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(71) Applicant *(for all designated States except US)*: **ARKEMA INC.** [US/US]; 2000 Market Street, Philadelphia, Pennsylvania 19103 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **VAN HORN, Brett L.** [US/US]; 562 B Street, King of Prussia, Pennsylvania 19406 (US). **BONNET, Philippe** [FR/FR]; 36 rue Camille Roy, F-69007 Lyon (FR).

(74) Agents: **BOYD, Steven D.** et al.; Arkema Inc., 2000 Market Street, Philadelphia, Pennsylvania 19103 (US).

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(54) Title: METHOD OF SELECTING REFRIGERANT-LUBRICANT COMBINATIONS

(57) Abstract: The present invention provides methods for selecting refrigerant and lubricant combinations for use in heat transfer cycle systems and provides methods for operating said heat transfer systems. More particularly, the invention provides methods to select lubricant and refrigerant combinations for a heat transfer cycle system wherein at the lower temperatures of the heat transfer cycle the refrigerant and lubricant are miscible and at the upper temperatures of the heat transfer cycle the refrigerant and lubricant are phase separated and such that the density phase inversion temperature of the combination is below the upper operating temperature of the heat transfer cycle.

METHOD OF SELECTING REFRIGERANT-LUBRICANT COMBINATIONS

Field of The Invention

The present invention relates to methods for selecting refrigerant and lubricant combinations for use in heat transfer cycle systems and provides methods for operating said heat transfer systems. More particularly, the invention relates to methods used to select lubricants and refrigerants combinations for a heat transfer cycle system wherein at the lower temperatures of the heat transfer cycle the refrigerant and lubricant are miscible and at the upper temperatures of the heat transfer cycle the refrigerant and lubricant are phase separated and such that the density phase inversion temperature of the combination is below the upper operating temperature of the heat transfer cycle.

Summary of the Invention

The miscibility between refrigerants and lubricants in heat transfer systems, such as vapor-compression refrigeration systems, is important in determining the performance of such systems. In many cases, miscibility between the lubricant and refrigerant at all conditions of operation is preferred in order to ensure adequate lubrication, sufficient circulation of lubricant in the system, and maintain efficient heat transfer in critical system components. However, many combinations of refrigerants and lubricants exhibit phase separation at elevated temperatures. A method of selecting refrigerant and lubricant combinations has been discovered that uses such phase separating combinations of refrigerants and lubricants that also exhibit the property of density phase inversion. At temperatures below the "phase inversion temperature" the lubricant-rich phase is less dense than the refrigerant-rich phase while at temperatures above the "phase inversion temperature" the refrigerant-rich phase is less dense than the lubricant-rich phase. The temperature at which a particular combination flips from one phase denser to the other, and thereby one phase on top to the other phase, is the phase inversion temperature.

An embodiment of the present invention is a method of selecting refrigerant and lubricant combinations in a heat transfer system, including but not limited to refrigeration vapor-compression-type systems, that incorporates at least one refrigerant and at least one

lubricant. In a further embodiement of the present invention, the method of selecting refrigerant and lubricant combinations is such that a lower operating temperature range is selected where the refrigerant and lubricant form a single phase and an upper operating temperature range is selected where the refrigerant and lubricant phase separate into refrigerant-rich and lubricant-rich phases. In a further embodient, the refrigerant-lubricant phase inversion temperature is between the lower operating temperature and upper operating temperature ranges. In a traditional refrigeration vapor-compression system, such as in refrigeration or air conditioning systems, such lower and upper operating temperatures may be the evaporator discharge temperature and compressor discharge temperature respectively.

The present method of selecting refrigerant and lubricant combinations will promote efficient oil return in the heat transfer system and help maintain efficient performance. For example, in the evaporator of a refrigeration vapor-compression cycle, immiscibility between the refrigerant and lubricant can lead to oil logging and excess oil hold up, which can insulate the evaporator to heat transfer, reducing the system efficiency. If the lubricant and refrigerant are miscible, the lubricant tends to be passed from the evaporator and returned back to the compressor. Therefore, a preferred embodiment of the present invention is where the refrigerant and lubricant combination is miscible at the lower temperatures of the heat transfer system to minimize oil logging.

Another issue is the potential for oil collecting in the receivers or reservoirs of heat transfer sytems. Typcially, if the lubricant and refrigerant are immiscible, a lubricant-rich phase may float on the surface of the denser refrigerant-rich phase in receivers or reservoirs, this places the lubricant-rich phase above the suction line for return to the compressor. This can lead to collection of the lubricant in these reservoirs and subsequent drainage of lubricants from the compressor, which can result in insufficient lubrication of the compressor parts leading to excessive wear and premature failure. If the temperature of such reservoirs or receivers is sufficiently above the phase inversion temperature of the refrigerant-lubricant combination, the lubricant-rich phase will sink to the bottom and be collected back to the compressor, thereby ensuring efficient oil return. If the temperature in such reservoirs or receivers is at or near the phase inversion temperature of the

refrigerant-lubricant combination, then the lubricant-rich and refrigerant-rich phases can form stable emulsions or mixtures with long settling times, again permitting efficient oil return. An embodiment of the present invention is that where the phase inversion point is between the upper and lower operating temperatures of the system and preferrably near or below the temperature of the receiver or reservoirs such that a lubricant-rich upper layer phase does not form in the receivers or reservoirs.

The miscibility behavior of the refrigerant and lubricant is very important in the compressor of the heat transfer system, where the lubrication is essential for proper operation and maintaining equipment life. If dissolved refrigerant decreases the viscosity of the lubricant too much, there may be insufficient lubrication in the compressor leading to excessive wear and premature failure. Another concern is that of flooded starts, where the compressor sump is flooded with refrigerant after shutdown. During startup, the presence of refrigerant can reduce lubricant viscosity resulting in inadequate compressor lubrication. This is particularly a concern with immiscible refrigerant/lubricant systems where two layers can form in the compressor sump with the refrigerant layer on the bottom. The withdrawal point where lubricant is normally drawn into the compressor bearings is at the bottom. In a preferred emodiment of the present invention, the temperature in the compressor is above the phase inversion temperature, thereby limiting the chance that refrigerant will displace lubricant in the compressor sump which will aid lubrication and avoid many problems of flooded starts. In a separate embodiment, the temperature in the compressor during idle periods is such that the refrigerant and lubricant are miscible.

Though not meant to limit the scope of the present invention, refrigerants of the present invention include compositions comprising hydrofluorocarbons (HFCs), hydrofluoroolefins (HFOs), hydrochlorofluorocarbons (HCFOs), hydrochlorofluorocarbons (HCFCs), hydrocarbons (HCs), carbon dioxide, ammonia, dimethyl ether, and/or mixtures thereof. Preferrably the refrigerant comprises a hydrofluoroolefin. More preferrably, the refrigerant comprises a fluorinated C3 to C6 alkene, more preferrably a fluorinated C3 to C4 alkene, even more preferrably a tri-, tetra-, or pentafluoro-propene, and even more preferrably a trifluoropropene, tetrafluoropropene,

and/or mixtures thereof. Exemplary trifluoropropenes include 3,3,3-trifluoropropene (HFO-1243zf). Exemplary tetrafluoropropenes include 2,3,3,3-tetrafluoropropene (HFO-1234yf) and 1,3,3,3-tetrafluoropropene (HFO-1234ze). 1,3,3,3-tetrafluoropropene (HFO-1234ze) can include the cis-isomer, trans-isomer, and mixtures thereof; preferably 1,3,3,3-tetrafluoropropene is predominantly the trans-isomer.

Exemplary HFCs include, but are not limited to, difluoromethane (HFC-32); 1-fluoroethane (HFC-161); 1,1-difluoroethane (HFC-152a); 1,2-difluoroethane (HFC-152); 1,1,1-trifluoroethane (HFC-143a); 1,1,2-trifluoroethane (HFC-143); 1,1,1,2-tetrafluoroethane (HFC-134a); 1,1,2,2-tetrafluoroethane (HFC-134); 1,1,1,2,2-pentafluoroethane (HFC-125); 1,1,1,3,3-pentafluoropropane (HFC-245fa); 1,1,2,2,3-pentafluoropropane (HFC-245ca); 1,1,1,2,3-pentafluoropropane (HFC-245eb); 1,1,1,3,3,3-hexafluoropropane (HFC-236fa); 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea); 1,1,1,3,3-pentafluorobutane (HFC-365mfc), 1,1,1,2,3,4,4,5,5,5-decafluoropropane (HFC-4310), and mixtures thereof. Exemplary hydrocarbons include, but are not limited to, propane, butane, isobutane, propylene, and mixtures thereof. Exemplary hydrochlorofluorocarbons include, but are not limited to, HCFC-22, HCFC-123, and mixtures thereof. Exemplary HCFOs include, but are not limited to, 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd), preferrably the trans-isomer, 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), and/or mixtures thereof.

Though not meant to limit the scope of the invention in any way, lubricants of the present invention, include but are not limited to: polyalkylene glycols (PAGs), polyol esters (POEs), polyvinyl ethers (PVEs), polyglycols, polyalkylene glycol esters, alkyl benzenes, mineral oils, polyalphaolefins, and/or mixtures thereof. PAG oils are preferrably homopolymers or copolymers consisting of two or more oxypropylene groups. PAG oils can be 'un-capped', 'single-end capped', or 'double-end capped'. Examples of commercial PAG oils include, but are not limited to, ND-8, Castrol PAG 46, Castrol PAG 100, Castrol PAG 150, Daphne Hermetic PAG PL, Daphne Hermetic PAG PR. Example commercial POE oils include, but are not limited to, Emkarate POE RL 32H, Emkarate POE RL 68H, Copeland Ultra 22CC, Copeland Ultra 32CC. The preferred viscosity of the lubricating oil is from about 10 to about 200 centistokes.

Example of refrigerant / lubricant combinations within the scope of the present invention include:

HFO-1234yf / PAG

HFO-1234yf / POE

HFO-1234yf / PVE

HFO-1234ze / PAG

HFO-1234ze / POE

HFO-1234ze / PVE

HFO-1243zf / PAG

HFO-1243zf / POE

HFO-1243zf / PVE

It is recognized the chemical composition of lubricants within the same family (eg. PAGs) can be different. Therefore, the miscibility behavior and inversion temperature can be different from one lubricant to the next even when used in combination with the same refrigerant. Therefore, the operation temperatures of the method of cooling of the present invention may change depending on the specific combinations of refrigerant and lubricant. A person of ordinary skill in the art would be able to determine the phase inversion temperature of a specific combination.

Heat transfer systems, including for refrigeration, air conditioning, and liquid chilling, are operated with one portion of the cycle at a the lower operating temperature range and another part of the cycle at the upper operating temperature range. These upper and lower temperature ranges will depend on the specific application. For example, the operating temperatures for low temperature refrigeration may be different than for automotive air conditioning or for water chillers. Preferrably, the upper operating temperature range is

from about +15°C to about +90°C, more preferrably from about +30°C to about +70°C. Preferrably, the lower operating temperature range is from about +25°C to about -60°C, more preferrably from about +15°C to about -30°C. For example, a low pressure liquid chiller may be operated at an evaporator temperature from about -10°C to +10°C and a condensor temperature from about +30°C to +55°C. For example, an air conditioner, such as for automotive AC, may operate with an evaporating temperature at 4°C and a condensing temperature of 40°C. For refrigeration, the lower operating temperature range may be depend upon the specific application. For instance, some typical application temperatures for refrigeration include: freezer (eg. ice cream): -15°F +/- 2°F (-26°C +/- 1.1°C); low temperature: 0°F +/- 2°F (-18°C +/- 1.1°C); medium temperature: 38°F +/- 2°F (3.3°C +/- 1.1°C). These examples are only informative and not meant to limit the scope of the present invention in any way. Other operating temperatures and operating temperature ranges may be employed within the scope of the present invention.

The compositions may also comprise additives, such as dyes, viscosity modifiers, anti-foaming agents, corrosion inhibitors, stabilizers, compatibilizers, anti-oxidants, pour point depressants, nanoparticles, flame suppressants an dmixtures thereof.

Another embodiment of the present invention is a method of operating a heat transfer system with a refrigerant-lubricant combination. In one embodiment, one portion of the heat transfer system is operated at a lower operating temperature range where the refrigerant and lubricant form a single phase. Another portion of the heat transfer system is operated at an upper operating temperature range where the refrigerant and lubricant separate into a refrigerant-rich phase and a lubricant-rich phase. In this emodiment of the present invention, the heat transfer system is operated where the density phase inversion temperature of the refrigerant/lubricant combination is between the upper and lower operating temperatures.

EXAMPLE 1

To a graduated pressure vessel was added approximately equal parts of HFO-1234yf and a commercial PAG lubricant (Castrol PAG 46). The components were mixed and allowed

to sit at ambient temperature to equilbrate. At ambient temperature (~20°C), the mixture was phase separated, with a lubricant-rich liquid phase floating on a refrigerant-rich liquid phase. To reduce the temperature of the mixture below ambient, the pressure vessel was placed in a contant temperature refrigerator or freezer and cooled until equilibrium was reached. At 8°C the mixture was miscible, showing only a single liquid phase. At -20°C the mixture was miscible with only a single liquid phase.

To raise the temperature of the mixture above ambient, the graduated pressure vessel was then placed in a constant temperature bath and heated in stages to from 25°C to 50°C, allowed to reach equilibrium at each stage, and the vessel contents were periodically observed. The mixture contained two liquid phases. At 30°C the two phases were very difficult to distinguish. At 35°C, the two phases were still difficult to distinguish but a liquid, refrigerant-rich phase was floating above a more lubricant-rich phase. At 40°C and higher, the portion of the sample that was the refrigerant-rich phase had increased and the two phases were more easily distinguished.

The graduated pressure vessel was removed from the contant temperature bath and allowed to cool. As the vessel cooled, the refrigerant-rich phase was observed to sink to the bottom of the vessel.

This example shows that the combination of HFO-1234yf with Castrol PAG 46 is miscible from 8°C to -20°C while being immiscble at +20°C and above, with a density phase inversion temperature of about +30°C.

EXAMPLE 2

A vapor-compression air conditioning system can be operated using the refrigerant/lubricant combination of Example 1, where the refrigerant is HFO-1234yf and the lubricant is Castrol PAG 46. The lower operating temperature range could be from about +8°C to about -20°C, while the upper operating temperature range could be from about 30°C and above. The air conditioning system would be operated according to the present invention, where the evaporator temperature is maintained at 4°C +/- 2°C, and the condensing temperature is maintained at about 40°C. Using these operating conditions,

the refrigerant and lubricant would be miscible at the coldest conditions in the air conditioning system while at the upper operating temperatures, the refrigerant and lubricant would be immiscible but where the refrigerant-rich phase is less dense.

Claims

1. A method for selecting a refrigerant and lubricant combination for a vapor-compression heat transfer system comprising:

a. determining a lower operating temperature range of a vapor-compression heat transfer system;

b. determining an upper operating temperature range of the vapor-compression heat transfer system; and

c. selecting a refrigerant selected from hydrofluorocarbons (HFCs), hydrofluoroolefis (HFOs), hydrochlorofluorocarbos (HCFCs), hydrochlorofluoroolefins (HCFOs), hydrocarbons (HCs), carbon dioxide, ammonia, dimethyl ether, or mixtures thereof at a first concentration and a lubricant selected from polyalkylene glycols (PAGs), polyol esters (POEs), polyvinyl ethers (PVEs), polyglycols, polyalkylene glycol esters, alkyl benzenes, mineral oils, polyalphaolefins, or mixtures thereof at a second concentration to wherein said refrigerant and said lubricant are miscible at a first temperature within said lower operating temperature range and produce a fluid system having a refrigerant-rich phase and a lubricant-rich phase at a second temperature within said upper operating temperature range provided that said second temperature is higher than said first temperature, wherein the lubricant-rich phase is denser relative to the refrigerant-rich phase at said second temperature.

2. The method of claim 1 wherein the phase inversion point of said refrigerant and lubricant combination is between the upper operating temperature range and the lower operating temperature range of the system.

3. The method of claim 1 wherein the hydrofluoroolefin is selected from the group consisting of C3 to C6 alkenes.

4. The method of claim 3 wherein said C3 to C6 alkene is selected from the group consisting of trifluoropropene, tetrafluoropropene, pentafluoropropene and mixtures thereof.

5. The method of claim 4 wherein said trifluoropropene, tetrafluoropropene is selected from the group consisting of 3,3,3-trifluoropropene (HFO-1243zf), 2,3,3,3-tetrafluoropropene (HFO-1234yf) and 1,3,3,3-tetrafluoropropene (HFO-1234ze).

6. The method of claim 1 wherein said higher operating temperature range is about +15°C to about +90°C and said lower operating temperature range is about -60°C to about +25°C.

7. The method of claim 1 wherein said higher operating temperature range is about +30°C to about +70°C and said lower operating temperature range is about -30°C to about +15°C.

8. The method of claim 1 wherein said fluid system further comprises one or more of additives selected from the group consisting of dyes, viscosity modifiers, anti-foaming agents, corrosion inhibitors, stabilizers, compatibilizers, anti-oxidants, pour point depressants, nanoparticles, flame suppressants and mixtures thereof.

9. A method for introducing a refrigerant and lubricant into a vapor-compression heat transfer device system comprising:

a. providing a vapor-compression heat transfer device comprising a heat transfer circuit, a compressor having an inlet side and an outlet side, a refrigerant and lubricant reservoir, wherein said reservoir is in fluid communication with the inlet side of the compressor and with said heat transfer circuit, and said heat transfer circuit is in fluid communication with said outlet side of the compressor;

b. determining the lower operating temperature range of the vapor-compression refrigeration device;

c. determining the upper operating temperature range of the vapor-compression refrigeration device;

d. selecting a refrigerant selected from hydrofluorocarbons (HFCs), hydrofluoroolefis (HFOs), hydrochlorofluorocarbos (HCFs), hydrochlorofluorocarbos (HCFs), hydrocarbons (HCs), carbon dioxide, ammonia, or mixtures thereof at a first concentration and selecting a lubricant selected from polyalkylene glycols (PAGs), polyol esters (POEs), polyvinyl ethers (PVEs), polyglycols, polyalkylene glycol esters, alkyl benzenes, mineral oils, polyalphaolefins, or mixtures thereof at a second concentration to produce a fluid system wherein said refrigerant and said lubricant are miscible at a first temperature within said lower operating temperature range and produce a fluid system having a refrigerant-rich phase and a lubricant-rich phase at a second temperature within said upper operating temperature range provided that said second temperature is higher than said first temperature, wherein the lubricant-rich phase is denser relative to the refrigerant-rich phase at said second temperature; and

e. introducing said refrigerant and lubricant into the vapor-compression heat transfer device.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 10/61258

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C09K 5/00 (2010.01)
USPC - 252/67,68
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)
USPC - 252/67,68

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 252/67,68

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWest: PGPB,USPT,USOC,EPAB,JPAB; Google; refrigerant, lubricant, HFC, HFO, HCFC, HCFO, HC, carbon dioxide, ammonia, dimethyl ether, PAG, POE, PVE, polyglycol, glycol, mineral oil, polyalphaolefin, miscible, upper, lower, dye, viscosity, foam, corrosion, pour, flame, trifluoropropene, tetrafluoropropene, density, inversion

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/0241562 A1 (THOMAS et al.) 01 October 2009 (01.10.2009) para [0010], para [0016]-[0019], para [0023], para [0037]-[0038], para [0044] and para [0046].	1-9
A	US 2007/0069175A1 (THOMAS et al.) 29 March 2007 (29.03.2007) entire document	1-9
A	US 2004/0089839A1 (THOMAS et al.) 13 May 2004 (13.05.2004) entire document	1-9

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"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
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve 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
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 February 2011 (07.02.2011)	18 FEB 2011

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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