

656376

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Australia

Patents Act 1990

Patent Request: Standard Patent

We, the Applicant/Nominated Person specified below, request we be granted a patent for the invention disclosed in the accompanying standard complete specification.

[70,71] **Applicant/Nominated Person:**
Shell Internationale Research Maatschappij B.V., a Netherlands company, of
Carel van Bylandtlaan 30, 2596 HR The Hague, The Netherlands

[54] **Invention Title:**
Fluid Composition for Compression Refrigeration

[72] **Inventors:**
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Basic Convention Application Details

[31]	Application No	[33]	Country	[32]	Date of Application
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	Basic Applicant:		Shell Internationale Research Maatschappij B.V.		

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Shell Internationale Research Maatschappij B.V.



Registered Patent Attorney



IRN:

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NOTICE OF ENTITLEMENT

I, Albertus Wilhelmus Joannes ZEESTRATEN, of Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands, being authorised by the Applicant/Nominated Person in respect of Application No. 16359/92 state the following:-

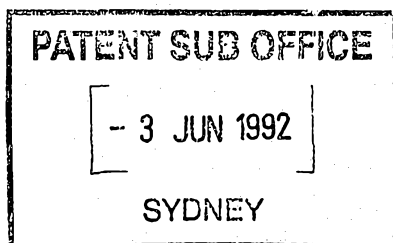
The Applicant/Nominated Person has entitlement from the actual inventor(s) as follows:-

The Applicant/Nominated Person is the assignee of the actual inventor(s).

The Applicant/Nominated Person is the applicant of the basic application(s) listed on the Patent Request.

The basic application(s) listed on the Patent Request is/are the application(s) first made in a Convention Country in respect of the invention.

DATED this _____ 16th day of April _____, 1992




.....
Albertus Wilhelmus Joannes ZEESTRATEN

A handwritten signature in dark ink, appearing to be 'AJ', is written over a horizontal dotted line. Below the line, the name 'Albertus Wilhelmus Joannes ZEESTRATEN' is printed.

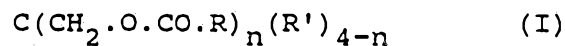


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- (71) Applicant(s)
SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
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- (56) Prior Art Documents
US 5008028
AU 638710 54480/90 C09K 5/04 C08K 5/02 C08L 67/04
- (57) Claim

1. A fluid composition for use in compression refrigeration comprising a mixture of
- (a) at least one fluorohydrocarbon and
 - (b) at least one carboxylic ester of a polyhydroxy compound, having the general formula



wherein n is 3 or 4, R' represents a methyl or ethyl group and each R independently represents a C₃₋₈ alkyl group containing 3 to 5 chain atoms.

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AUSTRALIA **656376**
PATENTS ACT 1990

COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

Name and Address
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Invention Title: Fluid Composition for Compression Refrigeration

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

FLUID COMPOSITION FOR COMPRESSION REFRIGERATION

This invention relates to fluid compositions for use in compression refrigeration, more particularly to such compositions containing fluorohydrocarbon refrigerant, to the preparation of such compositions and to their use as refrigeration fluid in compression refrigeration equipment.

Fluid compositions for use in compression refrigeration comprise mixtures of at least one refrigerant and at least one lubricant. Compression refrigeration equipment includes refrigerators and air-conditioners, including automobile, domestic and industrial air-conditioning systems. Problems of lubrication are particularly evident in automobile air-conditioning systems, because such systems are not separately lubricated, and a mixture of refrigerant and lubricant circulates through the entire system. It is therefore important that the refrigerant and the lubricant should be compatible (naturally soluble) over wide ranges of temperatures and concentrations.

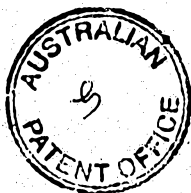
In the past, chlorofluorocarbons e.g. R-11 (CFC-11), R-12 (CFC-12) and R-113 (CFC-113) have generally been used as refrigerants.

JP-A-55-155093 discloses the use of chlorofluorocarbon refrigerants, specifically R-12

(HCFC-12) (dichlorodifluoromethane) and R-22 (chlorodifluoromethane), in combination with, as lubricant, neopentyl polyol esters containing 0.005 to 5% w of trimethyl phosphate. The neopentyl polyol is preferably trimethylolpropane or pentaerythritol, ~~esterified~~^{esterified} with straight-chain or branched saturated fatty acid esters, e.g. straight chain saturated fatty acids with 6 to 18 carbons such as caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, or stearic acid, and synthetic branched saturated fatty acids with 8 to 18 carbons such as isocaproic acid, 2-ethylhexoic acid, isononoic acid, isocapric acid, isolauric acid, isomyristic acid, isopalmitic acid or isostearic acid. 2-ethylhexoic acid is particularly preferred.

JP-A-61-171799 discloses the use of fluorocarbon refrigerants, the only named example of which is R-22 (HCFC-22) (chlorodifluoromethane), in combination with, as lubricant, an ester-type oil together with, e.g. 0.02 to 10% w of, a hydroxy aryl fatty acid. The ester-type oil is preferably an ester of a monohydric alcohol and a dicarboxylic acid, an ester of a polyhydric alcohol, e.g. a neopentyl polyol, and a monocarboxylic acid, or as ester of a polyhydric alcohol and a mixture of monocarboxylic and dicarboxylic acids.

Owing to the ozone-depletion potential of most common chlorofluorocarbons (CFC's), global controls on their manufacture and application have been agreed under the Montreal Protocol (September 1987). Hydrofluorocarbons (HFC's) have been identified as potential alternatives to CFC's. Examples of HFC's include R-23 (HFC-23) (trifluoromethane), R-134 (HFC-134) (1,1,2,2-tetrafluoroethane), R-134a



(HFC-134a) (1,1,1,2-tetrafluoroethane), R-143a
(HFC-143a) (1,1,1-trifluoroethane) and R-152a
(HFC-152a) (1,1-difluoroethane).

R-12 (CFC-12) (dichlorodifluoromethane) has been
5 widely used in automobile air-conditioning systems and
other compression-refrigeration equipment. R-134a
(HFC-134a) (1,1,1,2-tetrafluoroethane) has similar
vapour pressure to R-12 and can in principle be used
to replace R-12 without major redesign of existing
10 compression -refrigeration equipment.

The problem that arises in relation to
substitution of R-134a in place of R-12 is
compatibility with lubricants. R-12 is compatible
with mineral lubricating oils, whereas R-134a is not.

15 Polyalkylene glycols have been proposed as
lubricants, e.g. Research Disclosure 17483, October
1978, by Du Pont and US Patent No. 4,755,316.
However, of polyalkylene glycols it has been reported
(Financial Times Wednesday November 28 1990, p14) ("FT
20 article") that they "lubricated well but absorbed
water and after a while began to react with other
materials" in the compressors.

This same FT article states that "attention then
switched to synthetic oils called polyol esters.
25 Extensive testing of refrigeration equipment with
these ester lubricants over the last few months has
convinced the industry that they are the answer to its
prayers. A combination of R-134a coolant with ester
lubricant appears to work as well as R-12 plus mineral
30 oil in domestic fridges, car air conditioners and
small commercial refrigeration systems"

US Patent No. 4,851,144 proposes as lubricant
compositions miscible with hydrofluorocarbon and
hydrochlorofluorocarbon refrigerants, blends of
35 polyether polyols with esters selected from esters of

polyhydric alcohols with alkanolic acids and esters of
alkanedioic acids with alkanols. In comparative test
over temperature range -20°C to 85°C to determine
upper solution critical temperature (USCT) using
5 R-134a and various potential lubricants it was found
(Table 1, Column 4) that a pentaerythritol tetraester
of a mixture of alkanolic acids having 7-9 carbon
atoms, 25% in R-134a, had USCT 80°C and trimethylol
propane triheptonate, 16% w in R-134a, had USCT >83°C.

10 WO 90/12849 discloses liquid compositions useful
as refrigeration liquids in refrigerators and
air-conditioners, comprising a major amount of at
least one fluorine containing hydrocarbon containing
one or two carbon atoms, most preferably R-134a, and a
15 minor amount of at least one soluble organic lubricant
comprising at least one carboxylic ester of a
polyhydroxy compound containing at least 2 hydroxy
groups and characterised by the general formula



wherein R is a hydrocarbyl group, each R¹ is
independently hydrogen, a straight chain lower (i.e.
up to 7 carbon atoms) hydrocarbyl group, a branched
25 chain hydrocarbyl group, or a straight chain
hydrocarbyl group containing from 8 to about 22 carbon
atoms provided that at least one R¹ group is hydrogen,
a lower (i.e. up to 7 carbon atoms) straight chain
hydrocarbyl or a branched chain hydrocarbyl group, or
30 a carboxylic acid or carboxylic acid ester-containing
hydrocarbyl group, and n is at least 2.

Specific examples of polyhydroxy compounds listed
as useful in WO 90/12849 include ethylene glycol,
diethylene glycol, triethylene glycol, propylene
35 glycol, dipropylene glycol, glycerol, neopentyl

glycol, 1,2-, 1,3- and 1,4-butanediols,
pentaerythritol, dipentaerythritol,
tripentaerythritol, triglycerol, trimethylolpropane,
sorbitol, hexaglycerol, and
5 2,2,4-trimethyl-1,3-pentanediol.

Examples of carboxylic acids containing a
straight chain lower hydrocarbyl group include formic
acid, acetic acid, propionic acid, butyric acid,
pentanoic acid, hexanoic acid and heptanoic acid.

10 Examples of carboxylic acids wherein the hydrocarbyl
group is a branched chain hydrocarbyl group include
2-ethyl-n-butyric acid, 2-hexyldecanoic acid,
isostearic acid, 2-methylhexanoic acid,
15 3,5,5-trimethylhexanoic acid, 2-ethylhexanoic acid,
neoheptanoic acid, neodecanoic acid, and commercial
mixtures of branched chain carboxylic acids such as
the mixture identified as "Neo 1214" acid (trade mark)
from Exxon. Examples of higher molecular weight (8 to
20 about 22 carbon atoms) straight chain acids include
decanoic acid, dodecanoic acid, stearic acid, lauric
acid, and behenic acid.

Of the specific Examples in WO 90/12849, Example
6 describes reaction of trimethylolpropane with a
commercial C₈₋₁₀ straight chain methyl ester followed
25 by reaction with acetic anhydride. Example 9
describes (in the present tense) reaction of
pentaerythritol with neoheptanoic acid followed by
reaction with acetic anhydride to esterify remaining
hydroxyl groups.

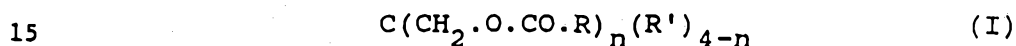
30 WO 90/12849 describes tests in which 0.5 g of
various candidate lubricants (ester) and 4.5g R-134a
(i.e. mixtures containing 10% w ester) are mixed and,
if the lubricant is soluble in the R-134a, temperature
is reduced until separation and/or precipitation
35 occurs. For Example 6 this temperature is -45°C. The

lowest value obtained is -50°C . No value is given for Example 9.

There has now surprisingly been found a defined class of polyol esters having significantly improved miscibility with R-134a, with respect to maximum and minimum miscibility temperatures, than any values hitherto reported.

According to the present invention there is provided a fluid composition for use in compression refrigeration comprising a mixture of

- (a) at least one fluorohydrocarbon and
- (b) at least one carboxylic ester of a polyhydroxy compound, having the general formula



wherein n is 3 or 4, R' represents a methyl or ethyl group and each R independently represents a C_{3-8} alkyl group containing 3 to 5 chain atoms.

The fluorohydrocarbon may be, for example trifluoromethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1-trifluoroethane or 1,1-difluoroethane, or a mixture of any two or more thereof but is preferably a tetrafluoroethane, more preferably 1,1,1,2-tetrafluoroethane (R-134a).

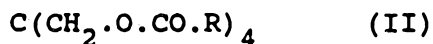
Fluid compositions of the invention may generally comprise, for example, 50 to 99% w of the at least one fluorohydrocarbon. Preferably the composition comprises a mixture containing 70 to 99% w, e.g. 80 to 98% w, of the at least one fluorohydrocarbon and 1 to 30% w, e.g. 2 to 20% w, of the at least one carboxylic ester.

Where n in formula I is 3, the esters are esters of trimethylolethane or, preferably,

trimethylolpropane. Most preferably in is 4, in which case the esters are esters of pentaerythritol.

Each R in formula I independently represents a C₃₋₈ alkyl group containing 3 to 5 chain atoms, By 3 to 5 chain atoms is meant that, starting with the carbon atom in R immediately adjacent the CH₂.O.CO. moiety, the longest linear chain of carbon atoms in the R moiety contains 3 to 5 carbon atoms. Thus, for example, a R moiety of formula -C(CH₃)₂CH₂CH₂CH₃ is a C₆ alkyl group containing 4 chain atoms, and a R moiety of formula -C(CH₃)(C₂H₅)₂ is a C₆ alkyl group containing 3 chain atoms. Preferably each R independently represents a C₄₋₆ alkyl group containing 3 to 4 chain atoms.

In accordance with a particularly preferred aspect of the invention there is provided a fluid composition for use in compression refrigeration comprising a mixture of at least one fluorohydrocarbon and at least one carboxylic ester of a polyhydroxy compound, wherein the at least one carboxylic ester of a polyhydroxy compound consists of at least one ester having the general formula



wherein ~~n is 3 or 4, and~~ each R independently represents a C₃₋₈ alkyl group containing 3 to 5 chain atoms, more preferably a C₄₋₆ alkyl group containing 3 or 4 chain atoms. It will be appreciated that formula II corresponds to formula I wherein n is 4.

Although each R moiety may be a C₃₋₅ n-alkyl group (straight-chain alkyl group), in such cases the esters of formula I and II tend to have viscosity at 40°C (DIN 51 562) less than 20 mm²/s.

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Preferably the ester of formula I or II is an ester having viscosity at 40°C (DIN 51 562) of at least 20 mm²/s wherein on average at least one R moiety is a branched alkyl group.

5 Fluid compositions in accordance with this invention may additionally include small quantities, e.g. 0.2 to 5%w, preferably 0.4 to 2.5%w, based on the weight of the at least one carboxylic ester, of each of one or more additives, such as thermal stabilisers
10 (e.g. glycidyl ethers, for example phenylglycidyl ether), antiwear agents (e.g. steel/steel antiwear agents, for example "SANCTICIZER 154" (trade mark) ex Monsanto, and/or steel/aluminium antiwear agents, for example "VANLUBE 672" (trade mark) ex Vanderbilt) and
15 metal passivators (e.g. copper passivators, for example "REOMET 39" (trade mark) ex Ciba Geigy).

The invention further comprises a process for the preparation of a fluid composition of the invention which comprises mixing at least one fluorohydrocarbon
20 with at least one carboxylic acid ester of formula I as defined above.

The invention also comprises the use of a fluid composition of the invention as refrigeration fluid in compression refrigeration equipment, e.g.
25 refrigerators and air-conditioners, including domestic and industrial air conditioning systems.

The carboxylic acid esters of formula I may readily be synthesised in known manner, e.g. by processes analogous to those described in WO 90/12849,
30 or by processes according to or analogous to that described hereinafter in Example 1.

The invention will be further understood from the following illustrative Examples.

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EXAMPLES 1 TO 12

Preparation of pentaerythritol tetrapentanoate (1)

5 To a mixture of pentaerythritol (227.9g, 2.0 mol) and pentanoic acid (887.2g, 8.6 mol) in a reactor fitted with a Dean and Stark trap was added, with stirring, under nitrogen, xylene (250ml) and methanesulphonic acid (40.8g, 0.4 mol). The resulting
10 mixture was stirred under nitrogen for 5 hours at 140°C, before being cooled to ambient temperature (20°C), washed with 1M aqueous sodium hydroxide solution (2 x 500ml), washed with 10% w/v aqueous sodium sulphate solution (6 x 500 ml), dried (Na₂SO₄)
15 filtered and evaporated under reduced pressure to yield pentaerythritol tetrapentanoate (1) (756g, 80%), characterised by viscosity at 40°C of 16.72 and at 100°C of 3.75 (DIN 51 562), viscosity index of 113 (DIN 150 2909) and saponification no. 484.7 (ASTM
20 D1962-67).

Following analogous procedures, there were prepared a number of additional pentaerythritol esters (Examples 2 to 12). Details of these esters are given in Table 1 below, together with their viscosities at
25 40°C and 100°C (DIN 51 562), viscosity indices (VI) (DIN ISO 2909), pour points (DIN ISO 3016) and saponification nos. (ASTM D 1962-67).

Miscibility of the various pentaerythritol esters with R134a refrigerant (1,1,1,2-tetrafluoromethane)
30 was determined using a cryostat, a thermostat and glass tubes prepared according to DIN 51 351. Mixtures of refrigerant and pentaerythritol ester (concentrations determined gravimetrically) containing respectively 2% w and 20% w pentaerythritol ester were
35 prepared in sealed glass tubes and the tubes were

completely immersed in the temperature-controlled bath of the thermostat or cryostat. The bath fluid was then heated up or cooled down at a rate of 2°C/minute, and the temperature of phase separation was noted.

5 Results are given in Table 1 following.

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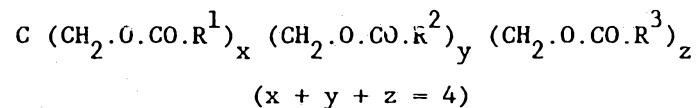
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TABLE I



Example	R ¹	x	R ²	y	R ³	z	Viscosity		V I	Pour Point °C	Sap. No.	Miscibility	
							mm ² /s 40°C	mm ² /s 100°C				min/2%	max/20%
1	(CH ₂) ₃ CH ₃	4	-	-	-	-	16.4	3.74	117	<-60	465	<-70/>100	<-70/>100
2	(CH ₂) ₂ CH ₃	4	-	-	-	-	16.0	3.47	87	-33	545	<-70/>100	<-70/>100
3	CH ₂ CH(CH ₃) ₂	4	-	-	-	-	42.1	5.58	51	-45	473	<-70/>100	<-70/>100
4	(CH ₂) ₃ CH ₃	3	C(CH ₃)(C ₂ H ₅) ₂	1	-	-	23.0	4.43	101	-60	440	<-70/>100	<-70/>100
5	(CH ₂) ₃ CH ₃	3	C(CH ₃) ₂ CH ₂ CH ₂ CH ₃	1	-	-	22.2	4.32	102	<-60	435	<-70/>100	<-70/>100
6	(CH ₂) ₃ CH ₃	2	C(CH ₃)(C ₂ H ₅) ₂	1	C(CH ₃) ₂ CH ₂ CH ₂ CH ₃	1	41.3	5.69	64	-48	398	<-70/>100	<-70/>100
7	(CH ₂) ₃ CH ₃	3	C(CH ₃)(C ₂ H ₅) ₂	0.5	C(CH ₃) ₂ CH ₂ CH ₂ CH ₃	0.5	25.5	4.67	99	-60	450	<-70/>100	<-70/>100
8	(CH ₂) ₃ CH ₃	3	C(CH ₃)(C ₂ H ₅) ₂	0.25	C(CH ₃) ₂ CH ₂ CH ₂ CH ₃	0.75	22.8	4.41	101	<-60	441	<-70/>100	<-70/>100
9	(CH ₂) ₃ CH ₃	2	CH(C ₂ H ₅)(CH ₂) ₃ CH ₃	2	-	-	28.9	4.94	91	-60	386	<-70/>100	-58/>100
10	(CH ₂) ₃ CH ₃	1.33	CH(C ₂ H ₅)(CH ₂) ₃ CH ₃	2.67	-	-	37.3	6.28	105	-57	347	-68/>100	-38/>100

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It will be seen that the ~~miscibility~~^{miscibility} data for the examples of the invention is significantly superior to that obtained for Comparative Examples A to D. This is particularly marked for Examples 1 to 8, in which all the groups R¹, R² and R³ are C₄₋₆ alkyl groups containing 3 or 4 chain atoms.

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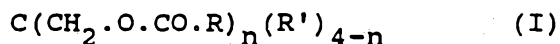


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CLAIMS

The claims defining the invention are as follows:

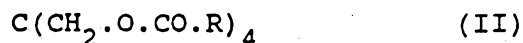
1. A fluid composition for use in compression refrigeration comprising a mixture of
- (a) at least one fluorohydrocarbon and
- (b) at least one carboxylic ester of a polyhydroxy compound, having the general formula



wherein n is 3 or 4, R' represents a methyl or ethyl group and each R independently represents a C₃₋₈ alkyl group containing 3 to 5 chain atoms.

2. A fluid composition according to Claim 1 wherein the fluorohydrocarbon is a tetrafluoroethane.
3. A fluid composition according to Claim 2 wherein the fluorohydrocarbon is 1,1,1,2-tetrafluoroethane.
4. A fluid composition according to any one of Claims 1 to 3 which comprises a mixture containing 70 to 99% w of the at least one fluorohydrocarbon and 1 to 30% w of the at least one carboxylic ester.
5. A fluid composition according to any one of Claims 1 to 4 wherein in formula I n is 4.

6. A fluid composition for use in compression refrigeration comprising a mixture of at least one fluorohydrocarbon and at least one carboxylic ester of a polyhydroxy compound, wherein the at least one carboxylic ester of a polyhydroxy compound consists of at least one ester having the general formula



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wherein ~~n is 3 or 4, and~~ each R independently represents a C₃₋₈ alkyl group containing 3 to 5 chain atoms.

7. A fluid composition according to any one of Claims 1 to 6 wherein in formula I or II each R independently represents a C₄₋₆ alkyl group containing 3 or 4 chain atoms.
8. A fluid composition according to any one of Claims 1 to 7 wherein the ester of formula I or II has viscosity at 40°C (DIN 51 562) of at least 20 mm²/s wherein on average at least one R moiety is a branched alkyl group.
9. A process for the preparation of a fluid composition according to any one of Claims 1 to 8 which comprises mixing at least one fluorohydrocarbon with at least one carboxylic ester of formula I as defined in Claim 1.
- ~~10. Use of a fluid composition according to any one of Claims 1 to 8 as refrigeration fluid in compression refrigeration equipment.~~
10. A fluid composition for use in compression refrigeration substantially as hereinbefore described with reference to any one of the Examples but excluding the comparative examples.
11. A process for the preparation of a fluid composition substantially as hereinbefore



-16-

described with reference to any one of the
Examples but excluding the comparative examples.

DATED this THIRTEENTH day of MAY 1992
Shell Internationale Research Maatschappij B.V.

Patent Attorneys for the Applicant
SPRUSON & FERGUSON

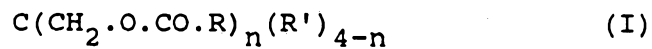
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ABSTRACT

FLUID COMPOSITION FOR COMPRESSION REFRIGERATION

This invention provides fluid compositions for use in compression refrigeration comprising mixtures of

- 5 (a) at least one fluorohydrocarbon and
(b) at least one carboxylic ester of a polyhydroxy compound, having the general formula



10 wherein n is 3 or 4, R' represents a methyl or ethyl group and each R independently represents a C₃₋₈ alkyl group containing 3 to 5 chain atoms.