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(54) Cleaning composition.

(57) The invention provides a cleaning composition containing as an active component an aliphatic fluorohydrocarbon represented by the formula
$C_nF_mH_{2n+2-m}$
wherein $4 \leq n \leq 6$ and $6 \leq m \leq 12$.

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CLEANING COMPOSITION

The present invention relates to a cleaning composition and more particularly to a cleaning composition which is suitable for removal of fluxes, fats and oils, dust, etc. deposited on IC components, components of precision instruments or the like.

In the manufacture of IC components, components of precision instruments, etc., cleaning has been heretofore conducted usually using an organic solvent to remove the fluxes, dust and the like which deposited on components during assembling. For such cleaning, 1,1,2-trichloro-1,2,2-trifluoroethane (R-113) has been widely used as the organic solvent. R-113 is nonflammable, low in toxicity and excellent in stability. Further, R-113, which has a proper solvency, can selectively dissolve only dirts and is unlikely to corrode metals, plastics, elastomers and the like. Printed boards to be cleaned for removal of fluxes are mostly composite products composed of metals, plastics, elastomers and the like. Also from this viewpoint, R-113 is beneficial.

However, use of R-113 is being restricted because R-113 would be likely to destroy the ozone layer in the stratosphere and may become the cause of cutaneous cancer.

It is an object of the present invention to provide a cleaning composition which is utterly unlikely to destroy the ozone layer and which is capable of accomplishing effective cleaning for removal of fluxes, oils and the like.

It is another object of the invention to provide a cleaning composition which has such a suitable solvency that it can selectively dissolve only dirts and it will not corrode metals, plastics, elastomers, etc.

We conducted extensive research to achieve the foregoing objects, and found the following. Specific aliphatic fluorohydrocarbons are (1) entirely free from the possibility of destroying the ozone layer because of the absence of chlorine in the molecule; (2) outstanding in the ability to remove fluxes, fats and oils, dust, etc.; and (3) capable of selectively dissolving only dirts without corroding composite products composed of metals, plastics, elastomers, etc. because of their proper solvency like that of R-113 heretofore used. The present invention has been accomplished based on these novel findings.

According to the present invention, there is provided a cleaning composition containing as an active component an aliphatic fluorohydrocarbon represented by the formula

$C_nF_mH_{2n}+2-m$

wherein $4 \leqq n \leqq 6$ and $6 \leqq m \leqq 12$.

The cleaning composition according to the invention contains as an active component an aliphatic fluorohydrocarbon represented by the formula

$C_nF_mH2n+2-m$

wherein $4 \leqq n \leqq 6$ and $6 \leqq m \leqq 12$. Such compound has never been used as a cleaning agent for removing fluxes, fats and oils, etc.

Examples of aliphatic fluorohydrocarbons present in the cleaning composition of the invention are compounds represented by the formulas $C_4F_6H_4$, $C_4F_8H_2$, $C_5F_7H_5$, $C_5F_8H_4$, $C_5F_9H_3$, $C_5F_{10}H_2$, $C_6F_9H_5$ and $C_6F_{12}H_2$, respectively. Preferred examples of aliphatic fluorohydrocarbons are 1, 1,2,3,4,4-hexafluorobutane ($HCF_2CFHCFHCF_2H$), 1,1,1,2,2,3,3,4-octafluorobutane ($CF_3CF_2CF_2CH_2F$), 1,1,2,2,3,3,4-heptafluoropentane ($HCF_2(CF_2)_2CFHCH_3$, 1,1,2,3,3,4,5,5-octafluoropentane ($HCF_2CFHCf_2CFHCF_2H$), 1,1,2,2,3,3,4,4,5,-nonafluoropentane ($HCF_2(CF_2)_3CH_2F$), 1,1,1,2,3,3,4,4,5,5,-decafluoropentane ($CF_3CF(CHF_2)CF_2CF_2H$), 1,1,1,2,2,3,3,4,4,-nonafluorohexane ($CF_3(CF_2)_3CH_2CH_3$), 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexane ($HCF_2(CF_2)_4CF_2H$), 2-trifluoromethyl-1,1,1,3,4,4,5,5,5-nonafluoropentane ($(CF_3)_2CHCFHCF_2CF_3$), etc. The above-exemplified alipahtic fluorohydrocarbons can be used singly or at least two of them are usable in mixture. The amount of the aliphatic fluorohydrocarbon to be contained in the cleaning composition of the invention is not specifically limited, usually about 70% by weight or more, preferably about 80% by weight or more.

The composition of the invention may contain at least one organic solvent selected from the group consisting of hydrocarbons, alcohols, esters and ketones in order to increase the solvency for dissolving fluxes. The amount of the organic solvent used is not specifically limited, usually about 30% by weight or less, preferably about 0.5 to about 10% by weight, more preferably about 1 to about 8% by weight, based on the whole amount of the cleaning composition of the invention. If the mixture of the aliphatic fluorohydrocarbon and the organic solvent can be an azeotropic composition, it is preferred to use the mixture as the azeotropic composition.

Useful hydrocarbons are not specifically limited. Preferred hydrocarbons are hexane, heptane, isoheptane, octane, isooctane, methylcyclopentane, cyclohexane, methylcyclohexane, toluene, etc.

Useful alcohols are not specifically limited. Preferred alcohols are chain saturated alcohols having about 1 to about 5 carbon atoms, such as methanol, ethanol, n-propanol, isopropanol, n-butyl alcohol, sec-butyl alcohol, isobutyl alcohol, tert-butyl alcohol, pentyl alcohol, sec-amyl alcohol, 1-ethyl-1-propanol, 2-methyl-1-butanol, isopentyl alcohol, tert-pentyl alcohol, 3-methyl-2-butanol, neopentyl alcohol, 2-ethyl-1-butanol, etc. Among them, methanol, ethanol, isopropanol, n-propanol, etc. are desirable.

Useful esters are not specifically limited. Preferred esters are esters of fatty acids having about 1 to about 5 carbon atoms with lower alcohols having about 1 to about 6 carbon atoms, such as methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, methyl propionate, ethyl propionate, propyl propionate, isopropyl propionate, methyl butyrate, ethyl butyrate, methyl valerate, etc. Among them, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, etc. are preferred.

Useful ketones are not specifically limited. Preferred ketones are those represented by the formula R-CO-R' wherein R and R' each represent a saturated hydrocarbon group having about 1 to about 4 carbon atoms. Examples of such ketones are acetone, 2-butanone, 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, etc. Among them, acetone, 2-butanone, 4-methyl-2-pentanone, etc. are preferred.

The composition of the invention may further contain ingredients heretofore used for this kind of cleaning compositions according to a particular application. Useful ingredients are surfactants and like auxiliary agents for cleaning compositions, stabilizers, hydrogen-containing chlorofluorohydrocarbons which would be less likely to destroy the ozone layer, hydrogen-containing fluorohydrocarbons and other hydrocarbons which are entirely free from the possibility of destroying the ozone layer, and so on. In removal of fluxes, fats and oils, dust, etc. using the cleaning composition of the invention, a conventional cleaning method can be employed. Such cleaning methods include, for example, manually wiping methods, immersion methods, spraying methods, oscillating methods, ultrasonic cleaning methods, steam cleaning methods, etc.

The cleaning composition of the invention is not prone at all to destroy the ozone layer and is capable of accomplishing effective cleaning for removal of fluxes. Having a proper solvency like that of R-113 heretofore used, the cleaning composition of the invention can selectively dissolve and remove only dirts (including fluxes, fats and oils, dust, etc.) without corroding composite products composed of metals, plastics, elastomers, etc.

The present invention will be described below in more detail with reference to the following examples.

Example 1

A test for ability to remove fluxes was carried out using the cleaning compositions Nos. 1 to 27 of the present invention listed below in Table 1 and containing as an active component 1,1,2,2,3,3,4-heptafluoropentane (7F pentane), 1,1,2,3,3,4,5,5-octafluoropentane (8F pentane) or 2-trifluoromethyl-1,1,3,4,4,5,5,5-nonafluoropentane (6FDH2).

A flux (trade name: Tamura F-AI-4, product of Tamura Seisakusho) was applied on the entire surface of a printed board (copper clad laminate). The coated board was preheated at 110 °C for 20 seconds and soldering was conducted at 250 °C for 5 seconds. After the soldering, the printed board was immersed in the cleaning composition of the invention, followed by one minute of ultrasonic cleaning. The degree of the removal of the flux was evaluated according to the following criteria. Table 1 shows the results.

A: Flux was removed satisfactorily
B: A slight quantity of flux remained unremoved
C: A considerable quantity of flux remained unremoved

Table 1

No.	Composition (wt.%)	Result of cleaning
1	7F pentane (100)	B
2	7F pentane (93) Ethanol (7)	A
3	7F pentane (92) Isopropanol (8)	A
4	7F pentane (95) Ethyl acetate (5)	A
5	7F pentane (92) 2-Butanone (8)	A
6	7F pentane (95) Methyl acetate (5)	A
7	7F pentane (93) Ethanol (5) Ethyl acetate (2)	A
8	7F pentane (94) Ethyl acetate (5) 2-Butanone (1)	A
9	7F-pentane (93) 2-Butanone (5) Ethanol (2)	A
10	8F pentane (100)	B
11	8F pentane (97) Ethanol (3)	A
12	8F pentane (95) Isopropanol (5)	A
13	8F pentane (96) Ethyl acetate (4)	A
14	8F pentane (95) 2-Butanone (5)	A

Table 1 (continued)

No.	Composition (wt.%)	Result of cleaning
15	8F pentane (96) Methyl acetate (4)	A
16	8F pentane (93) Ethanol (5) Ethyl acetate (2)	A
17	8F pentane (94) Ethyl acetate (5) 2-Butanone (1)	A
18	8F pentane (93) 2-Butanone (4) Ethanol (3)	A
19	6FDH2 (100)	B
20	6FDH2 (80) Ethanol (20)	A
21	6FDH2 (75) Isopropanol (25)	A
22	6FDH2 (80) Ethyl acetate (20)	A
23	6FDH2 (75) 2-Butanone (25)	A
24	6FDH2 (80) Methyl acetate (20)	A
25	6FDH2 (80) Ethanol (10) Ethyl acetate (10)	A
26	6FDH2 (75) Ethyl acetate (15) 2-Butanone (10)	A
27	6FDH2 (80) 2-Butanone (7) Ethanol (13)	A

Example 2

In order to check the influence on the plastics materials exerted by the cleaning compositions Nos. 1 to 18 used in Example 1, various plastics materials listed below in Table 2 were immersed in each composition at 50°C for 1 hour. On withdrawal, the variation (expressed in percentage) of the weight of each plastics material was measured and the degree of the influence was evaluated according to the following criteria. Table 2 shows the results.

0: Little or no influence was found (Variation of the weight: 0 to 1%)

1 : The plastics material was slightly swelled, but substantially no problem was caused (Variation of

the weight: 1 to 5%)

2: The plastics material was swelled and eroded (Variation of weight: 5 to 10%)

Table 2

Resin	Cleaning composition No.								
	1	2	3	4	5	6	7	8	9
ABS resin	0	0	0	0	0	0	0	0	0
Polycarbonate	0	0	0	0	0	0	0	0	0
Polystyrene	0	1	1	1	1	1	1	1	1
Polymethacrylate	0	1	1	1	1	1	1	1	1
Epoxy resin	0	0	0	0	0	0	0	0	0
Phenolic resin	0	0	0	0	0	0	0	0	0
Polyphenylene oxide	0	0	0	1	1	1	0	1	1

Table 2 (continued)

Resin	Cleaning composition No.								
	10	11	12	13	14	15	16	17	18
ABS resin	0	0	0	0	0	0	0	0	0
Polycarbonate	0	0	0	0	0	0	0	0	0
Polystyrene	0	1	1	1	1	1	1	1	1
Poly-methacrylate	0	1	1	1	1	1	1	1	1
Epoxy resin	0	0	0	0	0	0	0	0	0
Phenolic resin	0	0	0	0	0	0	0	0	0
Polyphenylene oxide	0	0	0	1	1	1	0	1	1

The results shown in Tables 1 and 2 reveal that the composition of the present invention is excellent in ability to effectively remove fluxes and does not erode the plastics materials.

Example 3

A flux (trade name: F-AL-4, product of Tamura Seisakusho) was applied on a printed board (10 cm x 10 cm) and the coated board was preheated at 110 °C. Soldering was conducted at 250 °C for 5 seconds. A test for ability to remove fluxes was conducted using the cleaning compositions of the invention as listed below in Table 3 by subjecting the printed board treated above to ultrasonic cleaning for 60 seconds and to vapor cleaning for 60 seconds.

After the cleaning, the degree of removal of the flux was evaluated by observing the printed board with the unaided eye and according to the following criteria. On the other hand, the amount of ionic residue was measured using an Omega meter 500 (trade name of a product of KENKO) and utilized for evaluation

according to the following criterion. Table 3 shows the results.

Criteria for evaluation of the degree of removal of flux with the unaided eye:

A: The flux was removed satisfactorily

B: A slight degree of flux remained unremoved

C: A considerable degree of flux remained unremoved

Criterion for evaluation by the amount of ionic residue: Exhibiting satisfactory ability to remove fluxes when the amount of the inonic residue is up to 2 μgNaCl/cm^2

Table 3

		Ability to remove fluxes	
	(wt%)	Result with unided eye	Ionic residue (μgNaCl/cm^2)
$HCF_2CFHCFHCF_2H/C_2H_5OH$	93/7	A	1.4
$/(CH_3)_2CHOH$	95/5	A	1.5
$/CH_3COOC_2H_5$	97/3	A	1.5
$/CH_3COC_2H_5$	95/5	A	1.8
$HCF_2(CF_2)_2CFHCH_3/C_2H_5OH$	90/10	A	1.5
$/C_3H_7OH$	92/8	A	1.6
$/CH_3COOC_2H_5$	95/5	A	1.6
$/CH_3COC_2H_5$	90/10	A	1.9
$HCF_2CFHCF_2CFHCF_2H/C_2H_5OH$	90/10	A	1.3
$/C_3H_7OH$	95/5	A	1.5
$/CH_3COOC_2H_5$	95/5	A	1.4
$/CH_3COC_2H_5$	90/10	A	1.6
$HCF_2(CF_2)_3CH_2F/C_3H_7OH$	95/5	A	1.5
$CF_3CF(CHF_2)CF_2CF_2H/C_3H_7OH$	94/6	A	1.7
$/CH_3COOC_2H_5$	92/8	A	1.6
$CF_3(CF_2)_3CH_2CH_3/(CH_3)_2CHOH$	90/10	A	1.6
$HCF_2(CF_2)_4CF_2H/C_2H_5OH$	88/12	A	1.5
$(CH_3)_2CHOH$	90/10	A	1.6
C_3H_7OH	92/8	A	1.7
$CH_3COOC_2H_5$	90/10	A	1.6

Example 4

A 100 mesh-cylindrical wire net (25^{ϕ} x 15^{H} mm) on which spindle oil was deposited was immersed in the cleaning composition of the invention heated to 60 °C, followed by 60 seconds of ultrasonic cleaning. The wire net was further immersed in a solvent heated to 40 to 60 °C and subjected to shaking with hands or to ultrasonic cleaning for 60 seconds. Thereafter, vapor cleaning was conducted for 60 seconds, whereby the cleaning composition was tested for degreasing ability. After the test, the quantity of oil remaining on the wire net was measured by an oil content meter (product of Horiba, Ltd.) and the degree of removal of oils was expressed in cleaning degree (%).

Table 4 below shows the composition of the cleaning compositions used and the cleaning degree.

Table 4

		Degreasing ability
	(wt.%)	Cleaning degree (%)
$HCF_2CFHCFHCF_2H$	100	99.6
$CF_3CF_2CF_2CH_2F$	100	99.3
$HCF_2(CF_2)_2CFHCH_3$	100	99.5
$HCF_2CFHCF_2CFHCF_2H$	100	99.6
$HCF_2(CF_2)_3CH_2F$	100	99.5
$CF_3CF(CHF_2)CF_2CF_2H$	100	99.3
$CF_3(CF_2)_3CH_2CH_3$	100	99.2
$HCF_2(CF_2)_4CF_2H$	100	99.2
$(CF_3)_2CHCFHCF_2CF_3$	100	99.1
$HCF_2CFHCFHCF_2H$/n-Heptane	70/30	99.9
/Cyclohexane	90/10	99.7
$CF_3CF_2CF_2CH_2F$/n-Heptane	70/30	99.9
/Cyclohexane	90/10	99.6

Table 4 (continued)

		Degreasing ability
	(wt.%)	Cleaing degree (%)
$HCF_2(CF_2)_2CFHCH_3$/n-Heptane	70/30	99.9
/Cyclohexane	90/10	99.7
HCF_2CFHCF_2CFH/n-Heptane	70/30	99.9
/Cyclohexane	90/10	99.7
$HCF_2(CF_2)_3CH_2F$/n-Heptane	70/30	99.9
/Cyclohexane	90/10	99.6
$CF_3CF(CHF_2)CF_2CF_2H$/n-Heptane	70/30	99.9
/Cyclohexane	90/10	99.7
$CF_3(CF_2)_3CH_2CH_3$/n-Heptane	70/30	99.8
/Cyclohexane	90/10	99.6
$HCF_3(CF_2)_4CF_2H$/n-Heptane	70/30	99.9
/Cyclohexane	90/10	99.7
$(CF_3)_2CHCFHCF_2CF_3$/n-Heptane	70/30	99.9
/Cyclohexane	90/10	99.6

As described above, the cleaning compositions of the present invention are excellent in degreasing ability.

Claims

1. A cleaning composition containing as an active component an aliphatic fluorohydrocarbon represented by the formula
$C_nF_mH_{2n+2-m}$
wherein $4 \leq n \leq 6$ and $6 \leq m \leq 12$.

2. A cleaning composition according to claim 1 wherein the aliphatic fluorohydrocarbon is at least one compound selected from the group consisting of compounds represented by the formulas $C_4F_5H_4$, $C_4F_8H_2$, $C_5F_7H_5$, $C_5F_8H_4$, $C_5F_9H_3$, $C_5F_{10}H_2$, $C_6F_9H_5$ and $C_6F_{12}H_2$, respectively.

3. A cleaning composition according to claim 1 wherein the aliphatic fluorohydrocarbon is at least one compound selected from the group consisting of 1,1,2,3,4,4-hexafluorobutane ($HCF_2CFHCFHCF_2H$), 1,1,1,2,2,3,3,4-octafluorobutane ($CF_3CF_2CF_2CH_2F$), 1, 1, 2,2,3,3,4-heptafluoropentane ($HCF_2(CF_2)_2CFHCH_3$, 1,1,2,3,3,4,5,5--octafluoropentane ($HCF_2CFHCF_2CFHCF_2H$), 1,1,2,2,3,3,4,4,5,-nonafluoropentane ($HCF_2(CF_2)_3CH_2F$), 1,1,1,2,3,3,4,4,5,5,-decafluoropentane ($CF_3CF(CHF_2)CF_2CF_2H$), 1,1,1,2,2,3,3,4,4,-nonafluorohexane ($CF_3(CF_2)_3CH_2CH_3$), 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexane ($HCF_2(CF_2)_4CF_2H$), and 2-trifluoromethyl-1,1,1,,3,4,4,5,5,5-nonafluoropentane ($(CF_3)_2CHCFHCF_2CF_3$).

4. A cleaning composition according to claim 1 which contains at least one organic solvent selected from hydrocarbons, alcohols, esters and ketones.

5. A cleaning composition according to claim 1 which contains at least 70% by weight of the aliphatic fluorohydrocarbon.

6. A cleaning composition according to claim 4 which contains about 30% by weight or less of the organic solvent.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 12 2748

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)
X	US-A-3 729 567 (R.C. TERRELL) * Claim 1 *	1-3	C 23 G 5/028 C 11 D 7/24
X	DE-A-2 124 458 (NATIONAL RESEARCH DEVELOPMENT CORP.) * Claims 1,4,8 *	1,2	C 11 D 7/50
X	EP-A-0 260 587 (HOECHST AG) * Claim 1; examples; page 9, compound 4 *	1,2	
A	FR-A-2 275 540 (ALLIED CHEMICAL CORP.) * Claims 1,5,6,7,8 *	1,4,5,6	
A	US-A-4 842 764 (E.A.E. LUND)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 23 G
C 11
D

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	13 March 91	LANDAIS A.M-R.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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