

Description

Title of Invention: Azeotropic Solvent Formulation of Hydrofluoroether and Organic Carbonates

5 Technical Field

The present invention relates to a composition comprising a dialkyl carbonate or a cyclic carbonate and a hydrofluoroether having the formula (I). The present invention further relates to a method for preparing the composition and the use of the composition.

Background Art

- 10 Restriction on commercialization of solvents is becoming increasingly stricter due to the hazardous nature of some solvents or its components in the case of mixed solvents. Solvents are used in applications such as precision cleaning in electronics, carriers for lubricant/coatings, vapour phase spot-free drying in wafer applications and aerosol formulations. It is therefore desirable that solvents have low environmental impact with respect to ozone depletion potential,
- 15 global warming potential, and worker exposure levels. The solvent should also be exempted from being a Volatile Organic Compound (VOC).

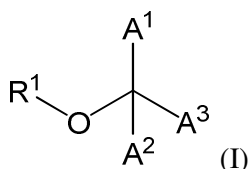
There is therefore a need to provide a composition that overcomes or at least ameliorates, one or more of the disadvantages described above.

Summary

- 20 In an aspect, there is provided a composition comprising:

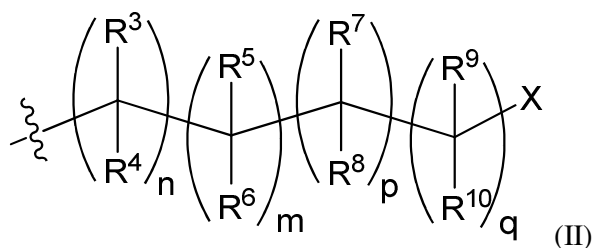
a dialkyl carbonate or a cyclic carbonate; and

a compound having the following formula (I):



wherein R¹ is selected from the group consisting of alkyl, alkenyl and alkynyl; and

- 25 A¹, A² and A³ are independently X or have the following formula (II):



wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are independently X or, $-CX_3$;

X is halogen;

n is an integer of at least 1;

5 m, p and q are independently 0 or an integer of at least 1; and

~~~~~represents where formula (II) attaches to formula (I).

Advantageously, the composition comprises a compound having formula (I). The compound having formula (I) is a hydrofluoroether. Fluorinated solvents derived from hydrofluoroethers, hydrofluoro olefins, and perfluoro ketones are recently considered to be environmentally benign and are therefore recommended to be used for above purposes.

Further advantageously, hydrofluoroethers of formula (I) are considered to be non-VOC, environmentally benign solvents. Advantageously, it may be used in many applications in precision cleaning, formulations, aerosols and as a solvent for lubricants. More advantageously, it forms azeotropic compositions with various hydrocarbon, alcoholic and chlorinated solvents, whereby the azeotrope increases the solvency of the hydrofluoroethers. The hydrofluoroether of formula (I) may be a Novec™ hydrofluoroether.

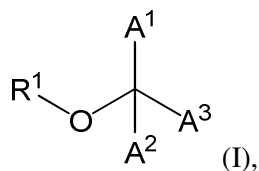
Advantageously, the composition comprises dialkyl carbonate or a cyclic carbonate. Dialkyl carbonates such as dimethyl carbonate has recently been recognised as a VOC exempted solvent by the United States Environmental Protection Agency (US EPA) due to favourable environmental properties. It has been recommended as an alternative to hazardous Methyl Ethyl Ketone (MEK) and amine-based solvents. Advantageously, dialkyl carbonates such as dimethyl carbonate exhibits good solvency both in terms of polarity and hydrogen-bonding, which makes it a more versatile solvent. Moreover, it is an aprotic solvent having low odour, low skin irritation and a 200 ppm exposure limit.

Advantageously, the composition comprising a hydrofluoroether and a dialkyl carbonate or cyclic carbonate may be an azeotrope.

In another aspect, there is provided a method for synthesizing a composition comprising:

a dialkyl carbonate or a cyclic carbonate; and

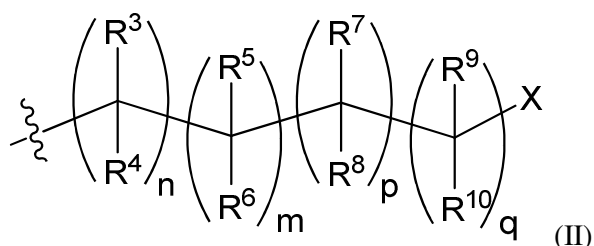
a compound having the following formula (I):



the method comprising the step of contacting the dialkyl carbonate with the compound having formula (I),

wherein  $\text{R}^1$  is selected from the group consisting of alkyl, alkenyl and alkynyl; and

5  $\text{A}^1$ ,  $\text{A}^2$  and  $\text{A}^3$  are independently X or have the following formula (II):



wherein  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$ ,  $\text{R}^8$ ,  $\text{R}^9$  and  $\text{R}^{10}$  are independently X or,  $-\text{CX}_3$ ;

X is halogen;

n is an integer of at least 1;

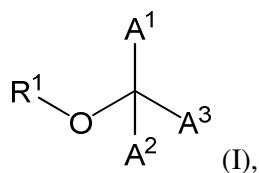
10 m, p and q are independently 0 or an integer of at least 1; and

~~~~~represents where formula (II) attaches to formula (I),

In another aspect, there is provided the use of a composition comprising:

a dialkyl carbonate or a cyclic carbonate; and

a compound having the following formula (I):

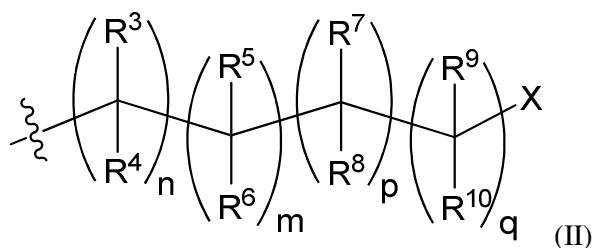


15

as a solvent,

wherein R^1 is selected from the group consisting of alkyl, alkenyl and alkynyl; and

A^1 , A^2 and A^3 are independently X or have the following formula (II):



wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are independently X or, $-CX_3$;

X is halogen;

n is an integer of at least 1;

5 m, p and q are independently 0 or an integer of at least 1; and

~~~~~ represents where formula (II) attaches to formula (I).

Advantageously, the solvent may be an azeotrope.

## Definitions

The following words and terms used herein shall have the meaning indicated:

10        "Alkyl" as a group or part of a group refers to a straight or branched aliphatic hydrocarbon group, preferably a  $C_1$ - $C_{50}$  alkyl, preferably a  $C_1$ - $C_{12}$  alkyl, more preferably a  $C_1$ - $C_{10}$  alkyl, most preferably  $C_1$ - $C_6$  unless otherwise noted. Examples of suitable straight and branched  $C_1$ - $C_6$  alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, t-butyl, hexyl, and the like. The group may be a terminal group or a bridging group.

15        "Alkenyl" as a group or part of a group denotes an aliphatic hydrocarbon group containing at least one carbon-carbon double bond and which may be straight or branched preferably having 2-12 carbon atoms, more preferably 2-10 carbon atoms, most preferably 2-6 carbon atoms, in the normal chain. The group may contain a plurality of double bonds in the normal chain and the orientation about each is independently E or Z. Exemplary alkenyl groups include, but are  
20        not limited to, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl and nonenyl. The group may be a terminal group or a bridging group.

25        "Alkynyl" as a group or part of a group means an aliphatic hydrocarbon group containing a carbon-carbon triple bond and which may be straight or branched preferably having from 2-12 carbon atoms, more preferably 2-10 carbon atoms, more preferably 2-6 carbon atoms in the normal chain. Exemplary structures include, but are not limited to, ethynyl and propynyl. The group may be a terminal group or a bridging group.

"Alkyloxy" refers to an alkyl group as defined herein that is singularly bonded to oxygen. The group may be a terminal group or a bridging group. If the group is a terminal group, it is bonded to the remainder of the molecule through the alkyl group.

"Alkyloxyalkyl" refers to an alkyloxy-alkyl- group in which the alkyloxy and alkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

"Aryl" as a group or part of a group denotes (i) an optionally substituted monocyclic, or fused polycyclic, aromatic carbocycle (ring structure having ring atoms that are all carbon) preferably having from 5 to 12 atoms per ring. Examples of aryl groups include phenyl, naphthyl, and the like; (ii) an optionally substituted partially saturated bicyclic aromatic carbocyclic moiety in which a phenyl and a C<sub>5-7</sub> cycloalkyl or C<sub>5-7</sub> cycloalkenyl group are fused together to form a cyclic structure, such as tetrahydronaphthyl, indenyl or indanyl. The group may be a terminal group or a bridging group. Typically, an aryl group is a C<sub>6</sub>-C<sub>18</sub> aryl group.

"Arylalkyl" means an aryl-alkyl- group in which the aryl and alkyl moieties are as defined herein. Preferred arylalkyl groups contain a C<sub>1-5</sub> alkyl moiety. Exemplary arylalkyl groups include benzyl, phenethyl, 1-naphthalenemethyl and 2-naphthalenemethyl. The group may be a terminal group or a bridging group. If the group is a terminal group, it is bonded to the remainder of the molecule through the alkyl group.

"Cyclic carbonate" refers to a carbonate ester or an ester of a carbonic acid, comprising a carbonyl group flanked by two alkyloxyalkyl groups and whereby the carbonate groups are linked by a 2- or 3-membered carbon bridge forming a cyclic compound. The bridging compound may be substituted or unsubstituted, for example with an alkyl group, a hydroxy group, a hydroxyalkyl, an aryl or an arylalkyl. Exemplary structures include, but are not limited to, ethylene carbonate (1,3-dioxolan-2-one), trimethylene carbonate (1,3-dioxan-2-one), propylene carbonate (4-methyl-1,3-dioxolan-2-one), butylene carbonate (4-ethyl-1,3-dioxolan-2-one), styrene carbonate (4-phenyl-1,3-dioxolan-2-one) and glycerol carbonate (4-hydroxymethyl-2-oxo-1,3-dioxolane).

"Hydroxyalkyl" refers to an alkyl group as defined herein in which one or more of the hydrogen atoms has been replaced with an OH group. A hydroxyalkyl group typically has the formula C<sub>n</sub>H<sub>(2n+1-x)</sub>(OH)<sub>x</sub>. In groups of this type n is typically from 1 to 10, more preferably from 1 to 6, most preferably from 1 to 3. x is typically from 1 to 6, more preferably from 1 to 4.

"Halogen" represents chlorine, fluorine, bromine or iodine.

"Azeotrope" refers to a constant boiling point mixture which is a mixture of two or more liquids whose proportions cannot be altered or changed by simple distillation. When an azeotrope is boiled, the vapour has the same proportions of constituents as the unboiled mixture.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

5 As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

10 Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have  
15 specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

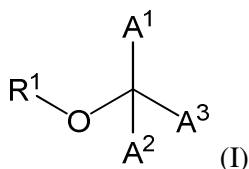
Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form  
20 part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

## Detailed Disclosure of Optional Embodiments

There is provided a composition comprising:

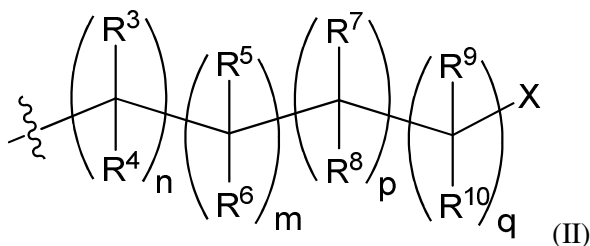
25 a dialkyl carbonate or a cyclic carbonate; and

a compound having the following formula (I):



wherein R<sup>1</sup> may be selected from the group consisting of alkyl, alkenyl and alkynyl; and

A<sup>1</sup>, A<sup>2</sup> and A<sup>3</sup> may independently be X or have the following formula (II):



wherein  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  may be independently X or,  $-CX_3$ ;

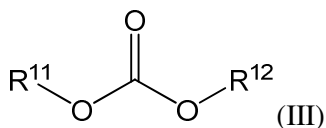
X may be halogen;

n may be an integer of at least 1;

5      m, p and q are independently 0 or an integer of at least 1; and

~~~~~ represents where formula (II) attaches to formula (I).

The dialkyl carbonate may have the following formula (III):



wherein R^{11} and R^{12} may independently be a branched or straight-chain alkyl group.

10 R^{11} and R^{12} may independently be selected from the group consisting of methyl, ethyl, propyl, isopropyl, cyclopropyl, butyl, butan-2-yl, 2-methylpropyl, tert-butyl, pentyl, 2-methylbutan-2-yl, 2,2-dimethylpropyl, 3-methylbutyl, pentan-2-yl, pentan-3-yl, 3-methylbutan-2-yl, 2-methylbutyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, and dodecyl.

The dialkyl carbonate may be dimethyl carbonate or diethyl carbonate.

15 The cyclic carbonate may be selected from the group consisting of ethylene carbonate, propylene carbonate, butylene carbonate, styrene carbonate and glycerine carbonate.

R^1 may be an alkyl.

R^1 may be methyl or ethyl.

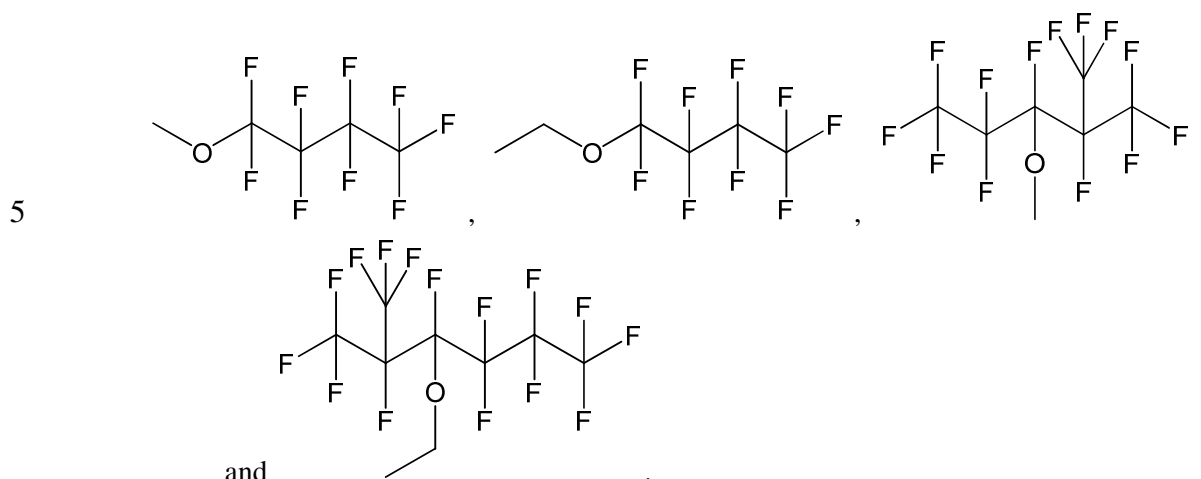
X may be fluorine.

20 At least one of A^1 , A^2 or A^3 may have formula (II).

A^1 may have formula (II) and A^2 and A^3 may be X. In such a case, in A^1 , n may be 4, m, p and q may be 0 and R^3 and R^4 may both be X.

A^1 and A^2 may have formula (II), and A^3 may be X. In such a case, in A^1 , n and m may be 1, p and q may be 0, R^3 , R^5 and R^6 may be X and R^4 may be CX_3 ; and in A^2 , n may be 2 or 3, m, p and q may be 0 and R^3 and R^4 may both be X.

The compound of formula (I) may be selected from the group consisting of:



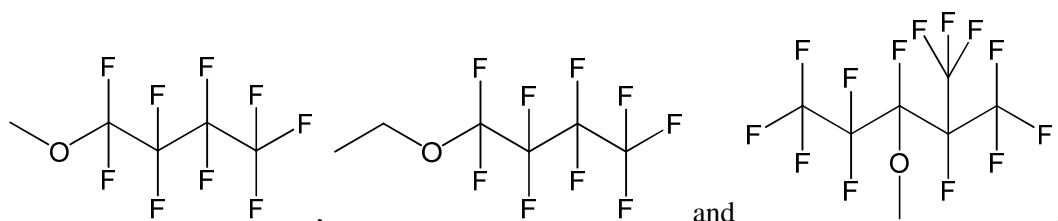
The dialkyl carbonate may be present at a range of 0.1 to 15% w/w, wherein the composition may have a total % w/w of 100%. The dialkyl carbonate may be present at a range of 0.1% to 0.2% w/w, 0.1% to 0.5% w/w, 0.1% to 1% w/w, 0.1% to 1.5% w/w, 0.1% to 2% w/w, 0.1% to 5% w/w, 0.1% to 10% w/w, 0.2% to 0.5% w/w, 0.2% to 1% w/w, 0.2% to 1.5% w/w, 0.2% to 2% w/w, 0.2% to 5% w/w, 0.2% to 10% w/w, 0.2% to 15% w/w, 0.5% to 1% w/w, 0.5% to 1.5% w/w, 0.5% to 2% w/w, 0.5% to 5% w/w, 0.5% to 10% w/w, 0.5% to 15% w/w, 1% to 1.5% w/w, 1% to 2% w/w, 1% to 5% w/w, 1% to 10% w/w, 1% to 15% w/w, 1.5% to 2% w/w, 1.5% to 5% w/w, 1.5% to 10% w/w, 1.5% to 15% w/w, 2% to 5% w/w, 2% to 10% w/w, 2% to 15% w/w, 5% to 10% w/w, 5% to 15% w/w, or 10% to 15% w/w.

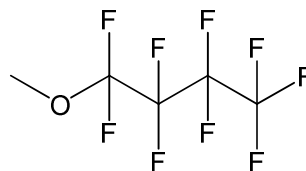
The dialkyl carbonate may be dimethyl carbonate and may be present at a range of 6 to 10% w/w, wherein the composition has a total %w/w of 100%.

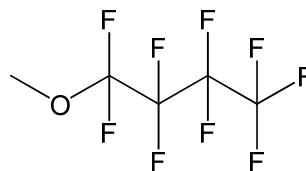
The composition may comprise:

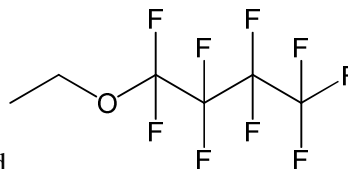
a dimethyl carbonate; and

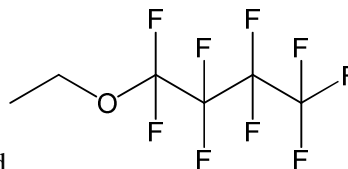
20 a compound selected from the group consisting of:

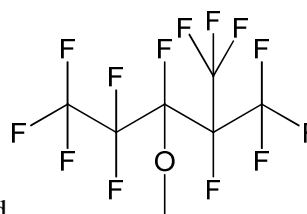


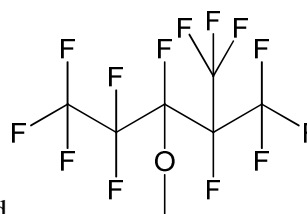


The composition may comprise dimethyl carbonate and , wherein the dimethyl carbonate may be present at a range of about 6 % w/w to about 7 % w/w, wherein the composition has a total %w/w of 100%.



- 5 The composition may comprise dimethyl carbonate and , wherein the dimethyl carbonate may be present at a range of about 8 % w/w to about 10 % w/w, wherein the composition has a total %w/w of 100%.



The composition may comprise dimethyl carbonate and , wherein the dimethyl carbonate may be present at about 7 % w/w, wherein the composition has a total %w/w of 100%.

- 10 The composition may be an azeotrope.

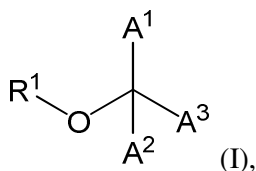
The composition may comprise a further solvent.

The further solvent may be trans-1,2-dichloroethene.

There is provided a method for synthesizing a composition comprising:

a dialkyl carbonate or a cyclic carbonate; and

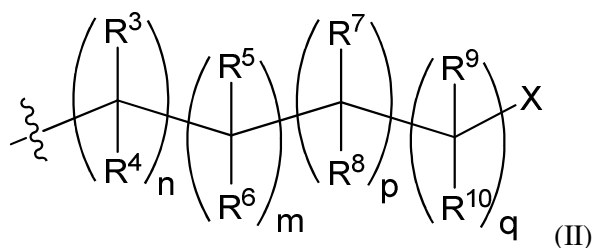
- 15 a compound having the following formula (I):



the method comprising the step of contacting the dialkyl carbonate with the compound having formula (I),

wherein R¹ may be selected from the group consisting of alkyl, alkenyl and alkynyl; and

- 20 A¹, A² and A³ may be independently X or may have the following formula (II):



wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} may be independently X or, $-CX_3$;

X may be halogen;

n may be an integer of at least 1;

5 m, p and q may be independently 0 or an integer of at least 1; and

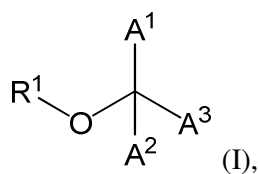
~~~~~ represents where formula (II) attaches to formula (I).

The contacting step may comprise refluxing the dialkyl carbonate or cyclic carbonate and the compound having formula (I) for a duration in the range of about 15 minutes to about 45 minutes, about 15 minutes to about 20 minutes, about 15 minutes to about 30 minutes, about 15 minutes to about 40 minutes, about 20 minutes to about 30 minutes, about 20 minutes to about 40 minutes, about 20 minutes to about 45 minutes, about 30 minutes to about 40 minutes, about 30 minutes to about 45 minutes, or about 40 minutes to about 45 minutes.

There is also provided a use of a composition comprising:

a dialkyl carbonate or a cyclic carbonate; and

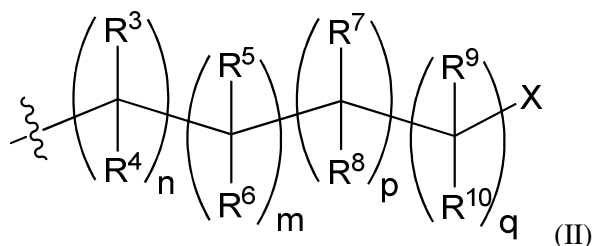
15        a compound having the following formula (I):



as a solvent,

wherein  $R^1$  may be selected from the group consisting of alkyl, alkenyl and alkynyl; and

$A^1$ ,  $A^2$  and  $A^3$  may be independently X or have the following formula (II):



wherein  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  may be independently X or,  $-CX_3$ ;

X may be halogen;

n may be an integer of at least 1;

m, p and q may be independently 0 or an integer of at least 1; and

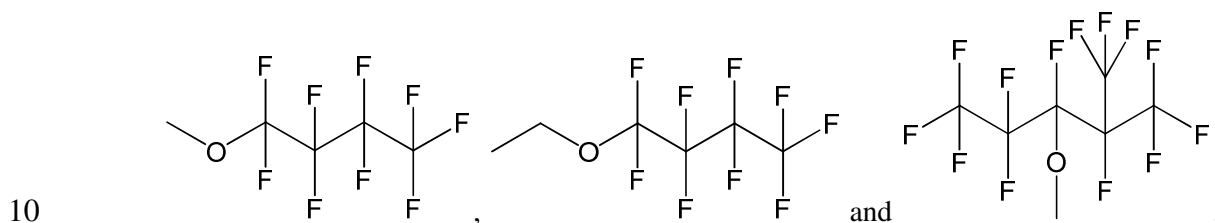
5  represents where formula (II) attaches to formula (I).

The solvent may be an azeotrope.

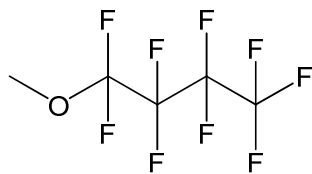
In using the composition, the composition may comprise:

a dimethyl carbonate; and

a compound selected from the group consisting of:

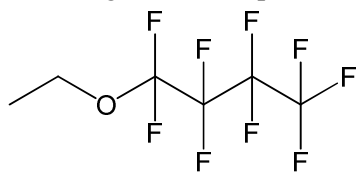


In using the composition, the composition may comprise dimethyl carbonate and



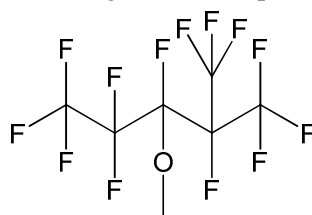
, wherein the dimethyl carbonate may be present at a range of about 6 % w/w to about 7 % w/w, wherein the composition has a total %w/w of 100%.

In using the composition, the composition may comprise dimethyl carbonate and



15 , wherein the dimethyl carbonate may be present at a range of about 8 % w/w to about 10 % w/w, wherein the composition has a total %w/w of 100%.

In using the composition, the composition may comprise dimethyl carbonate and



, wherein the dimethyl carbonate may be present at about 7 % w/w, wherein the composition has a total %w/w of 100%.

The composition may be used as a solvent for disc lubricant, coating, or aerosol, or in cleaning, rinsing or drying of a substrate.

## Brief Description of Drawings

5 The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

### Fig. 1

10 [Fig. 1] is a graph referring to the FTIR image of compositions comprising Novec™ 7100 with dialkyl carbonate or acetonitrile, or Novec™ 7200 with dialkyl carbonate, measured immediately after and 1 minute after application to a surface.

### Fig. 2

15 [Fig. 2] is a photographic image showing the surface wetting and spreading of Z-tetraol lubricant dissolved in different solvents. (D) is 7100-DMC; (A) is 7100AN, (V) is Vertrel XF and (I) is 71IPA.

### Fig. 3

[Fig. 3] shows the area% of the peaks in the gas chromatograms of 7100-DMC at various stages of evaporation of the 0.5% and 1.0% concentration mixtures.

## Examples

20 Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

## Example 1: Materials

Table 1. Raw materials used

| <b>FUNCTION</b>                                                                                                 | <b>CHEMICAL</b>                                                  | <b>SUPPLIER</b>                                                                   |
|-----------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| Fluorinated solvents -<br><br>Non-flammable, low surface tension, environmentally benign.                       | Novec™ hydrofluoroether 7100, 7200, 7300, 7500<br><br>Vertrel XF | 3M (Maplewood, Minnesota, USA)<br><br>Chemours (Wilmington, Delaware, USA)        |
| Carbonates –<br><br>High solvency, environmentally friendly, non-VOC (volatile organic solvent), polar aprotic. | dimethyl carbonate, diethyl carbonate                            | Sigma Aldrich (St. Louis, Missouri, USA)<br><br>Huntsman Corporation (Texas, USA) |

## Example 2: Formulations

- 5 A mixture of the hydrofluoroether and carbonates were refluxed in a round bottom flask for 30 minutes to equilibrate. The round bottom flask was attached with a distillation condenser fitted with a thermocouple connected to a digital thermometer which can read at increments of 0.1 °C accuracy. The constant boiling distillates were collected and analyzed using gas chromatography (GC) on an Agilent Technologies 5957C using column HP-5 FID.

Table 2: Formulations and Azeotropes

| Name     | Hydrofluoroether | Carbonate - %(w/w)         | Azeotrope/Boiling Point |
|----------|------------------|----------------------------|-------------------------|
| 7100-DMC | Novec™ 7100      | Dimethyl Carbonate – 6-7%  | Yes – 59 °C             |
| 7100-DEC | Novec™ 7100      | Diethyl Carbonate – 0-10%  | No                      |
| 7200-DMC | Novec™ 7200      | Dimethyl Carbonate – 8-10% | Yes – 73 °C             |
| 7200-DEC | Novec™ 7200      | Diethyl Carbonate – 10%    | No                      |
| 7300-DMC | Novec™ 7300      | Dimethyl Carbonate – 7%    | Yes – 83 °C             |
| 7300-DEC | Novec™ 7300      | Diethyl Carbonate – 10%    | No                      |
| 7500-DMC | Novec™ 7500      | Dimethyl Carbonate – 10%   | No                      |
| 7500-DEC | Novec™ 7500      | Diethyl Carbonate – 10%    | No                      |

### Example 3: Methods

#### Surface Tension

- 5 Surface Tension was measured by ASTM D971 standard, using the KSV Sigma Tensiometer Du Nuoy ring method.

#### Specific Gravity/Density

Density was measured using a hydrometer. Immersing it directly into the azeotrope mixture, the reading was directly made from the pre-graduated hydrometer.

#### 10 Turbidity (Kauri-Butanol Value or Kb value)

This was done following ASTM D1133 standard. Kauri resin was obtained from Shaman's Garden (Motueka, New Zealand)

- 15 20 ± 0.10 g of the adjusted kauri-butanol (KB) solution was weighed into a 250-mL Erlenmeyer flask. The temperature of the KB solution in the flask was checked to be 25 ± 5°C. If not, the Erlenmeyer flask and its contents were placed in a water bath or temperature controlled environment maintained at 25 ± 5°C and allowed to equilibrate for at least 30 minutes. If the flask was placed in a water bath, the flask from the water bath was removed. The sample dispensing device was filled with the solvent being tested. The contents of the flask was titrated with the solvent. The contents of the flask were swirled during the titration, periodically

stopping to observe the clarity of the print beneath the flask. The successive amounts of solvent added was gradually reduced as the end point approached. The end point was reached when the sharp outlines of 10-point print placed directly beneath the Erlenmeyer flask and observed through the liquid were first perceived to be obscured or blurred. The point where the print became illegible was considered to be past the end point. The temperature in the flask was checked immediately after the end point had been reached and if over 30°C or under 20°C, the titration was repeated. The volume of solvent, in millilitres, was designated to produce turbidity as C, based on the calculation below.

$$V = [65(C - B)/(A - B)] + 40$$

10 where:

A = toluene required to titrate 20 g of kauri-butanol solution (mL)

B = heptane-toluene blend required to titrate 20 g of kauri-butanol solution (mL); and

C = solvent under test required to titrate 20 g of kauri-butanol solution (mL).

### Water Solubility

15 0.1, 1, 10% water was added to the Azeotrope solvent and shaken well for 5 minutes. After allowing to settle, the top water layer was separated. The bottom azeotrope layer was titrated using a Karl-Fischer titrator. Water solubility content was directly obtained from the titration.

### Flammability/Flash Point

The azeotrope samples were analysed for Closed Cup Flash Point using ASTM D-3278-96 e-1.

20 No Flash Point was identified.

### Residue Analysis Using FTIR

The azeotrope mixture was analyzed using FTIR-ATR. The solvent was dripped on the probe and the spectrum was measured immediately to get the solvent composition. The measurement was taken again after 1 minute drying to allow the solvent to evaporate at ambient conditions.

### 25 Solvent Evaporation Studies with Dissolved Lubricant

The integrity of the mixed solvents in a coating bath was tested as follows:

- 0.5 % w/w and 1.0% w/w concentration of lubricant Z-Tetraol each dissolved in 7100-DMC (7wt% dimethylcarbonate in Novec™ 7100) were taken in a vial.
- Vials were kept open to facilitate the evaporation of solvent.
- 30 • Solvents were evaporated to 10, 25 and 50% by weight.
- The content of the remaining solvent composition was analyzed using gas chromatography (GC).

## Example 4: Physical Properties

The properties of the solvents are tabulated in Table 2. 7100-DMC (6 % w/w dimethylcarbonate in Novec™ 7100) and 7100AN (7 % w/w acetonitrile in Novec™ 7100) were found to have higher Kauri-Butanol value as compared to 7100 alone. However, AN is considered a Volatile Organic Compound (VOC), hence its replacement with 7100 is favourable. Further, 7100-DMC has < 1000ppm water solubility which will be very favourable for several applications.

Table 3: Properties of 7100-DMC compared with other azeotropes and solvents

| Properties               | DMC    | AN       | 7100          | 7100-DMC      | 7100AN        | VertrelXF     |
|--------------------------|--------|----------|---------------|---------------|---------------|---------------|
| BP                       | 90     | 82       | 61            | 59            | 55            | 55            |
| Azeotrope%               | -      | -        | -             | 6% DMC        | 7% AN         | -             |
| Surface Tension          | 28.5   | 29.2     | 13            | 14.2          | 14.4          | 14.1          |
| Density                  | 1.07   | 0.79     | 1.5           | 1.49          | 1.46          | 1.58          |
| Kb value                 | 34.2   | -        | 10            | 12.6          | 12.8          |               |
| Flammability/Flash Point | 18oC   | 2oC      | Non flammable | Non Flammable | Non Flammable | Non Flammable |
| Water Solubility         | 13 wt% | Miscible | 95ppm         | <1000ppm      | ~ 1%          | 480ppm        |
| Exposure Limit ppm       | 200    | 40       | 750           | 750/200       | 750/40        | 200           |
| ODP/GWP                  |        |          | 0/320         |               |               | 0/1650        |

DMC – Dimethyl carbonate

10 AN – Acetonitrile

7100 – Novec™ 7100

7100-DMC – Novec™ 7100 + Dimethyl carbonate

7100-AN – Novec™ 7100 + Acetonitrile

15 Flammability/flash point and exposure limit of the known solvents were taken from the Materials Safety Data Sheet (MSDS) of the respective solvents and ODP/GWP was taken from the Technical Data Sheet (TDS) of the respective solvents.

## Example 5: Environmental Properties

DMC is exempted from being a volatile organic compound (VOC) by the United States Environment Protection Agency (US EPA). The Maximum Incremental Reactivity (MIR) which is a measure of the ozone forming activity of a compound, of DMC is very small, measuring at 5.04 g O<sub>3</sub>/mole VOC, and 0/056 O<sub>3</sub>/gram VOC.

The exposure limits and toxicity data for DMC are more favourable than other common solvents. In Table 4, 7100-DMC comprises 7% w/w of dimethylcarbonate in Novec™ 7100.

Table 4: Comparison of Environmental Properties

| Properties                            | DMC    | 7100      | 7100-DMC | VertrelXF |
|---------------------------------------|--------|-----------|----------|-----------|
| Exposure Limit ppm                    | 200    | 750       | 750/200  | 200       |
| ODP/GWP                               | -      | 0/320     | < 320    | 0/1650    |
| Volatile Organic Compound             | Exempt | Exempt    | Exempt   | Exempt    |
| Acute Toxicity (4 hr. LC50 [Rat]) ppm |        | > 100,000 |          | 11000     |

\*ODP = ozone depleting potential, GWP = global warming potential

Exposure limit of the known solvents was taken from the Materials Safety Data Sheet (MSDS) of the respective solvents and ODP/GWP was taken from the Technical Data Sheet (TDS) of the respective solvents. Exposure limit of 7100-DMC is based on the individual exposure limits of 7100 and DMC, as mentioned in the respective MSDS.

The ODP/GWP for 7100-DMC was calculated based on the known ODP/GWP values of the respective component solvents and their relative proportions. GWP of DMC is not available, but the atmospheric lifetime of DMC is very small. In this regard, the calculations were made based on the assumption that the GWP of DMC will be close to 1.

It should be noted that typically, hydrocarbon solvents break down in the atmosphere quickly and does not contribute to GWP. There are two possible GWPs to be considered for hydrocarbons. 1) Direct GWP which is the direct contribution of the hydrocarbon molecule (in this case, DMC) and 2) Indirect GWP which is the GWP of the decomposed product of the molecule. Decomposition of DMC results in methanol and carbon dioxide, and the GWP of methanol is considered to be 0 and the GWP of carbon dioxide is considered to be 1. Accordingly, the GWP of DMC was considered to be 1, based on the GWP of its decomposition product, carbon dioxide.

## Example 6: Evaporation Efficiency

Novec™ 7100 and Novec™ 7200 azeotropes with dimethyl carbonate (DMC) was shown to evaporate readily without leaving any residues. The spectra in Fig. 1 show the FTIR of different compositions immediately and after 1 minute evaporation, and show the efficiency and the residue of the evaporation of the various solvents. In Fig. 1, 7100-DMC comprises 7% w/w of dimethylcarbonate in Novec™ 7100.

## Example 7: Application As An HDD Lubricant Deposition Solvent

A disposable glass vial was placed on a four-place balance and the mass ( $M_v$ ) recorded. The balance with the glass vial was tared and deposition solvent was added (varying from 1 g to 5 g) and the mass ( $M_s$ ) was recorded. The balance with the deposition solvent in the glass vial was tared again. The lubricant was added in a dropwise fashion using a disposable plastic pipette and the mass ( $M_L$ ) recorded. The glass vial was then mixed by hand for 10 seconds to 30 seconds and the solution clarity was visually observed and recorded. If the solution was hazy, the lubricant was considered to have exceeded the solubility limit of the deposition solvent. If the solution was clear, additional drops of lubricant were added to the glass vial, the mass ( $M_L$ ) was recorded, the glass vial was shaken, and the solution clarity was observed. This process was continued until a hazy solution was observed or more than 10% w/w (weight of lubricant to combined weight of lubricant and deposition solvent) was reached. After a hazy solution or more than 10% w/w of lubricant was reached, the glass vial with the solution was removed from the balance. The balance was tared and the final mass ( $M_F$ ) of the glass vial with deposition solvent and lubricant was measured and recorded. To account for the evaporative losses of the deposition solvent during the experiment, the mass of the vial and the mass of the lubricant added were subtracted from the total mass of the vial with the deposition solvent and lubricant to determine the final mass of deposition solvent ( $M_{S*}$ ) in the vial (i.e.,  $M_{S*} = M_F - M_v - M_L$ ). Solubility of the lubricant in deposition solvents was calculated as  $M_L / (M_L + M_{S*})$  and reported in % w/w (weight/weight).

Table 5: Solubility of lubricant Z-Tetraol in different solvents

| Solvent    | Wt.% Solubility of Z-Tetraol |
|------------|------------------------------|
| 7100       | <0.05%                       |
| Vertrel XF | > 10%                        |
| 7100DMC    | >5%                          |
| 7100AN     | > 5%                         |
| 71IPA      | > 5%                         |

Azeotropes of Novec™ 7100 showed equally good solvency of the Z-Tetraol Lubricant as compared to 7100AN (6 % w/w acetonitrile in Novec™ 7100) or 71IPA (4.5 % w/w isopropylalcohol in Novec™ 7100). However AN and IPA are VOCs. Vertrel XF, Novec™

7100 and DMC are registered as VOC exempt solvents under US EPA. However, while Vertrel XF showed better solvency than 7100-DMC (7 % w/w dimethylcarbonate in Novec™ 7100), as shown in Table 4, it has non-ideal ODP/GWP values compared to 7100-DMC. It should be noted that Vertrel XF is a hydrofluorocarbon which comes under the Montreal Protocol/Kigali Amendment scanner and it is in the process of being phased out. The unfavourable environmental profile (high GWP) of Vertrel XF results in high volume usage restrictions and also makes it subject to carbon tax in various countries.

Accordingly, it was shown that 7100-DMC is able to provide advantageous solvency while also being environmentally benign.

## 10 **Example 8: Surface Wetting**

Lubricant Z-Tetraol solution was dripped on a carbon-deposited finished media substrate. The solution wetting on the surface was noted, and following evaporation of the solvent, the lubricant deposition profile was checked visually.

As shown in Fig. 2, surface wetting using the lubricant Z-Tetraol, when deposited with 7100AN (6 % w/w acetonitrile in Novec™ 7100) and 71IPA (4.5 % w/w isopropylalcohol in Novec™ 7100), was not even, and the spread of the solvent droplet was not very well defined. In contrast, droplets of 7100-DMC (7 % w/w dimethylcarbonate in Novec™ 7100) and Vertrel XF wetted the surface well and showed uniform spread. 7100-DMC showed comparable results as Vertrel XF. However, as discussed above in Example 7, Vertrel XF has non-ideal ODP/GWP values compared to 7100-DMC. Accordingly, it was shown that 7100-DMC is able to provide advantageous surface wetting properties while also being environmentally benign.

## **Example 9: Solvent Evaporation Studies With Dissolved Lubricant**

Fig. 3 shows the area% of the peaks in the gas chromatograms at various stages of evaporation of the 0.5% w/w and 1.0% w/w concentration mixtures. It was shown that 7100-DMC is a stable azeotrope, as no change in the composition was observed.

## **Example 10: Application As Cleaning Solvent**

Contaminants such as hydrocarbons, light oils and greases on electronic parts after fabrication should be cleaned before assembly. This avoids out-gassing during operation and improves the life of exotic electronics.

Solvent cleaning was carried out in vapour degreasing machines. Vapour degreasing machines equipped with ultrasonication provides superior fine cleaning performances. 7100-DMC has a  $K_b$  value of 12.6 which is higher compared to pure 7100 and 71IPA, providing better solubility for hydrocarbon oils and greases. Moderately higher  $K_b$  values can be used to clean the last traces of hydrocarbons in precision cleaning.

Since 7100-DMC has dimethyl carbonate (DMC) as the polar component, this azeotrope potentially can be used as a rinsing agent in co-solvent systems. This helps to provide quick rinsing and drying of higher boiling point solvents, resulting in increased throughput and efficiency.

## 5 **Example 11: Application In Spot-Free Drying**

7100-DMC was mixed with pressurized nitrogen to form fine particles/a vapour mist. The pressurized 7100-DMC/N<sub>2</sub> mist was sprayed onto a substrate (wafers, glass etc.) in the chamber/jig coming out of a water tank. Because of the difference in surface tension (Marangoni phenomena) on the interface between the water particles and the mist, the water particles were repelled back to the water tank. The water was repelled so that there will not be any particles generated.

The water solubility of 7100-DMC is < 1000 ppm. This helps in the removal of water and will shorten the drying time of the solvent. Less water content in the solvent will avoid white water marks and spots being left on highly polished wafers.

## **Industrial Applicability**

5 The composition may be useful as a solvent, for example for lubricants for hard disc drives (HDD), in spot-free drying for semiconductor wafers, such as in Marangoni drying, in aerosol formulations, precision cleaning, and as a rinsing agent in co-solvent cleaning. The composition may be useful as an in situ oxygen booster in gasoline.

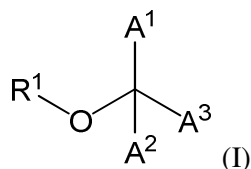
It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

## Claims

1. A composition comprising:

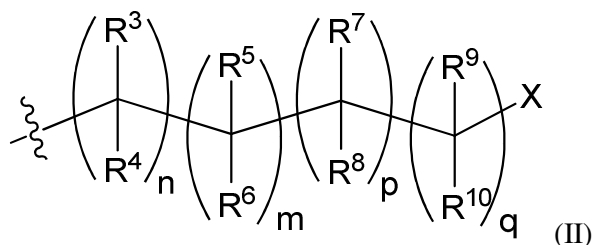
a dialkyl carbonate or a cyclic carbonate; and

a compound having the following formula (I):



wherein  $\text{R}^1$  is selected from the group consisting of alkyl, alkenyl and alkynyl; and

$\text{A}^1$ ,  $\text{A}^2$  and  $\text{A}^3$  are independently X or have the following formula (II):



wherein  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$ ,  $\text{R}^8$ ,  $\text{R}^9$  and  $\text{R}^{10}$  are independently X or,  $-\text{CX}_3$ ;

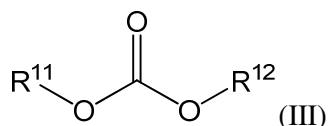
X is halogen;

n is an integer of at least 1;

m, p and q are independently 0 or an integer of at least 1; and

~~~~~ represents where formula (II) attaches to formula (I).

2. The composition according to claim 1, wherein the dialkyl carbonate has the following formula (III):

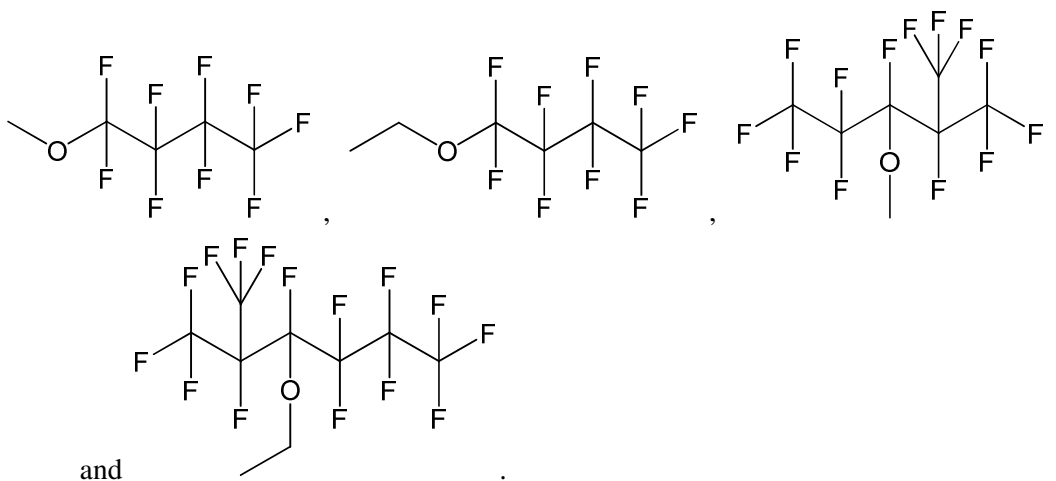


wherein R^{11} and R^{12} are independently a branched or straight-chain alkyl group.

3. The composition according to claim 2, wherein R^{11} and R^{12} are independently selected from the group consisting of methyl, ethyl, propyl, isopropyl, cyclopropyl, butyl, butan-2-yl, 2-methylpropyl, tert-butyl, pentyl, 2-methylbutan-2-yl, 2,2-dimethylpropyl, 3-

methylbutyl, pentan-2-yl, pentan-3-yl, 3-methylbutan-2-yl, 2-methylbutyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, and dodecyl.

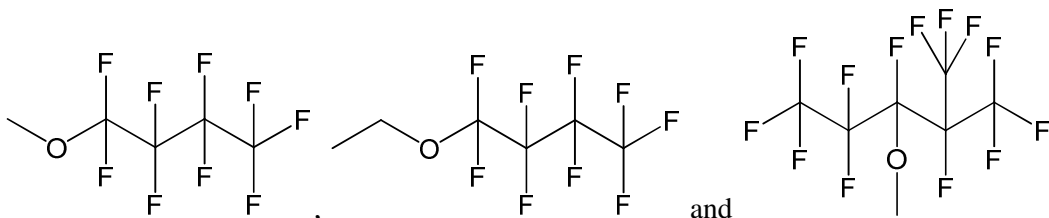
4. The composition according to any one of the preceding claims, wherein the dialkyl carbonate is dimethyl carbonate or diethyl carbonate.
5. The composition according to claim 1, wherein the cyclic carbonate is selected from the group consisting of ethylene carbonate, propylene carbonate, butylene carbonate, styrene carbonate and glycerine carbonate.
6. The composition according to any one of the preceding claims, wherein R^1 is an alkyl.
7. The composition according to any one of the preceding claims, wherein R^1 is methyl or ethyl.
8. The composition according to any one of the preceding claims, wherein X is fluorine.
9. The composition according to any one of the preceding claims, wherein at least one of A^1 , A^2 or A^3 has formula (II).
10. The composition according to claim 9, wherein A^1 has formula (II) and A^2 and A^3 are X.
11. The composition according to claim 10, wherein in A^1 , n is 4, m, p and q are 0 and R^3 and R^4 are both X.
12. The composition according to claim 9, wherein A^1 and A^2 have formula (II), and A^3 is X.
13. The composition according to claim 12, wherein in A^1 , n and m are 1, p and q are 0, R^3 , R^5 and R^6 are X and R^4 is CX_3 ; and in A^2 , n is 2 or 3, m, p and q are 0 and R^3 and R^4 are both X.
14. The composition according to any one of the preceding claims, wherein the compound of formula (I) is selected from the group consisting of:



15. The composition according to any one of the preceding claims, comprising:

a dimethyl carbonate; and

a compound selected from the group consisting of:



5 16. The composition according to any one of the preceding claims, wherein the dialkyl carbonate or cyclic carbonate is present at a range of 0.1 to 15% w/w, wherein the composition has a total % w/w of 100%.

10 17. The composition according to claim 16, wherein the dialkyl carbonate is dimethyl carbonate and is present at a range of 6 to 10% w/w, wherein the composition has a total %w/w of 100%.

18. The composition according to claim 16 or 17, wherein the composition is an azeotrope.

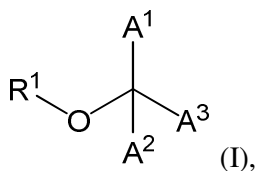
19. The composition according to any one of the preceding claims, comprising a further solvent.

15 20. The composition according to claim 19, wherein the further solvent is trans-1,2-dichloroethene.

21. A method for synthesizing a composition comprising:

a dialkyl carbonate or a cyclic carbonate; and

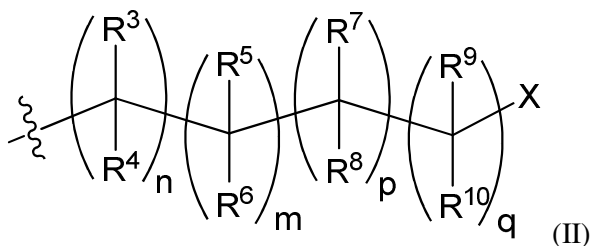
a compound having the following formula (I):



20 the method comprising the step of contacting the dialkyl carbonate with the compound having formula (I),

wherein R¹ is selected from the group consisting of alkyl, alkenyl and alkynyl; and

A¹, A² and A³ are independently X or have the following formula (II):



wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are independently X or, $-CX_3$;

X is halogen;

n is an integer of at least 1;

5 m, p and q are independently 0 or an integer of at least 1; and

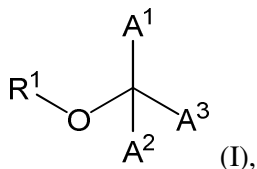
~~~~~ represents where formula (II) attaches to formula (I).

22. The method according to claim 21, wherein the contacting step comprises refluxing the dialkyl carbonate and the compound having formula (I) for a duration in the range of about 15 minutes to about 45 minutes.

10      23. Use of a composition comprising:

a dialkyl carbonate or a cyclic carbonate; and

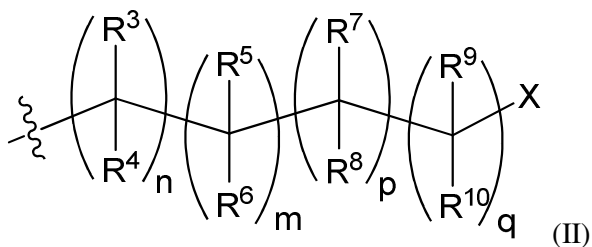
a compound having the following formula (I):



as a solvent,

15      wherein  $R^1$  is selected from the group consisting of alkyl, alkenyl and alkynyl; and

$A^1$ ,  $A^2$  and  $A^3$  are independently X or have the following formula (II):



wherein  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  are independently X or,  $-CX_3$ ;

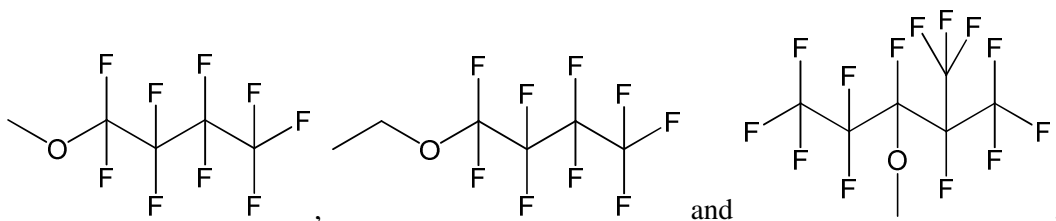
X is halogen;

n is an integer of at least 1;

m, p and q are independently 0 or an integer of at least 1; and

~~~~~represents where formula (II) attaches to formula (I).

- 5 24. The use according to claim 23, wherein the solvent is an azeotrope.
25. The use according to claim 23 or 24, wherein the composition comprises:
- a dimethyl carbonate; and
- a compound selected from the group consisting of:



- 10 26. The use according to any one of claims 23 to 25, wherein the composition is used as a solvent for disc lubricant, coating, or aerosol, or in cleaning, rinsing or drying of a substrate.