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2,3,3,3-Tetrafluor-propén alapú készítmény

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

A fordítást a szabadalmas az 1995. évi XXXIII. törvény 84/H. §-a szerint nyújtotta be. A fordítás tartalmi helyességét a Szellemi Tulajdon Nemzeti Hivatala nem vizsgálta.

COMPOSITION COMPRISING 2,3,3,3-TETRAFLUOROPROPENE

The present invention relates to a composition containing 2,3,3,3-tetrafluoropropene and a lubricant, suitable for use in air conditioning.

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

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

In the motor vehicle industry, the air conditioning systems of vehicles marketed in many countries have been changed from a chlorofluorocarbon (CFC-12) refrigerant to a hydrofluorocarbon (1,1,1,2-tetrafluoroethane: HFC-134a) refrigerant, 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 of a refrigerant to the greenhouse effect 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.

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

In the industrial sector, the refrigerating machines most commonly used are based on cooling by evaporation of a liquid refrigerant. After vaporization, the refrigerant is compressed and then cooled in order to return to the liquid state and thus continue the cycle.



For economic reasons, refrigerant compressors are very often reciprocating compressors with lubricated cylinders. In general, internal lubrication of the compressors is essential in order to reduce wear and heating of the moving members, complete their leak tightness and protect them against corrosion.

The main characteristics required of oils intended for refrigerant compressor lubrication are miscibility with the refrigerant, solubility, and thermal and chemical stability.

Thus, polyalkylene glycols (PAGs) have been developed as lubricants of HFC-134a in motor vehicle air conditioning.

Document US Pat No. 7,534,366 recommends the use of a PAG, in the form of a homopolymer or copolymer consisting of 2 or more oxypropylene groups and having a viscosity of 10 to 200 centiStokes at 37°C, in combination with HFO 1234yf in air conditioning.

Document EP 2119759 describes a composition for motor vehicle air conditioning comprising a lubricant based on polyol esters (POE) and the refrigerant 2,3,3,3-tetrafluoropropene. The applicant has now developed a refrigerant and lubricant pairing, suitable for use in air conditioning.

A subject of the present application is therefore a composition comprising at least one lubricant based on polyol esters (POEs) and a refrigerant F comprising at least 99.8% by weight of 2,3,3,3-tetrafluoropropene, from 0.5 to 500 ppm of 1,1,1,2,3-pentafluoropropene, from 0.5 to 500 ppm of 3,3,3-trifluoropropyne and from 1 to 1500 ppm of compounds containing 2 or 3 carbon atoms, optionally comprising an olefin bond (with the exclusion of HFO 1225ye and 3,3,3-trifluoropropyne).

Polyol esters are obtained by reaction of a polyol (an alcohol containing at least 2 hydroxyl groups -OH) with a monofunctional or plurifunctional carboxylic acid or with a mixture of monofunctional carboxylic acids. The water formed during this reaction is eliminated in order to prevent the reverse reaction (i.e. hydrolysis). This is because polyol esters are capable of reacting with water under certain conditions so as to reproduce the polyol.

The applicant has discovered that, despite this prejudice, it is possible to use the refrigerant F with POE in air conditioning, in particular in motor vehicle air conditioning where the risk of entry of moisture is higher. Generally, a motor vehicle air conditioning circuit comprises a drying filter such that the moisture level does not exceed approximately 1000 ppm.

According to the present invention, the preferred polyols are those having a neopentyl backbone, such as neopentyl glycol, trimethylol propane, pentaerythritol and dipentaerythritol; pentaerythritol is the preferred polyol.

The carboxylic acids may contain from 2 to 15 carbon atoms, it being possible for the carbon backbone to be linear or branched. Mention may in particular be made 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, adipic acid and succinic acid, and mixtures thereof.

Some alcohol functions are not esterified, but their proportion remains low. Thus, the POEs can comprise between 0 and 5 relative mol % of $\text{CH}_2\text{-OH}$ units relative to the $\text{---CH}_2\text{-O-(C=O)-}$ units.

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

Preferably, the composition according to the invention comprises at least one lubricant based on polyol esters (POEs) and a refrigerant F comprising at least 99.9% by weight of 2,3,3,3-tetrafluoropropene, from 0.5 to 250 ppm of 1,1,1,2,3-pentafluoropropene, from 0.5 to 250 ppm of 3,3,3-trifluoropropyne and from 1 to 500 ppm of compounds containing 2 or 3 carbon atoms, optionally comprising an olefin bond (with the exclusion of HFO 1225ye and 3,3,3-trifluoropropyne).

The composition which is particularly preferred comprises at least one lubricant based on polyol esters (POEs) and a refrigerant F comprising at least 99.95% by weight of 2,3,3,3-tetrafluoropropene, from 0.5 to 250 ppm of 1,1,1,2,3-pentafluoropropene, from 0.5 to

100 ppm of 3,3,3-trifluoropropyne and from 1 to 150 ppm of compounds containing 2 or 3 carbon atoms, optionally comprising an olefin bond (with the exclusion of HFO 1225ye and 3,3,3-trifluoropropyne).

According to a preferred embodiment of the invention, the POE(s) represent(s) between 10% and 50%, inclusive, by weight of the composition.

A subject of the present invention is also the use of the abovementioned composition in refrigeration, air conditioning, advantageously in motor vehicle air conditioning, and preferably in electric vehicles. In addition, this composition is thermally and/or chemically stable.

According to another preferred embodiment of the invention, the POE(s) represent(s) between 1% and 4%, inclusive, by weight of the composition. This composition preferably corresponds to that which circulates in the evaporator and the condenser of a motor vehicle air conditioning circuit.

EXPERIMENTAL SECTION

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 refrigerant systems".

The test conditions are as follows:

weight of fluid F: 2.2g

weight of lubricant: 5g

temperature: 200°C

duration: 14 days

The length of steel and the lubricant are introduced into a 42.2ml 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:

- 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.
- the length of steel is weighed (measurement of the rate of corrosion) and observed under a microscope.
- the lubricant is analysed: colour (by spectrophotometry, 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).

Two commercial lubricants were tested: the oil PAG ND8 and the oil POE Ze-GLES RB68. These lubricants initially contain 510 and 50 ppm of water respectively. Trials were then carried out by adding water so as to reach 1000 ppm of water in each lubricant.

The fluid F used for these trials contains 99.85% by weight of HFO 1234yf, 213 ppm of 3,3,3-trifluoropropyne, 30 ppm of HFO 1225ye and 1257 ppm of compounds containing 2 or 3 carbon atoms, optionally comprising an olefinic bond.

	PAG ND8		POE Ze-GLES RB68	
Water content	510 ppm	1000 ppm	50 ppm	1000 ppm
Byproducts in the gas phase:				
➤ from the fluid F				
➤ from the lubricant	1000 ppm	900 ppm	300 ppm	180 ppm
	3%	2.3%	1000 ppm	400 ppm
Rate of corrosion	< 5 µm/year	< 5 µm/year	< 5 µm/year	< 5 µm/year
Observation of the length of steel	Shiny	Shiny	Shiny, slightly blue	Shiny, slightly blue
Analysis of the lubricant:				
➤ colour	9 Gardner	9.5 Gardner	110 Hazen	250 Hazen
➤ water content	1500 ppm	4200 ppm	250 ppm	1100 ppm
➤ acid number	4.5 mg KOH/g	5 mg KOH/g	0.5 mg KOH/g	0.2 mg KOH/g

It is noted that, in the presence of the same moisture content, the fluid F is more stable in the presence of the POE.

Szabadalmi igénypontok

1. Készítmény, amely legalább egy poliol-észter (POE) alapú kenőanyagot és egy hűtőanyagot F tartalmaz, amely legalább 99,8 tömeg% 2,3,3,3-tetrafluor-propént, 0,5 - 500 ppm 1,1,1,2,3-pentafluor-propént, 0,5 - 500 ppm 3,3,3-trifluor-propint és 1 - 1500 ppm 2-3 szénatomos, adott esetben olefin kötést tartalmazó, vegyületeket tartalmaz a HFO-1225ye és a 3,3,3-trifluor-propin kivételével.

2. Az 1. igénypont szerinti készítmény, **azzal jellemezve, hogy** a hűtőanyag F legalább 99,9 tömeg% 2,3,3,3-tetrafluor-propént, 0,5 - 250 ppm 1,1,1,2,3-pentafluor-propént, 0,5 - 250 ppm 3,3,3-trifluor-propint és 1 - 500 ppm 2-3 szénatomos, adott esetben olefin kötést tartalmazó, vegyületeket tartalmaz a HFO-1225ye és a 3,3,3-trifluor-propin kivételével.

3. Az 1. vagy 2. igénypont szerinti készítmény, **azzal jellemezve, hogy** a hűtőanyag F legalább 99,95 tömeg% 2,3,3,3-tetrafluor-propént, 0,5 - 250 ppm 1,1,1,2,3-pentafluor-propént, 0,5 - 100 ppm 3,3,3-trifluor-propint és 1 - 150 ppm 2-3 szénatomos, adott esetben olefin kötést tartalmazó, vegyületeket tartalmaz a HFO-1225ye és a 3,3,3-trifluor-propin kivételével.

4. Az 1-3. igénypontok bármelyike szerinti készítmény, **azzal jellemezve, hogy** a POE-eket neopentil vázat tartalmazó poliolokból, mint neopentil-glikol, trimetilol-propán, pentaeritritol és dipentaeritritol, állítjuk elő.

5. Az 1-4. igénypontok bármelyike szerinti készítmény, **azzal jellemezve, hogy** a POE-eket egyenes vagy elágazó láncú 2-15 szénatomos karbonsavakból állítjuk elő.

6. Az 1-5. igénypontok bármelyike szerinti készítmény, **azzal jellemezve, hogy** a POE-(k) a készítmény 10 tömeg% és 50 tömeg% közötti részét képezik.

7. Az 1-6. igénypontok bármelyike szerinti készítmény alkalmazása légkondicionálásban.

A meghatalmazott:

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