(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 444 598 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **91102807.4**

(51) Int. Cl.5: **C11D 7/50**, C23G 5/028

(22) Date of filing: **26.02.91**

(30) Priority: **28.02.90 JP 48722/90**

(43) Date of publication of application:
04.09.91 Patentblatt 91/36

(84) Designated Contracting States:
BE DE ES FR GB GR IT NL

(71) Applicant: **DAIKIN INDUSTRIES, LIMITED**
Umeda Center Building 4-12 Nakazaki-nishi
2-chome Kita-ku
Osaka 530(JP)

(72) Inventor: **Omure, Yukio**
11-5, Daizozi 1-chome
Takatsuki-shi, Osaka-fu(JP)
Inventor: **Hanatani, Naoyoshi**
2-17-12, Kasuga-cho
Toyonaka-shi, Osaka-fu(JP)

(74) Representative: **Türk, Gille, Hrabal**
Brucknerstrasse 20
W-4000 Düsseldorf 13(DE)

(54) Azeotropic Solvent Composition

(57) An azeotropic solvent composition comprising a dichloropentafluoropropane and a fluorine alcohol. The composition is excellent in cleaning power, particularly rogin-flux cleaning power, incombustibility, chemical stability and selective solvent power, as well as has low boiling point, high solbility and easy control of the liquid composition of the solvent and easy recovering and reuse of the solvent. Especially, the composition does not corrode metals even in the presence of moisture, so, it can apply to various use conditions and various kinds of materials to be washed.

EP 0 444 598 A1

The present invention relates to an azeotropic solvent composition comprising a dichloropentafluoropropane (hereinafter referred to as "HCFC-225") and a fluorine alcohol.

Trichlorotrifluoroethane (hereinafter referred to as "CFC-113"), one of chlorofluoroethane compounds, is incombustible, low in toxity to living bodies and excellent in selective solvent power that it can dissolve fats and oils, greases, waxes, and the like without erosion of polymer substances such as plastics and rubbers. Accordingly, CFC-113 has hitherto been widely used alone or in the state of a mixture or azeotropic composition with another organic solvent as a solvent, a cleaning solvent, or the like.

Recently, a problem of environmental pollution that chlorofluoroethane compounds in which all hydrogen atoms of ethane are substituted by chlorine atoms and fluorine atoms (hereinafter referred to as "perhaloethanes") such as CFC-113 destroy the ozone layer surrounding the earth has been raised on a global scale. Therefore, it is urgently required to decrease the used amount of such perhaloethanes or to omit the use of the perhaloethane.

As one of methods decreasing the used amount of the perhaloethane, for example, a method using a mixed solvent of CFC-113 with an organic solvent other than the perhaloethanes has been studied. According to the method, however, the used amount of CFC-113 can be decreased no more than a certain extent, because the performances of the mixed solvent are lowered. Also, when using CFC as the mixed solvent, it is required to easily control the liquid composition of the solvent and to easily recover and reuse the solvent, moreover, it is desired that the mixed solvent can be applied to steam cleaning. For satisfying the requirements as mentioned above, it is necessary that the mixed solvents are azeotropic mixtures. It is not easy to find such a mixture. Thus, no useful substitute has been found.

On the other hand, though as to solvents containing no perhaloethane at all, various studies have been made, no useful substitute has been found, too.

Although mixed solvents of a halogenated organic solvent and a fluorine alcohol have been also known in Japanese Examined Patent Publication No. 12864/1971, azeotropic compositions of HCFC-225 and a fluorine alcohol have not been found out. Also, mixed solvents of a halogenated organic solvent, particularly fluorocarbon solvents, and a hydrocarbon alcohol have hitherto been well known. The mixted solvents have, however, a defect that an acid such as hydrochloric acid generates in the presence of moisture to corrode metals. Thus, when the mixed solvent is used, it is required to remove moisture, or use conditions or kinds of materials to be washed are limited.

An object of the present invention is to provide an azeotropic solvent composition containing no CFC-113, which has the improved rogin-flux cleaning power, which destroys scarcely the ozone layer, and which is incombustible.

This and other objects of the present invention will become apparent from the description hereinafter.

In accordance with the present invention, there is provided an azeotropic solvent composition comprising a dichloropentafluoropropane and a fluorine alcohol. The composition of the present invention, surprisingly, does not corrode metals even in the presence of moisture and is stable.

HCFC-225 used in the present invention has isomers such as 1,1-dichloro-2,2,3,3,3-pentafluoropropane [boiling point (bp) : 51 °C], 1,2-dichloro-1,2,3,3,3-pentafluoropropane (bp : 56 °C), 1,3-dichloro-1,2,2,3,3-pentafluoropropane (bp : 56.1 °C), 2,2-dichloro-1,1,3,3,3-pentafluoropropane (bp : 54 °C), 2,3-dichloro-1,1-2,3,3-pentafluoropropane (bp : 56 °C), 3,3-dichloro-1,1,2,2,3-pentafluoropropane (bp : 58 °C), 1,1-dichloro-1,2,3,3,3-pentafluoropropane (bp : 49 °C), 1,3-dichloro-1,1,2,3,3-pentafluoropropane (bp : 48 °C) and 1,2-dichloro-1,1,3,3,3-pentafluoropropane (bp : 50 °C).

HCFC-225 is incombustible, low in toxity to living bodies and chemically stable, and has the selective solvent power that it can wash and remove stains such as fats and oils, exerting scarcely influence on plastics, rubbers, metals, and the like. Moreover, HCFC-225 less destroys the ozone layer than CFC-113.

In the present invention, as the fluorine alcohol, there are exemplified alcohols having at least two fluorine atoms and not less than two carbon atoms in one molecule. More concretely, fluorine alcohols having the following formulas as mentioned below are cited;

CF_3CH_2OH

$H(CF_2CF_2)_aCH_2OH$

$H(CF_2\underset{\underset{CF_3}{|}}{CF})_bCH_2OH$

$H(CF_2CF_2)_c\underset{\underset{CH_3}{|}}{CHOH}$

$H(CF_2\underset{\underset{CF_3}{|}}{CF})_d\underset{\underset{CH_3}{|}}{CHOH}$

$F(CF_2CF_2)_eCH_2OH$

$F(CF_2\underset{\underset{CF_3}{|}}{CF})_fCH_2OH$

$F(CF_2CF_2)_gCH_2CH_2OH$

$F(CF_2\underset{\underset{CF_3}{|}}{CF})_hCH_2CH_2OH$

$F(CF_2CF_2)_iCH_2CH_2CH_2OH$

$F(CF_2\underset{\underset{CF_3}{|}}{CF})_jCH_2CH_2CH_2OH$

wherein each a, c, e, g and i is an integer of 1 to 5 and each b, d, f, h and j is an integer of 1 to 3.

Among them, trifluoroethanol (bp : 77°C), tetrafluoropropanol (bp : 107°C) and pentafluoropropanol (hereinafter referred to as "5FP", bp : 81°C) are more preferable. Furthermore, 5FP is more preferable because it is incombustible. The fluorine alcohols may be used alone or as an admixture thereof.

The composition of the present invention comprises HCFC-225 having the above-mentioned properties and the fluorine alcohol. Moreover, since the composition is azeotropic, it is easy to control the liquid composition of the solvent and to recover and reuse the solvent, so the composition can be applied to steam cleaning. Furthermore, the composition is very effective in electric and electronic industries as a cleaning solvent for removing rogin-flux used in soldering of printed-circuit board. The composition is also chemically stable, particularly is remarkably stable even in the presence of moisture and the metal, and has the selective solvent power that it can wash and remove only the stains, exerting no bad influence on plastics, rubbers, metals, and the like. Moreover, the composition less destroys the ozone layer than CFC-113 and is incombustible.

The mixture of HCFC-225 and the fluorine alcohol forms an azeotropic composition or an azeotropic like composition within the range of a weight ratio of HCFC-225 to the fluorine alcohol of 99.5 to 88.0/0.5 to

12.0, preferably 99.5 to 91.0/0.5 to 9.0. The azotropic composition has an azeotropic temperature of 47,5 ° to 57.5 ° C. Examples of the azeotropic mixture and the azeotropic like composition are, for instance, an azeotropic mixture (azeotropic point : 49.8 ° C) of 93.5 % by weight of 1,1-dichloro-2,2,3,3,3-pentafluoropropane (bp : 51 ° C) and 6.5 % by weight of pentafluoropropanol (5FP) (bp : 81 ° C), an azeotropic mixture (azeotropic point: 54.5 ° C) of 92.2 % by weight of 1,3-dichloro-1,2,2,3,3-pentafluoropropane (bp: 56.1 ° C) and 7.8 % by weight of 5FP (bp: 81 ° C), an azeotropic like composition of 93.5 to 92.2 % by weight of a mixture of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane, the weight ratio of 1,1-dichloro-2,2,3,3,3-pentafluoropropane to 1,3-dichloro-1,2,2,3,3-pentafluoropropane being 0.5 to 99.5/99.5 to 0.5, preferably 5 to 60/95 to 40, more preferably 20 to 50/80 to 50, and 6.5 to 7.8 % by weight of 5FP, and the like. The composition containing mainly HCFC-225 of the present invention is suitable for use not only as a cleaning solvent for removing the rogin-flux which is used in printed-circuit boards and which is difficult to be removed by a single component alone, but also in various uses in which CFC-113 has been generally used, for instance, as a degreasing solvent for removing paraffins, animal and vegetable oils, processing oils; as a cleaning solvent for removing mold release agents used in molding and processing of plastics; as a cleaning solvent for removing waxes used for temporarily fixing silicon wafers used in semiconductors, quartz and ceramics in their processing such as cutting or polishing, pressure sensitive adhesive tapes, paints, inks, and the like; as a disperse medium for ceramics or metal powder; as a drying dehydration desiccant; as a dry-cleaning solvent; and the like.

Although the composition of the present invention is chemically stable compared to solvents containing an aliphatic alcohol, a stabilizer can be included.

It is preferred that the stabilizers can be distilled together with the azeotropic composition of the invention or the mixture of the azeotropic composition and the stabilizer can form an azeotropic composition, in addition that the stabilizers have a large effect for stabilizing the composition.

Examples of the stabilizers as mentioned above are, for instance, aliphatic nitro compounds such as nitromethane, nitroethane and nitropropane; acetylene alcohols such as 3-methyl-1-butyne-3-ol and 3-methyl-1-pentyne-3-ol; epoxides such as glycidol, methyl glycidyl ether, allyl glycidyl ether, phenyl glycidyl ether, 1,2-butylene oxide, cyclohexene oxide and epichlorohydrin; ethers such as dimethoxymethane, 1,2-dimethoxyethane, 1,4-dioxane and 1,3,5-trioxane; unsaturated hydrocarbons such as hexene, heptene, octene, 2,4,4-trimethyl-1-pentene, pentadiene, octadiene, cyclohexene and cyclopentene; olefinic alcohols such as allyl alcohol, 1-butene-3-ol and 3-methyl-1-butene-3-ol; acrylates such as methyl acrylate, ethyl acrylate and butyl acrylate; and the like. The stabilizers may be used alone or as an admixture thereof. Among them, nitromethane is preferable. In addition thereto, other compounds may be used. In such a case as the stabilizer is used with the other compounds, synergic stabilizing effect can be obtained. Examples of the other compounds are, for instance, phenols such as phenol, trimethylphenol, cyclohexylphenol, thymol, 2,6-di-t-butyl-4-methylphenol, butylhydroxyanisole and isoeugenol; amines such as hexylamine, pentylamine, dipropylamine, diisopropylamine, diisobutylamine, triethylamine, tributylamine, pyridine, N-methylmorpholine, cyclohexylamine, 2,2,6,6-tetramethylpiperidine and N,N'-diallyl-p-phenylenediamine; toriazoles such as benzotriazole, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole and chlorobenzotriazole; and the like.

An amount of the stabilizer depends on the kind of the stabilizer, so it is suitably determined according to the kind of the used stabilizer. Generally, the amount is from 0.1 to 10 % by weight, preferably from 0.5 to 5 % by weight, based on the azeotropic composition. In such a case as nitromethane is used, an amount of nitromethane is from about 0.1 to 1.0 % by weight of the azeotropic composition.

The stabilizer is used in an amount such that the azeotropic composition is not impaired. Usually, since the stabilizer is used in a small amount such as not more than 1 % by weight, the addition of the stabilizer does not influence much the azeotropic composition.

The composition of the present invention is the same as or superior to CFC-113 in the flux cleaning power, incombustibility, chemical stability, and the like. The composition has the selective solvent power while it exerts scarcely influence on the plastics, rubbers, particularly metals. Also, the azeotropic solvent composition of the invention contains HCFC-225 destroying less the ozone layer than CFC-113 as the main component, is excellent in rogin-flux cleaning power, that is, it can remove the rogin-flux which cannot be removed sufficiently by using the single component alone with maintaining the excellent various properties of HCFC-225. Moreover, the composition is excellent in properties to be required as the azeotropic solvent composition, that is, it is low in boiling point, high in solubility, easy to control the liquid composition of solvent and easy to recover or reuse the solvent.

Especially, when the composition of the present invention is used, the metal cannot be corroded even in the presence of water, though the metal corrosion in the presence of water could not be avoided by the combination with the alcohol as conventionally used. Accordingly, the composition of the invention can be used in various use conditions and various kinds of materials to be washed.

The present invention is more specifically described and explained by means of the following Examples, in which all % and parts are by weight otherwise noted. It is to be understood that the present invention is not limited to the Examples and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

Example 1

A distillation flask was charged with 200 g of a mixture of 1,1-dichloro-2,2,3,3,3-pentafluoropropane (225ca, bp : 51 °C) and pentafluoropropanol (5FP, bp : 81 °C) in a weight ratio of 225ca to 5FP of 50/50. The mixture was distilled under normal pressure in a rectification towar having a theoritical plate number of 30 to give a distillate having an azeotropic point of 49.8 °C which was lower than the boiling point of each solvent.

As a result of gas chromatography analysis, it was confirmed that the distillate consisted of 93.5 % of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 6.5 % of pentafluoropropanol.

Using the obtained azeotropic mixture as a solvent, the flux cleaning power, effects on plastics, and stability were estimated according to the following tests, respectively.

[Flux cleaning power]

A rogin-flux commercially available under the trademark "MH-320V" from Kabushiki Kaisha Tamura Seisakusho is applied to a printed-circuit board (10 cm x 10 cm), and it is pre-heated at 110 °C. Then, the printed-circuit board is subjected to soldering (63Sn) at 250 °C for 5 seconds. Then, using 1 ℓ of a solvent shown in Table 1, dip cleaning is conducted for 1 minute and vapor cleaning is conducted for 1 minute.

The surface state of the printed-circuit board is observed with the naked eye. Also, an ionic residue remaining on the board is measured by using Omegameter® 500 commercially available from KENCO INDUSTRIES INC.

The results are shown in Table 1 as the results of the flux cleaning power test.

[Effects on plastics]

In 100 g of the solvent shown in Table 1 is dipped a plastic test piece shown in Table 1 (5 mm x 50 mm x 2 mm), and it is allowed to stand in a thermostat having a temperature of 50 °C for 5 minutes. Then, the test piece is taken out from the solvent, and immediately the weight and volume of the test piece are measured. The change of the weight and volume of the plastic test pieces are calculated, and the effects on plastics are estimated according to the following criteria:

◎ : A percentage of the increase of the weight or volume is from zero and less to than 2 %
○ : A percentage of the increase of the weight or volume is not less than 2 % and less than 5 %
△ : A percentage of the increase of the weight or volume is not less than 5 %
× : The plastic test piece is dissolved in the solvent.

The results are shown in Table 1 as the effects on plastics.

[Chemical stability]

A 100 mℓ glass bottle with a sealing stopper is charged with 100 g of the solvent shown in Table 1, 0.1 % of the solvent of water [in Comparative Examples 1 or 4 as mentioned below, 0.01 % of the solvent (225ca or 225cb alone) of water] and a metal, Aℓ or Zn, and the glass bottle was sealed. The glass bottle was placed in a thermostat having a temperature of 50 °C for 30 days.

In the meantime that the bottle was placed in the thermostat and after 30 days, whether the metal is corroded or not is estimated by observing the metal with the naked eye.

The results are shown in Table 1 as the chemical stability.

Comparative Examples 1, 2 and 3

The flux cleaning power, effects on plastics and chemical stability were examined in the same manner as in Example 1 except that as a solvent, 225ca alone (Comparative Example 1), 5FP alone (Comparative Example 2) or a mixture of 225ca and ethanol (225ca/ethanol = 97 % / 3 %) (Comparative Example 3) was used instead of the azeotropic mixture of 225ca/5FP.

The results are shown in Table 1.

Example 2

A mixture of 1,3-dichloro-1,2,2,3,3pentafluoropropane (225cb, bp: 56.1 °C) and 5FP (bp: 81 °C) in a weight ratio of 50/50 was distilled in the same manner as in Example 1 to give a distillate having an azeotropic point of 54.7 °C which was lower than the boiling point of each solvent.

As a result of gas chromatography analysis, it was confirmed that the distillate consisted of 92.2 % of 1,3-dichloro-1,2,2,3,3-pentafluoropropane and 7.8 % of 5FP.

As to the obtained azeotropic mixture, the flux cleaning power, effects on plastics and stability were measured in the same manner as in Example 1.

The results are shown in Table 1.

Example 3

A composition of a mixture of 55 % of 1,1-dichloro-2,2,3,3,3-pentafluoropropane(bp: 51 °C) and 45 % of 1,3-dichloro-1,2,2,3,3-pentafluoropropane (bp: 56.1 °C), and 5FP in a weight ratio of the mixture to 5FP being 50/50 was distilled in the same manner as in Example 1 to give a distillate. The distillate showed a stable boiling point within a narrow temperature range of 50 ° to 54.9 °C.

As a result of gas chromatorgraphy analysis, it was confirmed that the distillate consisted of 93.4 to 92.4 % of the mixture of 1,1-dichloro-2,2,3,3,3pentafluoropropane/1,3-dichloro-1,2,2,3,3pentafluoropropane (60 to 4 % :40 to 96 %) and 6.6 to 7.6 % of 5FP.

As to the obtained azeotropic like mixtures, the flux cleaning power, effects on plastics and stability were measured in the same manner as in Example 1.

The results are shown in Table 1.

Comparative Example 4

The flux cleaning power, effects on plastics and chemical stability were examined in the same manner as in Example 1 except that as a solvent, 225cb alone was used instead of the azeotropic mixture of 225ca/5FP.

The results are shown in Table 1.

Table 1

	Solvent	Flux cleaning power		Effects on plastics		
		Observation with the naked eye	Ionic residue ($\mu gNaC\ell/cm^2$)	ABS	Polycarbonate	Polystyrene
Ex. 1	225ca/5FP (93.5/6.5)	Clean surface (fine cleaning)	1.0	△	◎	○
Ex. 2	225cb/5FP (92.2/7.8)	Clean surface (fine cleaning)	1.1	△	◎	○
Ex. 3	225ca/225cb(55/45)*/5FP (93.2/6.8)	Clean surface (fine cleaning)	1.0	△	◎	○
	225ca/225cb(20/80)*/5FP (92.9/7.1)	Clean surface (fine cleaning)	1.2	△	◎	○
	225ca/225cb(5/95)*/5FP (92.4/7.6)	Clean surface (fine cleaning)	1.1	△	◎	○

(Note) * A weight ratio of 225ca/225cb

- continued -

- continued -

	Solvent	Chemical stability	
		Aℓ	Zn
Ex. 1	225ca/5FP (93.5/6.5)	No corrosion	No corrosion
Ex. 2	225cb/5FP (92.2/7.8)	No corrosion	No corrosion
Ex. 3	225ca/225cb(55/45)*/5FP (93.2/6.8)	No corrosion	No corrosion
	225ca/225cb(20/80)*/5FP (92.9/7.1)	No corrosion	No corrosion
	225ca/225cb(5/95)*/5FP (92.4/7.6)	No corrosion	No corrosion

- continued -

- continued -

	Solvent	Flux cleaning power		Effects on plastics		
		Observation with the naked eye	Ionic residue ($\mu gNaCl/cm^2$)	ABS	Polycarbonate	Polystyrene
Com. Ex. 1	225ca	White regidue on the surface (bad cleaning)	4.5	◎	◎	△
Com. Ex. 2	5FP	White regidue on the surface (bad cleaning)	2.3	×	×	◎
Com. Ex. 3	225ca/Ethanol (97/3)	Clean surface (fine cleaning)	1.0	△	◎	△
Com. Ex. 4	225cb	White regidue on the surface (bad cleaning)	4.6	◎	◎	△

- continued -

- continued -

	Solvent	Chemical stability	
		At	Zn
Com. Ex. 1	225ca	No corrosion	No corrosion
Com. Ex. 2	5FP	No corrosion	No corrosion
Com. Ex. 3	225ca/Ethanol (97/3)	No corrosion	The metal was corroded within 24 hours.
Com. Ex. 4	225cb	No corrosion	No corrosion

Claims

1. An azeotropic solvent composition comprising a dichloropentafluoropropane and a fluorine alcohol.

2. The composition of Claim 1, wherein the weight ratio of said dichloropentafluoropropane to said fluorine

alcohol is 99.5-88.0/0.5-12.0.

3. An azeotropic solvent composition comprising an azeotropic mixture of a dichloropentafluoropropane and a fluorine alcohol.

4. The composition of Claim 3, wherein the weight ratio of said dichloropentafluoropropane to said fluorine alcohol in said mixture is 99.5-88.0/0.5-12.0.

5. The composition of Claim 3, wherein said mixture is a mixture of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and pentafluoropropanol.

6. The composition of Claim 3, wherein said azeotropic mixture is a mixture of 93.5 % by weight of 1-1-dichloro-2,2,3,3,3-pentafluoropropane and 6.5 % by weight of pentafluoropropanol.

7. The composition of Claim 3, wherein said azeotropic mixture is a mixture of 1,3-dichloro-1,2,2,3,3-pentafluoropropane and pentafluoropropanol.

8. The composition of Claim 3, wherein said azeotropic mixture is a mixture of 92.2 % by weight of 1,3-dichloro-1,2,2,3,3-pentafluoropropane and 7.8 % by weight of pentafluoropropanol.

9. A composition comprising an azeotropic like composition of (A) 93.5 to 92.2 % by weight of a mixture of 0.5 to 99.5 % by weight of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 99.5 to 0.5 % by weight of 1,3-dichloro-1,2,2,3,3-pentafluoropropane, and (B) 6.5 to 7.8 % by weight of pentafluoropropanol.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91102807.4

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	GB - A - 1 321 375 (DONALD LOMAS) * Examples 1-6 * --	1	C 11 D 7/50 C 23 G 5/028
A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 14, No. 24, January 18, 1990 THE PATENT OFFICE JAPANESE GOVERNMENT page 5 C 677 * Kokai-No. 1-263 195(A) (DAIKIN IND LTD) * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 11 D
C 07 C 19/00
C 23 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	04-06-1991	SEIRAFI

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)