Abstract:
Mixtures of select neopentyl polyol esters are found to be highly miscible with the refrigerant R-32 over a wide temperature range. Working fluids are provided comprising R-32 and a polyol ester lubricant composition having a kinematic viscosity at 40°C of from 32 to 120 cSt, said lubricant composition comprising C5,10 alkylcarboxy esters di-pentaerythritol wherein at least 40 mol %, typically more, of the alkylcarboxylate groups of the alkylcarboxy esters are pentanoyl groups.
WORKING FLUIDS COMPRISING DIFLUOROMETHANE
AND DI-PENTAERYTHRITOL ESTER

This application claims benefit of U.S. Provisional Application No. 61/599,004 filed February 15, 2012, and U.S. Application No. 13/766,884 filed on February 14, 2013, the disclosure of which is incorporated herein by reference.

Provided are working fluids, suitable for heat transfer devices including refrigeration and air conditioning systems, said working fluid comprising a hydrofluorocarbon refrigerant, i.e., difluoromethane, also called R-32, and a polyol ester lubricant composition having a kinematic viscosity at 40 °C of from 32 to 120 cSt comprising linear and branched C<sub>5-10</sub> alkylcarboxy esters of di-pentaerythritol, wherein 40 mol % or more, typically 60 mol % or more of the C<sub>5-10</sub> alkylcarboxy esters of di-pentaerythritol are linear or branched C<sub>5</sub> alkylcarboxy esters. In many embodiments, difluoromethane is the predominate or sole refrigerant in the working fluid.

Heat transfer devices such as refrigerators, freezers, heat pumps and air conditioning systems are well known. In simple terms such devices operate via a cycle wherein a refrigerant of a suitable boiling point evaporates at low pressure taking heat from its surroundings, the vapor passes to a condenser where it condenses back to a liquid and gives off heat to its new surroundings, and then the condensate is returned to the evaporator completing the cycle. In addition to the mechanical parts of a refrigeration device such as a compressor etc., especially suited materials are needed including the refrigerant, suitable heat transfer materials, sealants to prevent loss of refrigerant and lubricants to allow for functioning of the movable parts of the device.

For example, a sufficient amount of the lubricant in the compressor to provide lubrication and sealing is desirable. The lubricant provides protection against wear of moving parts such as bearings under load, removes heat from the compressor, aids in preserving seals to prevent loss of refrigerant, seals clearances to ensure efficient compression of gas from low to high pressure and can be used to reduce noise (dampening).
The lubricant needs to have good low temperature flow properties and be thermally stable.

It is also necessary for a refrigeration lubricant to be compatible with the refrigerant. For example, in dealing with the compressor, the lubricating fluid is thought of as a solution of refrigerant dissolved in the lubricant. In other parts of the refrigerating system such as the evaporator, the oil may be thought of as lubricant dissolved in the refrigerant. Generally, it is desirable to have a high degree of miscibility between the lubricant and the refrigerant over the operating conditions (temperatures and pressures) of the entire refrigeration system and partial miscibility may cause problems with heat transfer and may also interfere with the return of oils to the compressor.

For example, the evaporator is the coldest part of the system and is a likely place for phase separation to occur, but the working fluid containing the lubricant must also perform at the higher temperatures encountered elsewhere in the system.

Refrigerant and lubricant combinations are therefore classified as completely miscible, partially miscible, or immiscible depending on their degree of mutual solubility. Partially miscible mixtures of refrigerant and lubricants are mutually soluble at certain temperatures and lubricant-in-refrigerant concentrations, and separate into two or more liquid phases under other conditions.

Concerns about ozone depletion and global warming have lead to replacement of traditional chlorofluorocarbon refrigerants with new or alternate materials. One example of an alternative to chlorofluorocarbon refrigerants, difluoromethane, is a highly efficient refrigerant without the harmful ozone depletion properties of chlorofluorocarbons. There are however technical hurdles that must be overcome in order to make full use of this highly desirable refrigerant.

The refrigerant R-32, i.e., difluoromethane, is a hydrofluorocarbon (HFC) with an ozone depleting potential (ODP) of 0 and a global warming potential (GWP) of 650. R-32 however is moderately flammable, but more importantly, insufficiently miscible with lubricants having the properties required for use in today's heat transfer systems. To overcome these technical hurdles, R-32 is used in blends, e.g., R-140A is an azeotropic (50%/50%) w/w mixture of difluoromethane (R-32) with pentafluoroethane (R-125); R-407A is an azeotropic mixture of difluoromethane with
nd tetrafluoroethane (R-134a). While overcoming some of the hurdles faced with R-32 when used alone, these blends are not as desirable from a performance or ecological point of view.

As stated, R-32 has a GWP of 650, which is considerably lower than that of refrigerant R-410A, GWP = 2100. R-410A has been considered as the replacement for R-22 (chlorodifluoromethane) HCFC refrigerant which has an ODP of 0.055 and GWP of 1810. R-32 also has a 10% higher volumetric capacity than R-410A, leading to a higher coefficient of performance (COP).

There has been a recent resurgence in the development of refrigeration and AC equipment that can run exclusively on R-32. R-32 operates at a higher pressure than R-410A but improvements in equipment design with improved economics have made the use of R-32 a practical consideration. Improvements in engineering controls to minimize flammability hazards, R-410A is considered non-flammable (A1 rating) while R-32 is considered moderately flammable (A2 rating), as well as the growing acceptance of flammable hydrocarbon refrigerants (A3 rating) for some application have increased the possibility of R-32 becoming a mainstream next generation low GWP refrigerant for new equipment.

One remaining issue standing in the way of R-32 acceptance is that the synthetic lubricants currently used with R-410A are not entirely suitable for use with R-32. The most commonly used lubricants with R-410A are polyol esters and polyvinyl ethers. The current commercial lubricants do not have suitable miscibility/solubility with R-32 over the entire operating range of the refrigeration/AC systems, especially at the more desirable lubricant viscosities. R-32 based equipment also run at higher discharge temperatures which puts additional requirements for thermal stability on the lubricant.

Synthetic ester based lubricants are effective refrigeration lubricants in many systems. The physical properties of the ester mixtures, for example, viscosity and the like, are dependent on the types of esters and the ratio of the esters present.

US Pat 6,444,626 discloses formulated fluids well suited for use as a coolant or lubricant comprising mixtures of pentaerythritol, di-pentaerythritol, tri-pentaerythritol and tetra-pentaerythritol esters as well as mixtures with the aforementioned esters and trimethylol polyol esters. The mixtures of pentaerythritol and poly-
s of US Pat 6,444,626 are prepared from a starting polyol which is predominately mono-pentaerythritol in a two step process following the general teaching of US Pat 3,670,013 by partially esterification the polyol under acidic conditions using less carboxylic acid than needed for full esterification under conditions that also lead to oligomerization of the polyol/ester. The following step completes the esterification of the hydroxy groups.

US Pat 5,486,302 discloses higher viscosity POE lubricants obtained by esterifying a polyol using branched chain carboxylic acids; unfortunately, these branched chain esters exhibit insufficient lubricity for use in certain heat transfer devices.

US 6,774,093 discloses a refrigeration lubricant comprising esters similar to those of US Pat 6,444,626, but with a much higher viscosity making it suitable for use with fluorinated refrigerants such as R-410A.

Co-pending US Pat Appl. No. 12/684,315 discloses refrigeration lubricants comprising mixtures of carboxy esters of mono-, di-, tri-, tetra- and higher oligomers of pentaerythritol, wherein at least 25% are esters of tetra-pentaerythritol or higher oligomers, useful with CO₂ as refrigerant. Co-pending US Pat Appl. No. 13/080,739 also discloses high viscosity lubricants useful with CO₂, which contain predominately esters of straight chain C₄-6 linear carboxylic acids, for example, n-pentanoic acid esters, and which comprise 30 wt % or more of esters of pentaerythritol oligomers containing 4 or more pentaerythritol groups.

It has been surprisingly found that certain mixtures of polyol esters comprising di-pentaerythritol carboxylate esters, wherein at least 40%, for example, at least 50, 60 or 70% of the carboxylate groups are pentanoyl, can provide a lubricant base stock ideally suited for use with R-32 refrigerant. Said alkylcarboxylate esters, and their blends with other neopentyl polyol esters, not only have higher than expected viscosity and R-32 miscibility, but also have excellent lubricity, film building and load bearing properties.

SUMMARY OF THE INVENTION
The invention provides a working fluid suitable for heat transfer devices comprising the hydrofluorocarbon refrigerant difluoromethane, i.e., R-32, and a polyol ester lubricant composition with a kinematic viscosity at 40°C of 32 cSt or higher, said lubricant composition comprising C₅-10 alkylcarboxy esters of di-pentaerythritol
mol %, 60 mol% or more of the alkylcarboxylate groups are pentanoyl groups.

While other types of refrigerants may be present, hydrofluorocarbon, i.e., HFC, refrigerants make up the majority of all refrigerants presents, in many embodiments, the refrigerant is predominately or exclusively made up of HFC refrigerants. In many embodiments the working fluid comprises difluoromethane as the predominate refrigerant and in certain particular embodiments the refrigerant consists essentially of difluoromethane, i.e., any refrigerant other than difluoromethane is present only in amounts that do not materially affect the basic and novel characteristic(s) of the invention.

The di-pentaerythritol polyol esters of the invention are conveniently prepared by known methods and can be blended with other polyol esters, for example, carboxylic acid esters of pentaerythritol, neopentyl glycol or trimethylol propane. In one embodiment, the polyol ester lubricant composition of the invention comprises a mixture of C5-10 alkylcarboxy esters of pentaerythritol and C5-10 alkylcarboxy esters of di-pentaerythritol wherein at least 50 mo%, typically 60 mol% or more, of all alkylcarboxylate groups are pentanoyl.

DESCRIPTION OF THE INVENTION
A working fluid comprising:
   i) a refrigerant comprising difluoromethane (R-32), and
   ii) a polyol ester lubricant composition comprising C5-10 alkylcarboxy di-pentaerythritol esters wherein at least 40 molar % of the alkylcarboxylate groups of the alkylcarboxy di-pentaerythritol esters are pentanoyl groups,

   wherein the polyol ester lubricant composition has a kinematic viscosity at 40 °C of 32 cSt, often greater than 40 cSt, for example, a kinematic viscosity at 40 °C of 50 cSt or higher or a kinematic viscosity at 40 °C of 60 cSt or higher.

The polyol ester lubricant composition comprises straight and branched C5-10 alkylcarboxy esters in a ratio of from 9:1 to 1:9 straight to branched chained esters.

The present lubricants have a kinematic viscosity at 40 °C of at least 32 cSt, 40 cSt, 46 cSt, 60 cSt or higher, and can be as high as 90, cSt, 100 cSt, 110, cSt, 120 cSt or 150 cSt. In most cases the viscosity at 40 °C will be from 32 to 120 cSt, e.g., from 32 to 100 cSt, e.g., 40 to 100 cSt, or from 46 to 100 cSt. Generally, the lubricant of the
viscosity grade of from 32 to 100, 48 to 100, and will function well in systems requiring, for example, ISO viscosity grades of 48, 68, 100, or some value in between.

The polyol ester lubricant composition can consist of a mixture of di-pentaerythritol esters, but in many embodiments the lubricant comprises a mixture of di-pentaerythritol esters with other neopentyl polyol esters, e.g., esters of neopentyl glycol, trimethylol propane, pentaerythritol, tri-pentaerythritol, and/or oligomers comprising 4 or more pentaerythritol monomers, having the same or lower viscosities, to yield the polyol ester lubricant composition with a kinematic viscosity at 40 °C of 32 to 100 cSt.

The di-pentaerythritol esters of the invention are mixtures of compounds of formula I:

\[
\begin{align*}
\text{R} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{R}
\end{align*}
\]

wherein each R is independently a linear or branched alkyl carbonyl of from 5 to 10 carbon atoms, wherein 60 mol%, often 70 mol%, 75 mol % or more of the alkyl carbonyls are C₅ alkylcarbonyls. The ratio of linear to branched alkyl carbonyl is from 9:1 to 1:9, often from 6:1 to 1:6, or 5:1 to 1:5.

At least 30%, for example 50%, 60%, or 75% by weight of all esters in the polyol ester lubricant composition are compounds of formula I, in one embodiment, 90% or more are compounds of formula I and in one particular embodiment, essentially all of the polyolesters in the lubricant composition are compounds of formula I.

In some embodiments, the di-pentaerythritol esters are blended with linear or branched C₅₋₁₀ alkylcarboxy esters of neopentyl glycol, trimethylol propane, pentaerythritol and pentaerythritol oligomers. In these blends, 50 mol% or more of
esters present are C₅ alkylcarboxy esters, and 60 mol%, 70 mol%, 75 mol % or more of all di-pentaerythritol esters are C₅ alkylcarboxy esters.

In one embodiment the polyol ester lubricant composition comprises a mixture of compounds of formula I and pentaerythhtol esters, i.e., compounds of formula II:

\[
\text{II,}
\]

wherein each R is independently a linear or branched alkyl carbonyl of from 5 to 10 carbon atoms. In such embodiments, the polyol ester lubricant composition can comprise from 30 to 70 wt% of di-pentaerythritol esters of formula I and 30 to 70 wt% of pentaerythhtol esters of formula II, wherein 50% or more of all C₅₋₁₀ alkylcarboxy esters are C₅ alkylcarboxy esters.

In other embodiments the polyol ester lubricant composition comprises a mixture of compounds of formula I and C₅₋₁₀ alkylcarboxylate esters of neopentyl glycol and/or trimethylol propane, or compounds of formula I and compounds of formula II with C₅₋₁₀ alkylcarboxylate esters of neopentyl glycol and/or trimethylol propane.

Although some commonly used polyol ester and polyvinyl ether lubricants are miscible with refrigerant R-32, or a refrigerant mixture which is predominately or essentially R-32, these lubricants have low viscosities, e.g., a kinematic viscosity at 40 °C of 32 cSt and are not as miscible at the wide temperature range as with lubricants of the present invention. Higher viscosity lubricants are preferred for many heat transfer systems, i.e., refrigeration, air conditioning etc., and in some cases required. Lubricants of the present invention have both the required range of R-32 miscibility and are available at the higher viscosities.

In the present application, "a" compound or "an" element means, unless otherwise specified, "one or more" compound or "element". "Majority" means 50% or more, typically more than 50%, and "predominately" means a significant majority, for example 70% or higher, in the case of the refrigerant, "predominately R-32" means
weight of the refrigerant is other than R-32, often less than 10% or 5%.

While each R in formulae I and II, as well as each alkyl carbonyl present on any other neopentyl alcohol ester of the invention, is independently an alkyl carbonyl of 5 to 10 carbon atoms, which can be linear or branched, at least 45% or more of all C\textsubscript{5-10} alkylcarboxlate esters, typically 50%, 60%, 70%, 75%, and at least 85% by weight, and often more, of all alkyl carbonyl groups in the lubricant composition are pentanoyl.

In many embodiments, the majority of all alkyl carbonyl groups are derived from a mixture of about 66% n-pentanoic acid and about 34% 2-methyl butanoic acid. For example, 60%, 70%, 80%, or 90% of all alkyl carbonyl groups are derived from a mixture of about 66% n-pentanoic acid and about 34% 2-methyl butanoic acid.

Typically, the ratio of linear to branched C\textsubscript{5-10} alkyl carbonyls present, is from 9:1 to 1:9, often from 6:1 to 1:6 or from 5:1 to 1:5, for example, from 3:1 to 1:3. Often, the ratio of linear to branched C\textsubscript{5} alkyl carbonyls is from 5:1 to 1:3, often from 3:1 to 1:1.

The mixture of the polyol esters of the invention are prepared by well known methods.

Small amounts of other compounds similar to those of formula I or II described above may be present in the working fluid. For example, incomplete esterification may lead to the presence of compounds wherein one or more R groups are hydrogen and higher oligomers showing greater degrees of branching are also possible depending on the synthetic method used.

It has been observed that the above lubricants have much improved miscibility with R-32 than similar lubricants containing larger amounts of linear or non-pentanoyl alkyl carbonyl groups.

The working fluid of the invention comprises the above lubricant and a refrigerant comprising R-32. The refrigerant may be a mixture of more than one HFC compound or contain non HFC compounds, but in generally the refrigerant is predominately R-32. For example, other refrigerants which may be present in the working fluid include CO\textsubscript{2}, ammonia and the like, but at least 85% by weight, and often more, of the
ypically at least 90% or 95%, and often more, of the refrigerant is R-32.

The mixing ratio of the polyol ester lubricant to the refrigerant is not particularly restricted, but the lubricant may be present in a ratio of 1 to 500 parts by weight, more preferably 2 to 400 parts by weight per 100 parts by weight of the refrigerant. In one embodiment the working fluid comprises 5 to 20 weight percent of the ester lubricant based on the weight of lubricant and refrigerant.

Examples of specific embodiments of the invention include:

A working fluid for a heat transfer device comprising:

i) a refrigerant comprising difluoromethane (R-32) and

ii) a polyol ester lubricant composition having a kinematic viscosity at 40 °C of from 32 to 120 cSt comprising linear and branched C_{5-10} alkylcarboxy esters of dipentaerythritol in a ratio of from 9:1 to 1:9, often from 6:1 to 1:6 or from 5:1 to 1:5, of linear to branched C_{5-10} alkylcarboxy esters, wherein 60 mol % or more for example 70 mol % or more, and often 75 mol % or more of the C_{5-10} alkylcarboxy esters of dipentaerythritol are linear or branched C_{5} alkylcarboxy esters; or

the working fluid described above wherein the a polyol ester lubricant composition has a kinematic viscosity at 40 °C of from 32 to 100 cSt, or 46 to 100 cSt.

A working fluid for a heat transfer device comprising:

i) a refrigerant comprising difluoromethane (R-32) and

ii) a polyol ester lubricant composition having a kinematic viscosity at 40 °C of from 32 to 120 cSt comprising the linear and branched C_{5-10} alkylcarboxy esters of dipentaerythritol described above and further comprising C_{5-10} alkylcarboxy esters of neopentyl glycol, trimethylol propane, pentaerythritol, tri-pentaerythritol, and/or oligomers comprising 4 or more pentaerythritol monomers, wherein 50 mol % or more of all the C_{5-10} alkylcarboxy esters are linear or branched C_{5} alkylcarboxy esters and wherein all the combination of all C_{5-10} alkylcarboxy esters present are in a ratio of from 9:1 to 1:9, from 6:1 to 1:6, or from 5:1 to 1:5 of linear to branched C_{5-10} alkylcarboxy esters;

the working fluid above wherein the polyol ester lubricant composition comprises
C₅₋₁₀ alkylcarboxy esters of di-pentaerythritol, and from 10 to 70 wt% C₅₋₁₀ alkylcarboxy esters of neopentyl glycol, trimethylol propane and/or pentaerythritol, wherein the wt % is based on the total weight of the polyol ester lubricant composition;

the working fluid above wherein the polyol ester lubricant composition comprises from 50 to 90 wt % C₅₋₁₀ alkylcarboxy esters of di-pentaerythritol, and from 10 to 50 wt% C₅₋₁₀ alkylcarboxy esters of neopentyl glycol, trimethylol propane and/or pentaerythritol; or

the working fluid above wherein the polyol ester lubricant composition comprises from 30 to 70 wt % C₅₋₁₀ alkylcarboxy esters of di-pentaerythritol, and from 30 to 70 wt% C₅₋₁₀ alkylcarboxy esters of pentaerythritol.

Any of the working fluids above wherein the refrigerant comprises R-32 and less than 15% by weight, for example, less than 10% by weight of the refrigerant, is other than R-32 and is selected from other hydrofluorocarbon refrigerants, C0₂, ammonia and hydrocarbon refrigerants, or wherein the refrigerant consists essentially of R-32.

The polyol esters ester can also be blended with other lubricants, such as polyalphaolefins, polyalkylene glycols, alkylated aromatics, polyvinyl ethers, mineral oils, other ester based lubricants including esters of pentaerythritol ologomers, vegetable oils etc., to form the lubricant composition. However, the mixture of polyol esters defined above is the majority, predominate or sole component of the lubricant composition used to prepare the working fluid and care must be used when adding other lubricant base stocks so that the desirable properties of the polyol ester composition relative to its use with the refrigerant is not diminished.

Thus, the working fluid of the invention may further comprise in addition to components i) and ii), one or more of a mineral oil, poly-a-olefin, alkylbenzenes, carboxylic acid ester other than the neopentyl polyol ester of component ii), polyether, polyvinyl ether, perfluropolyether, phosphoric acid ester or mixture thereof, although in small amounts, typically less than 10 wt%, less than 5 wt% and generally less than 2 wt%.
f the invention can comprise other components common to the
art, including additives, other lubricants etc. Common additives which may also be
present in the working fluid include antioxidants, extreme-pressure additives,
antiwear additives, friction reducing additives, defoaming agents, profoaming agents,
metal deactivators, acid scavengers and the like.

Examples of the antioxidants that can be used include phenolic antioxidants such
as 2,6-di-t-butyl-4-methylphenol and 4,4′-methylenebis(2,6-di-t-butylphenol); amine
antioxidants such as p,p-dioctylphenylamine, monooclyldiphenylamine,
phenothiazine, 3,7-dioctylphenothiazine, phenyl-1-naphthylamine, phenyl-2-
naphthylamine, alkylphenyl-1-naphthylamine, and alkylphenyl-2-naphthylamine;
sulfur-containing antioxidants such as alkyl disulfide, thiodipropionic acid esters and
benzothiazole; and zinc dialkyl dithiophosphate and zinc diaryl dithiophosphate.

Examples of the extreme-pressure additives, antiwear additives, friction reducing
additives that can be used include zinc compounds such as zinc dialkyl
dithiophosphate and zinc diaryl dithiophosphate; sulfur compounds such as
thiodipropionic acid esters, dialkyl sulfide, dibenzyl sulfide, dialkyl polysulfide,
alkylmercaptan, dibenzocthiophene and 2,2′-dithiobis(benzothiazole); sulfur/nitrogen
ashless antiwear additives such as dialkyldimercaptothiadiazoles and
methylenebis(N,N-dialkyldithiocarbamates); phosphorus compounds such as triaryl
phosphates such as tricresyl phosphate and triaryl phosphates; dialkyl or diaryl
phosphates; trialkyl or triaryl phosphites; amine salts of alkyl and dialkylphosphoric
acid esters such as the dodecylamine salt of dimethylphosphoric acid ester; dialkyl
or diaryl phosphites; monoalkyl or monoaryl phosphites; fluorine compounds such
as perfluoroalkyl polyethers, trifluorochooroethylene polymers and graphite fluoride;
silicon compounds such as a fatty acid-modified silicone; molybdenum disulfide,
graphite, and the like. Examples of organic friction modifiers include long chain fatty
amines and glycerol esters.

Examples of the defoaming and profoaming agents that can be used include
silicone oils such as dimethylpolysiloxane and organosilicates such as diethyl
silicate. Examples of the metal deactivators that can be used include benzotriazole,
tolyltriazole, alizarin, quinizarin and mercaptobenzothiazole. Furthermore, epoxy
compounds such as phenyl glycidyl ethers, alkyl glycidyl ethers, alkyl glycidyl
esters, epoxystearic acid esters and epoxidized vegetable oil, organotin compounds
and boron compounds may be added as acid scavengers or stabilizers.
Examples of moisture scavengers include trialkylorthoformates such as trimethylorthoformate and triethylorthoformate, ketals such as 1,3-dioxacyclopentane, and amino ketals such as 2,2-dialkyloxazolidines.

The working fluids comprising the present polyol esters and a refrigerant can be used in a wide variety of refrigeration and heat energy transfer applications. Non-limiting examples include all ranges of air conditioning equipment from small window air conditioners, centralized home air conditioning units to light industrial air conditioners and large industrial units for factories, office buildings, apartment buildings and warehouses. Refrigeration applications include small home appliances such as home refrigerators, freezers, water coolers, vending machines and icemakers to large scale refrigerated warehouses and ice skating rinks. Also included in industrial applications would be cascade grocery store refrigeration and freezer systems. Heat energy transfer applications include heat pumps for household heating and hot water heaters. Transportation related applications include automotive and truck air conditioning, refrigerated semi-trailers as well as refrigerated marine and rail shipping containers.

Types of compressors useful for the above applications can be classified into two broad categories; positive displacement and dynamic compressors. Positive displacement compressors increase refrigerant vapor pressure by reducing the volume of the compression chamber through work applied to the compressor’s mechanism. Positive displacement compressors include many styles of compressors currently in use, such as reciprocating, rotary (rolling piston, rotary vane, single screw, twin screw), and orbital (scroll or trochoidal). Dynamic compressors increase refrigerant vapor pressure by continuous transfer of kinetic energy from the rotating member to the vapor, followed by conversion of this energy into a pressure rise. Centrifugal compressors function based on these principles.

EXAMPLES
Working fluids comprising difluoromethane, i.e., R-32, and lubricants were prepared and the R-32/lubricant miscibility was determined at various temperatures wt %.

Examples 1-7 were prepared using di-pentaerythritol ester mixtures shown in Table 1.

Comparative Examples A-G were prepared using the Lubricants shown in Table 2.
nples, i-C5 is an ~ 66/34 mixture of pentanoic acid / 2-methylbutanoic acid, i-C9 is 3,5,5-trimethylhexanoic acid, PE is pentaerythritol, DiPE is dipentaerythritol, and PVE is poly vinyl ether.

Table 1

<table>
<thead>
<tr>
<th>Ex</th>
<th>Polyol</th>
<th>KV</th>
<th>VI</th>
<th>Mol % Carboxylic Acid</th>
<th>% C5</th>
<th>% of Acids</th>
<th>Branched</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>40°C</td>
<td>100°C</td>
<td>nC5</td>
<td>iC5</td>
<td>nC7</td>
<td>iC9</td>
</tr>
<tr>
<td>1</td>
<td>DiPE</td>
<td>63.2</td>
<td>9.3</td>
<td>127</td>
<td>0</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>DiPE</td>
<td>74.0</td>
<td>10.0</td>
<td>117</td>
<td>0</td>
<td>89</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>DiPE</td>
<td>86.7</td>
<td>11.1</td>
<td>115</td>
<td>0</td>
<td>85</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>DiPE</td>
<td>61.1</td>
<td>9.3</td>
<td>133</td>
<td>84</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>DiPE</td>
<td>94.6</td>
<td>11.7</td>
<td>114</td>
<td>0</td>
<td>75</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>DiPE</td>
<td>125.3</td>
<td>13.8</td>
<td>107</td>
<td>0</td>
<td>65</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>DiPE</td>
<td>166.0</td>
<td>16.1</td>
<td>101</td>
<td>0</td>
<td>50</td>
<td>0</td>
</tr>
</tbody>
</table>

As i-C5 is an ~ 2:1 mixture of pentanoic acid / 2-methylbutanoic acid, in Example 1-3 and 5-7, 67% of C5 alkyl carbonyl groups are derived from n-pentanoic acid and 33% are derived from 2-methylbutanoic acid.

Table 2

<table>
<thead>
<tr>
<th>Ex</th>
<th>Polyol</th>
<th>KV</th>
<th>Mol % Carboxylic Acid</th>
<th>% C5</th>
<th>% of Acids</th>
<th>Branched</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>40°C</td>
<td>nC5</td>
<td>iC5</td>
<td>nC7</td>
<td>iC9</td>
</tr>
<tr>
<td>A</td>
<td>PVE</td>
<td>68.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>PE</td>
<td>64.9</td>
<td>0</td>
<td>27</td>
<td>5</td>
<td>68</td>
</tr>
<tr>
<td>C</td>
<td>PE</td>
<td>46.2</td>
<td>0</td>
<td>39</td>
<td>10</td>
<td>51</td>
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<td>D</td>
<td>DiPE+PE</td>
<td>46.0</td>
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Table 3 lists the temperatures above which lubricant/ R-32 miscibility is observed for the above working fluids at various lubricant wt%. Two phases are apparent at the listed lubricant wt% when the temperature drops below that shown.
Table 3

<table>
<thead>
<tr>
<th>EX</th>
<th>ISO %</th>
<th>C5%</th>
<th>Branched %</th>
<th>Miscible Above (deg C)</th>
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</thead>
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<tr>
<td></td>
<td>Grade</td>
<td>Acid</td>
<td>Acid Content</td>
<td>5%</td>
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<tr>
<td>1</td>
<td>68</td>
<td>95%</td>
<td>37%</td>
<td>-53</td>
</tr>
<tr>
<td>2</td>
<td>68</td>
<td>89%</td>
<td>40%</td>
<td>-49</td>
</tr>
<tr>
<td>3</td>
<td>85</td>
<td>85%</td>
<td>44%</td>
<td>-38</td>
</tr>
<tr>
<td>4</td>
<td>68</td>
<td>84%</td>
<td>16%</td>
<td>-39</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>75%</td>
<td>51%</td>
<td>-32</td>
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<tr>
<td>6</td>
<td>65%</td>
<td>0.57%</td>
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<td>-62</td>
</tr>
<tr>
<td>7</td>
<td>50%</td>
<td>67%</td>
<td></td>
<td>-63</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ISO %</th>
<th>C5</th>
<th>Branched %</th>
<th>Miscible Above (deg C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade</td>
<td>Acid</td>
<td>Acid Content</td>
<td>5%</td>
</tr>
<tr>
<td>A</td>
<td>68</td>
<td>—</td>
<td>-10</td>
</tr>
<tr>
<td>B</td>
<td>68</td>
<td>27%</td>
<td>-20</td>
</tr>
<tr>
<td>C</td>
<td>46</td>
<td>39%</td>
<td>-24</td>
</tr>
<tr>
<td>D</td>
<td>46</td>
<td>53%</td>
<td>-38</td>
</tr>
<tr>
<td>E</td>
<td>32</td>
<td>32%</td>
<td>-16</td>
</tr>
<tr>
<td>F</td>
<td>32</td>
<td>43%</td>
<td>-20</td>
</tr>
<tr>
<td>G</td>
<td>32</td>
<td>—</td>
<td>-17</td>
</tr>
</tbody>
</table>

N.M. stands for not miscible.

A basic requirement for many refrigeration lubricants is that it form a single phase with the refrigerant at all concentrations above 0 °C. From the data above, this is achieved with each of the lubricants of di-pentaerythritol Examples 1-5, but not those of Examples 6, 7 and Comparative A-H.

In Examples 8-16, the highly miscible lubricants from Examples 1, 2 and 5 were blended with non-di-pentaerythritol ester lubricants and the R-32/lubricant miscibility was determined at various temperatures and wt%. Table 4 lists the acids from which the carboxylates are derived, some rounding errors are seen. The ratios shown are wt ratios. Table 5 lists the miscibility results.
1:2 mixture of the lubricant from Ex 2 with the lubricant of Comparative Ex B.

Examples 9-11 use 1:2, 1:1, and 1:2 mixtures of the lubricant from Example 1 with the lubricant of Comparative example B.

Example 12 uses a 3:2 mixture of the lubricant of Ex 1 with a pentaerythritol ester derived from a 72:28 mixture of n-pentanoic acid : 3,5,5-trimethylhexanoic acid.

Examples 13 and 14 use 9:1 and 4:1 mixtures of the lubricant from Ex 1 with n-heptanoyl esters of neo-pentyl glycol.

Example 15 uses a 3:1 mixture of the lubricant from Ex 1 with esters prepared from technical grade pentaerythritol comprising 80-95% pentaerythritol and 15-20% di-pentaerythritol and a 43:41:16 mixture of n-pentanoic, n-heptanoic and : 3,5,5- trimethylhexanoic acid.

Example 16 uses a 3:2 mixture of the lubricant from Ex 1 with the lubricant of Comparative Ex B.

Table 4

<table>
<thead>
<tr>
<th>EX</th>
<th>DiPE</th>
<th>Non- DiPE Ex</th>
<th>Ratio</th>
<th>ISO</th>
<th>Mol % Carboxylic Acid</th>
<th>%</th>
<th>%Acid</th>
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</thead>
<tbody>
<tr>
<td>8</td>
<td>2</td>
<td>B</td>
<td>1:2</td>
<td>68</td>
<td>0</td>
<td>51</td>
<td>63%</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>B</td>
<td>1:2</td>
<td>68</td>
<td>0</td>
<td>51</td>
<td>63%</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>B</td>
<td>1:1</td>
<td>68</td>
<td>0</td>
<td>62</td>
<td>57%</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>B</td>
<td>1:2</td>
<td>68</td>
<td>0</td>
<td>73</td>
<td>73%</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>G</td>
<td>3:2</td>
<td>32</td>
<td>0</td>
<td>46</td>
<td>34%</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>NPG</td>
<td>9:1</td>
<td>46</td>
<td>0</td>
<td>87</td>
<td>34%</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>NPG</td>
<td>4:1</td>
<td>32</td>
<td>0</td>
<td>78</td>
<td>31%</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>t-PE</td>
<td>3:1</td>
<td>46</td>
<td>0</td>
<td>73</td>
<td>29%</td>
</tr>
<tr>
<td>16</td>
<td>5</td>
<td>B</td>
<td>3:2</td>
<td>80</td>
<td>0</td>
<td>85</td>
<td>29%</td>
</tr>
</tbody>
</table>

A basic requirement for many refrigeration lubricants is that it must form a single phase with the refrigerant at all concentrations above 0 °C. From the data in Table 5 below, this is achieved with each of the blends of Examples 8-16.
<table>
<thead>
<tr>
<th>EX</th>
<th>DiPE</th>
<th>COMP</th>
<th>Ratio</th>
<th>ISO</th>
<th>Miscible Above (deg C)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>EX</td>
<td>EX</td>
<td>D:C</td>
<td>Grade</td>
<td>5 %</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>B</td>
<td>1:2</td>
<td>68</td>
<td>-30</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>B</td>
<td>1:2</td>
<td>68</td>
<td>-60</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>B</td>
<td>1:1</td>
<td>68</td>
<td>-60</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>B</td>
<td>1:2</td>
<td>68</td>
<td>-40</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>G</td>
<td>3:2</td>
<td>46</td>
<td>-50</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>NPG</td>
<td>9:1</td>
<td>46</td>
<td>-49</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>NPG</td>
<td>4:1</td>
<td>32</td>
<td>-45</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>t-PE</td>
<td>3:1</td>
<td>46</td>
<td>-45</td>
</tr>
<tr>
<td>16</td>
<td>5</td>
<td>B</td>
<td>3:2</td>
<td>80</td>
<td>-24</td>
</tr>
</tbody>
</table>
1. A working fluid for a heat transfer device comprising:
   i) a refrigerant comprising difluoromethane (R-32) and
   ii) a polyol ester lubricant composition having a kinematic viscosity at 40 °C of from 32 to 120 cSt comprising linear and branched C_{5-10} alkylcarboxy esters of di-pentaerythritol in a ratio of from 9:1 to 1:9 of linear to branched C_{5-10} alkylcarboxy esters, wherein 60 mol % or more of the C_{5-10} alkylcarboxy esters of di-pentaerythritol are linear or branched C_{5} alkylcarboxy esters.

2. The working fluid according to claim 1 wherein 70 mol % or more of the C_{5-10} alkylcarboxy esters of di-pentaerythritol are linear or branched C_{5} alkylcarboxy esters.

3. The working fluid according to claim 1 wherein 75 mol % or more of the C_{5-10} alkylcarboxy esters of di-pentaerythritol are linear or branched C_{5} alkylcarboxy esters.

4. The working fluid according to any one of claims 1, 2 or 3 wherein the ratio of linear to branched C_{5-10} alkylcarboxy esters is from 6:1 to 1:6.

5. The working fluid according to any one of claims 1, 2 or 3 wherein the ratio of linear to branched C_{5-10} alkylcarboxy esters is from 5:1 to 1:5.

6. The working fluid according to claim 1 wherein the a polyol ester lubricant composition has a kinematic viscosity at 40 °C of from 32 to 100 cSt.

7. The working fluid according to claim 1 wherein the a polyol ester lubricant composition has a kinematic viscosity at 40 °C of from 46 to 100 cSt.

8. The working fluid according to claim 1 wherein the polyol ester lubricant composition, further comprises linear or branched C_{5-10} alkylcarboxy esters of neopentyl glycol, trimethylol propane, pentaerythritol, tri-pentaerythritol, and/or oligomers comprising 4 or more pentaerythritol monomers, wherein 50 mol % or more of all the C_{5-10} alkylcarboxy esters are linear or branched C_{5} alkylcarboxy esters, and wherein all C_{5-10} alkylcarboxy esters present are in a ratio of from 9:1 to 1:9 of linear to branched C_{5-10} alkylcarboxy esters.
according to claim 8 wherein the polyol ester lubricant composition comprises from 30 to 90 wt % C₅₋₁₀ alkylcarboxy esters of di-
pentaerythritol, and from 10 to 70 wt% C₅₋₁₀ alkylcarboxy esters of neopentyl glycol, trimethylol propane and/or pentaerythritol, wherein the wt % is based on the total weight of the polyol ester lubricant composition.

10. The working fluid according to claim 9 wherein the polyol ester lubricant composition comprises from 50 to 90 wt % C₅₋₁₀ alkylcarboxy esters of di-
pentaerythritol, and from 10 to 50 wt% C₅₋₁₀ alkylcarboxy esters of neopentyl glycol, trimethylol propane and/or pentaerythritol.

11. The working fluid according to claim 8 wherein the polyol ester lubricant composition comprises from 30 to 70 wt % C₅₋₁₀ alkylcarboxy esters of di-
pentaerythritol, and from 30 to 70 wt% C₅₋₁₀ alkylcarboxy esters of pentaerythritol.

12. The working fluid according to any one of claims 8 through 11 wherein the a ratio of linear to branched C₅₋₁₀ alkylcarboxy esters is from 6:1 to 1:6.

13. The working fluid according to any one of claims 8 through 11 wherein the a ratio of linear to branched C₅₋₁₀ alkylcarboxy esters is from 5:1 to 1:5.

14. The working fluid according to any one of claims 1, 2, 3, or 6 through 11 wherein the refrigerant comprises R-32 and less than 15% by weight of the refrigerant is other than R-32 and is selected from other hydrofluorocarbon refrigerants, CO₂, ammonia and hydrocarbon refrigerants.

15. The working fluid according to any one of claims 1, 2, 3, or 6 through 11 wherein the refrigerant comprises R-32 and less than 10% by weight of the refrigerant is other than R-32.

16. The working fluid according to any one of claims 1, 2, 3, or 6 through 11 wherein the hydrofluorocarbon refrigerant consists essentially of R-32.

17. The working fluid according to any one of claims 1, 2, 3, or 6 through 11 further comprising one or more antioxidant, extreme-pressure additive, antiwear additive, friction reducing additive, defoaming agent, profoaming agent, metal deactivator, acid scavenger or mixture thereof.
# INTERNATIONAL SEARCH REPORT

**PCT/US2013/026302**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C10M171/00
ADD. C10N30/00 C10N40/30

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

CIOM

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

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

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>US 2011/240910 AI (CARR DALE [US] ET AL) 6 October 2011 (2011-10-06) paragraphs [0058], [0060]; claim 9; example 7; table 5</td>
<td>I-9, II-13, 16, 17</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

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*O* document referring to an oral disclosure, use, exhibition or other means.

*P* document published prior to the international filing date but later than the priority date claimed.

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**Y** document published after the international filing date or priority date and considered to be of particular relevance; the claimed invention cannot be considered to be an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

**A** document member of the same patent family.

**Date of the actual completion of the international search**

18 April 2013

**Date of mailing of the international search report**

06/05/2013

Name and mailing address of the ISA:

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer:

Bertrand, Samuel

Form PCT/ISA/210 (second sheet) (April 2005)
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