabilidad de la composición debido a la formación del isopentano de alto punto de ebullición hacia el final de la prueba de inflamabilidad. La cantidad mayor de isobutano

presente en la fase vapor al comienzo de la prueba de eliminación se cuantifica mediante la cantidad proporcionalmente mayor del **R125** de ebullición baja y retardante del fuego presente (y, en menor medida, **R134a**, que no es inflamable), mientras que la cantidad de butano puede reducirse debido al alto índice de solubilidad en aceite del isopentano presente incrementado.

Como consecuencia, se presentó la mezcla revisada siguiente a **ASHRAE** en junio de 2005 y recibió el número de refrigerante de **R424A** con una clasificación de seguridad de A1.

%

R134a	47,0
R125	50,5
Isopentano	0,6
Butano	1,0
Isobutano	0,9

Esta mezcla tiene un contenido en hidrocarburos total del 2,5 %, pero, cuando se tiene en cuenta el índice de solubilidad mayor del isopentano, la cantidad real de hidrocarburo se incrementa hasta el 4,3 %.

Con la explicación anterior, se establece claramente la presencia de una **actividad inventiva** para la solicitud de patente de invención de nuestro poderdante, y **NO puede afirmarse** que la identificación de la composición reivindicada fue una simple cuestión de elección.

Se adjunta una copia del informe de **ASHRAE** al que se hace referencia, junto con una copia de la patente concedida **EP 1765953** (ver **ANEXO 4**) para la misma invención de nuestro poderdante.

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Estas razones nos permiten afirmar que la **presente solicitud de patente de invención**, tal como ha sido definida en el nuevo pliego reivindicatorio no solamente es **NUEVA**, pues no ha sido descrita con anterioridad, sino que presenta **ALTURA INVENTIVA**, ya que no se desprende de forma evidente del estado de la técnica. Nótese que la tecnología descrita en la presente solicitud presenta enormes ventajas a la hora de ser utilizada para la obtención de Composiciones refrigerantes.

Por lo tanto, queda claramente demostrado que existen diferencias sustanciales entre los documentos **D1 y D2** con la **Composición Refrigerante** que se desea proteger en la presente solicitud de patente de invención de nuestro poderdante; para lo cual pone a consideración del Examinador Técnico de Patentes un **NUEVO CAPÍTULO REIVINDICATORIO** el cual incluye **doce Reivindicaciones (12)** que cumple con los requisitos de **NOVEDAD, NIVEL INVENTIVO Y APLICACIÓN INDUSTRIAL** exigidos por la Decisión 486 del Acuerdo de la Comisión de la Comunidad Andina; además, estamos dando respuesta al Concepto Técnico notificado mediante Oficio No. 17668 del 11 de noviembre de 2011.

Por lo anterior, solicito respetuosamente se proceda a **CONCEDER** la Patente de Invención titulada: **"COMPOSICION REFRIGERANTE DE UN HIDROFLUOROCARBURRO SELECCIONADO ENTRE R134a, R125, R143a y R227ea Y UN HIDROCARBURO SELECCIONADO DE UNA MEZCLA DE ISOPENTANO, BUTANO E ISOBUTANO"** a nombre de la sociedad **RPL HOLDINGS LIMITED**.

Atentamente,

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Acciones Judiciales – Administrativas
Derecho Comercial – Industrial
Asesoría – Contratos – Otros
Corresponsalia a Nivel Mundial

MDE



Mario Delgado Echeverry e Hijos Ltda.

Abogados Consultores – Marcas y Patentes

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Miembros ACPI – ASIPI - AIPPI



JAIME EDUARDO DELGADO VILLEGAS
C.C. No. 19.270.955 Bogotá
T.P. No. 43.308 C.S.J.

Anexos:

Anexo 1 Nuevas Reivindicaciones.

Anexo 2 Norma ASHRAE RS44

Anexo 3 SCE test results 2 5% butane 0 5% iso 23 oct.2002 y traducción

Anexo 4 EP 1765953

NUEVAS REIVINDICACIONES

1. Una composición refrigerante de un hidrofluorocarburo seleccionado entre R134a, R125, R143a y R227ea y un hidrocarburo seleccionado de una mezcla de isopentano, butano e isobutano, **CARACTERIZADA PORQUE** esta constituida en peso por:

R134a	de	53,2	a	39%
R125	de	45	a	55%
isopentano	de	0,6	a	1%
butano	de	0,6	a	3%
isobutano	de	0,6	a	2%

2. Una composición refrigerante de la Reivindicación 1, **CARACTERIZADA PORQUE** está constituida en peso por:

R134a	47,5%
R125	50,0%
isopentano	0,6%
butano	1,0%
isobutano	0,9%

3. Una composición refrigerante de acuerdo con cualquier Reivindicación precedente, **CARACTERIZADA PORQUE** la composición es no inflamable cuando se encuentra completamente en la fase vapor; y
siendo la composición tal que cuando se encuentra en un recipiente con vapor y líquido presentes, ni la fase vapor ni la fase líquida es inflamable; y
en la que en cualquier momento durante una fuga desde un espacio de la fase vapor en un recipiente ni la fase líquida ni la fase vapor es inflamable.

4. Una composición refrigerante de acuerdo con cualquier Reivindicación precedente, **CARACTERIZADA PORQUE** la proporción del hidrocarburo a hidrofluorocarburo en la fase vapor no difiere de la proporción equivalente en la fase líquida en más del 40% en equilibrio a 25° C.
5. Una composición refrigerante de la Reivindicación 4, **CARACTERIZADA PORQUE** la proporción no difiere en más del 30%.
6. Una composición refrigerante de la Reivindicación 4, **CARACTERIZADA PORQUE** la proporción no difiere en más del 20%.
7. Una composición refrigerante de acuerdo con cualquier Reivindicación precedente, **CARACTERIZADA PORQUE** la proporción de hidrocarburo a hidrofluorocarburo en la fase vapor no difiere de la composición formulada en más del 40% en equilibrio a 25° C.
8. Una composición refrigerante de acuerdo con la Reivindicación 7, **CARACTERIZADA PORQUE** la proporción no difiere en más del 30%.
9. Una composición refrigerante de acuerdo con la Reivindicación 8, **CARACTERIZADA PORQUE** la proporción no difiere en más del 20%.
10. Una composición refrigerante de acuerdo con cualquier Reivindicación precedente, **CARACTERIZADA PORQUE** durante una fuga desde el espacio de la fase vapor o espacio de fase

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líquida de un recipiente, la proporción de hidrocarburo a hidrofluorocarburo bien en la fase vapor o bien en la fase líquida no difiere de la composición formulada en más del 40% en equilibrio a 25° C.

11. Una composición refrigerante de acuerdo con la Reivindicación 10, **CARACTERIZADA PORQUE** la proporción no difiere en más del 40%.
12. Una composición refrigerante de acuerdo con la Reivindicación 11, **CARACTERIZADA PORQUE** la proporción no difiere en más del 20%.

23 October, 2002

Dan Etzold
United Suppliers of America, Inc.
228 Burnett Ave.
Maplewood, NJ 07040

**Update on the depletion test results for the blend
R125/R134a/R600/I-CP 5 (0.5, 0.47, 0.025, 0.005)**

SCE Inc. has completed first depletion test for the blend R125/R134a/R600/I-CP5. The newest version of computer depletion simulation programs REFLEAK AND REFPROP (ver 6 and 7) from NIST do not have in their component database an isopentane (I-CP5), so they could not be used to simulate the process.

An older version of this programs (DOS based ver. 5) included isopentane and therefore was used for preliminary assessment of the conditions at which a worst case fractionated formulation WCFF would occur.

Multiple computer simulation of the vapor phase leakage were performed for different fills (15% or 90% of tank volume) and temperatures. The starting point for the simulations was either WCF1 (0.49, 0.48, 0.025, 0.005) or WCF2 (0.51, 0.46, 0.025, 0.005).

The highest content of flammable components at the end of the depletion simulation occurred when starting with WCF2 and running the simulation at 23°C with the tank 90% filled. Therefore these conditions were chosen to run the depletion test.

The results of the test are shown on the attached charts. The solid lines refer to computer simulation, the points refer to the test results. The first chart shows all four components, the second shows only two components for clarity.

A significant difference between prediction and test was noted for butane. The predicted value for R600 at 95% weight loss was 7%, the test yield 1.6%. The butane also exhibits a different trend then the computer predicted.

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We didn't perform a full flammability test required by Ashrae to establish LFL of mixture remaining in tank, but we have checked one point for flammability. At ~96% of weight loss the mixture from the tank was put into a flammability test chamber at the concentration of ~11 % volume and ignited with a spark.

The flame didn't propagate throughout the flask, but a localized flamefront moving upward was noted.

Conclusions

1. The use of computer simulation to predict results of the fractionation can not be justified because the test results for butane do not confirm the computer predictions.
2. The mixture remaining in the tank at the end of depletion maybe flammable, as the one point test showed some borderline flammability.
3. Because the computer simulation is not justified, all the experimental depletion tests proposed would have to be performed to establish worst case fractionated formulation WCFF.

If you have any questions or you need more information, please call us at 847 925 8100.

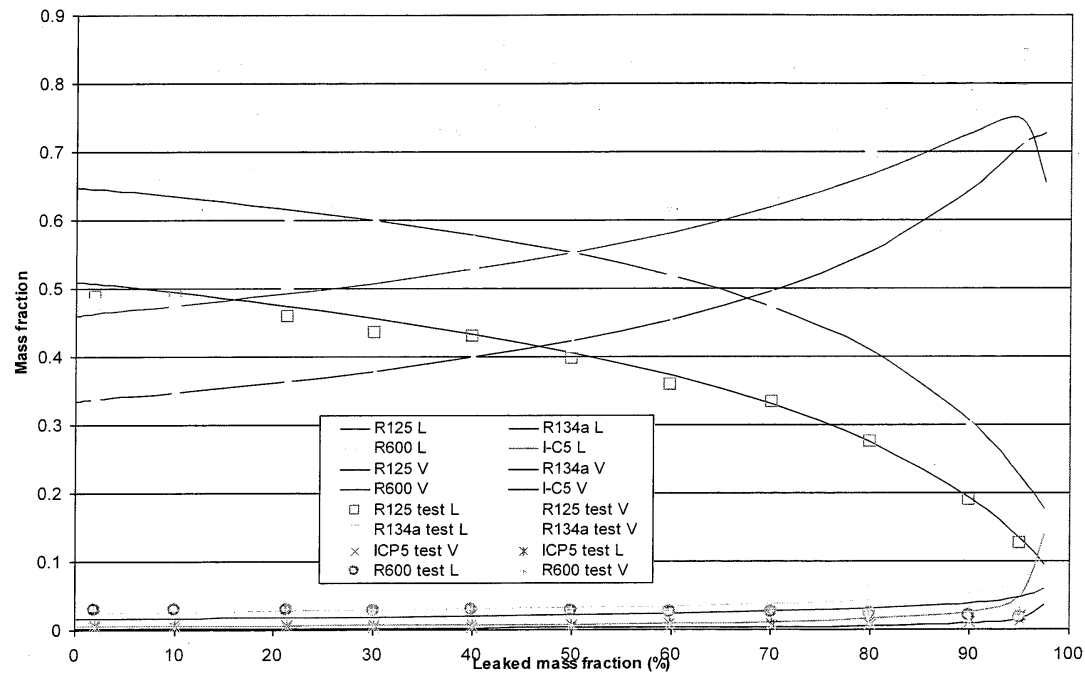
Regards,

Andrew Kusmierz

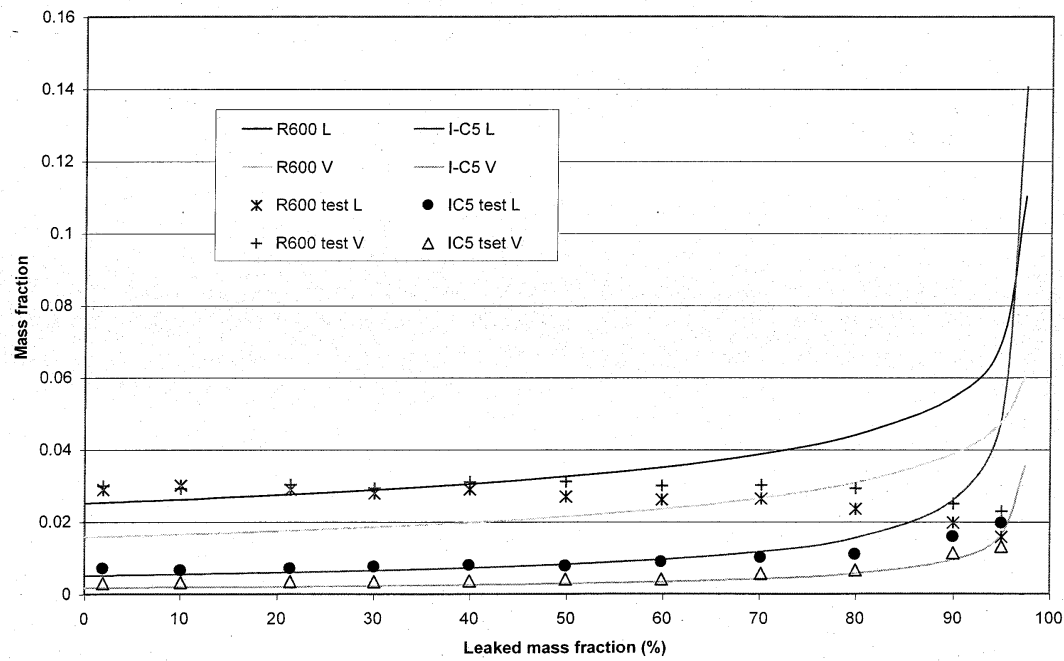
Abdollah Kashani

SCE, Inc.

Fractionation simulation and test results for
R125/R134a/R600/I-CP5 @ 23°C and 90% fill



Fractionation simulation and test results for
R125/R134a/R600/I-CP5 @ 23°C and 90% fill (only R600 and I-CP5 shown)



23 de octubre de 2002

Dan Etzold
United Suppliers of America, Inc.
228 Burnett Ave.
Maplewood, NJ 07040

**Actualización sobre los resultados de las pruebas de agotamiento para la mezcla
R125/R134a/R600/I-CP 5 (0,5, 0,47, 0,025, 0,005)**

SCE Inc. ha completado la primera prueba de agotamiento para la mezcla R125/R134a/R600/I-CP 5. Las últimas versiones de los programas de simulación de agotamiento REFLEAK y REFPROP (versiones 6 y 7) de NIST no tienen en su base de datos de componentes un isopentano (I-CP5), por lo que no pudieron usarse para simular el proceso.

Una versión anterior de estos programas (versión 5, basada en DOS) incluía isopentano y, por lo tanto, se usó para la evaluación preliminar de las condiciones en las que se produciría el peor caso de formulación fraccionada (WCFF por sus siglas en inglés).

Se realizaron múltiples simulaciones por ordenador de las fugas de la fase gaseosa para diferentes cargas (15 % o 90 % del volumen del depósito) y temperaturas. El punto de partida para las simulaciones fue, o bien la WCF1 (0,49, 0,48, 0,025, 0,005) o bien la WCF2 (0,51, 0,46, 0,025, 0,005).

El mayor contenido de componentes inflamables al final de la simulación de agotamiento se produjo partiendo de la WCF2 y llevando a cabo la simulación a 23 °C con el depósito lleno al 90 %. Por lo tanto, se escogieron estas condiciones para llevar a cabo la prueba de agotamiento.

Los resultados de la prueba se muestran en las gráficas adjuntas. Las líneas continuas se refieren a la simulación por ordenador, los puntos se refieren a los resultados de la prueba. La primera gráfica muestra los cuatro componentes, la segunda muestra sólo dos componentes, en aras de la claridad.

Se observó para el butano una diferencia significativa entre la predicción y la prueba. El valor predicho para R600 al 95 % de pérdida de peso era del 7 %, la prueba proporcionó un 1,6 %. El butano también presenta una tendencia diferente de la predicha por ordenador.

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No realizamos una prueba de inflamabilidad completa requerida por la Ashrae para establecer el LII (LFL por sus siglas en inglés) de la mezcla que quedó en el depósito, pero hemos comprobado un punto para la inflamabilidad. Al ~96 % de pérdida de peso, la mezcla del depósito se dispuso en una cámara para pruebas de inflamabilidad a la concentración del ~11 % en volumen y se prendió con una chispa.

La llama no se propagó a través del matraz, pero se observó un frente de llama localizado que se movía hacia arriba.

Conclusiones

- 1 No puede justificarse el uso de la simulación por ordenador para predecir los resultados del fraccionamiento debido a que los resultados de la prueba para el butano no confirman las predicciones por ordenador.
- 2 La mezcla que queda en el depósito al final del agotamiento puede ser inflamable ya que la prueba de un punto mostró algo de inflamabilidad límite.
- 3 Debido a que la simulación por ordenador no está justificada, deberían realizarse todas las pruebas de agotamiento experimentales propuestas para establecer el peor caso de formulación fraccionada WCFF.

Si tienen alguna duda o necesitan más información, les rogamos se pongan en contacto con nosotros en el número 847 925 8100.

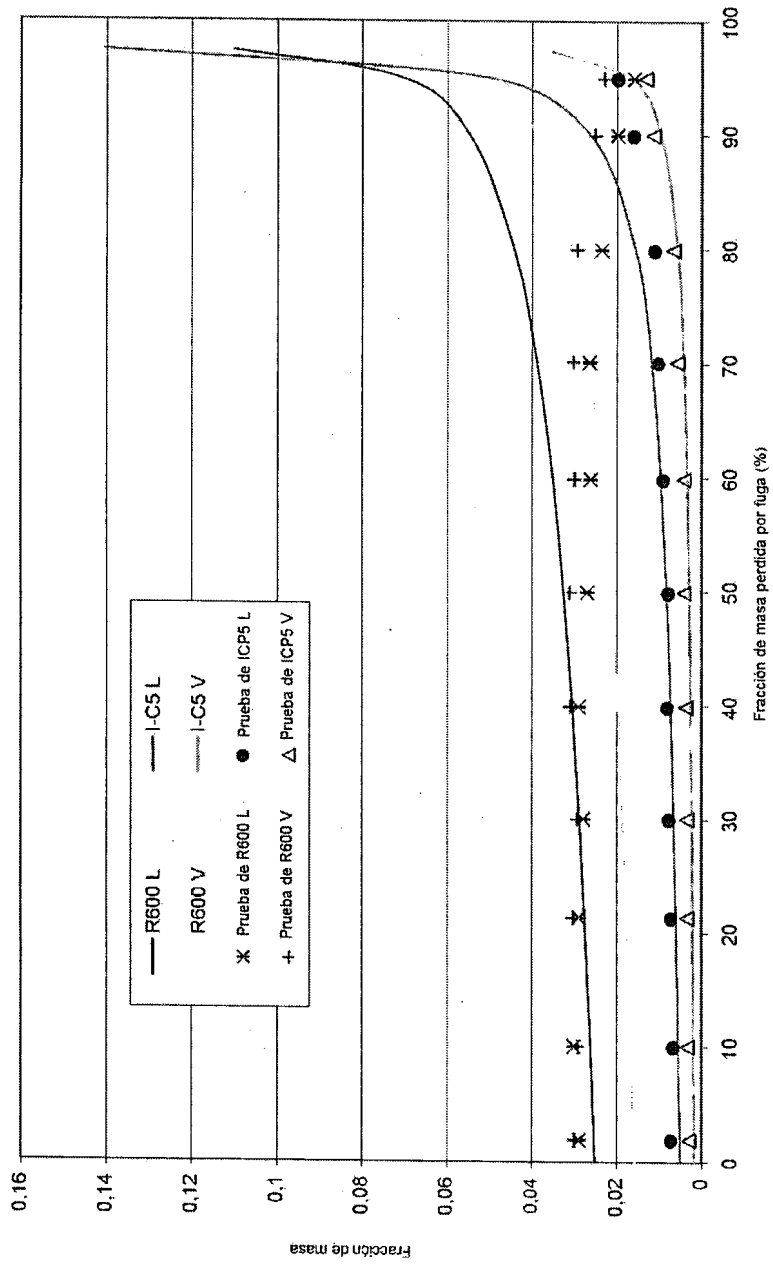
Atentamente,

Andrew Kusmierz

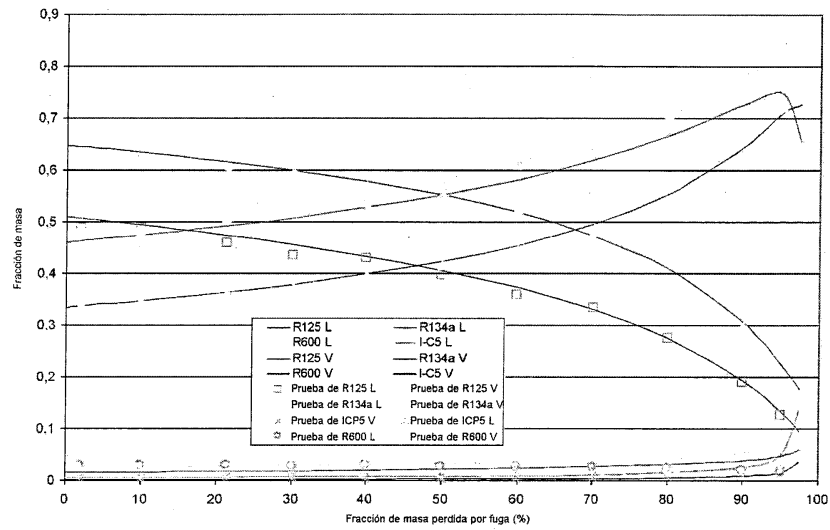
Abdollah Kashani

SCE, Inc.

Simulación de fraccionamiento y resultados de la prueba para
R125/R134a/R600/ICP5 a 23 °C y 90 % de carga (sólo se muestran R-600 e I-CP5)



Simulación de fraccionamiento y resultados de la prueba para
R125/R134a/R600/I-CP5 a 23 °C y 90 % de carga



USA UNITED SUPPLIERS OF AMERICA, INC.

SUBMISSION TO ASHRAE SSPC 34 COMMITTEE

**Request for Refrigerant Number Designation and Safety Classification
for
Refrigerant Blend R-125/134a/600a/600/601a (50.5, 47.0, 0.9, 1.0, 0.6)**

March 15, 2005

Submitted on behalf of
USA United Suppliers of America, Inc.
by
Safety Consulting Engineers, Inc.
Schaumburg, IL 60173
(847) 925 8100

Cover

1. Applicant:

USA United Suppliers of America, Inc.
303 Roosevelt Avenue
Spring Valley, NJ 10977
Phone # 800 270-3080
Fax # 877 774-5528
Attn: James Burke

2. Primary Contact:

Dan Etzold
USA United Suppliers of America, Inc.
303 Roosevelt Avenue
Spring Valley, NJ 10977
Phone # 800 270-3080
Fax # 877 774-5528
Voice mail # 800 992-0730
E-mail detzold@ptd.net

3. Refrigerant:

R-125/134a/600a/600/601a

4. Requested Actions:

Refrigerant Number	Composition (Weight %)	Safety Group	Composition Tolerances (%)	Remark
	R-125/134a/600a/600/601a (50.5, 47.0, 0.9, 1.0, 0.6)	A1	(±1.0, ±1.0, +0.1(-0.2), +0.1(-0.2), +0.1(-0.2))	Zeotrope

Administrative Information

Administrative Information

1. **Applicant Identification:**

- Applicant:

USA United Suppliers of America Inc.
303 Roosevelt Avenue
Spring Valley, NJ 10977
Phone # 800 270-3080
Fax # 877 774-5528

- Primary Contact

Dan Etzold
USA United Suppliers of America Inc.
303 Roosevelt Avenue
Spring Valley, NJ 10977
Phone # 800 270-3080
Fax # 877 774-5528
Voice mail # 800 992-0730
E-mail detzold@ptd.net

- Applicant's Interest:

USA United Suppliers of America, Inc. is the master distributor of the subject refrigerant originally developed by Refrigerant Solutions, Ltd., Cheshire, UK.

2. Data Certification

I/We certify that the information provided in this application (including its appendices) is true and accurate to the best of my/our knowledge and that no information that would affect classification of toxicity or flammability safety is being withheld. I/We further certify that I/we have reviewed ANSI/ASHRAE Standard 34-2004 (including all published addenda thereto) and that the information provided in this application is consistent with the requirements of that standard.

Applicant:
James R. Burke

Corporate Secretary
USA United Suppliers of America, Inc.

Date _____

Primary Contact:
Dan Etzold

Refrigerant Specialist
USA United Suppliers of America, Inc.

Date _____

3.

I/We understand that designations and safety classifications recommended for public review approval or publication are not assigned and may be revised or disapproved until actually published in an addendum or revision to Standard 34.

Applicant:
James R. Burke

Corporate Secretary
USA United Suppliers of America, Inc.

Date _____

Primary Contact:
Dan Etzold

Refrigerant Specialist
USA United Suppliers of America, Inc.

Date _____

Designation Information

Designation Information

1. Refrigerant Identification:

R-125/134a/600a/600/601a (50.5, 47.0, 0.9, 1.0, 0.6)
Refrigerant Blend
Zeotrope

2. Refrigerant Data:

A. Individual Component of R125/R134a/R600a/R600/R601a

Property	R125	R134a	R600a	R600	R601a
Chemical Name	pentafluoroethane	1,1,1,2-tetrafluoroethane	isobutane (2-methylpropane)	n-butane	isopentane (2-methylbutane)
Chemical Formula	CHF ₂ CF ₃	CH ₂ FCF ₃	CH ₃ (CH ₃)CHCH ₃	CH ₃ CH ₂ CH ₂ CH ₃	(CH ₃) ₂ CHCH ₂ CH ₃
Chemical Abstract Service Registry Number	354-33-6	811-97-2	78-28-5	106-97-8	78-78-4
Molecular Mass	120.02 g/mol	102.03 g/mol	58.12 g/mol	58.12 g/mol	72.15 g/mol
Freezing Point	-100.6°C (-149.1 °F)	-103.3 °C (-153.9)	-159.6°C (-255.28°F)	-138.3 °C (-216.9 °F)	-160.0 °C (-256.0 °F)
Normal Boiling Point	-48.1°C (-54.7 °F)	-26.1°C (-14.9°F)	-11.61°C (11.10°F)	-0.5°C (31.0°F)	28.0 °C (82.0 °F)
Saturated Vapor Pressure At 20°C(68°F)	1204.5 kPa	571.5 kPa	301.8 kPa	208.1 kPa	77.0 kPa
At 60°C(140°F)	3167.0 kPa	1682.0 kPa	868.3 kPa	639.0 kPa	273.0 kPa
Temperature at the Critical Point	66.2°C (151.1°F)	101.1°C (213.9°F)	134.7 °C (274.5 °F)	152 °C (305.6°F)	187.4 °C (369. 2 °F)

USA United Suppliers of America, Inc. Application to ASHRAE/ANSI Standard 34, March 07, 2005

Property	R125	R134a	R600a	R600	R601a
Specific Volume at the Critical Point	1.75 L/kg	1.95 L/kg	4.46 L/kg	4.38 L/kg	4.24 L/kg
Use and Typical Application Temperatures Evaporating Range Condensing Range	Blend component for alternatives like 402A, 402B, 404A, 407A, 407B, 407C, 407D, 408A, 410A, 410B, 507A. Sterilant, fire suppressant.	Domestic and commercial refrigeration, primary alternative for R12 and R500, blend component for 404A, 407A, 407B, 407C, 407D, 413A, 416A. Aerosol propellant. Evaporating temp typically -20 °C to +20 °C, condensing between 30 °C to 50 °C	Originally used for small refrigeration systems (1920-30) Now used as a blend component for refrigerants and aerosol propellants..	Blend component of alternatives to R12 and R500 (for example R416A). Primary uses as a fuel, aerosol propellant and a base material for solvents, rubbers, and plastics. Evaporating range -40 °C to 15 °C, condensing range 30 °C to 70 °C	Used only as a blend component to increase lubrication properties.

B. Refrigerant Blend of R125/134a/600a/600/601a

Property	Blend
(a) Formulation	R125/134a/600a/600/601a (50.5, 47.0, 0.9, 1.0, 0.6)
(b) Molecular Mass as Formulated	108.4 g/mol
(c) Molecular Mass of the Vapor at 60°C (140°F)	110.4 g/mol
(d) Temperature at 14.7 psia (101 kPa) Saturated liquid (Boiling Point) Saturated vapor (Dew point)	-39.1°C -33.3°C
(e) Maximum temperature glide At the normal boiling point At 20°C(68°F)	5.8°C 4.3°C
(f) Vapor Composition for the as formulated saturated liquid At normal boiling point At 20°C(68°F)	73.27, 25.22, 0.95, 0.48, 0.08 64.69, 33.76, 0.82, 0.57, 0.16
(g) Dew Point Vapor Pressure At 20°C(68°F) At 60°C(140°F)	752.9 kPa 2154.0 kPa
(h) Latent Heat of Vaporization At 60°C(140°F)	105.1 J/kg
(i) Specific Heat Ratio of Vapor At 60°C(140°F)	1.68
(j) Temperature at the Critical Point	87.5°C
(k) Specific Volume at the Critical Point	1.97 L/kg
(l) Pressure at the Critical Point	3845.3 kPa
(m) Heat of Combustion (calculated for nominal blend) (calculated for WCF)	2425.16 kJ/kg 2613.35 kJ/kg
(n) Use and Typical Application Temperatures Evaporating Range Condensing Range	R22 replacement -30°C to 15°C 20°C to 70°C
(m) Proposed composition tolerances for classification	R125=49.5-51.5 %wt. R134a=46.0-48.0 %wt. R600a=1.0-0.7 %wt. R600=1.1-0.8 %wt. R601a=0.7-0.4 %wt.
(o) Worst case formulation (WCF) of the blend	R125/134a/600a/600/601a (49.5, 47.7, 1.0, 1.1, 0.7)
(p) Worst case fractionated formulation (WCFF) of the blend WCFF1 WCFF2	R125/134a/600a/600/601a (14.37, 82.4, 0.31, 0.58, 2.34) (27.49, 69.1, 0.67, 0.98, 1.76)

NIST program Refprop 6.01 was used to calculate properties of the blend.

Toxicity Information

MSDS for the Blend and Individual Components

MSDS for the Blend R-125/134a/600a/600/601a

MSDS for R125

MSDS for R134a

MSDS for R600a (isobutane)

MSDS for R600 (butane)

MSDS for R601a (isopentane)

MSDS

Refrigerant Solutions Limited

8 Murieston Road

Hale

Altrincham

Cheshire, WA15 9ST

Tel: +44 (0) 161 926 9876

Fax: +44 (0) 161 926 9875

E-mail: rs@refsols.com

www.refsols.com

October 2001

PRODUCT SAFETY DATA SHEET

PRODUCT: RS-44

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND THE COMPANY/UNDERTAKING

1.1 Identification of the preparation: RS-44, liquefied refrigerant blend

1.2 Company

Refrigerant Solutions Limited
8 Murieston Road
Hale
Altrincham
Cheshire, WA15 9ST
Tel: +44 (0) 161 926 9876
Fax: +44 (0) 161 926 9875

USA Distribution:
USA United Suppliers of
America, Inc.
303 Roosevelt Avenue
Spring Valley, NJ 10977
Tel: 800 270-3080
Fax: 877 774-5528

13 Emergency telephone number (Outside USA) +44 (0) 161 926 9876
Emergency telephone number (USA) 800 270 3080

14 E-mail: rs@refsols.com
Web site: www.refsols.com

MSDS

PRODUCT SAFETY DATA SHEET

PRODUCT: RS-44

2. COMPOSITION/INFORMATION ON INGREDIENTS

Chemical Name	CAS-No	Weight %
Pentafluoroethane	354-33-6	50.5
1, 1, 1,2--tetrafluoroethane	811-97-2	47.0
Isobutane	78-28-5	0.9
Butane	106-97-8	1.0
Isopentane	78-78-4	0.6

3. HAZARDS IDENTIFICATION

Liquefied gas: May cause frostbite to skin and eyes.

4. FIRST-AID MEASURES

Eyes: If substance has got into the eyes immediately wash out with plenty of water for at least 15 minutes. Keep eye wide open while rinsing.

Skin: May cause frostbite. Wash frost-bitten area immediately with plenty of water. Do not remove clothing. Wash affected skin with warm water. If skin irritation persists, call a physician.

Inhalation: Move to fresh air in case of accidental inhalation of vapours. Oxygen or artificial respiration if needed. Do not apply artificial respiration if patient is breathing. Consult a physician after significant exposure. Do not give adrenaline or similar drugs.

Ingestion: Do not induce vomiting without medical advice. Call a physician immediately. Do not give drugs from adrenaline-ephedrine group.

General advice: Consult a physician for severe cases.

MSDS

PRODUCT SAFETY DATA SHEET

PRODUCT: RS-44

5. FIRE-FIGHTING MEASURES

5.1 Suitable extinguishing media:

The product itself does not burn. Extinguish with carbon dioxide, dry chemical, foam or water spray, as appropriate for surrounding area.

5.2 Extinguishing media which must not be used for safety reasons

None

5.3 Specific hazards:

Possibility of generating hazardous reactions during a fire due to the presence of F groups. Fire or intense heat may cause violent rupture of packages

5.4 Special protection equipment for fire fighters:

In the event of fire, wear self-contained breathing apparatus. Suitable protective clothing

5.5 Specific methods:

Standard procedure for chemical fires. In the event of fire, cool exposed containers with water spray.

6. ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions:

Use Personal protective equipment Evacuate personnel to safe areas. Ensure adequate ventilation. Avoid contact with skin, eyes and inhalation of vapour.

6.2 Methods for clearing up:

Shut off leaks if without risk. Let the liquid evaporate. Ensure adequate ventilation.

7. HANDLING AND STORAGE

7.1 Handling: Provide sufficient air exchange and/or exhaust in work rooms. Do not puncture or drop container.

7.2 Storage: Keep containers tightly closed in a cool, dry well-ventilated place away from direct sunlight. Keep away from heat and sources of ignition.

MSDS

PRODUCT SAFETY DATA SHEET

PRODUCT: RS-44

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

- 8.1 Engineering measures: Ensure adequate ventilation, especially in confined areas.
- 8.2 Personal protection equipment:
- Respiratory protection: In case of insufficient ventilation wear suitable respiratory equipment, preferably a compressed airline breathing apparatus.
 - Hand protection: Impervious gloves (butyl rubber).
 - Eye protection: Wear as appropriate: safety glasses, goggles. Wear face-shield and protective suit for abnormal processing problems.
 - Skin and body protection: Chemical resistant apron, long sleeved clothing, safety shoes.
- 8.3 Exposure limit: Occupational Exposure Limit 1000 ppm (TWA).

9. PHYSICAL AND CHEMICAL PROPERTIES

- 9.1 Appearance: Compressed liquefied gas
- 9.2 Colour: Colourless
- 9.3 Odour: Very faint ether-like
- 9.4 Boiling point/range: -39.1°C
- 9.5 Critical temperature: 87.5 °C
- 9.6 Critical pressure: 3845.3 kPa

MSDS

PRODUCT SAFETY DATA SHEET

PRODUCT: RS-44

Cont.		
9.7	Vapour pressure:	982.2 kPa at 25°C
9.8	Liquid density:	1173 kg/m ³ at 25°C
9.9	Water solubility:	Insoluble
9.10	Flash point:	Not applicable
9.11	Flammability:	Non-flammable
9.12	Explosion limit	Not applicable
9.13	Auto-ignition temperature:	Not determined

10. STABILITY AND REACTIVITY

10.1	Stability:	Stable at normal conditions. No decomposition if stored and applied as directed.
10.2	Conditions to avoid:	Fire/sources of heat.
10.3	Materials to avoid:	Strong oxidizing agents, alkali metals, alkaline earth metals, finely divided aluminum.
10.4	Hazardous decomposition products:	Hydrogen fluoride by thermal decomposition and hydrolysis.

11. TOXICOLOGICAL INFORMATION

11.1	Acute toxicity:	HFC 125 : LC 50 inhalation (Rat)/4h: >769,000 ppm HFC 134a: LC 50 inhalation (Rat)/4h: >359,300 ppm Isopentane: LC50 inhalation (Rat)/4h, 434,564 ppm Butane: LC50 inhalation (Rat)/4h, 272,000 ppm Isobutane: LC50 inhalation (Rat)/4h, 142,500 ppm
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MSDS

PRODUCT SAFETY DATA SHEET

PRODUCT: RS-44

Cont.

11.2 Irritation:

- Skin: slightly irritating, may cause frostbite
- Eyes: slightly irritating

12 ECOLOGICAL INFORMATION

Behaviour in the environment:

Mobility:

Product is volatile when not under pressure.

Persistence/degradability:

All the components decompose comparatively rapidly in the lower atmosphere and all have relatively short atmospheric lifetimes demonstrated below:

HFC 134a	14.6 years
HFC 125	32.6 years
Isopentane	approximately 10 years
Butane	approximately 10 years
Isobutane	approximately 10 years

Bioaccumulation:

Not bioaccumulable.

Destination of the product:

Effects on the aquatic environment:

Discharge of the product will enter the atmosphere. No long term aqueous contamination due to low solubility.

MSDS

PRODUCT SAFETY DATA SHEET

PRODUCT: RS-44

13. DISPOSAL CONSIDERATIONS

Waste treatment: Refrigerant Products Limited will take back product for reclamation provided RS-44 has not been mixed with any other products. If RS-44 is mixed with other refrigerants, the mixture can be destroyed by high temperature incineration in an approved facility capable of absorbing and neutralizing the by-products.

14. TRANSPORT INFORMATION

- 14.1 International regulations: UN number: 3163
- Rail/road (RID/ADR): Class: 2
Item number: 2A
Hazard identification number: 20
Labeling: 2
 - Sea (IMO/IMDG): Class: 2.2
Labeling: Gas comprime flammable
Not classified as a marine pollutant
 - Air (ICAO-IATA): Class: 2.2
Labeling: Non-flammable gas
- 14.2 United Kingdom: Rail/road. Substance Identification number: 3163
- 14.3 Note: Given the possible evolution of transport regulations for hazardous materials, it is recommended to check their validity

15 REGULATORY INFORMATION

Classification according to European Directive on classification of hazardous preparations 88/379/EEC. Not classified as dangerous. The product does not need to be labeled in accordance with EC directives.

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PRODUCT SAFETY DATA SHEET

PRODUCT: RS-44

Cont.

R-phrases: No R-phrases

S-phrases: S7/9 - Keep container tightly closed in a well-ventilated place
S24/25 - Avoid contact with skin and eyes
S47- Keep at temperature not exceeding 500C
S51- Use only in well ventilated areas
S61- Avoid release to the environment

16. OTHER INFORMATION

The information provided in this Product Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as guidance for safe handling, use, processing, storage transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process unless specified in the text.

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Fractionation Information

1.0 FRACTIONATION ANALYSIS

Fractionation simulations and testing have been conducted for the original refrigerant blend: R-125/134a/600a/600/601a defined as follows:

Component	%w/w	Tolerances
Pentafluoroethane (R125)	50.5	±1%
1,1,1,2-tetrafluoroethane (R134a)	47.0	±1%
Isobutane (R600a)	0.9	+0.1%, -0.2%
n-butane (R600)	1.0	+0.1%, -0.2%
Isopentane (R601a)	0.6	+0.1%, -0.2%

The purpose of the fractionation analysis is to identify the composition changes affecting flammability of the refrigerant's worst case manufacturing mixture during an isothermal vapor leak. The worst case manufacturing mixture (WCF) composition is defined for this blend as the composition containing the highest amount (percentage) of flammable components within the manufacturing tolerance range (+0.1%, -0.2 % for R600a, R600 and R601a) and the lowest amount of R125 (because of its flame suppressant properties). The worst case manufacturing composition (WCF) for the above original mixture is then defined as:

Component	%w/w
Pentafluoroethane (R125)	49.5
1,1,1,2-tetrafluoroethane (R134a)	47.7
Isobutane (R600a)	1.0
n-butane (R600)	1.1
Isopentane (R601a)	0.7

The simulations include:

- Leakage of the refrigerant worst case manufacturing mixture (WCF) at different temperatures and liquid loading of the cylinder evaluated by computer simulation and testing.

- Leakage and recharge of the refrigerant worst case manufacturing mixture at room temperature of the cylinder evaluated by computer simulation and testing.

2.0 FRACTIONATION SIMULATIONS

2.1

2.1 Computer simulation

The theoretical fractionation was performed by computer simulation using NIST developed program REFLEAK ver. 2.1.

Seven simulations were carried out for isothermal vapor leak process for the worst case manufacturing mixture:

- (a) 90% liquid filled tank at 54.4°C (130°F)
- (b) 90% liquid filled tank at 23°C (73.4°F)
- (c) 73% liquid filled tank at -28.9°C (-20.2 °F) (BP of the WCF + 10°C)
(the program refused to run at 90% loading)
- (d) 15% liquid filled tank at 60°C (140°F)
- (e) 15% liquid filled tank at 23°C (73.4°F)
- (f) 15% liquid filled tank at -28.9°C (-20.2 °F) (BP of the WCF + 10°C)

Another simulation was conducted for isothermal leak refill process at:

- (a) 15% liquid filled tank at 23°C (73.4°F)

2.2 Fractionation (Depletion) Test and Composition Measurements

An isothermal vapor depletion of the worst-case formulation was carried out first at 23°C (73.4°F) and 90% loading configuration resulting in the final worst-case fractionated formulation obtained with the computer simulation. The results of the test didn't verify the computer model for one component. The isopentane concentration didn't increase at the end of the test as much as model predicted. **The isopentane concentration at 95% depletion from the model was ~400% higher then the experimental value.** The predicted concentration values for

all the remaining four components (R125, R134a, R600a, and R600) were in good agreement with test. In order to establish a credible concentration values for isopentane and find out a worst case fractionated formulation (WCFF) all seven depletion tests have been conducted. The WCFFs found in this analysis are based on test data, while simulation data was retain on the graphs to verify the depletion of the other four components (R125, R134a, R600a, and R600).

2.2.1 Setup

The apparatus consisted of a 1000-ml Stainless Steel cylinder equipped with a dip tube, needle valves with sampling ports, a 25-liter isolated and cooled tank (cooling bath), immersion cooler and a circulator, Teflon high pressure hose, and an electronic gas mass flow meter. A GX 6000 scale and a stopwatch completed the setup. The high-pressure hose was used to connect the cylinder sample port to the flow meter.

2.1.2 Procedure

The 1000-ml cylinder was filled at 90% or 15% liquid with the final worst-case formulation blend and was conditioned at its test temperature in the cooling bath (or worm bath) overnight.

Once the composition of the initial vapor and liquid samples were measured, the cylinder was placed on a balance and gross weight was recorded. The cylinder was then placed in the appropriate bath (at the corresponding depletion temperature) in the upright position (for vapor depletion) and the cylinder needle valve opened slowly until the vapor flow out of the cylinder was 2% mass/hour.

After 2% of the initial weight of the refrigerant leaked out from the cylinder, the needle valve was closed to stop the leak. Liquid and vapor samples were taken and analyzed by Gas Chromatography. This procedure was repeated at 10%, 20%...90% loss increments. The last sample if possible was taken at 95% of mass loss. The test stopped if there was no more liquid in the tank, or no more vapor coming out of tank.

A Hewlett-Packard GC with thermal conductivity detector (TCD) and a Haysep D 80/100 column with helium as a carrier gas was used to determine the concentration of the gases at different fractionation levels. The oven temperature was 100°C for 8 min, ramped to 160°C and kept for 16 min.

A vapor sample was taken directly from a vapor port on the tank; the liquid sample was trapped into pre-vacuumed small cylinder and 1 ml of it was then injected into GC.

Final fractionation test data is reported in Figure 1 through 14 and Table 2 through 9. The resulting test data points for vapor and liquid phase are superimposed on the computer simulation data.

2.3 Results

Comparison of the simulation data to the test data indicates that the computer model is satisfactory in predicting the fractionation behavior of the four components of the blend (R125, R134a, R600a and R600), **but is not acceptable in predicting concentration values of isopentane (R601a)**. Therefore all the flammable component concentrations were derived from the experimental data.

The Figures 1 through 14 contain both simulation and test data. The continuous lines represent computer-modeling data; the points refer to experimental data. Because the R600a, R600 and R601a amounts are very small comparing to R125 and 134a and they don't really show well on the graphs containing all five components (full range), the part of the graph containing flammables (low range) was expanded to show better their behavior. The candidate WCFFs resulting from this analysis are shown in Table 1.

TABLE 1. WCFF SELECTION

Loading	Temperature	Total % wt. of flammables	Phase	Corresponding R125 %wt.	Mass Loss
90%	54.4 °C	3.41	liquid	27.49	90% (end)
90%	23 °C	3.23	liquid	14.37	95% (end)
90%	-28.9 °C	3.36	vapor	68.50	2% (initial)
15%	60 °C	3.01	liquid	41.50	20% (end of liquid)
15%	23 °C	2.75	liquid	32.24	70% (end of liquid)
15%	-28.9 °C	3.24	vapor	48.06	2% (initial)
15% Leak&refill	23 °C	2.77	liquid	37.17	20% (end of 5 th refill)

The highest ratio of total flammables to R125 was found for 90% loading at 23°C in liquid phase at the end of depletion.

The highest amount of flammables was found for 90% loading at 54.4°C in liquid phase at the end of depletion.

Therefore **WCFFs** are defined as :

WCFFs	R125	R134a	R600a	R600	R601a
WCFF1	14.37	82.4	0.31	0.58	2.34
WCFF2	27.49	69.1	0.67	0.98	1.76

TABLE 2
FRACTIONATION TEST RESULTS FOR 90% FILLED TANK @54.4°C

Leaked Mass %wt	R125 L %wt	R134a L %wt	R 600a L %wt	R600 L %wt	R601a L %wt	R125 V %wt	R134a V %wt	R 600a %wt	R600 V %wt	R601a V %wt	Total Flamm. In liquid	Total Flamm. In vapor
0	49.66	47.52	1.00	1.11	0.71	59.05	38.46	1.10	1.01	0.38	2.82	2.49
2	49.32	47.86	0.99	1.11	0.72	58.79	38.71	1.10	1.01	0.39	2.82	2.50
10	47.96	49.21	0.99	1.1	0.74	57.75	39.72	1.08	1.02	0.43	2.83	2.53
20	47.91	49.3	0.97	1.08	0.75	57.44	40.03	1.05	1.01	0.46	2.8	2.52
30	46.81	50.36	0.96	1.08	0.79	56.91	40.6	1.03	1.02	0.44	2.83	2.49
40	44.88	52.27	0.95	1.09	0.82	55.19	42.35	1.02	1	0.44	2.86	2.46
50	42.78	54.36	0.89	1.07	0.9	53.28	44.22	0.99	1.02	0.49	2.86	2.5
60	40.75	56.36	0.88	1.05	0.96	51.31	46.1	0.98	1.06	0.56	2.89	2.6
70	39.19	57.81	0.86	1.08	1.06	48.2	49.16	0.95	1.07	0.63	3	2.65
80	33.3	63.52	0.78	1.04	1.35	43.76	53.61	0.88	1.01	0.74	3.17	2.63
90	27.49	69.1	0.67	0.98	1.76	36.65	60.49	0.81	1	1.05	3.41	2.86

\$2

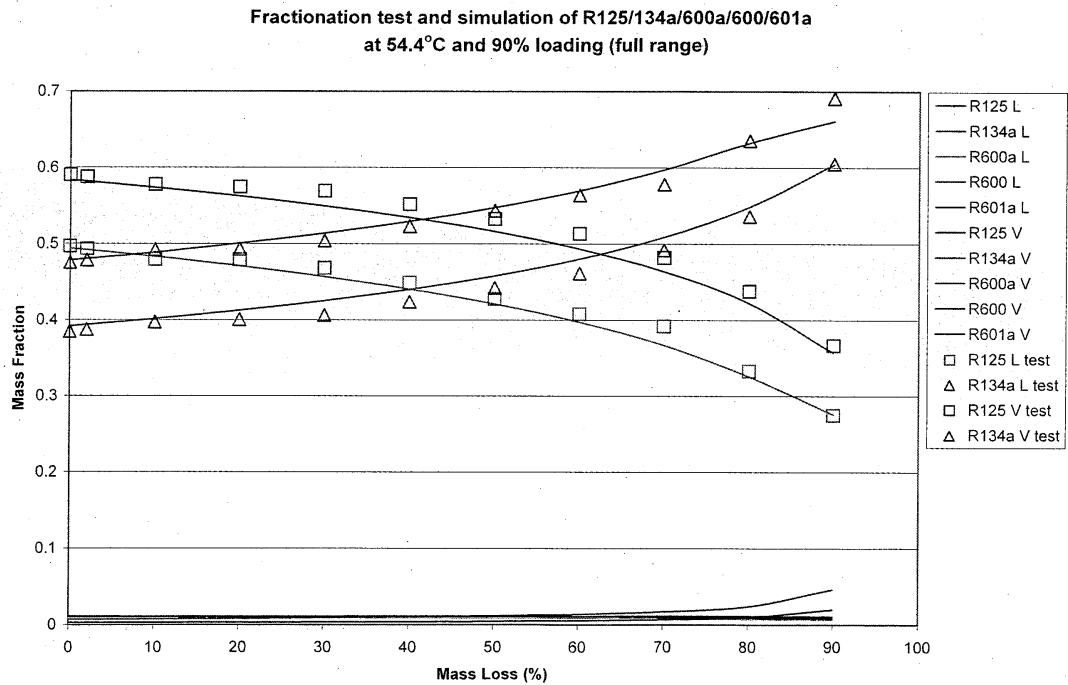


Figure 1. 90% loading at 54.4°C (full range)

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Fractionation test and simulation of R125/134a/600a/600/601a
at 54.4°C and 90% loading (low range)

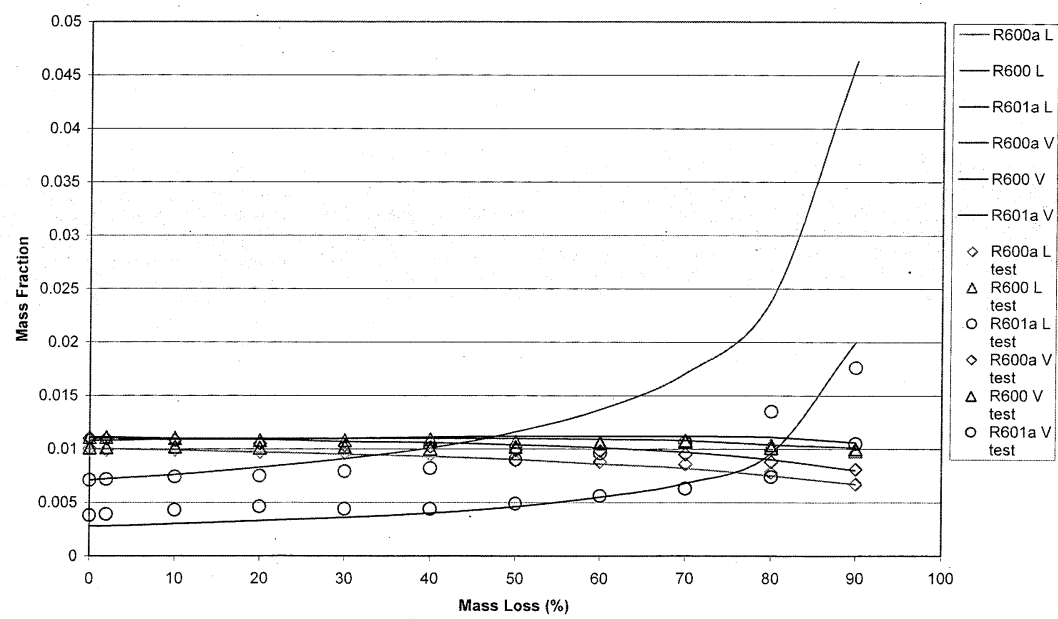


Figure 2. 90% loading at 54.4°C (low range)

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TABLE 3
FRACTIONATION TEST RESULTS
FOR 90% FILLED TANK @-28.9°C

Leaked Mass %wt	R125 L %wt	R134a L %wt	R 600a L %wt	R600 L %wt	R601a L %wt	R125 V %wt	R134a V %wt	R 600a %wt	R600 V %wt	R601a V %wt	Total Flamm. In liquid	Total Flamm. In vapor
0	50.33	46.88	1.03	1.10	0.65	68.66	28.00	1.67	1.33	0.34	2.78	3.34
2	50.06	47.20	0.98	1.08	0.66	68.50	28.14	1.71	1.33	0.32	2.72	3.36
10	48.68	48.68	0.96	1.04	0.66	67.36	29.34	1.61	1.35	0.34	2.65	3.30
20	45.80	51.66	0.84	1.00	0.71	65.16	31.65	1.50	1.31	0.36	2.54	3.18
30	44.54	52.96	0.80	0.97	0.74	62.90	34.04	1.37	1.28	0.41	2.50	3.06
40	42.11	55.48	0.71	0.92	0.80	59.63	37.45	1.20	1.25	0.48	2.42	2.93
50	36.25	61.51	0.56	0.81	0.88	54.74	42.48	1.01	1.18	0.58	2.24	2.77
60	29.44	68.59	0.36	0.62	0.98	48.96	48.45	0.85	1.05	0.68	1.96	2.58
70	23.69	74.52	0.23	0.48	1.09	40.41	57.41	0.52	0.83	0.83	1.80	2.18
80	14.22	84.32	0.07	0.25	1.14	26.19	72.01	0.22	0.53	1.03	1.46	1.78
84.47	8.26	90.30	0.05	0.15	1.24	18.58	79.79	0.12	0.34	1.17	1.44	1.63

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Fractionation simulation of R125/134a/600a/600/601a
at (-28.9)°C and 73% loading . Fractionation test at 90% loading (full range).

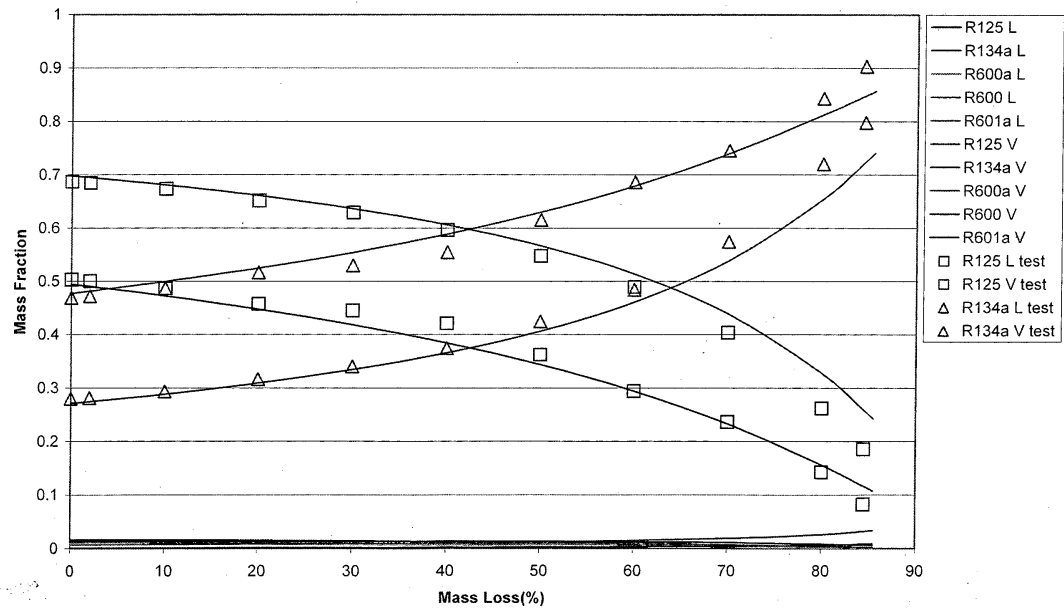


Figure 3. Test for 90% loading at (-28.9)°C. Simulation at 73% loading and (-28.9)°C (full range)

Fractionation simulation of R125/134a/600a/600/601a
at (-28.9)°C and 73% loading. Fractionation test at 90% loading (low range).

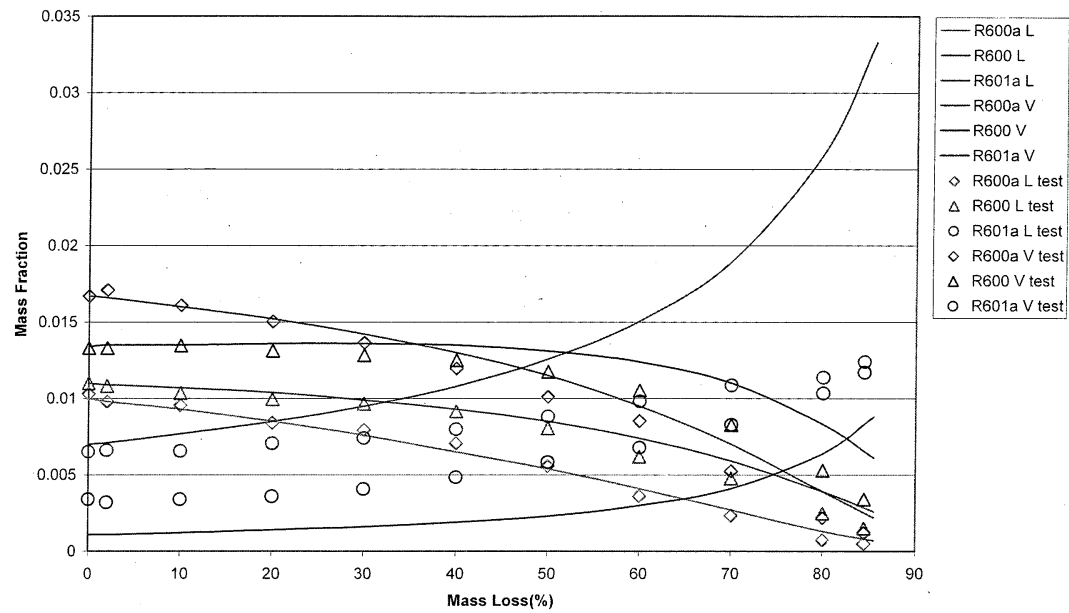


Figure 4. Test for 90% loading at (-28.9)°C. Simulation at 73% loading and (-28.9)°C (low range)

TABLE 4
FRACTIONATION COMPUTER SIMULATION RESULTS
FOR 90% FILLED TANK @23°C

Leaked Mass %wt	R125 L %wt	R134a L %wt	R 600a L %wt	R600 L %wt	R601a L %wt	R125 V %wt	R134a V %wt	R 600a %wt	R600 V %wt	R601a V %wt	Total Flamm. In liquid	Total Flamm. In vapor
0	49.43	47.76	1	1.1	0.7	62.76	34.68	1.24	1.13	0.19	2.8	2.56
2	49.15	48.04	0.99	1.1	0.71	62.52	34.93	1.24	1.13	0.19	2.8	2.56
10	47.95	49.22	0.97	1.1	0.76	61.46	35.98	1.22	1.14	0.2	2.83	2.56
20	46.28	50.86	0.94	1.09	0.83	59.96	37.47	1.2	1.15	0.23	2.86	2.58
30	44.35	52.74	0.9	1.08	0.92	58.21	39.21	1.17	1.15	0.25	2.9	2.57
40	42.11	54.92	0.86	1.07	1.04	56.12	41.3	1.14	1.16	0.29	2.97	2.59
50	39.45	57.5	0.81	1.04	1.2	53.56	43.85	1.09	1.16	0.34	3.05	2.59
60	36.19	60.64	0.74	1.01	1.42	50.32	47.08	1.03	1.16	0.41	3.17	2.6
70	32.04	64.57	0.65	0.96	1.78	46	51.39	0.95	1.14	0.52	3.39	2.61
80	26.48	69.68	0.54	0.87	2.44	39.79	57.56	0.82	1.09	0.74	3.85	2.65
90	18.29	76.35	0.37	0.72	4.27	29.68	67.41	0.6	0.94	1.37	5.36	2.91
95	12.36	78.55	0.27	0.6	8.22	21.57	74.61	0.43	0.78	2.61	9.09	3.82
97.48	8.85	69.28	0.26	0.66	20.95	16.62	76.4	0.34	0.69	5.95	21.87	6.98

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TABLE 5
FRACTIONATION TEST RESULTS
FOR 90% FILLED TANK @23°C

Leaked Mass %wt	R125 L %wt	R134a L %wt	R 600a L %wt	R600 L %wt	R601a L %wt	R125 V %wt	R134a V %wt	R 600a %wt	R600 V %wt	R601a V %wt	Total Flamm. In liquid	Total Flamm. In vapor
0	50.27	46.93	1.04	1.07	0.7	62.79	34.48	1.27	1.09	0.37	2.81	2.73
2	49.67	47.47	1.01	1.08	0.76	62.78	34.37	1.36	1.08	0.4	2.85	2.84
10	48.48	48.66	1	1.07	0.79	61.94	35.18	1.33	1.12	0.42	2.86	2.87
20	46.76	50.41	0.97	1.06	0.8	60.56	36.65	1.23	1.13	0.43	2.83	2.79
30	45.04	52.05	0.94	1.06	0.92	58.88	38.39	1.19	1.1	0.44	2.92	2.73
40	43.54	53.59	0.9	1.03	0.93	56.96	40.2	1.18	1.15	0.51	2.86	2.84
50	40.3	56.89	0.84	1.01	0.97	54.67	42.56	1.11	1.1	0.53	2.82	2.74
60	37.69	59.46	0.79	0.99	1.08	51.83	45.3	1.09	1.13	0.64	2.86	2.86
70	33.43	63.68	0.7	0.94	1.24	48.02	49.14	1	1.09	0.75	2.88	2.84
80	28.3	68.78	0.59	0.86	1.47	42.01	55.14	0.89	1.07	0.9	2.92	2.86
90	18.79	78.22	0.38	0.68	1.93	32.85	64.39	0.63	0.92	1.21	2.99	2.76
95	14.37	82.4	0.31	0.58	2.34	23.79	73.31	0.51	0.8	1.6	3.23	2.91

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Fractionation test and simulation at 23°C for 90% loading
of R125/134a/600a/600/601a (full range)

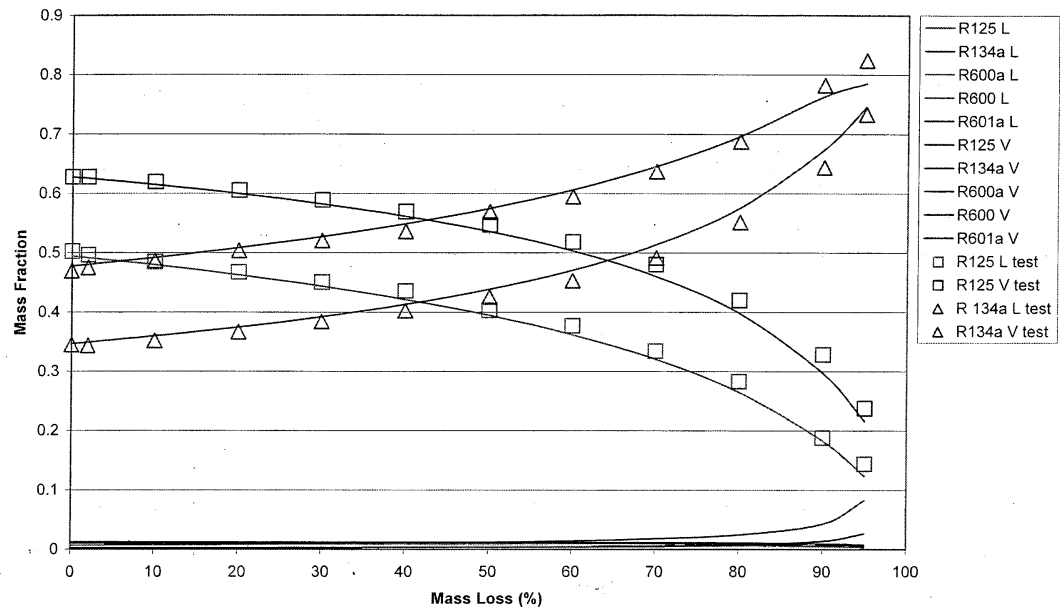


Figure 5. 90% loading at 23°C (full range).

Fractionation test and simulation at 23°C for 90% loading
of R125/134a/600a/600/601a (low range)

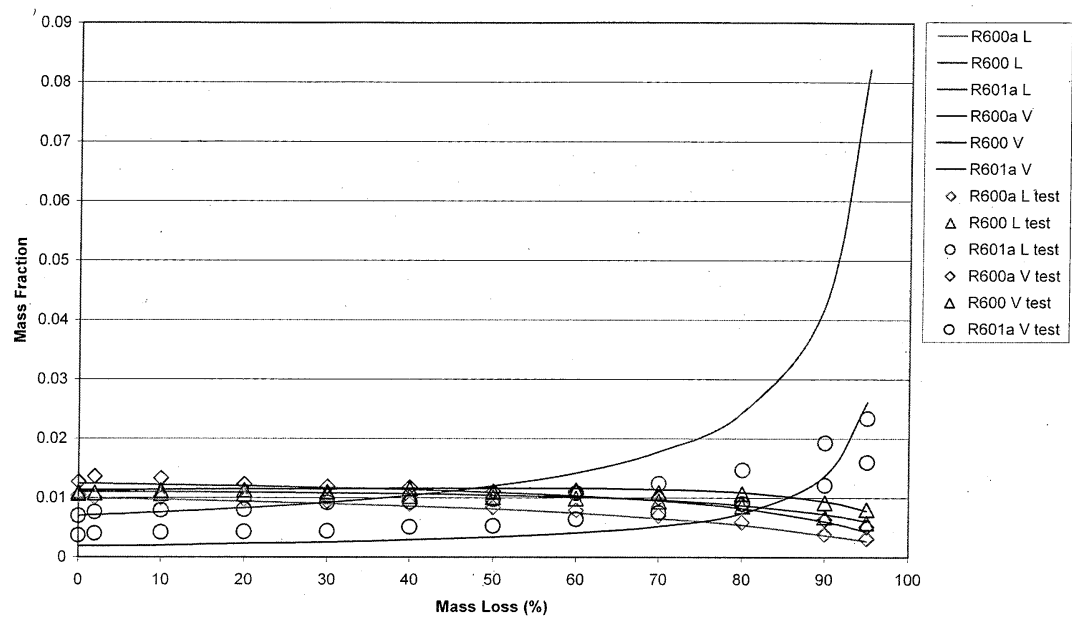


Figure 6. 90% loading at 23°C (low range).

TABLE 6
FRACTIONATION TEST RESULTS
FOR 15% FILLED TANK @60°C

Leaked Mass %wt	R125 L %wt	R134a L %wt	R 600a L %wt	R600 L %wt	R601a L %wt	R125 V %wt	R134a V %wt	R 600a %wt	R600 V %wt	R601a V %wt	Total Flamm. In liquid	Total Flamm. In vapor
0	44.05	53.01	0.94	1.08	0.91	52.99	44.38	1.07	1.05	0.52	2.93	2.64
2	43.27	53.76	0.96	1.09	0.92	52.35	44.98	1.06	1.06	0.55	2.97	2.67
10	42.63	54.41	0.95	1.07	0.94	51.7	45.67	1.04	1.04	0.55	2.96	2.63
20	41.55	55.44	0.94	1.06	1.01	50.76	46.61	1.02	1.03	0.57	3.01	2.62
30	42.62	54.44	0.91	1.04	0.98	50.82	46.46	1.02	1.05	0.65	2.82	2.66
40	48.88	48.29	1.01	1.07	0.74	49.52	47.81	0.99	1.03	0.64	2.82	2.66
50	49.08	48.15	1.03	1.07	0.67	49.37	47.49	1	1.01	0.66	2.77	2.67

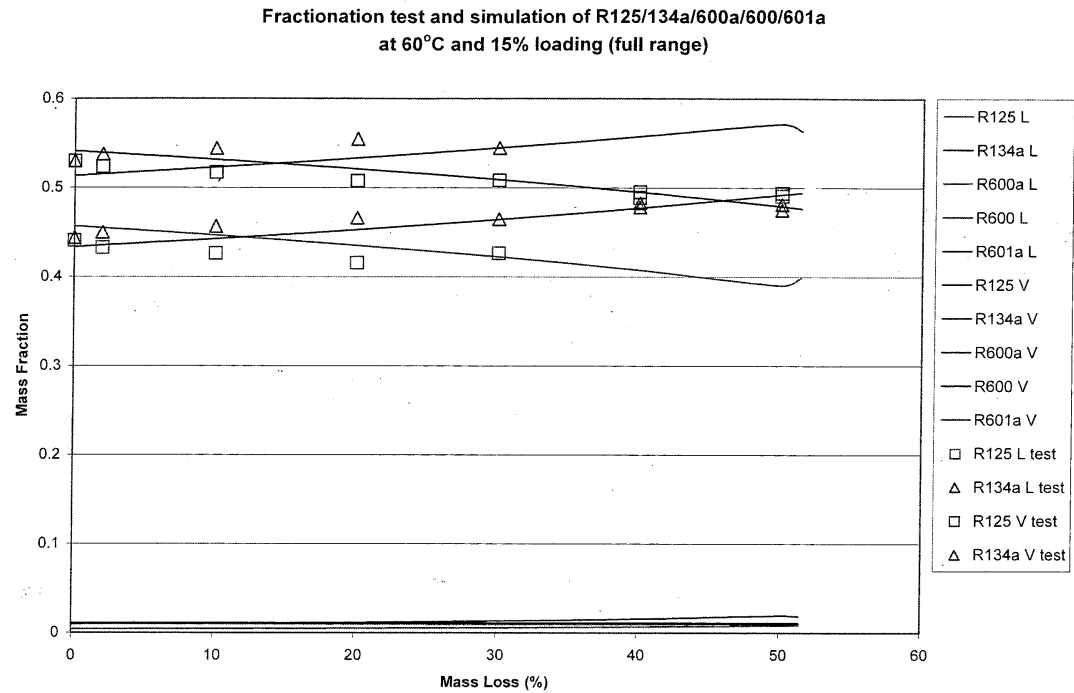


Figure 7. 15% loading at 60°C (full range)

Fractionation test and simulation of R125/134a/600a/600/601a
at 60°C and 15% loading (low range)

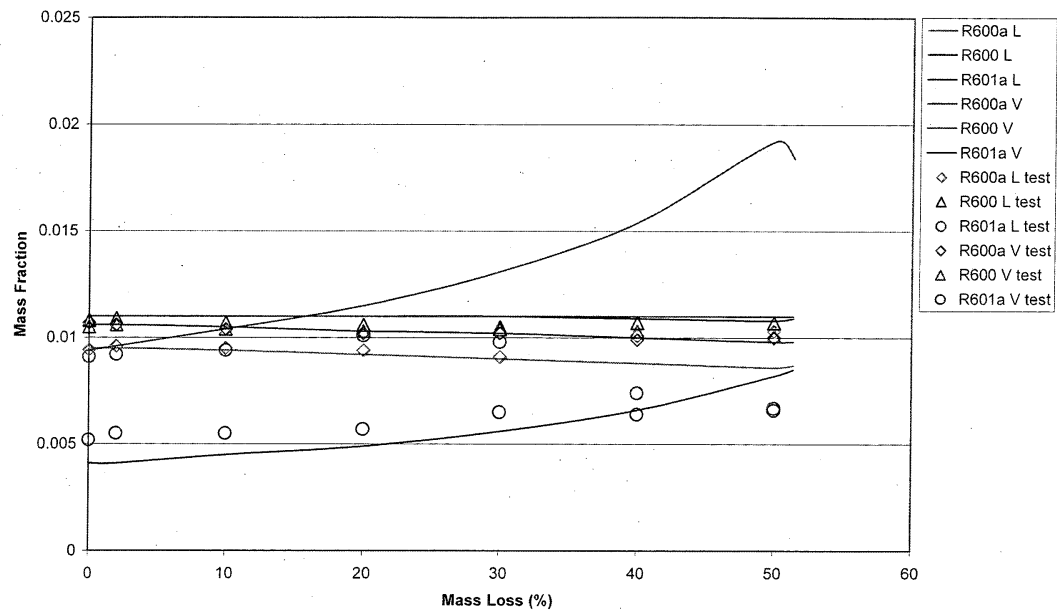


Figure 8. 15% loading at 60°C (low range)

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TABLE 7
FRACTIONATION TEST RESULTS
FOR 15% FILLED TANK @-28.9°C

Leaked Mass %wt	R125 L %wt	R134a L %wt	R 600a L %wt	R600 L %wt	R601a L %wt	R125 V %wt	R134a V %wt	R 600a %wt	R600 V %wt	R601a V %wt	Total Flamm. In liquid	Total Flamm. In vapor
0	49.44	47.82	1.03	1.07	0.64	68.73	28.04	1.63	1.30	0.30	2.74	3.23
2	49.35	48.06	0.96	1.01	0.61	68.28	28.47	1.70	1.26	0.28	2.58	3.24
10	47.21	50.25	0.91	0.97	0.66	66.83	30.08	1.51	1.24	0.34	2.54	3.09
20	44.49	53.13	0.80	0.92	0.67	64.06	32.88	1.42	1.26	0.38	2.39	3.06
30	41.61	56.09	0.71	0.87	0.71	61.14	35.80	1.39	1.24	0.42	2.29	3.05
40	38.42	59.44	0.56	0.82	0.76	57.86	39.26	1.22	1.18	0.47	2.14	2.88
50	33.25	64.61	0.51	0.77	0.86	55.51	41.73	1.08	1.15	0.53	2.14	2.76
60	28.21	69.70	0.46	0.68	0.95	51.72	45.68	0.91	1.03	0.66	2.08	2.60
70	23.28	75.07	0.24	0.43	0.98	43.50	54.18	0.65	0.87	0.80	1.65	2.32
80	17.40	81.11	0.16	0.32	1.01	32.94	65.03	0.36	0.64	1.03	1.49	2.03

Fractionation test and simulation of R125/134a/600a/600/601a
at (-28.9)°C and 15% loading (full range)

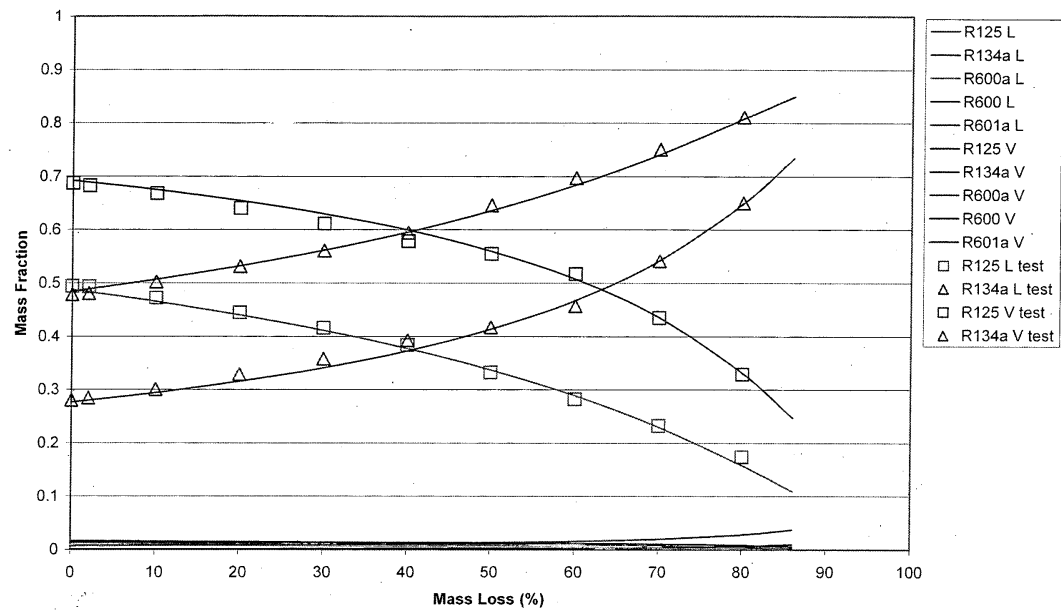


Figure 9. 15% loading at (-28.9) °C (full range)

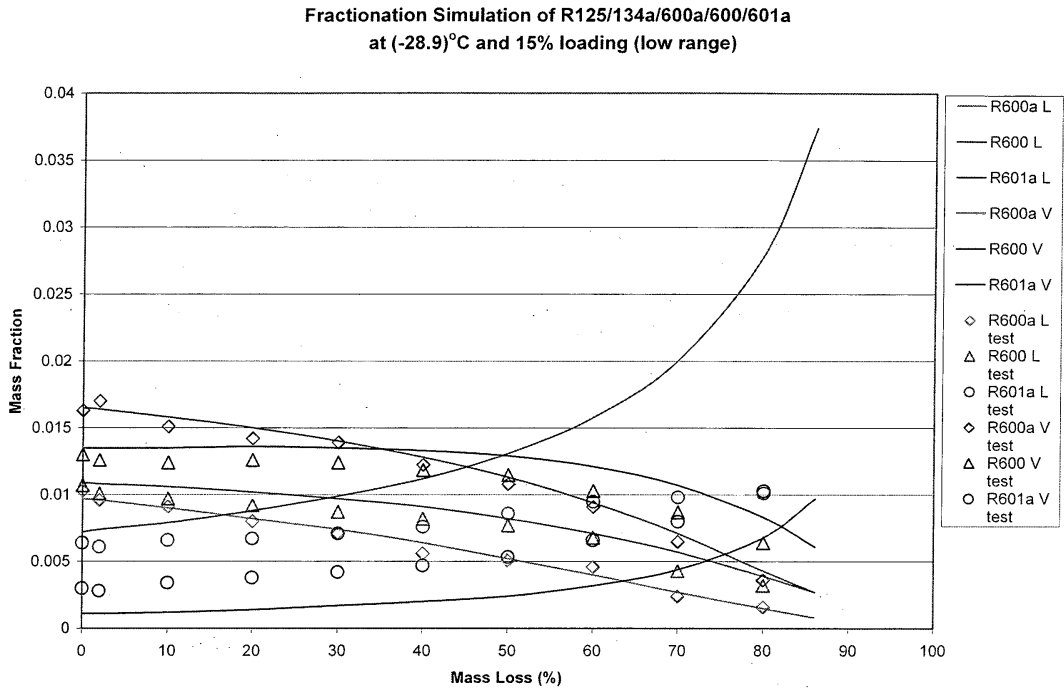


Figure 10. 15% loading at (-28.9) °C (low range)

TABLE 8
FRACTIONATION TEST RESULTS
FOR 15% FILLED TANK @23°C

Leaked Mass %wt	R125 L %wt	R134a L %wt	R 600a L %wt	R600 L %wt	R601a L %wt	R125 V %wt	R134a V %wt	R 600a %wt	R600 V %wt	R601a V %wt	Total Flamm. In liquid	Total Flamm. In vapor
0	46.93	50.27	0.99	1.08	0.72	59.82	37.44	1.24	1.13	0.38	2.79	2.75
2	46.32	50.95	0.97	1.06	0.69	59.76	37.44	1.27	1.14	0.38	2.72	2.79
10	45.05	52.26	0.93	1.05	0.71	59.50	37.73	1.22	1.17	0.38	2.69	2.77
20	43.21	54.06	0.92	1.03	0.78	58.07	39.13	1.23	1.15	0.42	2.73	2.80
30	42.16	55.12	0.87	1.02	0.83	56.28	40.87	1.20	1.16	0.48	2.72	2.84
40	39.86	57.28	0.87	1.04	0.95	54.82	42.42	1.16	1.15	0.46	2.86	2.77
50	37.89	59.40	0.80	0.97	0.94	53.00	44.31	1.10	1.09	0.49	2.71	2.68
61	34.41	62.87	0.73	0.93	1.06	49.31	48.06	1.01	1.04	0.58	2.72	2.63
70	32.24	65.01	0.68	0.89	1.18	46.25	51.15	0.94	1.01	0.64	2.75	2.59
80	44.30	52.97	0.91	1.03	0.79	44.48	52.87	0.92	1.01	0.73	2.73	2.66

Fractionation test and simulation for R125/134a/600a/600/601a
at 23°C and 15% loading (full range)

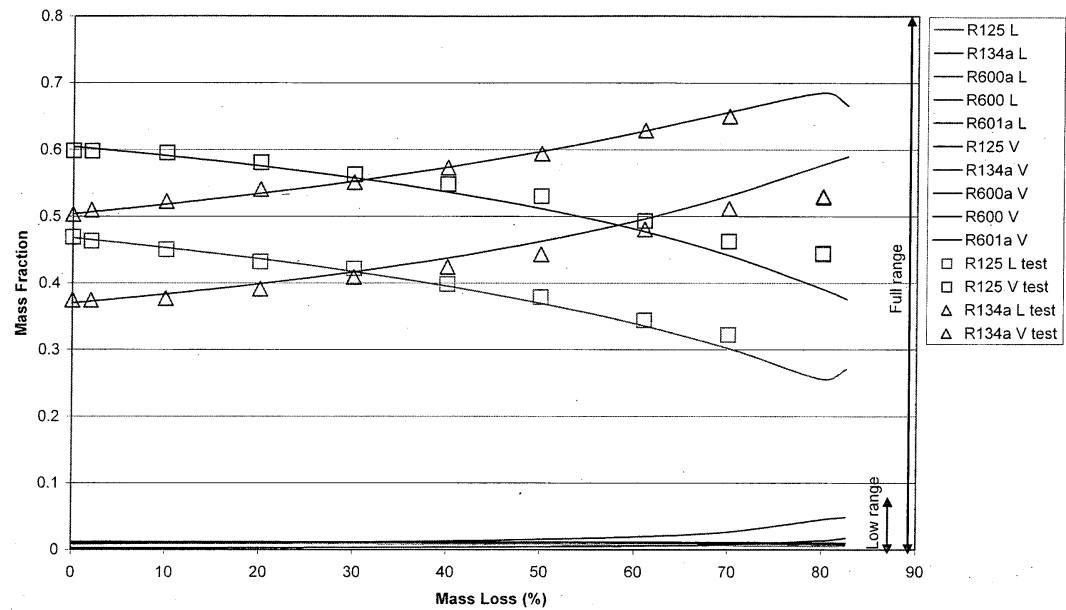


Figure 11. 15% loading at 23°C (full range)

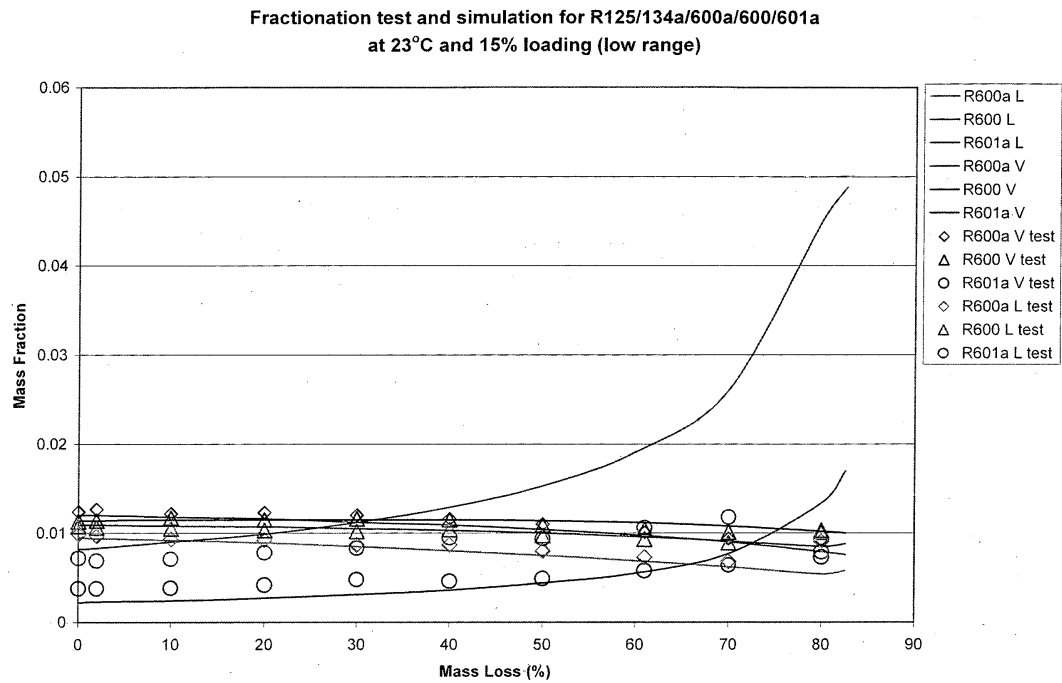


Figure 12. 15% loading at 23°C (low range)

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TABLE 9
FRACTIONATION TEST RESULTS
FOR LEAK AND REFILL OF 15% FILLED TANK @23°C

Leaked Mass %wt	R125 L %wt	R134a L %wt	R 600a L %wt	R600 L %wt	R601a L %wt	R125 V %wt	R134a V %wt	R 600a %wt	R600 V %wt	R601a V %wt	Total Flamm. In liquid	Total Flamm. In vapor
0	46.11	51.12	0.99	1.04	0.75	60.01	37.48	1.19	1.00	0.32	2.78	2.51
10	44.55	52.70	0.94	1.02	0.79	58.89	38.47	1.21	1.03	0.40	2.75	2.64
20	42.66	54.56	0.92	1.01	0.85	57.42	39.91	1.19	1.06	0.43	2.78	2.68
0	44.17	53.05	0.95	1.03	0.80	58.44	38.90	1.21	1.06	0.39	2.78	2.66
10	42.34	54.89	0.92	0.99	0.86	57.09	40.24	1.17	1.05	0.45	2.77	2.67
20	41.12	56.15	0.88	0.96	0.90	55.41	41.89	1.11	1.02	0.57	2.74	2.70
0	42.84	54.36	0.92	1.03	0.84	57.09	40.34	1.15	1.00	0.42	2.79	2.57
10	41.12	56.14	0.86	0.98	0.90	55.66	41.67	1.14	1.06	0.47	2.74	2.67
20	39.30	57.99	0.81	0.97	0.93	54.14	43.16	1.11	1.04	0.55	2.71	2.70
0	41.25	56.08	0.84	0.97	0.86	56.01	41.29	1.16	1.07	0.47	2.67	2.70
10	40.59	56.73	0.84	0.95	0.90	54.69	42.63	1.14	1.06	0.48	2.69	2.68
20	38.69	58.55	0.82	0.97	0.96	53.06	44.25	1.10	1.05	0.55	2.75	2.70
0	41.41	55.86	0.86	0.98	0.89	55.41	41.87	1.15	1.08	0.49	2.73	2.72
10	39.70	57.65	0.79	0.94	0.92	53.92	43.46	1.08	1.04	0.50	2.65	2.62
20	37.99	59.31	0.78	0.94	0.98	52.29	45.09	1.06	1.01	0.55	2.70	2.62
0	40.38	56.90	0.81	0.97	0.94	54.57	42.75	1.12	1.06	0.51	2.72	2.69
10	38.67	58.56	0.80	0.97	1.00	52.98	44.34	1.08	1.04	0.56	2.77	2.68
20	37.17	60.06	0.78	0.96	1.03	51.63	45.72	1.04	1.04	0.57	2.77	2.65

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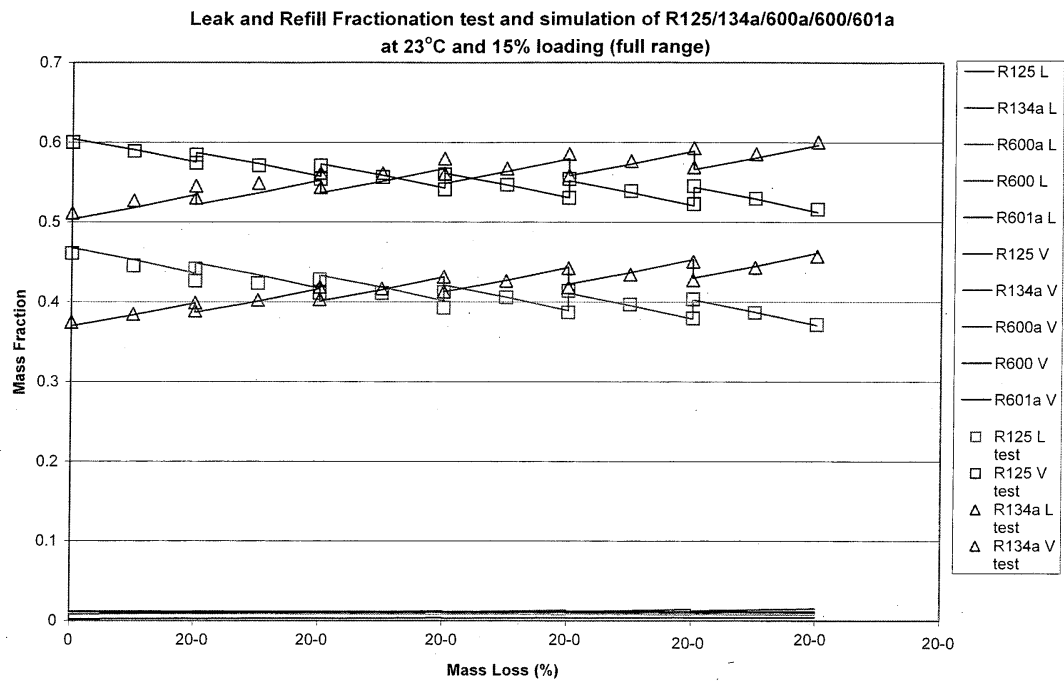


Figure 13. Leak and refill 15% loading at 23°C (full range)

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Leak and Refill Fractionation Simulation of R125/134a/600a/600/601a
at 23°C and 15% loading (low range)

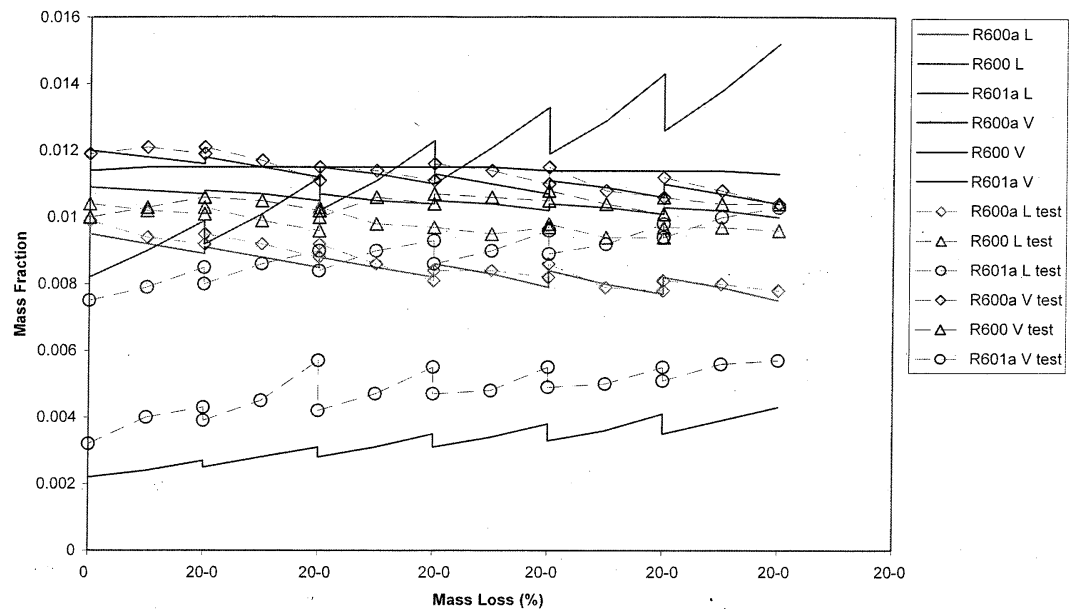


Figure 14. Leak and refill 15% loading at 23°C (low range)

Flammability Information

Flammability Information

1.0 Flame Propagation

Flammability criteria tests have been conducted on the worst case manufactured (WCF) and worst case fractionated compositions (WCFFs) of the original refrigerant mixture R-125/134a/600a/600/601a (50.5, 47.0, 0.9, 1.0, 0.6). Emphasis was placed on identifying the shift of the flammable range of the refrigerant's worst case manufacturing (if any) due to a change in the overall mixture composition after an isothermal leak (fractionation) from the refrigerant system. Series of flammability tests were performed at both the worst case manufactured and worst case fractionated mixtures:

- WCF; R-125/134a/600a/600/601a (49.5, 47.7, 1.0, 1.1, 0.7) at 100°C
- WCFF1; R-125/134a/600a/600/601a (14.37, 82.4, 0.31, 0.58, 2.34) at 60°C
- WCFF2; R-125/134a/600a/600/601a (27.49, 69.1, 0.67, 0.98, 1.76) at 60°C

2.0 Flammability of Worst Case Manufactured and Fractionated Compositions

2.1 Test Setup and Procedure

The tests were performed using a 12-liter flask per ASHRAE standards. Tests were conducted at 100°C for WCF, at 60°C for WCFF and at atmospheric pressure. Refer to Figure 1 for the setup.

The flask consists of a one-necked glass test vessel. A stirrer was also used to mix the gases (air/refrigerant) in the glass flask. For the test, a liquid quantity of the blend mixture was injected and vaporized into a pre-vacuumed cylinder. A measured amount of gas is then introduced into the flask (by partial pressure), the flask is then brought back to atmospheric pressure using 50% relative humidity air. The stirrer was turned on to obtain complete mixing and attainment of thermal equilibrium. After five minutes of mixing, the stirrer was then turned off. An electric spark (15,000V, 30 mA) was created to ignite the gas mixture inside the flask. Visual observation of the flame propagation beyond a 90° fan from the tip of the electrodes to the vessel was considered as a reaction.

The flask was purged with dry compressed air to clean out residue after each trial. The quantity of the blend sample in air was varied between trials until the composition, which could just sustain propagation of the flame was determined.

2.2 Test Results

The flammability test results for WCF; R-125/134a/600a/600/601a (49.5, 47.7, 1.0, 1.1, 0.7) performed at 100°C are shown in Table 1.

The results for WCFF1; R-125/134a/600a/600/601a (14.37, 82.4, 0.31, 0.58, 2.34) at 60°C are shown in Table 2.

The results for WCFF2; R-125/134a/600a/600/601a (27.49, 69.1, 0.67, 0.98, 1.76) at 60°C are shown in Table 3.

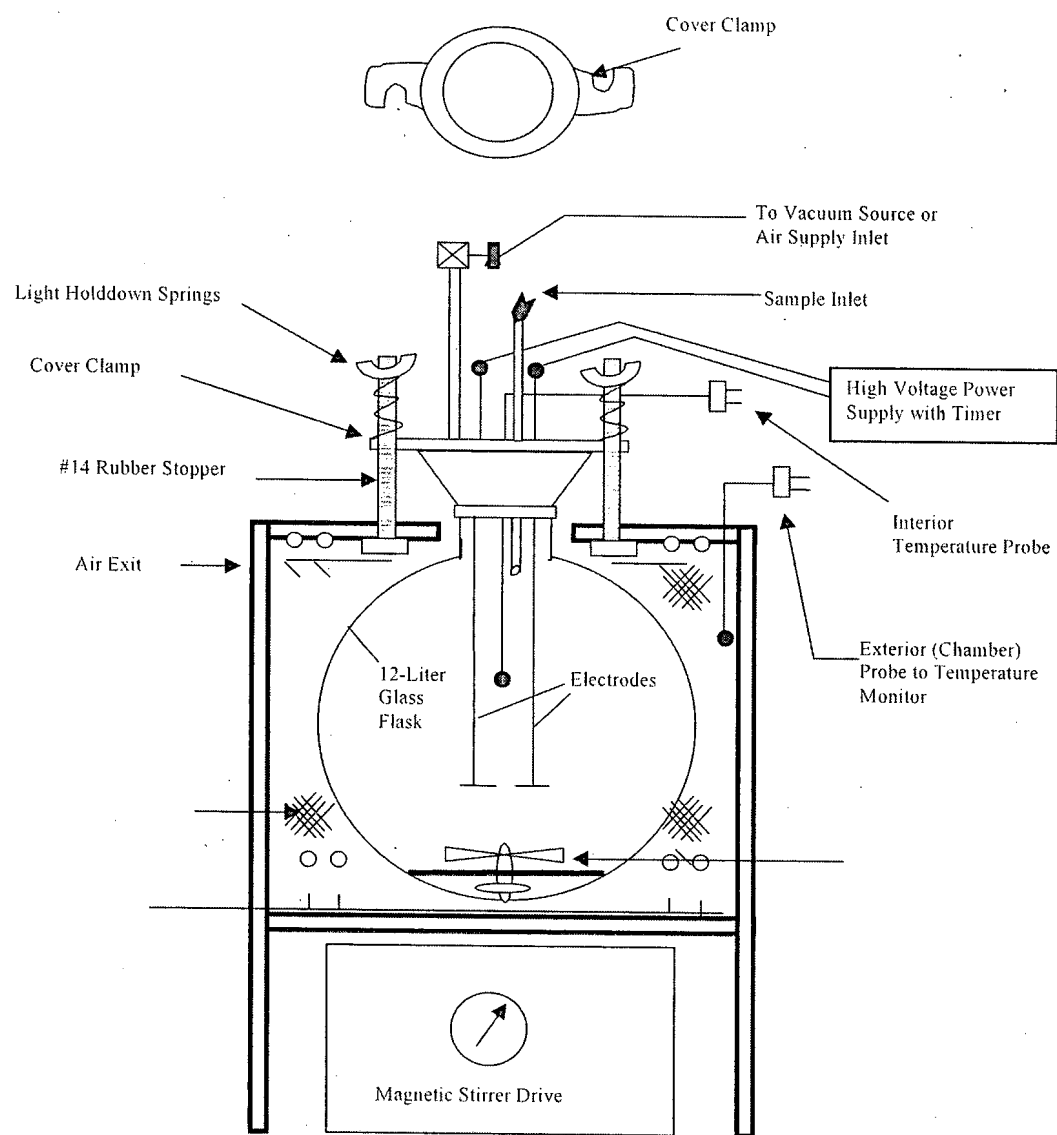


Figure 1. Flammability chamber setup

Flask Volume:	12-liter	Air Relative:	50%
Test Temperature:	100°C		(0.0086 gm _{H₂O})/gm _{air}

CONCENTRATION (% by volume)	RESULTS	
	GO	NO GO
2		X
3		X
4		X
5		X
6		X
7		X
8		X
9		X
10		X
11		X
12		X
13		X
14		X
15		X
16		X
17		X
18		X
19		X
20		X
22		X
24		X
26		X
28		X
30		X

Flask Volume:	12-liter	Air Relative: 50%
Test Temperature:	60°C	(0.0086 gm _{H2O})/gm _{air}

CONCENTRATION (% by volume)	RESULTS	
	GO	NO GO
2		X
3		X
4		X
5		X
6		X
7		X
8		X
9		X
10		X
11		X
12		X
13		X
14		X
15		X
16		X
17		X
18		X
19		X
20		X
22		X
24		X
26		X
28		X
30		X

Flask Volume:	12-liter	Air Relative: 50%
Test Temperature:	60°C	(0.0086 gm _{H2O})/gm _{air}

CONCENTRATION (% by volume)	RESULTS	
	GO	NO GO
2		X
3		X
4		X
5		X
6		X
7		X
8		X
9		X
10		X
11		X
12		X
13		X
14		X
15		X
16		X
17		X
18		X
19		X
20		X
22		X
24		X
26		X
28		X
30		X

Flammability Information



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The file contains technical information submitted after
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Description

[0001] This invention relates to refrigerant compositions which have no adverse effect on stratospheric ozone and to compositions which are for use both in refrigeration and air conditioning systems designed to use Ozone Depleting Substances (ODS) CFC12 (dichlorodifluoromethane), CFC502 (azeotrope of chloropentafluoromethane and chlorodifluoromethane) and HCFC22 (chlorodifluoromethane) and additionally in new equipment. These new refrigerant compositions are compatible with lubricants commonly found in refrigeration and air conditioning systems.

[0002] The compositions may also be used in equipment designed for non ozone depleting substances.

[0003] It is well known that chlorofluorocarbons (CFCs) such as CFC12 and CFC502 and hydrochlorofluorocarbons such as HCFC22 while being energy efficient, non flammable and of low toxicity migrate to the stratosphere where they are broken down by ultra violet light to attack the ozone layer. These Ozone Depleting Substances are in the process of being replaced by non ozone depleting alternatives such as hydrofluorocarbons (HFCs) which are also non flammable, efficient and of low toxicity. There are six main HFCs, namely HFC134a, HFC32, HFC125, HFC143a, HFC227ea and HFC152a, which either individually or blended into mixtures can replace CFCs and HCFCs. While HFC134a, HFC227ea and HFC152a can be used to replace ODS directly, HFC32, HFC143a, and HFC125 are generally found in blends as replacements for ODS. However, HFCs do not have adequate solubility in traditional lubricants such as mineral and alkylbenzene oils so that synthetic oxygen containing lubricants have been introduced specifically for new equipment. These new lubricants are expensive and hygroscopic.

[0004] Refrigerant blends such as R404A, R507, R410A, R407C and others have been commercialised as replacements for CFCs and HCFCs but, because these compositions contain only HFC components, they cannot be used with the traditional lubricants commonly found in use with CFCs and HCFCs. If these blends are to be used to replace CFCs and HCFCs in existing equipment, the major chemical manufacturers recommend that no more than 5% of the -traditional lubricant in the system be retained so that a virtual complete change of lubricant to a synthetic oxygen containing lubricant resulting in a full retrofit is required, which is often costly and technically unsatisfactory..

[0005] Although equipment manufacturers have adapted their units to operate with HFC blends, they do not always find the commercially available products as satisfactory as the CFCs and HCFCs that these new refrigerants are replacing. In particular to ensure adequate oil return, hydrocarbon lubricants, such as mineral oil, have been replaced by oxygen containing lubricants, notably polyol esters and polyalkylene glycols. Unfortunately these materials are liable to absorb atmospheric moisture, especially during maintenance, which can contribute to excessive corrosion and wear in equipment thus reducing its reliability. A key objective of this patent is to provide HFC/hydrocarbon blends that enable the continued use of hydrocarbon oils in both existing and new equipment.

[0006] Additionally some refrigerants, such as R07C, have wide temperature glides ($> 4^{\circ}\text{C}$) in the evaporator and condenser, whereas equipment manufacturers, based on their experience with CFC/HCFC single fluids or azeotropes, prefer refrigerants with low glides. A further key objective of this invention, therefore, is to provide HFC/hydrocarbon blends that can substitute for CFC 12, HCFC 22 and azotrope 502 (CFC 115/HCFC 22) both allowing the continued use of hydrocarbon lubricants in equipment and minimising the temperature glides in the heat exchangers.

[0007] The present invention relates to refrigerant compositions, which are non flammable under all conditions of fractionation as defined under ASHRAE Standard 34, and which can be used to replace ODS in an existing unit without the need to change the lubricant or make any significant change to the system hardware. In new equipment the refrigerant compositions allow the continued use of hydrocarbon oils, although the manufacturers may take the opportunity to modify their units to optimise the performances of the new refrigerants, for example by selecting the most appropriate lengths of capillary tubes. Where the ingress of moisture or other problems are being experienced with oxygen containing oils the new compositions allow such oils to be replaced by hydrocarbon oils

[0008] It is known in the art that the addition of a small amount of hydrocarbon to a refrigerant composition containing an HFC or HFC mixtures can result in sufficient hydrocarbon being dissolved in the lubricant to be transported around the system so that lubrication of the compressor is maintained at all times. It is obvious that the greater the hydrocarbon content of the composition the greater the ability of the refrigerant to transport the lubricant back to the compressor. However, too high a hydrocarbon content can lead to flammable mixtures. Although flammable refrigerants are acceptable in some applications, this invention relates to non flammable compositions for use in equipment where flammable refrigerants are prohibited. However, it is not well understood how to achieve non flammable compositions under all conditions including fractionation of the refrigerant compositions which can take place during a leak of the refrigerant from the system or during storage.

[0009] Not all HFCs are non flammable as defined under ASHRAE Standard 34. HFC143a and HFC32 have not received a non flammable rating by ASHRAE. This invention relates to compositions of refrigerants which not only covers blends of non flammable HFCs with hydrocarbons but also blends of flammable HFCs, non flammable HFCs and hydrocarbons in selected proportions such that all such compositions are non flammable during fractionation while providing similar refrigerating effects and thermodynamic performances as the ODS they replace, namely CFC12, CFC502 and HCFC22.

[0010] While this invention relates to refrigerant compositions which can be used with traditional lubricants such as mineral and alkylbenzene oils, they are also suitable for use with synthetic oxygen containing lubricants.

[0011] In formulating HFC/hydrocarbon blends to replace CFC 12, CFC 502 and HCFC 22 in specific applications it is generally necessary to use one or more lower boiling HFCs, with one or more higher boiling HFCs. In this context preferred lower boiling HFCs are HFC 32, HFC 143a and HFC 125, and higher boiling HFCs are HFC 134a, HFC 134, HFC 227ea and HFC 152a.

[0012] To avoid flammability in the blend, or in a fraction generated by a leak, for example as defined by ASHRAE Standard 34, the total amount of hydrocarbon should be minimised. At the same time the quantity of the hydrocarbon mixture dissolved in the oil needs to be maximised for good oil return, especially at those locations in the circuit where the oil is at its most viscous, for example the evaporator. A single higher boiling hydrocarbon, such as pentane or *iso*-pentane, would certainly show higher solubility in the oil than a lower boiling hydrocarbon. However, as the result of a leak, for example from a cylinder, a higher boiling hydrocarbon will concentrate in the liquid phase. The amount of hydrocarbon will, therefore, need to be limited in order to avoid generating a flammable mixture towards the end of the leak.

[0013] This problem could be avoided by using only a low boiling hydrocarbon such as propane or *iso*-butane. However, this has 2 disadvantages. Firstly, lower boiling hydrocarbons are less soluble than higher boiling hydrocarbons in hydrocarbon lubricants in the evaporator when present at similar weights % as formulated in the blend. Consequently they are less effective at ensuring good oil return. Secondly, because of their higher volatility they tend to concentrate in the vapour phase of a blend. Their concentration therefore needs to be restricted to avoid generating flammable mixtures at the beginning of a leak. This problem is exacerbated if the one or more of the lower boiling HFCs is also flammable.

[0014] Surprisingly we have found that the best approach to formulating HFC/HC refrigerant blends is to use combinations of two and preferably three hydrocarbons with different boiling points. This allows the total amount of hydrocarbon of the blend to be reduced while simultaneously the amount dissolved in the oil in the evaporator is increased.

[0015] This invention has the following advantage. Hydrocarbon components facilitate oil return, but, because of their flammability, restrict the weights of flammable HFCs, notably HFC 143a that can be included. Inclusion of these fluids can be valuable in achieving the required balance of thermodynamic properties, so minimising the amounts of hydrocarbon present allows more scope in formulating preferred blends.

[0016] The blending of HFCs to achieve the desired balance of physical properties appropriate to various cooling applications is well known and a variety of products are available commercially, for example R407C, R410A and R410B. Although these have been selected for specific applications in combination with oxygen containing synthetic lubricants, simply adding 2 or 3 hydrocarbon components to these products does not achieve the preferred products for use with hydrocarbon lubricants. Firstly, the hydrocarbon components contribute to the overall thermodynamic properties of the blend so will affect the preferred ratios of the HFCs. Secondly, the ratio of flammable to non-flammable HFCs will need to be selected to ensure non-flammability, for example, as required by the ASHRAE 34 Standard.

[0017] Blends of HFC125, HFC134a, HFC143a, HFC227ea are particularly preferred as replacements for CFCs and HCFCs. Both HFC125 (pentafluoroethane) and R227ea are non flammable under all operating conditions and in addition are fire suppressants, an application for which they have been developed by the fire fighting industry. The presence of HFC227ea provides a twofold advantage of reducing the flammability of the composition and also enhances oil return to the compressor due to emulsification of the lubricant in the presence of a hydrocarbon.

[0018] Blends of HFC 134a, HFC227ea, HFC125 and mixtures of selected hydrocarbon additives have been found to be preferred replacements for CFC12 in centrifugal chillers. It has been found that the interaction of hydrocarbon additives in such mixtures facilitates non flammable mixtures during all conditions of leakage during fractionation so that non flammability can be achieved according to ASHRAE Standard 34. The presence of hydrocarbons results in the lubricant being returned to the compressor. The presence of R227ea enables the requisite molecular weight of the blend to match that of CFC12 and additionally facilitates non flammability due to its fire retardant properties. The presence of R125 increases the capacity of the blend. The resulting mixtures are a close match for CFC12 in thermodynamic and system performance.

[0019] Surprisingly it has been found that given the same percentage content of hydrocarbon additive in the refrigerant composition, increasing the HFC125 content of the composition results in flammable mixtures being created during fractionation. This is very surprising since it would seem obvious that the greater the amount of HFC125 in the composition the less would be the likelihood to generate a flammable mixture during fractionation. The reasons for this apparent anomaly relate to the pressure/temperature relationship between the quantities of HFC125 and HFC134a in the mixture and the amount and type of hydrocarbon and/or hydrocarbon mixture. The following refrigerant compositions were made up and leaked away until the cylinder was almost liquid empty according to ASHRAE Standard 34:

	%	
	Blend 1	Blend 2
R134a	48.0	21.0

(continued)

	%	
	Blend 1	Blend 2
5 R125	49.0	76.0
butane	2.7	2.5
isopentane	0.3	0.5

10 [0020] Blend 2 with the considerably higher HFC125 content was found to create a flammable composition during fractionation, while Blend 1 with a lower HFC125 content remained non flammable throughout fractionation.

[0021] In GC 2727427 N A Roberts teaches that, if a hydrocarbon with at least four carbon atoms other than methyl propane (isobutane) is used, surprisingly the flammability of the fractionated composition is greatly reduced. Surprisingly, we have now found that the inclusion of isobutane with appropriately chosen hydrocarbons does not result in flammable compositions during fractionation. It has been found that the selection of the hydrocarbon additive or mixtures thereof with the HFC components is critical to achieving non flammability under all operating conditions and as defmed under ASHRAE Standard 34.

20 [0022] In US5,800,730 it is stated that HFC 134a needs to be added to blends of HFC125 and HFC143a as a replacement for CFC502 in order to avoid a flammable mixture (example 3). Surprisingly we have found that by excluding HFC134a, changing the proportion of HFC125 to HFC143a and adding a selected range of hydrocarbons results in a composition which is non flammable during fractionation and a close match for R502 with regard to thermodynamic performance.

25 [0023] In US5,211.867, azeotropic compositions are claimed of R125 and R143a. It is a key feature of this invention that a specially selected hydrocarbon or mixtures of hydrocarbons are present in order to facilitate oil return to the compressor. Surprisingly it has been found that, despite the flammability of HFC143a, the selection of a hydrocarbon or mixtures of hydrocarbons enables the compositions to be non flammable during fractionation. The combination of a high boiling hydrocarbon such as isopentane (BP 27°C) with butane (BP -0.5°C) and isobutane (BP -11.5°C) avoids build up of hydrocarbon content in the liquid phase during a leakage while the more volatile isobutane is countered in the vapour phase by the fire suppressant HFC125 due to the latter's higher vapour pressure and lower boiling point (BP -45°C). In order for the composition to be non flammable, the HFC125 content of the composition is above the azeotropic composition so that the content of HFC143a is reduced but without affecting the refrigerating performance of the composition as a replacement for CFC502.

35 [0024] Although the addition of hydrocarbons to HFCs has been previously described, it has not been previously appreciated that the volatilities of the hydrocarbons need to be matched to the application for which the refrigerant is intended. For example R12 is employed as the refrigerant in domestic freezers with evaporating temperatures of --22°C, in domestic fridges with evaporating temperatures of ~-5°C, and in mobile air conditioning with evaporating temperatures of ~-5°C. An important aspect of this invention is to formulate HFC/HC blends that ensure good oil return in these disparate applications while also ensuring that the refrigerant blend remains non-flammable according to the chosen criterion. For applications with evaporators operating at temperatures above -5°C the higher boiling hydrocarbons are preferred. Specially preferred are isopentane, alone or mixed with butane. For applications with the evaporators operating in the range -20°C to -5°C mixtures of hydrocarbons containing a higher, an intermediate and a lower boiling point component are preferred. Especially preferred are blends containing isopentane, butane and isobutane. For evaporators operating below -20°C HC mixtures containing isobutane and butane are preferred with optionally some isopentane.

45 [0025] US-B-6629419 discloses refrigerant composition consisting of R134a, R125, isopentane and butane. EP-A-0779352 discloses compositions consisting of R134a, R125, butane and isobutane. US2004/026655 discloses refrigerant compositions comprising R134a, R227ea and R125 and a hydrocarbon US-B-6526764 discloses refrigerants comprising R32, R125, R134a and R143a.

[0026] According to the present invention a refrigerant composition which may find application as a replacement or substitute for R22 consists essentially of:

50 R134a	53.2 to 39%
R125	45 to 55%
isopentane	0.6 to 1%
butane	0.6 to 3%
55 isobutane	0.6 to 2%.

[0027] A particularly preferred consists essentially of:

R134a	47.5%
R125	50%
isopentane	0.6%
butane	1%
isobutane	0.9%.

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- 10 [0028] In a first preferred embodiment the hydrocarbon is present in an amount of 0.6 to 4% and wherein the composition is non-flammable when completely in the vapour phase.
- [0029] In a second preferred embodiment the hydrocarbon is present in an amount of 0.6 to 4% and wherein when the composition is in a container both vapour and liquid present, neither vapour nor liquid phase is flammable.
- [0030] In a third preferred embodiment the hydrocarbon is present in an amount of 0.6 to 4% and wherein at any time during a leak from a vapour space in a container neither the liquid phase nor the vapour phase is flammable.
- 15 [0031] In a fourth preferred embodiment the hydrocarbon is present in amount of 0.6 to 4% and wherein at any time during a leak from a liquid space in a container neither the liquid phase nor vapour phase is flammable.
- [0032] According to a fifth preferred embodiment the hydrocarbon is present in an amount of 0.6 to 4% and wherein the proportion of hydrocarbon to hydrofluorocarbon in the vapour phase does not differ from the equivalent proportion in the liquid phase by more than 40%, more preferably not by more than 30%, most preferably not by more than 20% at equilibrium at 25°C.
- 20 [0033] In a sixth preferred embodiment hydrocarbon is present in amount of 0.6 to 4% and wherein the proportion of hydrocarbon to hydrofluorocarbon in the vapour phase does not differ from the formulated composition by more than 40%, preferably by not more than 30%, most preferably by not more than 20% at equilibrium at 25°C.
- [0034] In particularly preferred compositions in accordance with either the fifth or sixth preferred compositions above, during a leak from the vapour space or liquid space in a container, the proportion of hydrocarbon to hydrofluorocarbon in either of the vapour phase or the liquid phase does not differ from the formulated composition by more than 40%, more preferably by not more than 30%, most preferably by not more than 20% at equilibrium at 25°C.
- [0035] Preferred compositions in accordance with this invention meet two or more of the criteria of the preferred embodiment.
- 30 [0036] The hydrocarbon component consists of a mixture of isopentane, butane and isobutane.
- [0037] The amount of isopentane is preferably about 0.6 to 1%.
- [0038] The amount of butane is preferably about 0.6 to 3%, most preferably about 0.6 to 2%.
- [0039] The amount of isobutane is preferably about 0.6 to 2%, most preferably about 0.6 to 1%.
- 35 [0040] Percentages and other proportions referred to in this specification are by weight unless indicated otherwise and are selected to total 100% from within the ranges disclosed.
- [0041] The invention is further described by means of example but not in a limitative sense.

Replacement for R22 in Room Air Conditioning

40 **EXAMPLE**

- [0042] Blends comprising fluids selected from R134a, R125, 600, 600a and 601a.
- [0043] The performances of various blends were evaluated in a typical static air conditioning cycle using the NIST CYCLE D program. The modelling conditions are given below.

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COOLING DUTY DELIVERED	10 kW
EVAPORATOR	
Midpoint fluid evaporation temperature	7.0°C
Superheating	5.0°C
50 Suction line pressure drop (in saturated temperature)	1.5°C
CONDENSER	
Midpoint fluid condensing temperature	45.0°C
Subcooling	5.0°C
55 Discharge line pressure drop (in saturated temperature)	1.5°C
LIQUID LINE/SUCTION LINE HEAT EXCHANGER	
Efficiency	0.3

(continued)

	COOLING DUTY DELIVERED	10 kW
	COMPRESSOR	
5	Electric motor efficiency	0.85
	Compressor isentropic efficiency	0.7
	Compressor volumetric efficiency	0.82
	PARASITIC POWER	
10	Indoor fan	0.3 kW
	Outdoor fan	0.4kW
	Controls	0.1kW

[0044] The results of analysing the performances in an air-conditioning unit using these operating conditions are shown in the Table. For comparison the performances of R22 and R407C are also shown.

Table - Replacements for R22 especially in fixed orifice expansion units

	Refrigerant	R-22	R407C	1	2	3	4	5
20	R134a wt%			42.2	44.3	46.3	47.8	49.3
	R125 wt%			55	53	51	49	48
	R601a			0.8	0.9	0.6	0.8	1
	R600			0.8	1	1.4	1.5	1
25	R600a			1.2	0.8	0.7	0.9	0.7
	Discharge pressure (bar)	17.91	19.30	16.05	15.78	15.64	15.37	15.27
30	Discharge temperature (°C)	104.7	92.5	78.3	78.6	78.7	78.9	79.1
	COP (system)	2.49	2.47	2.48	2.48	2.49	2.49	2.49
	Capacity (kW/m3)	3067	3172	2671	2635	2619	2580	2566
	Glide in evaporator (°C)	0	4.8	4.0	4.1	3.7	3.9	4.1
35	Glide in condenser (°C)	0	4.7	3.8	3.9	3.7	3.9	4.0

Claims

1. A refrigerant composition consisting by weight essentially of:

	R134a	53.2 to 39%
45	R125	45 to 55%
	isopentane	0.6 to 1%
	butane	0.6 to 3%
	isobutane	0.6 to 2%.

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

	R134a	47.5%
55	R125	50%
	isopentane	0.6%
	butane	1%
	isobutane	0.9%.

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3. A composition as claimed in any preceding claim wherein the composition is non-flammable when completely in the vapour phase; and wherein when the composition is in a container with both vapour and liquid present; neither vapour nor liquid phase is flammable; and
5 wherein at any time during a leak from a vapour space in a container neither the liquid phase nor the vapour phase is flammable.
4. A composition as claimed in any preceding claim wherein the proportion of hydrocarbon to hydrofluorocarbon in the vapour phase does not differ from the equivalent proportion in the liquid phase by more than 40% at equilibrium at
10 25°C.
5. A composition as claimed in claim 4 wherein the proportion does not differ by more than 30%.
6. A composition as claimed in claim 4 wherein the proportion does not differ by more than 20%.
15
7. A composition as claimed in any preceding claim wherein the proportion of hydrocarbon to hydrofluorocarbon in the vapour phase does not differ from the formulated composition by more than 40% at equilibrium at 25°C.
8. A composition as claimed in claim 7 wherein the proportion does not differ by more than 30%.
20
9. A composition as claimed in claim 8 wherein the proportion does not differ by more than 20%.
10. A composition as claimed in any preceding claim wherein during a leak from the vapour space or liquid space of a container, the proportion of hydrocarbon to hydrofluorocarbon in either of the vapour phase or the liquid phase does
25 not differ from the formulated composition by more than 40% at equilibrium at 25°C.
11. A composition as claimed in claim 10 wherein the proportion does not differ by more than 40%.
12. A composition as claimed in claim 11 wherein the proportion does not differ by more than 20%.
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Patentansprüche

1. Kältemittelzusammensetzung gewichtsmäßig im Wesentlichen bestehend aus:
35

R134a	53,2 bis 39%
R125	45 bis 55%
Isopentan	0,6 bis 1%
Butan	0,6 bis 3%
Isobutan	0,6 bis 2%.

2. Kältemittelzusammensetzung, wie in Anspruch 1 beansprucht, im Wesentlichen bestehend aus:
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R134a	47,5%
R125	50%
Isopentan	0,6%
Butan	1%
Isobutan	0,9%.

3. Zusammensetzung, wie in einem der vorangehenden Ansprüche beansprucht, wobei die Zusammensetzung nicht-
55 brennbar ist, wenn sie vollständig in der Dampfphase ist, und wobei, wenn sich die Zusammensetzung in einem Behälter befindet, wobei sowohl Dampf als auch Flüssigkeit vorhanden ist, weder eine Dampf- noch eine Flüssigphase brennbar ist; und wobei zu jeder Zeit während eines Lecks von einem Dampfraum in einem Behälter weder die Flüssigphase noch

die Dampfphase brennbar ist.

4. Zusammensetzung, wie in einem der vorangehenden Ansprüche beansprucht, wobei sich das Verhältnis von Kohlenwasserstoff zu Fluorkohlenwasserstoff in der Dampfphase von dem gleichwertigen Verhältnis in der Flüssigphase nicht um mehr als 40% im Gleichgewicht bei 25°C unterscheidet.
5. Zusammensetzung, wie in Anspruch 4 beansprucht, wobei sich das Verhältnis nicht um mehr als 30% unterscheidet.
6. Zusammensetzung, wie in Anspruch 4 beansprucht, wobei sich das Verhältnis nicht um mehr als 20% unterscheidet.
7. Zusammensetzung, wie in einem der vorangehenden Ansprüche beansprucht, wobei sich das Verhältnis von Kohlenwasserstoff zu Fluorkohlenwasserstoff in der Dampfphase von der formulierten Zusammensetzung nicht um mehr als 40% im Gleichgewicht bei 25°C unterscheidet.
8. Zusammensetzung, wie in Anspruch 7 beansprucht, wobei sich das Verhältnis nicht um mehr als 30% unterscheidet.
9. Zusammensetzung, wie in Anspruch 8 beansprucht, wobei sich das Verhältnis nicht um mehr als 20% unterscheidet.
10. Zusammensetzung, wie in einem der vorangehenden Ansprüche beansprucht, wobei sich während eines Lecks von dem Dampfraum oder einem Flüssigkeitsraum eines Behälters das Verhältnis von Kohlenwasserstoff zu Fluorkohlenwasserstoff in entweder der Dampfphase oder der Flüssigphase von der formulierten Zusammensetzung nicht um mehr als 40% im Gleichgewicht bei 25°C unterscheidet.
11. Zusammensetzung, wie in Anspruch 10 beansprucht, wobei sich das Verhältnis nicht um mehr als 40% unterscheidet.
12. Zusammensetzung, wie in Anspruch 11 beansprucht, wobei sich das Verhältnis nicht um mehr als 20% unterscheidet.

Revendications

1. Composition réfrigérante composée essentiellement, en poids, de :

R134a :	53,2% à 39%
R125 :	45% à 55%
Isopentane :	0,6% à 1%
Butane :	0,6% à 3%
Isobutane :	0,6% à 2%.

2. Composition réfrigérante selon la revendication 1, composée essentiellement de :

R134a :	47,5%
R125 :	50%
Isopentane :	0,6%
Butane :	1%
Isobutane :	0,9%

3. Composition selon l'une quelconque des revendications précédentes, laquelle composition est ininflammable lorsqu'elle se trouve complètement en phase gazeuse ; et
 - laquelle composition, lorsqu'elle se trouve dans un conteneur dans lequel les phases gazeuses et liquides sont toutes les deux présentes, aucune des phases n'est inflammable; et
 - lors d'une fuite depuis un espace occupé par la phase gazeuse dans un conteneur, ni la phase liquide ni la phase gazeuse ne sont à aucun moment inflammables.

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4. Composition selon l'une quelconque des revendications précédentes, dans laquelle la proportion d'hydrocarbure au hydrofluorocarbure en phase gazeuse ne se différencie pas plus de 40% à l'équilibre à 25°C de son équivalent en phase liquide.
- 5 5. Composition selon la revendication 4, dans laquelle la proportion ne différencie pas plus de 30%.
6. Composition selon la revendication 4, dans laquelle la proportion ne se différencie pas plus de 20%.
- 10 7. Composition selon l'une quelconque des revendications précédentes, dans laquelle la proportion d'hydrocarbure au hydrofluorocarbure en phase gazeuse ne se différencie pas plus de 40% à l'équilibre à 25°C de la composition telle que formulée.
8. Composition selon la revendication 7, dans laquelle la proportion ne se différencie pas plus de 30%.
- 15 9. Composition selon la revendication 8, dans laquelle la proportion ne se différencie pas plus de 20%.
- 20 10. Composition selon l'une quelconque des revendications précédentes, dans laquelle pendant une fuite depuis un espace occupé par la phase gazeuse ou un espace occupé par la phase liquide, dans un conteneur, la proportion d'hydrocarbure au hydrofluorocarbure en phase gazeuse ou en phase liquide ne se différencie pas plus de 40% à l'équilibre à 25°C de la composition telle què formulée.
- 25 11. Composition selon la revendication 10, dans laquelle la proportion ne se différencie pas plus de 30%.
12. Composition selon la revendication 11, dans laquelle la proportion ne se différencie pas plus de 20%.

REFERENCES CITED IN THE DESCRIPTION

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