

(19)



(11)

EP 2 876 153 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

27.05.2015 Bulletin 2015/22

(51) Int Cl.:

C11D 7/50 (2006.01)

C23G 5/028 (2006.01)

C23G 5/032 (2006.01)

(21) Application number: **13194066.0**

(22) Date of filing: **22.11.2013**

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

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(54) **Non-flammable compositions and use of these compositions**

(57) The invention relates to certain non-flammable compositions containing 1,1,1,3,3-pentafluorobutane (R365mfc), 1,2-dichloroethylene, ethoxynonafluorobutane (HFE-7200), and a linear C1 to C4 alcohol as well as to mixtures containing these compositions and to the

use of these non-flammable compositions or these mixtures, especially as precision cleaning agents for solid surfaces and for flushing, especially of refrigeration systems.

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Description

[0001] The invention relates to certain non-flammable compositions comprising 1,1,1,3,3-pentafluorobutane (R365mfc), 1,2-dichloroethylene, ethoxynonafluorobutane (HFE-7200) and a linear C1 to C3 alcohol, to mixtures comprising these non-flammable compositions and to their use, especially as cleaning and/or drying agents for solid surfaces and for flushing, especially of refrigeration systems.

[0002] Fully halogenated chlorofluorinated hydrocarbons (CFCs), in particular 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113), were widely used as solvents in industry for degreasing and cleaning various surfaces. In addition to their use in electronics in cleaning soldering, they were also conventionally used for degreasing metal components or for cleaning mechanical components of high quality and of high precision. In these various applications, CFC-113 was most often used in combination with other organic solvents, preferably in the form of azeotropic or pseudo-azeotropic compositions. For example, CFC-113 was used in combination with trans-1,2-dichloroethylene in compositions formerly known as Freon® MCA and Freon® SMT. Such compositions could also be used as cleaning agents in the refrigeration industry.

[0003] However, CFC-113, as well as other fully halogenated chlorofluoroalkanes, was suspected of being involved in the destruction of the stratospheric ozone layer.

[0004] Consequently, compositions with reportedly lower ozone-layer destruction potential were disclosed in WO 2000/56833 and include compositions of 1,1,1,3,3-pentafluorobutane and 1,1,1,2,3,4,4,5,5-decafluoropentane or nonafluoromethoxybutane with the optional addition of trans-1,2-dichloroethylene (TDCE), n-propyl bromide (nPB), acetone, methanol, ethanol or isopropanol.

[0005] In applications where the potential of fire is of concern, it is desirable for the cleaning compositions to be non-flammable in both liquid and vapour phase, during usage. Accordingly, one of the objectives of the present invention is to provide non-flammable compositions.

[0006] During usage and/or when discharged to the atmosphere, a composition of a mixture may change, what might cause the composition remaining or the composition being discharged to become flammable or to exhibit unacceptable performance. Accordingly, it is another objective of this invention to provide compositions forming azeotropes or pseudo-azeotropes.

[0007] The HFCs that have been proposed as replacement for CFCs might have not sufficient solvency for electronics soils such as hydrocarbon or silicon oils and flux residues, or soils of the refrigeration industry. Accordingly, it is yet another object of the present invention to provide HFC-based cleaning compositions that exhibit acceptable solubility for electronics soils notably suited for cleaning printed circuit boards and/or soils in the refrigeration industry, notably as flushing agents for cleaning

air conditioning systems. One example of a measure of solvency power is the Kauri-butanol value ("Kb value"). Accordingly, it is yet another objective of the invention to provide a cleaning composition with an improved Kauri-butanol value.

[0008] Additionally, it is an objective of the present invention to provide compositions with a low global warming potential (GWP) and/or with a low ozone-depletion potential.

[0009] There is still a need in the electronics and refrigeration industry for compositions that provide advantageous compositions with regard to the aforementioned problems.

[0010] The compositions of the present invention solve one or more of at least the aforementioned problems confronting the cleaning and refrigeration industries.

[0011] Consequently, the present invention relates to non-flammable compositions consisting or consisting essentially of 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration of 5-20 wt %, 1,2-dichloroethylene in a concentration of 30-88.9 wt %, ethoxynonafluorobutane (HFE-7200) in a concentration of 1-40 wt %, and at least one linear C1 to C4 alcohol in a concentration of 0.1-10 wt %, preferably consisting or consisting essentially of 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration of 10-15 wt %, 1,2-dichloroethylene in a concentration of 70-84.9 wt %, ethoxynonafluorobutane (HFE-7200) in a concentration of 5-20 wt %, and at least one linear C1 to C4 alcohol in a concentration of 0.1-5 wt %, more preferably consisting or consisting essentially of 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration of 10-15 wt %, 1,2-dichloroethylene in a concentration of 75-79.1 wt %, ethoxynonafluorobutane (HFE-7200) in a concentration of 10-15 wt %, and at least one linear C1 to C4 alcohol in a concentration of 0.1-5 wt %, even more preferably consisting or consisting essentially of 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration of 12-13 wt %, 1,2-dichloroethylene in a concentration of 74-76 wt %, ethoxynonafluorobutane (HFE-7200) in a concentration of 10-11 wt %, and at least one linear C1 to C4 alcohol in a concentration of 1-2 wt %.

[0012] The term "linear C1 to C4 alcohol" is intended to denote a compound including at least one hydroxyl group attached to a non-branched alkyl chain. Very suitable examples include methanol, ethanol, n-propanol, n-butanol and mixtures thereof. Methanol, ethanol, and n-propanol are preferred, ethanol is especially preferred. Another C1 to C4 alcohol is isobutanol.

[0013] Unless specified otherwise, the weight percentages in the present specification are all relative to the total weight of the composition.

[0014] The term "flammable" is meant to denote any flammability determined according to any applicable standard, and is preferably as defined in DIN/EN/ISO 13736.

[0015] The term "consisting essentially of" as used herein is intended to denote a composition comprising the components as specified as well as other compo-

nents in trace amounts wherein the presence of the other components does not change the essential characteristics of the specified subject matter.

[0016] HFE-7200 is commercially available from 3M and consists of the two isomers $(\text{CF}_3)_2\text{CFCF}_2\text{OC}_2\text{H}_5$ (CAS No. 163702-06-5) and $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{OC}_2\text{H}_5$ (CAS No. 15 163702-05-4).

[0017] 1,2-Dichloroethylene exists in two isomeric forms, cis-1,2-dichloroethylene and trans-1,2-dichloroethylene. For the purposes of the present invention, 1,2-dichloroethylene is understood to mean, without distinction, one or the other isomer or a mixture of these. In a preferred embodiment, the 1,2-dichloroethylene consists essentially of trans-1,2-dichloroethylene.

[0018] In another preferred embodiment, the compositions of the present invention are azeotropic or pseudo-azeotropic. An azeotrope as used herein is a specific system containing at least two components in which, at a given temperature and a given pressure, the composition in the liquid phase is equal to the composition in the vapour phase. A pseudo-azeotrope as used herein is a specific system containing at least two components in which, at a given temperature and a given pressure, the composition in the liquid phase is substantially equal to the composition in the vapour phase. In practice, their composition remains substantially constant in solvent cleaning operations, as well as in operations for recovering spent solvents by distillation.

[0019] In another preferred embodiment, the non-flammable compositions have a GWP of < 500, preferably < 350, more preferably < 250, most preferably < 150. The Global Warming Potential (GWP) as used herein is determined using the 100-yr ITH, IPCC2001 method.

[0020] The invention also relates to mixtures comprising the inventive non-flammable compositions as described above and further comprising at least one propellant.

[0021] The propellant assists in the delivery of the composition to the point of use. Representative propellants comprise air, nitrogen, carbon dioxide, difluoromethane, trifluoromethane, fluorinated ethanes, especially 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,2-trifluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,2,2-tetrafluoroethane, and pentafluoroethane. The propellant may be included in the composition in an amount of > 0, preferably equal to or more than 5 parts, more preferably equal to or more than 10 parts by weight per 100 parts by weight of the composition according to the invention. Preferably, the amount of the propellant is equal to or less than 40 parts, preferably equal to or less than 30 parts by weight per 100 parts by weight of composition according to the invention. Mixtures wherein the propellant is comprised in an amount of 1 to 25 parts per 100 parts of the composition according to the invention are especially suitable for flushing.

[0022] The mixture can further comprise a stabilizer. The stabilizer can be present in an amount of up to or equal to 5 wt %, preferably up to or equal to 2 wt %, more

preferably up to or equal to 0.5 wt % relative to the total weight of the mixture. The stabilizer is intended to stabilize the components of the composition against undesired side reactions during storage, transportation or use. Examples of suitable stabilizers are epoxides, unsaturated hydrocarbons, nitroalkanes, diketones, brominated compounds, and other alcohols than the linear C1 to C4 alcohols according to the invention.

[0023] The compositions according to the invention can be used in the same applications and according to the same techniques as the prior compositions based on CFC-113.

[0024] The compositions can be used, for example, as cleaning agents in general, especially as surface cleaning agent, e.g. for cleaning parts, for example, precision parts, made of plastics or inorganic material. The term "cleaning" includes, for example, cleaning textiles, degreasing in general, for example, degreasing animal hides, surface cleaning, for example cleaning, especially degreasing of metal, glass, or ceramics parts; for example, cleaning of optical lenses, cleaning of electronic devices, e.g. printed circuit boards contaminated by a pickling flux and residues from this flux, or cleaning solid chemicals insoluble in the composition. Solid objects can be desiccated to remove the water adsorbed at the surface of solid objects.

[0025] Accordingly, the present invention also relates to method of use of the non-flammable compositions or the mixtures as described above as cleaning agents, preferably as precision cleaning agents, or as degreasing agents. Preferably, the non-flammable composition or the mixture is in the vapour phase during the cleaning. Especially preferred is a method of use as a cleaning agent or as a degreasing agent for printed circuit boards contaminated by a pickling flux and residues from this flux or as desiccating agent for removing water adsorbed at the surface of solid objects. Alternatively, they also can be used as mold-release agents or for defluxing electronic components and for degreasing metals.

[0026] Also preferably, the propellant-containing mixtures are used for flushing of refrigeration equipment. The interior surface of compression refrigeration equipment, for example, used for climatisation of rooms, space for storing goods, or automobiles (mobile air conditioning, MAC) sometimes needs cleaning from residues, for example, when the refrigerant has to be changed, or had evaporated because of a leakage or has to be removed for repair. The residue be located in lines or other parts of the apparatus, e.g. in the compressor. The residue comprises refrigerant, compressor lubricant, e.g. mineral oil, naphthenes or polyol ethers, metal particles or rust. By contact with the composition according to the present invention, the inner surface of the equipment is recovered substantially free of residue. The way of contacting is not critical. The composition preferably is flushed in liquid phase through the equipment. The vapour pressure of the propellant moves the composition through the equipment.

[0027] Accordingly, the present invention also relates to a method of use of the non-flammable compositions as described above and preferably the mixtures as described above for cleaning of interior surfaces of refrigeration equipment, especially by flushing the refrigeration equipment. More preferably the refrigeration equipment is an air-conditioner.

[0028] The non-flammable compositions and the mixture of the present invention can even be applied as blowing agents for preparing plastic foams or for spraying liquids or as refrigerants.

[0029] The compositions, with or without a propellant, can be prepared in a very simple manner by mixing the constituents. Constituents which are gaseous at ambient pressure and temperature can be added in liquid form under pressure or by adding them to the other constituents under condensation.

[0030] The invention advantageously provides compositions which are non-flammable, despite their content of 1,2-dichloroethylene and the linear C1 to C4 alcohols, which per se are flammable.

[0031] The examples below, without implied limitation, illustrate the invention in a more detailed way.

Examples

Example 1 : Preparation of a quaternary composition

[0032] Trans-1,2-dichloroethylene is mixed with 1,1,1,3,3-pentafluorobutane, ethoxynonafluorobutane (HFE-7200) and ethanol in a weight ratio of 70:15:10:5. Flammability test with the composition of example 1 :

[0033] The flammability test is performed according to DIN/EN/ISO 13736 in a closed cup of 75 ml inner volume. The cup also comprises a stirrer and a probe to determine the temperature of the liquid to be tested, and means to rise the temperature. In the lid of the cup, a device is contained which allows to direct a test flame to the surface of the liquid the combustibility of which has to be determined. The apparatus used had a thermo detector which responds to fast rise of the measured temperature (indicating that a flame occurred).

[0034] The stirrer rotated slowly (about 30 rpm). The liquid in the cup is slowly warmed up. Whenever the temperature rose by 0.5°C, the test flame is ignited and it was checked if the thermo sensor responded. The tested composition is non-flammable.

Example 2 : Use of the composition of example 1 for vapour degreasing

[0035] Metal parts can be greased on the surface to protect them against corrosion. Adhering grease can also be caused by the application of drawing wax, drawing grease or drawing oil during shaping the metal parts. The step of cleaning high-precision metal parts is performed in a vapour degreaser.

[0036] A vapour immersion unit which has two solvent-

filled sumps can be applied. A boil cleaning tank comprises a solvent mixture which, additional to a higher-boiling solvent component additionally comprises the non-flammable composition described above. A rinsing tank only comprises the non-flammable composition described above.

[0037] The metal parts are assembled in a basket and immersed into the boil cleaning tank to dissolve adhering grease. They are then removed and immersed into the rinsing tank wherein adhering solvent mixture from the boil cleaning tank is rinsed. The parts then are covered with the lower-boiling composition of the rinsing tank. The basket is then removed from the rinsing tank and kept in the gas space above tanks. The solvent adhering on the surface of the metal parts passes into the vapour phase. Near the top of the vapour degreaser are three sets of cooled coils where the vapour condenses before it can escape from the unit. The condensed vapour flows back to a clean condensate tank and can be reused. A part of the vapour is fed to a drying unit to remove water from it. The degreased dry metal parts can then be removed from the vapour degreaser.

Example 3 : Preparation of a mixture comprising a stabilizer and a propellant

[0038] 15 wt % 1,1,1,3,3-pentafluorobutane (R365mfc), 70 wt % 1,2-trans-dichloroethylene which comprises about 0.5 wt % isopropanol as stabilizer, and 10 wt % ethoxynonafluorobutane (HFE-7200) and 5 wt % ethanol are mixed. This basic composition is filled into a container, and 10 parts 1,1,1,2-tetrafluoroethane are condensed into the container.

Example 4 : Flushing MAC apparatus using the composition of the present invention

[0039] The mixture of example 3 is applied in a method for flushing a mobile air conditioning apparatus.

[0040] The refrigerant is removed beforehand. A storage tank containing the composition is connected to the apparatus, and respective valves are opened. The composition is flushed through the lines and parts of the apparatus including the compressor. Residual oil and solids are removed during the treatment. The composition after leaving the apparatus is collected in a tank and can be conditioned for reuse by distillation. The flushed apparatus is clean and degreased and can be refilled with refrigerating agent.

[0041] The inventive compositions show an improved solvent strength, especially for inorganic and /or polar organic impurities. This is a benefit especially for removing solder-, brazing-, inorganic impurities as well as for the use in water displacement equipment.

[0042] Surprisingly, it has been found that inventive mixtures also show azeotropic behaviour.

Claims

1. A non-flammable composition consisting or consisting essentially of
 - (a) 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration of 5-20 wt %,
 - (b) 1,2-dichloroethylene in a concentration of 30-88.9 wt %,
 - (c) ethoxynonafluorobutane (HFE-7200) in a concentration of 1-40 wt %, and
 - (d) at least one linear C1 to C4 alcohol in a concentration of 0.1-10 wt %.
2. The non-flammable composition of claim 1 consisting or consisting essentially of
 - (a) 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration of 10-15 wt %,
 - (b) 1,2-dichloroethylene in a concentration of 70-84.9 wt %,
 - (c) ethoxynonafluorobutane (HFE-7200) in a concentration of 5-20 wt %, and
 - (d) at least one linear C1 to C4 alcohol in a concentration of 0.1-5 wt %.
3. The non-flammable composition of claim 2 consisting or consisting essentially of
 - (a) 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration of 10-15 wt %,
 - (b) 1,2-dichloroethylene in a concentration of 75-79.1 wt %,
 - (c) ethoxynonafluorobutane (HFE-7200) in a concentration of 10-15 wt %, and
 - (d) at least one linear C1 to C4 alcohol in a concentration of 0.1-5 wt %.
4. The non-flammable composition of claim 3 consisting or consisting essentially of
 - (a) 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration of 12-13 wt %,
 - (b) 1,2-dichloroethylene in a concentration of 74-76 wt %,
 - (c) ethoxynonafluorobutane (HFE-7200) in a concentration of 10-11 wt %, and
 - (d) at least one linear C1 to C4 alcohol in a concentration of 1-2 wt %.
5. The non-flammable composition of any one of claims 1 to 4 wherein the linear C1 to C4 alcohol is methanol, ethanol or propanol, preferably the linear C1 to C4 alcohol is ethanol.
6. The non-flammable composition of any one of claims 1 to 5 which is azeotropic.
7. The non-flammable composition of any one of claims 1 to 5 which is pseudo-azeotropic.
8. The non-flammable composition of any one of claims 1 to 7 which has a GWP of < 500, preferably < 350, more preferably < 250, most preferably < 150.
9. A mixture comprising the non-flammable composition of any one of claims 1 to 8 and further comprising at least one propellant.
10. The mixture of claim 9 wherein the propellant is comprised in an amount of 1 to 25 parts per 100 parts of the non-flammable composition.
11. A method of use of the non-flammable composition of any one of claims 1 to 8 or the mixture of any one of the claims 9 to 11 as a cleaning agent, preferably as precision cleaning agent, or as degreasing agent.
12. The method of use of claim 11, wherein the non-flammable composition is in the vapour phase.
13. The method of use of any one of claims 11 to 12 as a cleaning agent or as a degreasing agent for printed circuit boards contaminated by a pickling flux and residues from this flux or as desiccating agent for removing water adsorbed at the surface of solid objects.
14. A method of use of the non-flammable composition of any one of the claims 1 to 8 or the mixture of any one of the claims 9 to 10 for cleaning of interior surfaces of refrigeration equipment, especially by flushing the refrigeration equipment.



EUROPEAN SEARCH REPORT

Application Number
EP 13 19 4066

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	FR 2 929 956 A1 (ARKEMA FRANCE [FR]) 16 October 2009 (2009-10-16) * page 6, line 24 - line 27; claims * -----	1-14	INV. C11D7/50 C23G5/028 C23G5/032
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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 16 April 2014	Examiner Culmann, J
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EPO FORM 1503 03.82 (F04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
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