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(54) **Precision cleaning compositions**

(57) The invention relates to certain compositions of hydrofluoroalkanes, hydrofluoroalkenes, hydrofluoroethers or hydrofluoroketones with 1,2-dichloroethylene and fatty acid esters as well as mixtures comprising these

compositions and the use of the same especially as cleaning and/or drying agents for solid surfaces and for flushing, especially of refrigeration systems.

EP 3 012 318 A1

Description

[0001] The invention relates to certain compositions comprising, consisting or consisting essentially of a fluorinated compound selected from the group consisting of a hydrofluoroalkane, a hydrofluoroalkene, a hydrofluoroether and a hydrofluoroketone, together with 1,2-dichloroethylene and a fatty acid ester. Furthermore, the invention relates to mixtures comprising these 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, CFC-113 has been replaced from these compositions with compounds reportedly characterised by lower ozone-layer destruction potential such as hydrofluoroalkanes, hydrofluoroalkenes, hydrofluoroethers and hydrofluoroketones.

[0005] For example, SOLVOKANE® S, an azeotropic mixture of 1,1,1,3,3-pentafluorobutane (R365mfc), 1,2-dichloroethylene and 1H-imidazole-1-ethanol, 4,5-dihydro-, 2-nortall-oil alkyl derivs. is available from Solvay Fluor GmbH and has been widely used in the precision cleaning industry.

[0006] However, there is still a need in the electronics and refrigeration industry for advantageous compositions with regard to the problems as detailed in the following:

[0007] In precision cleaning applications, water displacement capacity and sufficient solvency for electronics soils such as oils and flux residues, or soils of the refrigeration industry are essential characteristics of suitable compositions. Accordingly, it is an object of the present invention to provide compositions that exhibit an advantageous water displacement capacity and/or advantageous solubility for electronics soils.

[0008] Surfactants are commonly used in the compositions for precision cleaning applications. However, some of the surfactants raise concerns with regard to their environmental and/or toxic properties. Consequently, it is another objective of the present invention to provide compositions with improved environmental and/or toxicological properties.

[0009] 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.

[0010] 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.

[0011] 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.

[0012] The compositions of the present invention solve one or more of at least the aforementioned problems confronting the cleaning and refrigeration industries.

[0013] Consequently, the present invention relates a composition comprising, consisting or consisting essentially of (a) at least one fluorinated compound selected from the group consisting of a hydrofluoroalkane, a hydrofluoroalkene, a hydrofluoroether and a hydrofluoroketone, (b) 1,2-dichloroethylene, and (c) at least one fatty acid ester of a polyol.

[0014] The weight percentages in the present specification are all relative to the total weight of the composition.

[0015] The term "consisting essentially of" as used herein is intended to denote a composition comprising the components as specified as well as other components in trace amounts wherein the presence of the other components does not change the essential characteristics of the specified subject matter.

[0016] The term "hydrofluoroalkane" as used herein is intended to denote a hydrocarbon, which is partially fluorinated. The hydrofluoroalkane preferably comprises 3 to 7 carbon atoms. Also preferably, the number of fluorine atoms is equal to or higher than the number of hydrogen atoms. Especially preferred are pentafluoropropanes, for example, 1,1,1,3,3-pentafluoropropane (HFC-245fa), 1,1,2,2,3-pentafluoropropane (HFC-245ca), hexafluoropropanes, heptafluoropropanes, especially 1,1,1,2,3,3,3-heptafluoropropane, pentafluorobutanes, for example, 1,1,1,3,3-pentafluorobutane and 2-methyl-1,1,1,3,3-pentafluoropropane (HFC-365 mps), hexafluorobutanes, for example, 1,1,1,4,4,4-hexafluorobutane, and decafluoropentanes, for example 1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFC-43-10-mee).

[0017] The term "hydrofluoroalkene" denotes compounds consisting of carbon, hydrogen and fluorine which can be

aliphatic or alicyclic and comprise at least one C-C double bond and preferably comprise 3 to 7 carbon atoms. Also preferably, the ratio of fluorine atoms to hydrogen atoms is higher than 2:1. Pentafluoropropene compounds are very suitable. The term "pentafluoropropene" includes cis-1,2,3,3,3-pentafluoropropene, trans-1,2,3,3,3-pentafluoropropene, 1,1,2,3,3-pentafluoropropene and 1,1,3,3,3-pentafluoropropene. Preferably, the at least one fluorinated compound is 1,1,1,3,3-pentafluorobutane (R365mfc), which can be obtained from Solvay Fluor GmbH.

[0018] The term "hydrofluoroether" denotes a hydrocarbon, which is fluorinated and which comprises at least one "C-O-C" moiety. Furthermore, the term "a hydrofluoroether" is intended to denote the presence of a single compound selected from the class of hydrofluoroethers or a mixture of two or more compound from the class of hydrofluoroethers. Examples of suitable hydrofluoroethers comprise HFE-7200 and HFE-7100. 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). HFE-7100 is also commercially available from 3M.

[0019] The term "hydrofluoroketone" denotes a fluorinated hydrocarbon which comprises at least one ketone functionality. For example, 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone can be applied.

[0020] 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.

[0021] The term "fatty acid ester" denotes an ester of a fatty acid, i.e. a dehydration product of a reaction of an alcohol with a fatty acid. Suitable saturated fatty acids are for example caprylic acid, capric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid and cerotic acid. Suitable unsaturated fatty acids comprise palmitoleic acid, sapienic acid, oleic acid and linoleic acid. Preferably, the fatty acid is lauric acid $(\text{CH}_3(\text{CH}_2)_{10}\text{COOH})$.

[0022] The term "polyol" denotes alcohols with at least three hydroxyl groups. Preferably, the polyol is a sugar alcohol or a dehydrated sugar alcohol. Suitable examples for sugar alcohols are maltitol, sorbitol, xylitol, erythritol, and isomalt.

[0023] The term "dehydrated sugar alcohol" denotes a compound derived from the dehydration of a sugar alcohol. Most preferably, the dehydrated sugar alcohol is sorbitan. Sorbitan is a mixture of isomeric compounds derived from the dehydration of sorbitol. The mixture can vary, but usually comprises 1,4-anhydrosorbitol, 1,5-anhydrosorbitol and 1,4,3,6-dianhydrosorbitol.

[0024] Preferably, the fatty acid ester is sorbitan monolaurate (CAS# 1338-39-2).

[0025] 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.

[0026] Preferably, the compositions of this invention are non-flammable. 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.

[0027] 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.

[0028] In a preferred embodiment, the composition is comprising, consisting or consisting essentially of (a) at least one fluorinated compound selected from the group consisting of hydrofluoroalkanes, hydrofluoroalkenes, a hydrofluoroethers and hydrofluoroketones in a concentration from 50 to 95 wt %, (b) 1,2-dichloroethylene in a concentration from 4.99 to 45 wt%, and (c) a fatty acid ester of a polyol in a concentration of 0.01 to 5 wt%, more preferably of (a) 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration from 50 to 95 wt %, (b) 1,2-dichloroethylene in a concentration from 4.99 to 45 wt%, and (c) sorbitan monolaurate in a concentration of 0.01 to 5 wt%, even more preferably of (a) 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration from 65 to 80 wt %, (b) 1,2-dichloroethylene in a concentration from 25 to 35 wt%, and (c) sorbitan monolaurate in a concentration of 0.5 to 2.5 wt% and most preferably of (a) 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration of around 69.5 wt %, (b) 1,2-dichloroethylene in a concentration of around 29.5 wt%, and (c) sorbitan monolaurate in a concentration of around 1 wt%.

[0029] The invention also relates to mixtures comprising the inventive non-flammable compositions as described above and further comprising at least one stabilizer and/or at least one propellant.

[0030] The stabilizer can be present in an amount of up to or equal to 5 wt %, preferably up to or equal to 2 %, 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 alcohols. A preferred stabilizer is isopropanol.

[0031] 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.

[0032] 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.

[0033] 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.

[0034] 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, 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.

[0035] Preferably, the propellant-containing mixtures are used for flushing of refrigeration equipment. The interior surface of compression refrigeration equipment, for example, used for climatization 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.

[0036] 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.

[0037] 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.

[0038] Surfactants are compounds that lower the surface tension between two liquids or between a liquid and a solid. It has been surprisingly found that the fatty acid esters of the polyols according to this invention are very advantageous surfactants for the inventive compositions and result in an improved water displacement index as compared to the mixtures of the prior art.

[0039] Furthermore, the inventive compositions have favourable ecological characteristics as both the polyols as well as the fatty acids can be derived from natural sources.

[0040] Additionally, the inventive compositions show improved toxicological characteristics. For example, sorbitan monolaurate is even approved as food additive and designated the number E493.

[0041] The examples below, without implied limitation, illustrate the invention in a more detailed way.

Examples

Example 1 : Preparation of the composition

[0042] Trans-1,2-dichloroethylene was mixed with 1,1,1,3,3-pentafluorobutane in a weight ratio of 70 to 30 and 500 ppm sorbitan monolaurate was added. Flammability test with the composition of example 1 :

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 has a thermo detector which responds to fast rise of the measured temperature (indicating that a flame occurred).

[0043] The stirrer rotates slowly (about 30 rpm). The liquid in the cup is slowly warmed up. Whenever the temperature rises by 0.5°C, the test flame is ignited and checked if the thermo sensor responded. The composition is non-flammable, i.e. no flashpoint is detected.

Example 2 : Determination of the water displacement index

[0044] Stainless-steel hexagon nuts of size M4 were placed in a stainless-steel basket (diameter: 10 cm). Total weight of basket and nuts was determined accurately (around 400 g total weight). The basket was immersed in tap water (250 ml). Upon removal of the basket from the water, water was allowed to drip for 1 min and the residual water loading was determined as the difference of the weight of the basket before and after the water bath.

[0045] Afterwards, the basket was submersed in the test composition and the basket was vertically agitated 10 times with slow rotation. The water layer formed on top of the test composition was decanted. Upon removal of the basket from the test composition, the liquid was allowed to drip for 1 min and the residual water was determined by weighing.

[0046] The water displacement index was determined as the ratio of water adhered to the basket and nuts before and after submersing them into the test composition.

[0047] Average results from three repetitions:

Test mixture	Water displacement index
Solvokane® S	68
Composition of example 1	90

[0048] The results clearly show the surprising improvement of the inventive mixture over the prior art.

Claims

1. A composition comprising, consisting or consisting essentially of

- (a) at least one fluorinated compound selected from the group consisting of a hydrofluoroalkane, a hydrofluoroalkene, a hydrofluoroether and a hydrofluoroketone,
- (b) 1,2-dichloroethylene, and
- (c) at least one fatty acid ester of a polyol.

2. The composition according to claim 1 wherein the at least one fluorinated compound is 1,1,1,3,3-pentafluorobutane (R365mfc).

3. The composition according to claim 1 or 2 wherein the polyol is a sugar alcohol or a dehydrated sugar alcohol.

4. The composition according to claim 3 wherein the polyol is sorbitan.

5. The composition according to any one of claims 1 to 4 wherein the fatty acid ester is sorbitan monolaurate.

6. The composition of claim 1 comprising, consisting or consisting essentially of

- (a) at least one fluorinated compound selected from the group consisting of hydrofluoroalkanes, hydrofluoroalkenes, a hydrofluoroethers and hydrofluoroketones in a concentration from 50 to 95 wt %,
- (b) 1,2-dichloroethylene in a concentration from 4.99 to 45 wt%, and
- (c) a fatty acid ester of a polyol in a concentration of 0.01 to 5 wt%.

7. The composition of claim 6 comprising, consisting or consisting essentially of

- (a) 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration from 50 to 95 wt %,
- (b) 1,2-dichloroethylene in a concentration from 4.99 to 45 wt%, and

(c) sorbitan monolaurate in a concentration of 0.01 to 5 wt%.

8. The composition of claim 7 comprising, consisting or consisting essentially of

- 5 (a) 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration from 65 to 80 wt %,
(b) 1,2-dichloroethylene in a concentration from 25 to 35 wt%, and
(c) sorbitan monolaurate in a concentration of 0.025 to 1 wt%.

9. The composition of claim 8 comprising, consisting or consisting essentially of

- 10 (a) 1,1,1,3,3-pentafluorobutane (R365mfc) in a concentration of 69 to 71 wt %,
(b) 1,2-dichloroethylene in a concentration of 29 to 31 wt%, and
(c) sorbitan monolaurate in a concentration of around 0.05 wt%.

15 10. A mixture comprising the composition of any one of claims 1 to 9 and further comprising at least one stabilizer and/or at least one propellant.

11. A mixture comprising the composition of any one of claims 1 to 9 or the mixture of claim 10 and further comprising at least one stabilizer.

20 12. A method of use of the composition of any one of claims 1 to 9 or the mixture of claim 10 or 11 as a cleaning agent, precision cleaning agent or degreasing agent.



EUROPEAN SEARCH REPORT

Application Number
EP 14 19 0230

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	WO 2014/096417 A1 (SOLVAY SA [BE]) 26 June 2014 (2014-06-26) * page 1, line 5 - page 2, line 22; claims; examples *	1-12	INV. C11D1/66 C11D3/24 C11D7/50 C23G5/028
A	WO 2008/095881 A1 (SOLVAY FLUOR GMBH [DE]) 14 August 2008 (2008-08-14) * page 1, line 1 - page 2, line 24; claims; examples *	1-12	
A	WO 2009/110926 A1 (ARKEMA INC [US]) 11 September 2009 (2009-09-11) * page 2, lines 20-27 * * page 8, last paragraph * * claims *	1-12	
			TECHNICAL FIELDS SEARCHED (IPC)
			C11D C23G
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 26 March 2015	Examiner Péntek, Eric
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			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 14 19 0230

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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