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(54) Title: AZEOTROPIC COMPOSITIONS CONTAINING PERFLUORINATED CYCLOAMINOETHER

(57) Abstract

An azeotropic composition includes a perfluorinated cycloaminoether and an organic solvent.

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AZEOTROPIC COMPOSITIONS CONTAINING PERFLUORINATED CYCLOAMINOETHER

The invention relates to azeotropes.

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) have been used commonly in a wide variety of solvent applications such as drying, cleaning (e.g., the removal of flux residues from printed circuit boards), and vapor degreasing. CFCs and HCFCs also commonly have been used as physical blowing agents to generate cells in foamed plastic materials. However, CFCs and HCFCs have been linked to the destruction of the earth's protective ozone layer, and replacements have been sought. The characteristics sought in replacements, in addition to low ozone depletion potential, typically have included low boiling point, low flammability, and low toxicity. Solvent replacements also should have a high solvent power.

It is known that azeotropes possess some properties that make them useful solvents. For example, azeotropes have a constant boiling point, which avoids boiling temperature drift during processing and use. In addition, when a volume of an azeotrope is used as a solvent, the properties of the solvent remain constant because the composition of the solvent does not change. Azeotropes that are used as solvents also can be recovered conveniently by distillation.

A number of azeotropic and azeotrope-like compositions that include a perfluorinated compound and an organic solvent are known in the art.

Zuber, U.S. Pat. No. 4,169,807 describes an azeotropic composition containing water, isopropanol, and either perfluoro-2-butyl-tetrahydrofuran or

perfluoro-1,4-dimethylcyclohexane. The inventor states that the composition is useful as a vapor phase drying agent.

Van der Puy, U.S. Pat. No. 5,091,104 describes an "azeotropic-like" composition containing t-butyl-2,2,2-trifluoroethyl ether and perfluoromethylcyclohexane. The inventor states that the composition is useful for cleaning and degreasing applications.

Fozzard, U.S. Pat. No. 4,092,257 describes an azeotrope containing perfluoro-n-heptane and toluene.

Batt et al., U.S. Pat. No. 4,971,716 describes an "azeotrope-like" composition containing perfluorocyclobutane and ethylene oxide. The inventor states that the composition is useful as a sterilizing gas.

Shottle et al., U.S. Pat. No. 5,129,997 describes an azeotrope containing perfluorocyclobutane and chlorotetrafluorethane.

Merchant, U.S. Pat. No. 4,994,202 describes an azeotrope containing perfluoro-1,2-dimethylcyclobutane and either 1,1-dichloro-1-fluoroethane or dichloro-trifluoroethane. The inventor states that the azeotrope is useful in solvent cleaning applications and as a blowing agent. The inventor also notes that "as is recognized in the art, it is not possible to predict the formation of azeotropes. This fact obviously complicates the search for new azeotrope compositions" (col. 3, lines 9-13).

Azeotropes including perfluorohexane and hexane, perfluoropentane and pentane, and perfluoroheptane and heptane are also known.

There currently is a need for alternative azeotrope compositions that can be used in solvent and other applications. Preferably these compositions would be non-flammable, have good solvent power, and cause little if any damage to the ozone layer.

Preferably, also, the azeotrope composition would consist of readily available and inexpensive solvents.

The invention features azeotropic compositions comprising, and preferably consisting essentially of, a perfluorinated cycloaminoether and at least one organic solvent. The azeotropic compositions exhibit good solvent properties and, as a result, can replace CFCs and HCFCs in solvent applications in which low boiling CFCs and HCFCs are used. The preferred compositions are non-flammable and typically have boiling points lower than both the cycloaminoether and the organic solvent. The preferred compositions also cause little, if any, ozone depletion, and have low toxicity.

"Azeotropic composition", as used herein, is a mixture of the perfluorinated cycloaminoether and one or more organic solvents, in any quantities, that if fractionally distilled will produce a distillate fraction that is an azeotrope of the perfluorinated compound and the organic solvent(s). The characteristics of azeotropes are discussed in detail in Merchant, U.S. Pat. No. 5,064,560 (see, in particular, col. 4, lines 7-48).

"Perfluorinated cycloaminoether", as used herein, is a perfluoro compound that includes a ring structure including a nitrogen (amine) linkage and an oxygen (ether) linkage. A perfluoro compound is one in which all of the hydrogen atom bonding sites on the carbon atoms in the molecule have been replaced by fluorine atoms, except for those sites where substitution of a fluorine atom for a hydrogen atom would change the nature of the functional group present (e.g., conversion of an aldehyde to an acid fluoride). Examples of perfluorinated cycloaminoethers are described in Owens et al. U.S. Pat. No. 5,162,384 (see in particular col. 3, line 49-col. 4, line 46).

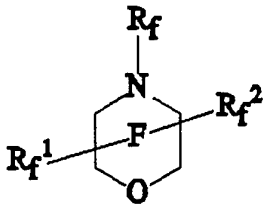
A HCFC is a compound consisting only of carbon, fluorine, chlorine, and hydrogen. A HFC is a compound consisting only of carbon, hydrogen, and fluorine. A hydrocarbon is a compound consisting only of carbon and hydrogen. All of these compounds can be saturated or unsaturated, branched or unbranched, and cyclic or acyclic.

The invention also features an azeotrope including a perfluorinated cycloaminoether and an organic solvent.

The azeotropic compositions are suitable for a wide variety of uses in addition to solvent applications. For example, the compositions can be used as blowing agents, as carrier solvents for lubricants, in cooling applications, for gross leak testing of electronic components, and for liquid burn-in and environmental stress testing of electronic components.

Other features and advantages of the invention will be apparent from the description of the preferred embodiment thereof, and from the claims.

The more preferred perfluorinated cycloaminoethers are N-aliphatic morpholines having the following structure:



In the formula, R_f is a perfluoroaliphatic group, saturated or unsaturated, having 1 to 4 carbon atoms, and R_f^1 and R_f^2 are, independently, a fluorine atom or a perfluoroaliphatic saturated or unsaturated group

having 1 to 4 carbon atoms. The total number of carbon atoms in the compound preferably does not exceed 12, and more preferably it does not exceed 10. The designation "F" inside the ring is a conventional symbol that denotes that the saturated ring is fully fluorinated, that is, all ring carbon atoms are bonded to fluorine atoms, except as depicted. The compounds are commercially available or known in the literature. Examples include perfluoro-N-ethylmorpholine, perfluoro-N-methylmorpholine and perfluoro-N-isopropylmorpholine.

The preferred organic solvents include HCFCs (e.g., 1-fluoro-1,1-dichloroethane, 1,1,1-trifluoro-2,2-dichloroethane, 1,1-dichloro-2,2,3,3,3-pentafluoropropane, and 1,3-dichloro-1,1,2,2,3-pentafluoropropane), HFCs (e.g., 1,1,2,2-tetrafluorocyclobutane, 1,1,2-trifluoroethane, 1-hydro-perfluoropentane, 1-hydro-perfluorohexane, 2,3-dihydro-perfluoropentane, and 2,2,3,3-tetrahydro-perfluorobutane), chlorinated hydrocarbons (e.g, methylene chloride, 1,2-dichloroethane, and trans-1,2-dichloroethylene, hydrocarbons (e.g., cyclopentane and 2,2,4-trimethylpentane), ethers (e.g., t-butyl methyl ether, t-butyl amyl ether and tetrahydrofuran), ketones (e.g., acetone), esters (e.g., t-butyl acetate), siloxanes (e.g., hexamethyldisiloxane), and alcohols (e.g, t-butanol, methanol, ethanol, and isopropanol). The solvents can be cyclic or acyclic, branched or unbranched, and typically will have boiling points of between 20°C and 125°C. The more carbon atoms in the solvent molecule, the higher the boiling point of the solvent. Typically, the solvent will include between 1 and 12 carbon atoms. The solvent selected preferably has a boiling point of within about 40°C of the boiling point of the perfluorinated cycloaminoether included in the composition. Where flammability is a concern, the

boiling point of the solvent more preferably is within about 25°C to 40°C above the boiling point of the perfluorinated cycloaminoether.

The preferred azeotropic compositions preferably include about the same quantities, by weight, of the cycloaminoether and the organic solvent(s) as the azeotrope formed between them. This in particular avoids significant boiling temperature drift and significant change in solvent power of the composition when the composition is used as a solvent. Preferably, the quantity by weight of the perfluorinated cycloaminoether and the organic solvent in the azeotropic composition is within 10%, and more preferably within 5%, of the average quantity of the cycloaminoether and the solvent found in the azeotrope formed between them. Thus, for example, if an azeotrope between a particular perfluorinated cycloaminoether and an organic solvent contains on average 60% by weight of the cycloaminoether and on average 40% by weight of the solvent, the preferred azeotropic composition includes between 54% and 66% (more preferably between 57% and 63%) of the cycloaminoether by weight, and between 36% and 44% (more preferably between 38% and 42%) of the solvent by weight. The same general guidelines apply when an azeotrope includes more than one organic solvent.

The more preferred azeotropic compositions are a single phase under ambient conditions, i.e., at room temperature and atmospheric pressure.

To determine whether a particular combination of a perfluorinated cycloaminoether and organic solvent will form an azeotrope, the particular combination can be screened by methods known in the art. For example, a composition can be carefully distilled through a four foot, perforated plate internal bellows silvered column of 45 physical plates or, alternatively, a six plate

Snyder column. The initial distillate is collected, and analyzed by GLC, e.g., using a three foot Porapak P or a six foot Hayesep Q column and a thermal conductivity detector with the appropriate corrections for thermal conductivity difference between the components. In some cases a second distillation using the composition determined in the first distillation may be carried out and the composition of the distillate analyzed at intervals over the course of the distillation. If a solvent mixture is found to form a azeotrope, the composition of the azeotrope can be determined by known methods.

Examples of the azeotropes of the invention are provided in Table 1. In Table 1, component A is the perfluorinated morpholine, and components B and C are the organic solvents. The compositions are listed in weight percents. Flammability was determined either by measurement of the flash point according to ASTM test method D-3278-89, or by contact with an ignition source.

TABLE 1

Ex.	Component A	Component B	Component C	Azeotropic Composition (A:B)	Azeo-trope (A:B)	Boiling Point	Flam-mable	Note
1	perfluoro-N-methyl-morpholine	1,1,2,2-tetrafluoro-cyclobutane		50/50	67/33	39-41°C	no	
2	perfluoro-N-methyl-morpholine	1,1,1-trifluoro-2,2-dichloroethane		50/50	14/86	26.5°C	no	
3	perfluoro-N-methyl-morpholine	1-fluoro-1,1-dichloroethane		50/50	45/55	27°	no	
4	perfluoro-N-methyl-morpholine	1,2-trans-dichloroethylene		80/20	68/32	34°C		two phases
5	perfluoro-N-methyl-morpholine	cyclopentane		50/50	81/19	36°C	yes	
6	perfluoro-N-methyl-morpholine	t-butyl-methyl ether		50/50	81/19	41°C	yes	
7	perfluoro-N-methyl-morpholine	t-amyl-methyl ether		50/50 93/7	93/7	44°C	no	
8	perfluoro-N-methyl-morpholine	2,2,4-trimethyl-pentane		50/50	98/2	51°C	no	
9	perfluoro-N-ethyl-morpholine	1-fluoro-1,1-dichloroethane		50/50	22/78	32°C	no	

10	perfluoro-N-ethyl-morpholine	1,1,2,2-tetrafluoro-cyclobutane		50/50	42/58	50°C	yes	
11	perfluoro-N-ethyl-morpholine	2,2,4-trimethylpentane		90/10	90/10	71°C	no	
12	perfluoro-N-methyl-morpholine	t-butyl-alcohol		90/10	93/7	41°C	no	two phases
13	perfluoro-N-methyl-morpholine	1,1,2,2-tetrafluoro-cyclobutane	acetone	60/30/10		37°C	no	
14	perfluoro-N-methyl-morpholine	1,1,2,2-tetrafluoro-cyclobutane	isopropyl alcohol	60/30/10	60/38/2	40°C	no	
15	perfluoro-N-methyl-morpholine	hexamethyl-disiloxane		90/10	96/4	52°C	no	
16	perfluoro-N-methyl-morpholine	t-butyl-acetate		93/7	96/4	52°C	no	
17	perfluoro-N-methyl-morpholine	1,1,2,2-tetrafluoro-cyclobutane	t-butyl alcohol	61/30/9	60/38/2	41°C	no	
18	perfluoro-N-methyl-morpholine	2,3-dimethyl-pentane	t-butyl alcohol	80/10/10	93/2.5/4.5	52°C	no	
19	perfluoro-N-ethyl-morpholine	hexamethyl-disiloxane		90/10	87/13	70°C	yes	
20	perfluoro-N-methyl-morpholine	t-amyl-methyl ether	t-butyl alcohol	61/30/9		51°C		two phases

21	perfluoro-N-methyl-morpholine	1,1,2,2,-tetrafluoro-cyclobutane	ethanol	64/31/5	71/26/3	38°C	No	
22	perfluoro-N-ethyl-morpholine	t-butyl acetate		90/10		69°C		two phases
23	perfluoro-N-methyl-morpholine	cyclohexane		8/90/10		48°C		two phases

The azeotropic compositions of the invention can be used in a variety of applications. For example, the azeotropic compositions can be used to clean electronic articles such as printed circuit boards, magnetic media, disk drive heads and the like, and medical articles such as syringes and surgical equipment. The contaminated articles may be cleaned by contacting the article with the azeotropic composition, generally while the composition is boiling or otherwise agitated. The azeotropic compositions can be used in a variety of specific cleaning procedures, such as those described in Tipping et al., U.S. Pat. No. 3,904,430; Tipping et al., U.S. Pat. No. 3,957,531; Slinn, U.S. Pat. No. 5,055,138; Sluga et al., U.S. Pat. No. 5,082,503; Flynn et al., U.S. Pat. No. 5,089,152; and Slinn, U.S. Pat. No. 5,143,652; and Anton, U.S. Pat. No. 5,176,757.

The cleaning ability of some preferred azeotropes were evaluated by ultrasonic washing and/or vapor degreasing coupons of various materials. Ultrasonic washing was performed in a Branson 1200 ultrasonic bath at 19.4°C by immersing the coupon in the solvent. Vapor degreasing was performed in a Multicore soldering bath by immersing the coupon in the refluxing vapor of the solvent. The coupons were parallelepiped approximately 2.5 mm x 5 mm x 1.6 mm of 316 stainless steel, copper, aluminum, carbon steel, acrylic, or a printed-circuit board. Initially, coupons were cleaned with Freon 113 and then weighed to ±0.0005 g. A coupon was soiled by immersing a portion of it in the soil (Medi Kay heavy mineral oil, light machine oil, heavy machine oil, bacon grease, or Alpha 611 solder flux), removing it from the soil and weighing it. The soiled coupon was then cleaned by ultrasonic washing or vapor degreasing for 30 s and then weighed. Next, the coupon was the cleaned for an additional 30 s and then weighed. Finally, the coupon was cleaned for an additional 2 min and weighed. Weight of soil removed

as a percentage of that loaded (determined by difference) is reported in Tables 2-7 for a total cleaning time of 3 min. The Freon 113 in Tables 2-6 is included for comparison. For some of the coupons the reuslts show that greater than 100% of the contaminant was removed. It is believed that this may be because the initial cleansing with Freon 113 did not remove all of the contaminant that was originally on the coupons.

Table 2

% MINERAL OIL REMOVED FROM COUPONS AT 3 MINUTES - ULTRASONIC WASHING

	Carbon S	Copper	SS	Alum	PCB	Acrylic
Freon 113	100	100	100	100	N/A	100
Example 11	100	100	100	100	N/A	100
Example 18	105	100	100	100	N/A	100
Example 7	100	111	100	100	N/A	100

Table 3

% BACON GREASE REMOVED FROM COUPONS AT 3 MINUTES - ULTRASONIC WASHING

	Carbon S	Copper	SS	Alum	PCB	Acrylic
Freon 113	101	100	100	100	N/A	100
Example 11	88	98	97	93	N/A	98
Example 18	100	100	100	101	N/A	100
Example 7	109	100	100	100	N/A	100

Table 4

% LIGHT OIL REMOVED FROM COUPONS AT 3 MINUTES - ULTRASONIC WASHING

	Carbon S	Copper	SS	Alum	PCB	Acrylic
Freon 113	100	100	100	100	N/A	100
Example 11	101	100	101	100	N/A	100
Example 18	100	100	100	101	N/A	100
Example 7	100	100	99	100	N/A	100

Table 5

% HEAVY MACHINE OIL REMOVED FROM COUPONS AT 3 MINUTES - ULTRASONIC WASHING

	Carbon S	Copper	SS	Alum	PCB	Acrylic
Freon 113	100	100	100	100	N/A	100
Example 11	100	100	99	100	N/A	100
Example 18	100	100	100	100	N/A	100
Example 7	100	100	100	100	N/A	100

Table 6

CFC 113--VAPOR DEGREASING FOR 1.5 MINUTES - % OIL REMOVED

	Carbon S	Copper	SS	Alum	PCB	Acrylic
MINERAL OIL	99	100	100	101	99	100
BACON GREASE	99	100	100	99	100	100
MACHINE OIL	100	100	100	100	100	100
LIGHT OIL	100	100	100	100	99	100

Table 7

EXAMPLE 11 --VAPOR DEGREASING FOR 3.0 MINUTES - % OIL REMOVED

	Carbon S	Copper	SS	Alum	PCB	Acrylic
MINERAL OIL	99	103	102	101	98	98
BACON GREASE	94	96	87	87	94	85
MACHINE OIL	97	99	99	98	95	96
LIGHT OIL	100	101	102	100	96	97

An azeotrope having the composition of Example 18 in Table 1 was used as the solvent in water displacement, as described in Flynn U.S. Pat. No. 5,089,152 ("Flynn"). This azeotrope was used in the procedure described in example 1 of Flynn, using 0.2% by weight of the amidol surfactant in example 2a in Table 1 of Flynn, and was found to be effective in displacing water.

Some of the azeotropic compositions of the present invention are useful for cleaning sensitive substrates such as films, including coated films and film laminates. Many such films are sensitive to organic solvents and water, which can dissolve or degrade the film, or the coating. Thus, the azeotropic compositions that are used to clean films preferably include organic solvents that do not cause degredation of the film or coating. Examples of organic solvents that are suitable for film-cleaning applications include t-amyl methyl ether, hexamethyldisiloxane, isooctane, t-butanol, and 2,3-dimethylpentane.

A sample of exposed photographic film was marked on both sides (coated and uncoated sides) with a grease pencil. The sample was then suspended in the vapor above a boiling sample of the azeotropic composition of Example 7 for a period of 30 seconds. The film was then wiped with a cotton or paper pad to remove residual amounts of the azeotrope and marking. The

film sample was then visually inspected to reveal only a slight residue of the marking from the grease pencil. Both sides were cleaned equally and there appeared to be no degradation of either the film or the photographic emulsion.

This test was then repeated using another sample of exposed, marked photographic film, which was placed in the vapor above a boiling sample of the azeotropic composition of Example 18. Visual inspection of the sample revealed a slight residue. There was no apparent damage to either the film or the emulsion.

A third sample of exposed, marked photographic film was contacted with the azeotropic composition of Example 15, at room temperature. After one minute the sample was removed, wiped, and inspected. The sample revealed no traces of the grease pencil, and no apparent damage to either the film or the emulsion.

A fourth sample of exposed, marked photographic film was contacted with the liquid azeotrope of Example 18 at room temperature. After four minutes, the sample was removed, wiped, and inspected. The cleansed sample revealed no traces of the grease pencil.

A fifth sample of exposed photographic film was marked on both sides and contacted with the liquid azeotrope of Example 18 at 36°C, with ultrasonic agitation. After three minutes, the sample was removed, wiped, and inspected. The cleansed sample revealed no traces of the grease pencil. The azeotropic compositions also can be used as blowing agents, according to the procedures described Owens et al., U.S. Pat. No. 5,162,384.

Other embodiments are within the claims.

What is claimed is:

1. An azeotropic composition comprising a perfluorinated cycloaminoether and at least one organic solvent.

2. A composition according to claim 1, wherein said perfluorinated cycloaminoether is selected from the group consisting of perfluorinated N-aliphatic morpholine, perfluoro-N-methylmorpholine, perfluoro-N-ethylmorpholine and perfluorinated morpholine.

3. A composition according to any of claims 1 or 2, wherein said organic solvent is selected from the group consisting of hydrochlorofluorocarbon, hydrofluorocarbon, ether, hydrocarbon, alcohol, ketone, ester and siloxane.

4. A composition according to any of claims 1 to 3, wherein said composition comprises two organic solvents.

5. A composition according to any of claims 1 to 4, wherein said composition includes within 10% of the quantity, by weight, of said perfluorinated cycloaminoether as is contained in the azeotrope formed between said perfluorinated cycloaminoether and said organic solvent.

6. A composition according to any of claims 1 to 4, wherein said composition includes within 10% of the quantity, by weight, of said organic solvent as is contained in the azeotrope formed between said perfluorinated cycloaminoether and said organic solvent.

7. A composition according to any of claims 1 to 6, wherein said composition is a single phase under ambient conditions.

8. A method of removing a contaminant from an article, comprising contacting said article with an azeotropic composition according to any of claims 1 to 7 to remove said contaminant from said article.

INTERNATIONAL SEARCH REPORT

Interna l Application No
PCT/US 94/02189

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C23G5/036 C11D7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C23G C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 091 104 (VAN DER PUY) 25 February 1992 cited in the application see the abstract ---	1,8
A	US,A,4 994 202 (MERCHANT) 19 February 1991 cited in the application see the abstract ---	1,8
A	PATENT ABSTRACTS OF JAPAN vol. 7, no. 171 (C-178) 28 July 1983 & JP,A,58 079 078 (DAIKIN KOGYO KK) 12 May 1983 see abstract ---	1,8
A	EP,A,0 509 739 (MINNESOTA MININ AND MANUFACTURING COMPANY) 21 October 1992 see claim 4 ---	1,8
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 162 384 (OWENS ET AL) 10 November 1992 cited in the application	1,8

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat l Application No
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-5091104	25-02-92	NONE		
US-A-4994202	19-02-91	AU-B-	642365	14-10-93
		AU-A-	7239391	10-10-91
		CN-A-	1054790	25-09-91
		EP-A-	0527740	24-02-93
		HU-A-	62027	29-03-93
		JP-T-	5504951	29-07-93
		WO-A-	9113946	19-09-91
EP-A-0509739	21-10-92	US-A-	5089152	18-02-92
		CN-A-	1065810	04-11-92
		JP-A-	5117696	14-05-93
		US-A-	5125978	30-06-92
US-A-5162384	10-11-92	AU-A-	2429992	27-04-93
		CA-A-	2115439	01-04-93
		EP-A-	0603213	29-06-94
		WO-A-	9306163	01-04-93