STABLE 2,3,3,3-TETRAFLUOROPROPENE COMPOSITION

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ABSTRACT
The invention relates to a stable composition (CS) comprising at least x wt.-% 2,3,3,3-tetrafluoropropene (99.8≤x≤100), at most y wt.-% unsaturated compound(s) (Ia) (0≤y≤0.2) selected from among 3,3,3-trifluoropropene (HFO-1225ye) and the positional isomers of 2,3,3,3-tetrafluoropropene, such as 1,3,3,3-tetrafluoropropene (isomers Z and E) and 1,1,2,3-tetrafluoropropene, and, optionally, at most 500 ppm of 3,3,3-trifluoropropyne and/or at most 200 ppm 1,1,1,2,3-pentafluoropropene (HFO-1225ye).
STABLE 2,3,3,3-TETRAFLUOROPROPENE COMPOSITION

[0001] The present invention relates to a stable composition including 2,3,3,3-tetrafluoropropene capable of being used in refrigeration and air conditioning.

[0002] The problems presented by substances which deplete the atmospheric ozone layer were dealt with at Montreal, where the protocol was signed imposing a reduction on the production and use of chlorofluorocarbons (CFCs). This protocol has formed the subject of amendments which have required the abandoning of CFCs and have extended regulation to other products, including hydrochlorofluorocarbons (HCFCs).

The refrigeration and air conditioning industries have invested a great deal in the replacement of these refrigerants and it is because of this that hydrofluorocarbons (HFCs) have been marketed.

[0003] In the motor vehicle industry, the air conditioning systems of commercial vehicles have been changed in many countries from a refrigerant comprising chlorofluorocarbon (CFC-12) to that of hydrofluorocarbon (HFC-134a), which is less harmful to the ozone layer. However, from the viewpoint of the objectives set by the Kyoto protocol, HFC-134a (GWP = 1430) is regarded as having a high heating power. The contribution to the greenhouse effect of a refrigerant is quantified by a criterion, the GWP (Global Warming Potential), which summarizes the heating power by taking a reference value of 1 for carbon dioxide.

[0004] Hydrofluorolefins (HFOs) have a low heating power and thus meet the objectives set by the Kyoto protocol. The document JP 4-110388 discloses 2,3,3,3-tetrafluoropropene (HFO-1234yf) as heat transfer agent in refrigeration, air conditioning and heat pumps.

[0005] In addition to having good properties as a heat transfer agent, in order for a refrigerant to be accepted commercially, it must in particular be thermally stable and be compatible with lubricants. This is because it is highly desirable for the refrigerant to be compatible with a lubricant used in the compressor present in the majority of refrigeration systems. This refrigerant and lubricant combination is important for the use and the effectiveness of the refrigeration system; in particular, the lubricant has to be sufficiently soluble in the refrigerant throughout the operating temperature range.

[0006] According to the document WO 2008/042066, as fluorolefins are capable of decomposing on contact with moisture, oxygen or other compounds when they are used as refrigerant, possibly at high temperature, it is recommended to stabilize them with at least one amine.

[0007] Other stabilizing agents, such as benzophenone derivatives, lactones and some phosphorus-comprising compounds, have also been proposed for stabilizing fluorolefins (WO 2008/027596, WO 2008/027516 and WO 2008/027515).

[0008] Furthermore, the document EP 2 149 543 describes a process for the purification of 1,1,1,2,3-pentafluoropropane, a starting material in the manufacture of HFO-1234yf, in order to obtain a product having a 1,1,1,2,3-pentafluoropropane (HFO-1225ye) content of less than 500 ppm and a trifluoropropylene content of less than 50 ppm.

[0009] The Applicant Company has now developed a 2,3,3-tetrafluoropropene composition which makes it possible to improve the thermal stability when it is used in refrigeration systems.

[0010] A subject-matter of the present invention is thus a stable composition (SC) comprising at least 8% by weight of 2,3,3,3-tetrafluoropropene (99.8% ≤ x ≤ 100%), at most 7% by weight of unsaturated compound(s) (la) (0 ≤ y ≤ 0.2) chosen from 3,3,3-trifluoropropene (HFO-1243zf) and the positional isomers of 2,3,3,3-tetrafluoropropene, such as 1,3,3,3-tetrafluoropropene (Z and E isomers) and 1,1,2,3-tetrafluoropropene, and optionally at least 500 ppm of 3,3,3-trifluoropropene and/or at most 200 ppm of 1,1,1,2,3-pentafluoropropene (HFO-1225ye).

[0011] The stable composition according to the present invention can additionally comprise at least one of the compounds (lb) chosen from 1,1,1,2-tetrafluoropropane (HFC-254eb), 1,1,1,3,3-pentafluoropropane (HFC-245eb), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,2-trifluoroethane (HFC-143), 1,1,1,2,3,3-hexafluoropropane, hexafluoropropane, cyclohexafluoropropane and 1,1,1,3,3-pentafluoropropene (HFO-1225ye).

[0012] The combined compounds (lb) present in the composition according to the present invention represent at most 500 ppm.

[0013] Preferably, the SC composition comprises at least 99.85% by weight of 2,3,3,3-tetrafluoropropene, at most 7% by weight of unsaturated compound(s) (la) (0 ≤ y ≤ 0.15) chosen from 3,3,3-trifluoropropene (HFO-1243zf) and the positional isomers of 2,3,3,3-tetrafluoropropane, such as 1,3,3,3-tetrafluoropropene (Z and E isomers) and 1,1,2,3-tetrafluoropropene, and optionally at most 200 ppm of 3,3,3-trifluoropropene and/or at most 5 ppm of 1,1,1,2,3-pentafluoropropene (HFO-1225ye).

[0014] The SC composition which is particularly preferred comprises at least 99.9% by weight of 2,3,3,3-tetrafluoropropene, at most 6% by weight of unsaturated compound(s) (la) (0 ≤ y ≤ 0.1) chosen from 3,3,3-trifluoropropene (HFO-1243zf) and the positional isomers of 2,3,3,3-tetrafluoropropene, such as 1,3,3,3-tetrafluoropropene (Z and E isomers) and 1,1,2,3-tetrafluoropropene, and optionally at most 200 ppm of 3,3,3-trifluoropropene and/or at most 5 ppm of 1,1,1,2,3-pentafluoropropene (HFO-1225ye).

[0015] According to a preferred embodiment of the invention, the SC composition comprises from 99.85 to 99.98% by weight of 2,3,3,3-tetrafluoropropene, from 0.02 to 0.15% by weight of unsaturated compound(s) (la) chosen from 3,3,3-trifluoropropene (HFO-1243zf) and the positional isomers of 2,3,3,3-tetrafluoropropene, such as 1,3,3,3-tetrafluoropropene (Z and E isomers) and 1,1,2,3-tetrafluoropropene, and optionally at most 200 ppm of 3,3,3-trifluoropropene and/or at most 5 ppm of 1,1,1,2,3-pentafluoropropene (HFO-1225ye) and/or at most 400 ppm of compounds (lb).

[0016] The stable composition according to the invention exhibits the advantage of being able to be obtained directly by a process for the manufacture of 2,3,3,3-tetrafluoropropene, optionally after at least one separation stage.

[0017] Another subject-matter of the present invention is 2,3,3,3-tetrafluoropropene which has a purity of greater than or equal to 99.8% by weight and less than 100% by weight and which comprises at most 0.2% by weight of unsaturated compounds (la), optionally at most 500 ppm of 3,3,3-trifluoropropene and/or at most 200 ppm of 1,1,1,2,3-pentafluoropropane and/or at most 500 ppm of compounds (lb).

[0018] An additional subject-matter of the present invention is 2,3,3,3-tetrafluoropropene which has a purity of greater than or equal to 99.9% by weight and less than 100% by weight and which comprises at most 0.1% by weight of...
unsaturated compounds (Ia), optionally at most 200 ppm of 3,3,3-trifluoropropyne and/or at most 5 ppm of 1,1,1,2,3-
pentfluoropropane and/or at most 500 ppm of compounds (lb).

[0019] 2,3,3,3-Tetrafluoropropene can be obtained from
hexafluoropropene (HFP) in at least 4 reaction stages: (i)
hydrogenation of HFP in the presence of a hydrogenation
catalyst in a solid phase to give 1,1,1,2,3,3-hexafluoropro-
pane; (ii) dehydrofluorination of the 1,1,1,2,3,3-hexafluoro-
propane obtained in stage (i) in the liquid phase using an
alkali metal hydroxide or in the gas phase in the presence of a
dehydrohalogenation catalyst to give 1,1,1,2,3-pentafluoro-
propane; (iii) hydrogenation of the HF/1-O-1225ye obtained in
(ii) in the presence of a hydrogenation catalyst in the solid
phase to give 1,1,1,2,3-pentafluoropropane; (iv) dehydroflu-
orination of the HFC-245eb obtained in stage (iii) in the liquid
phase using an alkali metal hydroxide or in the gas phase in
the presence of a dehydrohalogenation catalyst to give 2,3,3,
3-tetrafluoropropene.

[0020] 2,3,3,3-Tetrafluoropropene can be obtained from
hexafluoropropene (HFP) in at least 2 reaction stages: (i)
hydrogenation of HFP in the presence of a hydrogenation
catalyst in the solid phase to give 1,1,1,2,3-pentafluoropro-
pane; (ii) dehydrofluorination of the HFC-245eb obtained in
stage (i) in the liquid phase using an alkali metal hydroxide or
in the gas phase in the presence of a dehydrohalogenation
catalyst to give 2,3,3,3-tetrafluoropropene.

[0021] The 2,3,3,3-tetrafluoropropene according to the
present invention can be obtained from HFP according to a
process as described above after a purification of the HFC-
245eb and/or after purification of the 2,3,3,3-tetrafluoro-
propene.

Thus, the HFC-245eb, prior to the dehydrofluorination stage,
is, for example, purified by distillation at an absolute
pressure of 6 bar and at a column bottom temperature of
80°C and a top temperature of 50°C with approximately 30 theoretical
plates and a reflux ratio of approximately 37.

[0022] After the final dehydrofluorination stage, the HF-
O-1234yf is subjected to double distillation. The first distillation
is carried out at an absolute pressure of approximately 13 bar,
a column bottom temperature of approximately 60°C and a
top temperature of approximately 40°C and with approxi-
mately 35 theoretical plates and a reflux ratio of approxi-
mately 500. The second distillation is carried out at an abso-
lute pressure of approximately 11 bar, a column bottom
temperature of approximately 105°C, and a top temperature of
approximately 44°C and with approximately 30 theoretical
plates at a reflux ratio of approximately 4.

[0023] The 2,3,3,3-tetrafluoropropene can also be obtained
from 1,1,1-trifluoro-2-chloropropane by hydrofluorination in
the liquid or gas phase in the presence of a fluorination cata-
lyst. The 2,3,3,3-tetrafluoropropene thus obtained can be
purified to give the 2,3,3,3-tetrafluoropropene according to
the present invention.

[0024] The compositions according to the present inven-
tion are capable of being used as heat transfer agent in sta-
tionary or motor-vehicle air conditioning, refrigeration and
heat pumps.

[0025] Another subject-matter of the present invention is the
compositions as described above in combination with a
lubricant.

[0026] Mention may in particular be made, as lubricant, of
polyol esters (POEs), polyalkylene glycols (PAGs), polyalky-
lene glycol esters and polyvinyl ethers (PVEs).

[0027] The PAG lubricants are in the oxyalkylene homo-
or copolymer form. The preferred PAGs are homopolymers
composed of oxypropylene groups with a viscosity of 10 to
200 centistokes at 40°C, advantageously between 30 and 80 centistokes.
The hydroxyl groups at the ends of the oxyalkylene homo- or copolymer chains can be more or less replaced by
—O—C,H, groups where n=1 to 10; the group with
n=1 being preferred. The PAGs which may be suitable are those
having hydroxyl groups for each ending or
—O—C,H, groups.

[0028] Mention may in particular be made, as POEs, of
esters of carboxylic acids having a linear or branched carbon
chain of 2 to 15 atoms and of polyols having a neopentyl
backbone, such as neopentyl glycol, trimethylolpropane,
pentaerythritol and dipentaerythritol; pentaerythritol is
the preferred polyol. Esters of carboxylic acids having a carbon
chain of 4 to 9 atoms are preferred.

[0029] Mention may in particular be made, as carboxylic
acid of 4 to 9 carbon atoms, of n-pentanoic acid, n-hexanoic
acid, n-heptanoic acid, n-octanoic acid, 2-ethylhexanoic acid,
2,2-dimethylpentanoic acid, 3,5,5-trimethylhexanoic acid,
adic acid and succinic acid.

[0030] Some alcohol functional groups are not esterified;
however, the proportion remains low.

[0031] The POE oils selected can comprise between 0 and
5 relative mol % of CH, —O— units with respect to the
—CH, —O— (C—O)— units.

The preferred POE lubricants are those having a viscosity of
1 to 1000 centistokes (cSt) at 40°C, preferably of 10 to 200
CSt and advantageously of 30 to 80 cSt.

EXPERIMENTAL PART

[0032] The thermal stability trials are carried out according
to Standard ASHRAE 97-2007: “sealed glass tube method to
test the chemical stability of materials for use within refrig-
entor systems”.

The test conditions are as follows:
Weight of fluid: 2.2 g
Weight of lubricant: 5 g

Temperature: 200°C.

Duration: 14 days

Lengths of steel are introduced into tubes.
The length of steel and the lubricant are introduced into a 42.2
ml glass tube. The tube is subsequently evacuated under
vacuum and then the fluid F is added thereto. The tube is then
welded in order to close it and placed in an oven at 200°C for
14 days.

At the end of the test, various analyses are carried out:

[0036] the gas phase is recovered in order to be analysed
by gas chromatography: the main impurities were
identified by GC/MS (coupled gas chromatography/mass
spectrometry). The impurities coming from the fluid
F and those coming from the lubricant can thus be
combined.

[0037] the length of steel is weighed (measurement of
the rate of corrosion) and observed under a microscope.

[0038] the lubricant is analysed: colour (by spectropho-
tometry, Labomat DR Lange LICO220 model
MLG131), water content (by Karl Fischer coulometry,
Mettler DL37) and acid number (by quantitative
determination with 0.01N methanolic potassium hydroxide).
The lubricant used in the tests is a commercial PAG oil: PAG ND8.
The fluid used for these trials comprises essentially HFO-1234yf (at least 99.9% by weight) and then 300 ppm of HFO-1243zf, 500 ppm of E HFO-1234ze and 300 ppm of HFO-1243zf+500 ppm of E HFO-1234ze are respectively added to the fluid.

<table>
<thead>
<tr>
<th>Content of ppm ppm ppm ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>E HFO-1234ze</td>
</tr>
<tr>
<td>HFO-1243zf added</td>
</tr>
</tbody>
</table>

Byproducts in the gas phase:

<table>
<thead>
<tr>
<th>Rate of corrosion</th>
<th>Analysis of the oil:</th>
</tr>
</thead>
<tbody>
<tr>
<td>from the fluid</td>
<td>600 ppm 600 ppm 900 ppm 900 ppm</td>
</tr>
<tr>
<td>from the fluid</td>
<td>&lt;5 µm/year</td>
</tr>
</tbody>
</table>

The examples show that the presence of the compounds (Ia) is not harmful to the thermal stability, either of the HFO-1234yf composition or of the lubricant, and in some cases improves it.

1. Stable composition comprising at least about 99.8 to 100% by weight of 2,3,3,3-tetrafluoropropene, at most about 0 to 0.2% by weight of unsaturated compound selected from the group consisting of 3,3,3-trifluoropropene (HFO-1243zf), the positional isomers of 2,3,3,3-tetrafluoropropene, 1,1,2,3-tetrafluoropropene, and mixtures thereof.

2. Stable composition according to claim 1, characterized in that it further comprises at least one compound selected from the group consisting of 1,1,1,2,3-pentafluoropropene (HFC-254eb), 1,1,1,2,3,3-pentafluoropropene (HFC-245eb), 1,1,2,3,3-hexafluoropropene, hexafluoropropene, cyclohexafluoropropene, 1,1,1,3,3-pentafluoropropene, and mixtures thereof.

3. Stable composition according to claim 2, characterized in that the compound comprises at most 500 ppm of the stable composition.

4. Stable composition according to claim 1, characterized in that it comprises at least 99.85% by weight of 2,3,3,3-tetrafluoropropene, at most about 0 to 0.15% by weight of unsaturated compound selected from the group consisting of 3,3,3-trifluoropropene (HFO-1243zf), the positional isomers of 2,3,3,3-tetrafluoropropene, 1,1,2,3-tetrafluoropropene, and mixtures thereof.

5. Stable composition according to claim 1, characterized in that it comprises at least 99.9% by weight of 2,3,3,3-tetrafluoropropene, at most about 0 to 0.1% by weight of unsaturated compound selected from the group consisting of 3,3,3-trifluoropropene (HFO-1243zf), the positional isomers of 2,3,3,3-tetrafluoropropene, 1,1,2,3-tetrafluoropropene, and mixtures thereof.

6. Stable composition according to claim 1, characterized in that it comprises from 99.85 to 99.98% by weight of 2,3,3,3-tetrafluoropropene, from 0.02 to 0.15% by weight of unsaturated compound(s) (Ia) chosen from 3,3,3-trifluoropropene (HFO-1243zf) and the positional isomers of 2,3,3,3-tetrafluoropropene, such as 1,3,3,3-tetrafluoropropene (Z and E isomers) and 1,1,2,3-tetrafluoropropene, and optionally at most 200 ppm of 3,3,3-trifluoropropene and/or at most 5 ppm of 1,1,1,2,3-pentafluoropropene (HFO-1225ye) and/or at most 400 ppm of compounds (Ib).

(canceled)

8. Stable composition according to claim 1, characterized in that it further comprises a lubricant.

9. Stable composition according to claim 8, characterized in that the lubricant is selected from the group consisting of polyol esters (POEs), polyalkylene glycols (PAGs), polyalkylene glycol esters, polyvinyl ethers (PVEs) and mixtures thereof.

10. 2,3,3,3-Tetrafluoropropene which has a purity of greater than or equal to 99.8% by weight and less than 100% by weight and which comprises at most 0.2% by weight of unsaturated compound selected from the group consisting of 3,3,3-trifluoropropene (HFO-1243zf), the positional isomers of 2,3,3,3-tetrafluoropropene, 1,1,2,3-tetrafluoropropene, and mixtures thereof.

11. 2,3,3,3-Tetrafluoropropene according to claim 10, characterized by a purity of greater than or equal to 99.9% by weight and less than 100% by weight and comprising at most 0.1% by weight of unsaturated compound selected from the group consisting of 3,3,3-trifluoropropene (HFO-1243zf), the positional isomers of 2,3,3,3-tetrafluoropropene, 1,1,2,3-tetrafluoropropene, and mixtures thereof.

12. Stable composition according to claim 1, characterized in that it further comprises up to about 500 ppm of 3,3,3-trifluoropropene.

13. Stable composition according to claim 1, characterized in that it further comprises up to about 200 ppm of 1,1,1,2,3-pentafluoropropene (HFC-245eb).

14. Stable composition according to claim 4, characterized in that it further comprises up to about 250 ppm of 3,3,3-trifluoropropene.

15. Stable composition according to claim 4, characterized in that it further comprises up to about 50 ppm of 1,1,1,2,3-pentafluoropropene (HFO-1225ye).

16. Stable composition according to claim 5, characterized in that it further comprises up to about 200 ppm of 3,3,3-trifluoropropene.

17. Stable composition according to claim 5, characterized in that it further comprises up to about 5 ppm of 1,1,1,2,3-pentafluoropropene (HFC-245eb).

18. Stable composition according to claim 10, characterized in that it further comprises up to about 500 ppm of 3,3,3-trifluoropropene.

19. Stable composition according to claim 10, characterized in that it further comprises up to about 200 ppm of 1,1,1,2,3-pentafluoropropene (HFO-1225ye).

20. Stable composition according to claim 10, characterized in that it further comprises up to about 500 ppm of a compound selected from the group consisting of 1,1,1,2,3-tetrafluoropropene (HFC-254eb), 1,1,1,2,3-pentafluoropropene (HFO-245eb), 1,1,2,3-tetrafluoroethane (HFC-134a), 1,1,2-trifluoroethane (HFC-143), 1,1,1,2,3,3-hexafluoropropene, hexafluoropropene, cyclohexafluoropropene, 1,1,1,3,3-pentafluoropropene (HFC-1225ye) and mixtures thereof.
21. Stable composition according to claim 11, characterized in that it further comprises up to about 200 ppm of 3,3,3-trifluoropropyne.

22. Stable composition according to claim 11, characterized in that it further comprises up to about 5 ppm of 1,1,1,2,3-pentafluoropropene.

23. Stable composition according to claim 11, characterized in that it further comprises up to about 500 ppm of a compound selected from the group consisting of 1,1,1,2-tetrafluoropropane (HFC-254eb), 1,1,1,2,3-pentafluoropropane (HFC-245eb), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,2-trifluoroethane (HFC-143), 1,1,1,2,3,3-hexafluoropropene, hexafluoropropene, cyclohexafluoropropene, 1,1,1,3,3-pentafluoropropene (HFO-1225zc) and mixtures thereof.

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