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<p>(21) 国際出願番号 PCT/JP97/04298</p> <p>(22) 国際出願日 1997年11月25日(25.11.97)</p> <p>(30) 優先権データ 特願平8/318126 1996年11月28日(28.11.96) JP</p> <p>(71) 出願人 (米国を除くすべての指定国について) ダイキン工業株式会社(DAIKIN INDUSTRIES, LTD.)(JP/JP) 〒530 大阪府大阪市北区中崎西2丁目4番12号 梅田センタービル Osaka, (JP)</p> <p>(72) 発明者; および</p> <p>(75) 発明者/出願人 (米国についてのみ) 井手 哲(IDE, Satoshi)(JP/JP) 柴沼 俊(SHIBANUMA, Takashi)(JP/JP) 〒566 大阪府摂津市西一津屋1番1号 ダイキン工業株式会社 淀川製作所内 Osaka, (JP)</p> <p>(74) 代理人 弁理士 三枝英二, 外(SAEGUSA, Eiji et al.) 〒541 大阪府大阪市中央区道修町1-7-1 北浜TNKビル Osaka, (JP)</p>		<p>(81) 指定国 AU, BR, CA, CN, ID, KR, US, 欧州特許 (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>添付公開書類 国際調査報告書</p>
<p>(54) Title: METHOD OF CHARGING MIXED COOLING MEDIUM</p> <p>(54) 発明の名称 混合冷媒の充填方法</p> <p>(57) Abstract To use a non-azeotropic mixture consisting of HFC32 (23 wt.%), HFC125 (25 wt.%) and HFC134a (52 wt.%) as a cooling medium, the mixture in a container on the supply side such as a bomb is made to have a composition of HFC31 (23.5 to 25.0 wt.%), HFC125 (23.5 to 25.0 wt.%) and HFC134a (50.0 to 53.0 wt.%), and extracted from ththe liquid phase at a temperature not higher than 40 °C. The change of the composition due to the charging is within an allowable range of cooling performance.</p>		

Abstract

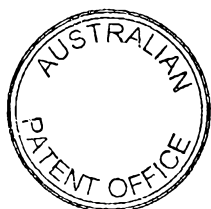
The present invention provides a method for charging a refrigerant blend characterized in that, in case of employing as refrigerant a non-azeotropic blend

5 comprising 23% by weight of difluoromethane, 25% by weight of pentafluoroethane and 52% of 1,1,1,2-tetrafluoroethane, composition change associated with transfer is allow to fall within the permissible range of performance of the non-azeotropic refrigerant blend by

10 adjusting a composition of the non-azeotropic blend in a feeding container such as bomb to 23.5-25.0% by weight of difluoromethane, 23.5-25.0% by weight of pentafluoroethane and 50.0-53.0% by weight of 1,1,1,2-tetrafluoroethane followed by discharging the non-

15 azeotropic blend from a liquid phase at 40°C or less. According to the charging method, composition change associated with transfer of non-azeotropic HFC32/HFC125/HFC134a refrigerant blend may be allowed to fall within the permissible range of performance of

20 refrigerant.



Specification

METHOD FOR CHARGING REFRIGERANT BLEND

Technical Field

The present invention relates to a method for
5 charging a non-azeotropic refrigerant blend comprising
23% by weight of difluoromethane, 25% by weight of
pentafluoroethane and 52% by weight of 1,1,1,2-
tetrafluoroethane used as a working fluid for vapor
compression refrigeration cycle.

10

Background Art

Vapor compression refrigeration cycle to
perform cooling and heating of fluids by the use of state
change of material such as evaporation and condensation
has found a widespread use for applications such as an
15 air-conditioner, refrigerator, hot-water supplier, etc.
A variety of working fluids which are applied for the
vapor compression refrigeration cycle, especially
fluorocarbon refrigerants, have been developed and
practically used. Among the fluids, HCFC22
20 (monochlorodifluoromethane) is widely used as a
refrigerant in a heating and cooling system for air-
conditioning.

However, chlorofluorocarbons were recently
found to be responsible for the destruction of the ozone
25 layer when released into the stratosphere and eventually



exert seriously adverse effects on the ecosystem including human on the earth. Then, a worldwide agreement calls for the restriction of use and in the future total abolition thereof. Under these
5 circumstances, there is an urgent demand for developing a new refrigerant which has no or little potential to cause the problem of depleting the ozone layer.

As attempts to make up for insufficient performances of a single component refrigerant by the use
10 of refrigerant blends, many proposals for using non-azeotropic refrigerant blends have recently been raised (e.g., Japanese Unexamined Patent Publication No. 79288/1989, Japanese Examined Patent Publication No. 55942/1994, and Japanese Unexamined Patent Publication
15 No. 287688/1991).

A non-azeotropic mixture causes a composition change during phase change such as evaporation and condensation, since a component having lower boiling point is likely to be evaporated and a component having
20 higher boiling point is likely to be condensed. The tendency of composition change is pronounced in the case of evaporation, i.e., phase change from liquid to vapor, and the tendency is particularly pronounced as differences of boiling point between components are
25 larger. Therefore, when such a non-azeotropic blend is



transferred from one container to another, it is common practice to discharge it from liquid phase so as not to arise the phase change. However, even in the case of discharging a refrigerant blend from liquid phase, phase change as much as a few percent occurs in the case where the differences in boiling points are large between components. This is because discharging the blend causes a decrease of pressure and increase of the gaseous space, resulting in evaporation of lower-boiling-point components from liquid phase. A few percent of composition change cause a significant change in performances of refrigerant, and the change not only results in a decrease in capability and efficiency of the refrigerant, but also adversely affects safety of refrigerants such as flammability.

In particular, when using as a refrigerant a non-azeotropic blend comprising 23% by weight of difluoromethane (thereafter referred to as "HFC32"), 25% by weight of pentafluoroethane (thereafter referred to as "HFC125") and 52% by weight of 1,1,1,2-tetrafluoroethane (thereafter referred to as "HFC134a"), which is considered as the most promising substitute for HCFC22, the composition change thereof caused during transfer of the refrigerant from a bomb and like feeding container, to an air-conditioner is a serious problem, since ASHRAE



STANDARD (1994) establishes the permissible composition range of HFC32 (21-25% by weight), HFC125 (23-27% by weight) and HFC134a (50-54% by weight).

As a method to solve the problem, Japanese
5 Unexamined Patent Publication No. 157810/1996 proposes a method for allowing the composition to fall within the range of the tolerance of the composition by increasing in the blend composition lower boiling point components beforehand which are decreased with composition change.

10 Since a permissible range of performance of refrigerant is usually within $\pm 3\%$ by weight, in particular $\pm 2\%$ by weight with respect to the standard value, a biased composition concerning lower-boiling-point components according to the method enlarges
15 differences of performance of refrigerant from the standard value.

Disclosure of the Invention

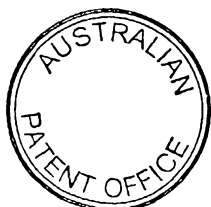
The inventors conducted extensive research on a method for charging a liquid gas so as to solve the
20 problem associated with the composition change which occurs when a non-azeotropic blend comprising three types of liquid gases having different boiling points and stored in a sealed vessel is transferred from a liquid-containing container to another container.

25 As a result, the inventors found a method for



charging a refrigerant blend characterized in that in case of employing a non-azeotropic mixture comprising 23% by weight of difluoromethane, 25% by weight of pentafluoroethane and 52% by weight of 1,1,1,2-
5 tetrafluoroethane as refrigerant, composition change associated with transfer of the refrigerant blend may be allowed to fall within the permissible range of performance of refrigerant blend by adjusting a blend composition in a bomb and like feeding container to 23.5-
10 25.0% by weight of difluoromethane, 23.5-25.0% by weight of pentafluoroethane and 50.0-53.0% by weight of 1,1,1,2-tetrafluoroethane, followed by discharging the refrigerant from the liquid phase at not more than 40 °C.

The invention relates to a method for charging
15 a refrigerant blend characterized in that in case of employing a non-azeotropic mixture comprising 23% by weight of difluoromethane, 25% by weight of pentafluoroethane and 52% by weight of 1,1,1,2-tetrafluoroethane as refrigerant, composition change
20 associated with transfer of the refrigerant falls within the permissible range of performance of refrigerant, by adjusting the blend component in a bomb and like feeding container to about 23.5-25.0% by weight of difluoromethane, about 23.5-25.0% by weight of
25 pentafluoroethane and about 50.0-53.0% by weight of



1,1,1,2-tetrafluoroethane, followed by discharging the refrigerant from the liquid phase at not more than about 40 °C.

In addition, the present invention relates to a
5 method for producing a vapor compression refrigerating
equipment with a composition range of 23% by weight of
difluoromethane, 25% by weight of pentafluoroethane and
52% by weight of 1,1,1,2-tetrafluoroethane comprising
discharging a liquid phase in a feeding container which
10 has a blend composition of about 23.5-25.0% by weight of
difluoromethane, about 23.5-25.0% by weight of
pentafluoroethane and about 50.0-53.0% by weight of
1,1,1,2-tetrafluoroethane at not more than about 40 °C
and transferring it to a main body of the vapor
15 compression refrigerating equipment.

According to the invention, the temperature during discharge of the liquid phase in feeding container is up to about 40°C, preferably about 20-30°C.

According to the production method of the
20 invention, known refrigerating equipments may be widely
used as the main body of vapor compression refrigerating
equipment.

The non-azeotropic refrigerant blend comprising
23% by weight of difluoromethane, 25% by weight of
25 pentafluoroethane and 52% by weight of 1,1,1,2-



tetrafluoroethane is, in particular, an object of the invention. However, the idea of the invention may be applied to other composition ranges, or, liquid gases of non-azeotropic compositions comprising other components
5 having different boiling points. A blend comprising difluoromethane and 1,1,1,2-tetrafluoroethane, and a blend comprising pentafluoroethane, 1,1,1-trifluoroethane and 1,1,1,2-tetrafluoroethane may be exemplified.

Examples of the vapor compression refrigerating
10 equipment of the invention are an air-conditioner, freezer, refrigerator and hot-water supplier.

Feeding containers according to the present invention are not specifically limited insofar as the container is a sealed container capable of storing a
15 refrigerant blend. For example, a bomb is exemplified. As equipments to which a refrigerant blend is transferred and charged, any equipment which utilizes vapor compression refrigeration cycle can be used. Said equipments include, but are not specifically limited to,
20 an air-conditioner, freezer, refrigerator, hot-water supplier, etc.

Examples

The present invention is illustrated with reference to the following examples, but it is to be
25 understood that the invention is not limited to the



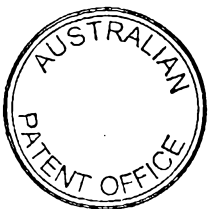
examples unless the scope of the invention is departed from.

Example 1 and Comparative example 1

To a 10 liter sealed container, 9 kg of a non-
5 azeotropic mixture of difluoromethane (HFC32), penta-
fluoroethane (HFC125) and 1,1,1,2-tetrafluoroethane
(HFC134a) having the upper limit composition (25.0/25.0/5
0.0% by weight; example 1) or the lowest limit
composition (21.0/25.0/54.0% by weight; comparative
10 example 1) of the permissible range with respect to the
standard composition (23.0/25.0/52.0% by weight) was
charged. The container was placed into a thermostatic
chamber in which the temperature was maintained at 10°C
or 40°C.

15 The mixture from the liquid phase was then
transferred to another empty container at a rate of 900
g/min by means of a pump. A portion of the charging gas
was withdrawn through a sampling valve located on a
charging pipe near the liquid phase and the composition
20 was analyzed by gas chromatography.

Performance of refrigerant composition at the
beginning and end of charging was compared under
conditions of refrigeration cycle that evaporating
temperature was 0°C; condensing temperature was 50°C;
25 overheating and supercooling were 0°C to determine



23.5/23.5/53.0 (the lowest limit) was transferred.

The conditions of transfer were the same as those of example 1 except that temperature of thermostatic chamber was 40°C which was the worst condition. The results are shown in table 2.

Example 3

Performance of refrigerant composition of example 2 charged at 40°C was compared under conditions of refrigeration cycle that evaporating temperature was 0°C; condensing temperature was 50°C; overheating and supercooling were 0°C. The results of example 3 together with the results of example 2 are shown in Table 2.

Table 2.

Transfer Ratio and Analysis of Collected Gas Composition

	HFC			Coefficient of Refrigerating Performance		Capacity	
	32	125	134a	(difference)	(Difference)	KJ/m ³	(wt.%)
Standard Composition	23.0	25.0	52.0	3.94 (0)	2947	(0)	
Example 2							
lowest limit beginning	23.3	23.4	53.3	3.95 (+0.3)	2941	(-0.2)	
end	22.1	22.4	55.5	3.97 (+0.8)	2889	(-2.0)	

Composition change associated with transfer of non-azeotropic HFC32/HFC125/HFC134a refrigerant blend used as a working fluid for vapor compression



refrigeration cycle may be allowed to fall within the permissible range ($\pm 3\%$ by weight, preferably $\pm 2\%$ by weight) of performance of refrigerant (coefficient of performance, refrigerating capacity), whereby a
5 significant change in performances and an increase in flammability of refrigerant can be prevented.



CLAIMS

1. A method for charging a refrigerant blend characterized in that, in case of employing as refrigerant a non-azeotropic blend comprising 23% by weight of difluoromethane, 25% by weight of pentafluoroethane and 52% of 1,1,1,2-tetrafluoroethane, composition change associated with transfer is allow to fall within the permissible range of performance of the non-azeotropic refrigerant blend by adjusting a composition of the non-azeotropic blend in a feeding container such as bomb to 23.5-25.0% by weight of difluoromethane, 23.5-25.0% by weight of pentafluoroethane and 50.0-53.0% by weight of 1,1,1,2-tetrafluoroethane followed by discharging the non-azeotropic blend from a liquid phase at 40°C or less.

2. The method for charging a refrigerant blend according to claim 1 wherein the composition change associated with the transfer is allowed to fall within $\pm 3\%$ by weight of performance of the non-azeotropic refrigerant blend.

3. A method for producing a vapor compression refrigerating equipment with a composition range of 23% by weight of difluoromethane, 25% by weight of pentafluoroethane and 52% by weight of 1,1,1,2-tetrafluoroethane comprising discharging a liquid phase



in a feeding container with a blend composition of 23.5-25.0% by weight of difluoromethane, 23.5-25.0% by weight of pentafluoroethane and 50.0-53.0% by weight of 1,1,1,2-tetrafluoroethane at not more than 40 °C and transferring
5 it to a main body of the vapor compression refrigerating equipment.

