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(54) **Title**: HEAT TRANSFER COMPOSITIONS AND METHODS

(57) **Abstract**: Compositions, methods and systems which comprise or utilize a multi-component mixture comprising: (a) HFC-32; (b) HFC-125; (c) HFO-1234yf and/or HFO-1234ze; (d) HFC-134a. In certain non-limiting aspects, such refrigerants may be used as a replacement for R-404A.

HEAT TRANSFER COMPOSITIONS AND METHODS

CROSS REFERENCES TO RELATED APPLICATIONS

The present application claims the priority benefit of U.S. Provisional Application No. 61/598,056, filed on February 13, 2012, the contents of which are incorporated herein by reference.

The present application is also related to as a continuation-in-part of and claims the priority benefit of U.S. Application 13/099,218, filed May 2, 2011 (currently pending), which is a continuation-in-part of International Application No. PCT/US2010/034120, filed May 7, 2010, which in turn claims the benefit of U.S. Provisional Application Serial Nos. 61/176,773, filed May 8, 2009 (expired); 61/240,786, filed September 9, 2009 (expired), 61/247,816, filed October 1, 2009 (expired), 61/329,955, filed April 30, 2010 (expired). International Application No. PCT/US2010/034120 is also a continuation of U.S. Application 12/511,954, filed July 29, 2009 (currently pending). Each of the above-identified applications is incorporated in its entirety herein by reference.

The present application is related to as a continuation-in-part of and claims the priority benefit of U.S. Application 13/182,591, filed July 14, 2011 (currently pending), which in turn claims the priority benefit of U.S. Provisional Application No. 61/364,373, filed on July 14, 2010 (expired), the contents of which are incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates to compositions, methods and systems having utility in refrigeration applications, with particular benefit in medium and low temperature refrigeration applications, and in particular aspects to refrigerant compositions for replacement of refrigerant HFC-404A for heating and cooling applications and to retrofitting medium and low temperature refrigerant systems, including systems designed for use with HFC-404A.

BACKGROUND

Mechanical refrigeration systems, and related heat transfer devices such as heat pumps and air conditioners, using refrigerant liquids are well known in the art for industrial, commercial and domestic uses. Fluorocarbon based fluids have found widespread use in many residential, commercial and industrial applications, including as the working fluid in systems such as air conditioning, heat pump and refrigeration systems. Because of certain suspected environmental problems, including the relatively high global warming potentials associated with the use of some of the compositions that have heretofore been used in these applications, it has become increasingly desirable to use fluids having low or even zero ozone depletion and global warming potentials, such as hydrofluorocarbons ("HFCs"). For example, a number of governments have signed the Kyoto Protocol to protect the global environment and setting forth a reduction of CO2 emissions (global warming). Thus, there is a need for a low- or non-flammable, non-toxic alternative to replace certain of high global warming HFCs.

One important type of refrigeration system is known as a "low temperature refrigeration system." Such systems are particularly important to the food manufacture, distribution and retail industries in that they play a vital role in ensuring that food which reaches the consumer is both fresh and fit to eat. In such low temperature refrigeration systems, a commonly used refrigerant liquid has been HFC-404A (the combination of HFC-125:HFC-143a:HFC134a in an approximate 44:52:4 weight ratio is referred to in the art as HFC-404A or R-404A). R-404A has an estimated high Global Warming Potential (GWP) of 3922.

There has thus been an increasing need for new fluorocarbon and hydrofluorocarbon compounds and compositions that are attractive alternatives to the compositions heretofore used in these and other applications. For example, it has become desirable to retrofit chlorine-containing refrigeration systems by replacing chlorine-containing refrigerants with non-chlorine-containing refrigerant compounds that will not deplete the ozone layer, such as hydrofluorocarbons (HFC's). Industry in general and the heat transfer industry in particular are continually seeking new fluorocarbon based mixtures that offer alternatives to, and are considered environmentally safer substitutes for, CFCs and HCFCs. It is generally considered

important, however, at least with respect to heat transfer fluids, that any potential substitute must also possess those properties present in many of the most widely used fluids, such as excellent heat transfer properties, chemical stability, low- or no- toxicity, non-flammability and/or lubricant compatibility, among others.

With regard to efficiency in use, it is important to note that a loss in refrigerant thermodynamic performance or energy efficiency may have secondary environmental impacts through increased fossil fuel usage arising from an increased demand for electrical energy.

Furthermore, it is generally considered desirable for CFC refrigerant substitutes to be effective without major engineering changes to conventional vapor compression technology currently used with CFC refrigerants.

Flammability is another important property for many applications. That is, it is considered either important or essential in many applications, including particularly in heat transfer applications, to use compositions which are non-flammable. Thus, it is frequently beneficial to use in such compositions compounds which are nonflammable. As used herein, the term "nonflammable" refers to compounds or compositions which are determined to be nonflammable as determined in accordance with ASTM standard E-681, dated 2002, which is incorporated herein by reference. Unfortunately, many HFC's which might otherwise be desirable for used in refrigerant compositions are not nonflammable as that term is used herein. For example, the fluoroalkane difluoroethane (HFC-152a) and the fluoroalkene 1,1,1–trifluorpropene (HFO-1243zf) are each flammable and therefore not viable for use in many applications.

Applicants have thus come to appreciate a need for compositions, and particularly heat transfer compositions, that are highly advantageous in heating and cooling systems and methods, particularly vapor compression heating and cooling systems, and even more particularly low temperature refrigerant systems, including systems which are used with and/or have been designed for use with HFC-404A.

SUMMARY

Applicants have found that the above-noted needs, and other needs, can be satisfied by compositions, methods and systems which comprise or utilize a multi-

component mixture, that in certain embodiments, comprises: (a) from about 10% to about 35% by weight of HFC-32; (b) from about 10% to about 35% by weight of HFC-125; (c) from greater than 0% to about 30% by weight of HFO-1234ze; (d) from about 10% to about 35% by weight of HFC-134a, (e) optionally but preferably from greater than about 0% to about 30% by weight of HFO-1234yf, and optionally (f) up to about 10% by weight of CF_3I and/or up to about 5% by weight of HFCO-1233ze, from about 0% to about 30% by weight of HFO-1234yf and with the weight percent being based on the total of the components (a) – (f) in the composition.

In certain preferred embodiments, HFC-32 is provided in an amount from about 15% to about 30% by weight, and in further preferred embodiments is provided in an amount from about 20% to about 30% by weight, with the weight percent being based on the total of the components (a) – (f) in the composition.

In certain preferred embodiments, HFC-125 is provided in an amount from about 10% to about 30% by weight, and in further preferred embodiments is provided in an amount from about 20% to about 30% by weight, with the weight percent being based on the total of the components (a) – (f) in the composition.

In certain preferred embodiments, HFO-1234yf is provided in an amount from about or greater than 0% to about 25% or from about or greater than 0% to about 22% by weight of HFO-1234yf, with the weight percent being based on the total of the components (a) – (f) in the composition. In the same or alternative embodiments, HFO-1234ze is provided in an amount from about 1% to about 30% by weight of HFO-1234ze or from about 5% to about 30% by weight of HFO-1234ze, with the weight percent being based on the total of the components (a) – (f) in the composition.

In certain preferred embodiments, HFC-134a is provided in an amount from about 15% to about 35% by weight, and in further preferred embodiments is provided in an amount from about 15% to about 30% by weight, with the weight percent being based on the total of the components (a) – (f) in the composition.

In further embodiments, the composition has a weight ratio of HFC-32:HFC-125 of from about 0.9:1.2 to about 1.2:0.9. In further, or alternative, embodiments the composition has a weight ratio of HFO-1234ze:HFO-1234yf of about 5:1 to about 0.1:1 or a weight ratio of HFO-1234ze:HFO-1234yf of between about 3:1 to about 0.2:1. In

even further, or alternative, embodiments, the composition has a weight ratio of 134a to a combination of HFO-1234ze and HFO-1234yf between about 5:7 to about 1:1 or of about 4:6.

The present invention provides also methods and systems which utilize the compositions of the present invention, including methods and systems for heat transfer and for retrofitting existing heat transfer systems. Certain preferred method aspects of the present invention relate to methods of providing relatively low temperature cooling, such as in low temperature refrigeration systems. Other preferred method aspects of the present invention provide methods of retrofitting an existing refrigeration system, preferably low temperature refrigeration systems, designed to contain and/or containing R-404A refrigerant comprising introducing a composition of the present invention into the system without substantial engineering modification of said existing refrigeration system.

The term HFO-1234ze is used herein generically to refer to 1,1,1,3-tetrafluoropropene, independent of whether it is the cis- or trans- form. The terms "cisHFO-1234ze" and "transHFO-1234ze" are used herein to describe the cis- and trans- forms of 1,1,1,3-tetrafluoropropene respectively. The term "HFO-1234ze" therefore includes within its scope cisHFO-1234ze, transHFO-1234ze, and all combinations and mixtures of these.

DETAILED DESCRIPTION OF THE INVENTION

Low temperature refrigeration systems are important in many applications, such as to the food manufacture, distribution and retail industries. Such systems play a vital role in ensuring that food which reaches the consumer is both fresh and fit to eat. In such low temperature refrigeration systems, one of the refrigerant liquids which has been commonly used has been HFC-404A, which has an estimated high Global Warming Potential (GWP) of 3922. Applicants have found that the compositions of the present invention satisfy in an exceptional and unexpected way the need for alternatives and/or replacements for refrigerants in such applications, particularly and preferably HFC-404A, that at once have lower GWP values and provide substantially non-flammable, non-toxic fluids that have a close match in cooling capacity and/or efficiency

to HFC-404A in such systems.

The present invention may also encompass medium temperature refrigeration composition, systems and methods. According to certain preferred embodiments, the present methods and systems involve evaporator temperatures of from above about -15°C to about 5°C. An example of such a medium temperature system and method involves providing cooling in the fresh food compartment of a residential refrigerator.

HEAT TRANSFER COMPOSITIONS

The compositions of the present invention are generally adaptable for use in heat transfer applications, that is, as a heating and/or cooling medium, but are particularly well adapted for use, as mentioned above, in medium and low temperature refrigeration systems, and preferably in low temperature systems, that have heretofor used HFC-404A and/or systems that have heretofor used R-22.

Applicants have found that use of the components of the present invention within the broad and narrowed ranges described herein is important to achieve the advantageous but difficult to achieve combinations of properties exhibited by the present compositions, particularly in the preferred systems and methods, and that use of these same components but substantially outside of the identified ranges can have a deleterious effect on one or more of the important properties of the compositions, systems or methods of the invention.

In certain preferred embodiments, compositions of the present invention comprise, consist essentially of, or consist of: (a) difluoromethane (HFC-32); (b) pentafluoroethane (HFC-125); (c) HFO-1234ze, HFO-1234yf or combinations thereof; (d) 1,1,1,2-tetrafluoroethane (HFC-134a); and optionally (e) CF_3I and/or 1233ze.

HFC-32 may be provided in an amount of from greater than 0 wt.% to about 50 wt.% by weight of the compositions, in certain preferred aspects in an amount of from about 10 wt.% to about 40 wt.% by weight of the compositions, in further preferred aspects in an amount of from about 10 wt.% to about 35 wt.% by weight of the compositions, in even further preferred aspects in an amount of from about 15 wt.% to about 30 wt.% by weight of the compositions, and in even further preferred aspects in an amount of from about 20 wt.% to about 30 wt.% by weight of the compositions, each

based on the total weight of the components (a) – (e).

HFC-125 may be provided in an amount of from greater than 0 wt.% to about 50 wt.% by weight of the compositions, in certain preferred aspects in an amount of from about 10 wt.% to about 40 wt.% by weight of the compositions, in further preferred aspects in an amount of from about 10 wt.% to about 35 wt.% by weight of the compositions, in even further preferred aspects in an amount of from about 10 wt.% to about 30 wt.% by weight of the compositions, and in even further preferred aspects in an amount of from about 20 wt.% to about 30 wt.% by weight of the compositions, each based on the total weight of the components (a) – (e).

HFO-1234ze may be provided in an amount of from greater than 0 wt.% to about 30 wt.% by weight of the compositions, in certain preferred aspects in an amount of from about 1 wt.% to about 30 wt.% by weight of the compositions, and in further preferred aspects in an amount of from about 5 wt.% to about 30 wt.% by weight of the compositions, each based on the total weight of the components (a) – (e).

HFO-1234yf, when present in such compositions, may be provided in an amount of from about or greater than 0 wt.% to about 30 wt.% by weight of the compositions, in certain preferred aspects in an amount of from about or greater than 0 wt.% to about 25 wt.% by weight of the compositions, and in further preferred aspects in an amount of from about or greater than 0 wt.% to about 30 wt.% by weight of the compositions, each based on the total weight of the components (a) – (e).

HFC-134a may be provided in an amount of from greater than 0 wt.% to about 50 wt.% by weight of the compositions, in certain preferred aspects in an amount of from about 5 wt.% to about 40 wt.% by weight of the compositions, in further preferred aspects in an amount of from about 10 wt.% to about 35 wt.% by weight of the compositions, in even further preferred aspects in an amount of from about 15 wt.% to about 35 wt.% by weight of the compositions, and in even further preferred aspects in an amount of from about 15 wt.% to about 30 wt.% by weight of the compositions, each based on the total weight of the components (a) – (e).

Highly preferred combinations of properties are achieved for compositions having a weight ratio of HFC-32:HFC-125 of from about 0.9:1.2 to about 1.2:0.9, with a ratio of about 1:1 being preferred in certain embodiments. Applicants have found that highly

preferred combinations of properties are also achieved for compositions having a weight ratio of HFO-1234ze:HFO-1234yf of from about 5:1 to about 0.1:1 or between about 0.2:1 to 3:1.

For the purposes of convenience, the combination HFO-1234ze and HFO-1234yf is referred to herein as the "tetrafluoropropene component" or "TFC," and in certain embodiments highly preferred combinations of properties can be achieved for composition which comprise a weight ratio of HFC-134a:TFC of from about 5:7 to about 1:1, with a ratio of about 4:6 being preferred in certain embodiments.

Although it is contemplated that either isomer of HFO-1234ze may be used, applicants have found that it is preferred, in certain embodiments, that the HFO-1234ze comprise transHFO-1234ze, and preferably comprise transHFO-1234ze in major proportion, and in certain embodiments consist essentially of transHFO-1234ze.

As mentioned above, applicants have found that the compositions of the present invention are capable of achieving a difficult to achieve combination of properties, including particularly low GWP. By way of non-limiting example, the following Table A illustrates the substantial improvement in GWP exhibited by certain compositions of the present invention in comparison to the GWP of HFC-404A, which has a GWP of 3922.

TABLE A

Composition of the Invention (weight fraction, based on identified components)	Name	GWP	GWP as a Percentageof R404A GWP
R125/R134a/R143a(0.44/0.04/0.52)	R404A	3922	
R32/R125/R134a/1234ze/1234yf (0.25/0.25/0.21/0.20/0.09)	A1	1344	34%
R32/R125/R134a/1234yf(0.25/0.25/0.2/0.3)	A2	1330	34%
R32/R125/R134a/1234ze/1234yf (0.26/0.26/0.21/0.17/0.1)	A3	1386	35%
R32/R125/R134a/1234ze (0.26/0.26/0.21/0.27)	A4	1386	35%
R32/R125/R134a/1234ze/1234yf (0.26/0.26/0.21/0.07/0.20)	A5	1386	35%

The compositions of the present invention may include other components for the purpose of enhancing or providing certain functionality to the composition, or in some cases to reduce the cost of the composition. For example, refrigerant compositions according to the present invention, especially those used in vapor compression systems, include a lubricant, generally in amounts of from about 30 to about 50 percent

by weight of the composition, and in some case potentially in amount greater than about 50 percent and other cases in amounts as low as about 5 percent. Furthermore, the present compositions may also include a compatibilizer, such as propane, for the purpose of aiding compatibility and/or solubility of the lubricant. Such compatibilizers, including propane, butanes and pentanes, are preferably present in amounts of from about 0.5 to about 5 percent by weight of the composition. Combinations of surfactants and solubilizing agents may also be added to the present compositions to aid oil solubility, as disclosed by U.S. Patent No. 6,516,837, the disclosure of which is incorporated by reference. Commonly used refrigeration lubricants such as Polyol Esters (POEs) and Poly Alkylene Glycols (PAGs), PAG oils, silicone oil, mineral oil, alkyl benzenes (ABs) and poly(alpha-olefin) (PAO) that are used in refrigeration machinery with hydrofluorocarbon (HFC) refrigerants may be used with the refrigerant compositions of the present invention. Commercially available mineral oils include Witco LP 250 (registered trademark) from Witco, Zerol 300 (registered trademark) from Shrieve Chemical, Sunisco 3GS from Witco, and Calumet R015 from Calumet. Commercially available alkyl benzene lubricants include Zerol 150 (registered trademark). Commercially available esters include neopentyl glycol dipelargonate, which is available as Emery 2917 (registered trademark) and Hatcol 2370 (registered trademark). Other useful esters include phosphate esters, dibasic acid esters, and fluoroesters. In some cases, hydrocarbon based oils are have sufficient solubility with the refrigerant that is comprised of an iodocarbon, the combination of the iodocarbon and the hydrocarbon oil might more stable than other types of lubricant. Such combination may therefore be advantageous. Preferred lubricants include polyalkylene glycols and esters. Polyalkylene glycols are highly preferred in certain embodiments because they are currently in use in particular applications such as mobile air-conditioning. Of course, different mixtures of different types of lubricants may be used.

Other additives not mentioned herein can also be included by those skilled in the art in view of the teachings contained herein without departing from the novel and basic features of the present invention.

HEAT TRANSFER METHODS AND SYSTEMS

The present methods, systems and compositions are thus adaptable for use in connection with a wide variety of heat transfer systems in general and refrigeration systems in particular, such as air-conditioning (including both stationary and mobile air conditioning systems), refrigeration, heat-pump systems, and the like. In certain preferred embodiments, the compositions of the present invention are used in refrigeration systems originally designed for use with an HFC refrigerant, such as, for example, R-404. The preferred compositions of the present invention tend to exhibit many of the desirable characteristics of R-404A but have a GWP that is substantially lower than that of R-404A while at the same time having a capacity and/or efficiency that is substantially similar to or substantially matches, and preferably is as high as or higher than R-404A. In particular, applicants have recognized that certain preferred embodiments of the present compositions tend to exhibit relatively low global warming potentials ("GWPs"), preferably less than about 2500, more preferably less than about 2400, and even more preferably not greater than about 2300. In certain embodiments, the present compositions have a GWP of about 1500 or less, and even more preferable of less than about 1000.

In certain other preferred embodiments, the present compositions are used in refrigeration systems which had contained and/or had originally been designed for use with R-404A. Preferred refrigeration compositions of the present invention may be used in refrigeration systems containing a lubricant used conventionally with R-404A, such as mineral oils, polyalkylbenzene, polyalkylene glycol oils, and the like, or may be used with other lubricants traditionally used with HFC refrigerants. As used herein the term "refrigeration system" refers generally to any system or apparatus, or any part or portion of such a system or apparatus, which employs a refrigerant to provide cooling. Such refrigeration systems include, for example, air conditioners, electric refrigerators, chillers (including chillers using centrifugal compressors), and the like.

As mentioned above, the present invention achieves exceptional advantage in connection with systems known as low temperature refrigeration systems. As used herein the term "low temperature refrigeration system" refers to vapor compression refrigeration systems which utilize one or more compressors and a condenser

temperature of from about 35°C to about 45°C. In preferred embodiments of such systems, the systems have an evaporator temperature of from about – 40°C and less than about -15°C, more preferably from about -35°C to about -25°C, with an evaporator temperature preferably of about -32°C. Moreover, in preferred embodiments of such systems, the systems have a degree of superheat at evaporator outlet of from about 0°C to about 10°C, with a degree of superheat at evaporator outlet preferably of from about 4°C to about 6°C. Furthermore, in preferred embodiments of such systems, the systems have a degree of superheat in the suction line of from about 15°C to about 25°C, with a degree of superheat in the suction line preferably of from about 20°C to about 25°C.

In one non-limiting embodiment, the heat transfer compositions of the present invention may be used to retrofit an existing refrigeration system with or without having to substantially modify the system and with or without having to drain completely the existing refrigerant. In one aspect, part of the refrigerant charge is drained from the system, which may include more than 5%, 10%, 25%, 50%, 75% or the like. The removed refrigerant charge is then replaced with one or a combination of the non-flammable, low GWP refrigerants discussed herein.

In alternative embodiments, rather than partially draining the existing system, the refrigerants of the present invention may be used to "top off" existing systems after a partial refrigerant leak. Many commercial systems, for example, have relatively high refrigerant leak rates which require routine addition of refrigerant over the life of the system. In one method of the present invention, a refrigerant system is provided with less than the full or designed charge of refrigerant in the system, which, in preferred embodiments, occurs as a result of leakage of refrigerant from the system, and a refrigerant composition of the present invention is used to recharge the system, preferably during normal recharge maintenance. If the system leaked R404A, for example, it would be recharged with one or a combination of the blends identified herein. The present methods permit such to occur while substantially maintaining capacity of the system, maintaining or improving energy efficiency (lower electricity consumption which equates to lower operating cost for the users), and lowering the GWP of the refrigerant contained in the system (lowering environmental impact). In

preferred embodiments, such a method can be performed regardless of how much refrigerant has leaked, preferably without a blend calculation, and provides a simple (and low cost) way to reduce environmental impact associated with recharging of an existent system without deviating from the routine maintenance schedule of the system.

In accordance with the foregoing, applicants' have recognized that even relatively large amounts of R404A when used in combination with the blends of the present invention, whether in the form of an unintentional contaminant, as an intentionally added ingredient or as the remaining refrigerant after a system replacement or recharge, do not have a substantially deleterious effect on the performance of the refrigerants and/or refrigeration systems of the present invention. Conversely, applicants have also come to recognize that relatively large amounts of the blends of the present invention in R404A, whether in the form of an unintentional contaminant or as an intentionally added ingredient, do not have a substantially deleterious effect on the performance of the refrigerant. Accordingly, whereas in other cases the presence of such a contaminant might otherwise disqualify the use of the refrigerant with the contaminant, applicants have come to recognize that the use of such mixtures of refrigerants will generally be acceptable for the intended purpose. Accordingly, one advantage of the methods and compositions of the present invention is that, from a workability standpoint, there is generally not a great incentive to ensure that R404A is entirely absent from the low GWP refrigerants, and vice versa, and under such circumstances there is an increased possibility that, in the absence of the methods provided by the present invention, substantial and severe problems would arise with the operation of many existing automatic purge systems. However, the present methods overcome these problems and add reliability, safety and efficiency to the systems.

EXAMPLES

The following examples are provided for the purpose of illustrating the present invention but without limiting the scope thereof.

EXAMPLE 1: Performance Parameters – Low Temperature System

The coefficient of performance (COP) is a universally accepted measure of

refrigerant performance, especially useful in representing the relative thermodynamic efficiency of a refrigerant in a specific heating or cooling cycle involving evaporation or condensation of the refrigerant. In refrigeration engineering, this term expresses the ratio of useful refrigeration to the energy applied by the compressor in compressing the vapor. The capacity of a refrigerant represents the amount of cooling or heating it provides and provides some measure of the capability of a compressor to pump quantities of heat for a given volumetric flow rate of refrigerant. In other words, given a specific compressor, a refrigerant with a higher capacity will deliver more cooling or heating power. One means for estimating COP of a refrigerant at specific operating conditions is from the thermodynamic properties of the refrigerant using standard refrigeration cycle analysis techniques (see for example, R.C. Downing, FLUOROCARBON REFRIGERANTS HANDBOOK, Chapter 3, Prentice-Hall, 1988).

A low temperature refrigeration system is provided. In the case of such a system illustrated in this Example, the condenser temperature is set to 40.55°C, which generally corresponds to an outdoor temperature of about 35°C. The degree of subcooling at the expansion device inlet is set to 5.55°C. The evaporating temperature is set to -31.6°C, which corresponds to a box temperature of about -26°C. The degree of superheat at evaporator outlet is set to 5.55°C. The degree of superheat in the suction line is set to 13.88°C, and the compressor efficiency is set to 65%. The pressure drop and heat transfer in the connecting lines (suction and liquid lines) are considered negligible, and heat leakage through the compressor shell is ignored. Several operating parameters are determined for the compositions A1 – A5 identified in Table A above in accordance with the present invention, and these operating parameters are reported in Table 1 below, based upon HFC-404A having a COP value of 100%, a capacity value of 100% and a discharge temperature of 97.6°C

TABLE 1

Name	GWP	Evaporator Glide (°C)	Capacity (%)	COP (%)
R404A	3922	0.5	100%	100%

Name	GWP	Evaporator Glide (°C)	Capacity (%)	COP (%)
A1	1344	4.9	96%	110%
A2	1330	3.5	103%	108%
A3	1386	4.7	99%	109%
A4	1386	5.4	95%	110%
A5	1386	3.9	102%	109%

As can be seen from the Table 1 above, applicants have found that the compositions of the present invention are capable of at once achieving many of the important refrigeration system performance parameters close to the parameters for R-404A, and in particular sufficiently close to permit such compositions to be used as a drop-in replacement for R-404A in low temperature refrigeration systems and/or for use in such existing systems with only minor system modification. For example, compositions A1 – A5 exhibit capacities in this low temperature refrigeration system that are within about 8%, and even more preferably within about 5% of that of R404A. All these blends efficiencies (COP) higher that R404A by as much as 10% which is very desirable. Especially in view of the improved GWP of compositions A1 – A5, these compositions of the present invention are excellent candidates for use as drop-in replacements for low temperature refrigeration systems originally containing and/or designed to contain R-404A.

Since many existing low temperature refrigeration systems have been designed for R-404A, or for other refrigerants with properties similar to R-404A, those skilled in the art will appreciate the substantial advantage of a refrigerant with low GWP and superior efficiency which can be used as replacement for R-404A or like refrigerants with relatively minimal modifications to the system. Furthermore, those skilled in the art will appreciate that the present compositions are capable of providing substantial advantage for use in new or newly designed refrigeration systems, including preferably, low temperature refrigeration systems.

EXAMPLE 2: Retrofit Parameters – Low Temperature System

It is contemplated that in certain embodiments the present invention provides

retrofitting methods which comprise removing at least a portion of the existing refrigerant from the system and replacing at least a portion of the removed refrigerant with a composition of the present invention, preferably without substantial modification of the system and even more preferably without any change in major system components, such as compressors, condensers, evaporators, and expansion valves. Due to certain characteristics of low temperature refrigeration systems, including particularly low temperature refrigeration systems containing or designed to contain R404A refrigerant, it is important in certain embodiments that such systems are capable of exhibiting reliable system operating parameters with drop-in refrigerants. Such operating parameters include:

- High-Side Pressure that is within about 105%, and even more preferably within about 103% of the high side pressure of the system using R404A. This parameter is important in such embodiments because it allows the use of existing pressure components.
- Discharge Temperature that is preferably lower than about 130°C, and even more preferably lower than about 125°C. The advantage of such a characteristic is that it permits the use of existing equipment without activation of the thermal protection aspects of the system, which are preferably designed to protect compressor components. This parameter is advantageous in that it avoids the use of costly controls such as liquid injection to reduce discharge temperature.
- Lower suction pressures are acceptable if they do not cause the system to go into sub-atmospheric pressure at low evaporation temperatures. This positive pressure is required to ensure that the system has always positive pressure, avoiding any contamination with humid air in case of leak. To evaluate this requirement, one would employ a property called “Normal Boiling Temperature” (NBT: boiling temperature at atmospheric pressure) of the fluid in question. This NBT should be as close as possible to the one of the fluid replaced (R404A) and at least lower than the lowest evaporation temperature found in typical commercial systems (example: -40ºC).

The above-noted and other operating parameters are determined for the compositions A1 – A5 identified in Table A above in accordance with the present

invention, and these operating parameters is reported in Table 2 below:

TABLE 2

Name	Discharge Pressure (%)	Discharge Temp. (°C)	Suction Pressure (%)	Normal Boiling Temp. (°C)
R404A	100%	91.9	100%	-46.2
A1	96%	117.7	78%	-44.9
A2	103%	113.4	87%	-46.1
A3	99%	118.3	80%	-45.3
A4	95%	120.4	76%	-44.8
A5	97%	116	85%	-45.9

In certain preferred embodiments, the replacement step is a drop-in replacement in the sense that no substantial redesign or modification of the system is required and no major item of equipment needs to be replaced in order to accommodate the refrigerant of the present invention. That is the case with the compositions A1 – A5, which in general can be used in most retrofit procedures without any change of major components. In all compositions A1 – A5, the discharge pressure and temperature is below the limit and the Normal Boiling Temperature is similar to R404A therefore they can be used in most existent refrigeration systems.

EXAMPLE 3: Performance Parameters

A medium temperature refrigeration system is provided. In the case of such a system illustrated in this Example, the condenser temperature is set to 40.55°C, which generally corresponds to an outdoor temperature of about 35°C. The degree of subcooling at the expansion device inlet is set to 5.55°C. The evaporating temperature is set to -3.88°C, which corresponds to a box temperature of about 1.66°C. The degree of superheat at evaporator outlet is set to 5.55°C. The degree of superheat in the suction line is set to 13.88°C, and the compressor efficiency is set to 65%. The pressure drop and heat transfer in the connecting lines (suction and liquid lines) are considered negligible, and heat leakage through the compressor shell is ignored.

Several operating parameters are determined for the compositions A1 – A5 identified in Table A above in accordance with the present invention, and these operating parameters are reported in Table 3 below, based upon HFC-404A having a COP value of 100%, a capacity value of 100% and a discharge temperature of 76°C.

TABLE 3

Name	GWP	Evaporator Glide (°C)	Capacity (%)	COP (%)
R404A	3922	0.5	100%	100%
A1	1344	5.4	99%	106%
A2	1330	3.9	104%	105%
A3	1386	5.1	101%	106%
A4	1386	5.9	98%	107%
A5	1386	4.4	103%	105%

As can be seen from the Table 3 above, applicants have found that the compositions of the present invention are capable of at once achieving many of the important refrigeration system performance parameters close to the parameters for R-404A, and in particular sufficiently close to permit such compositions to be used as a drop-in replacement for R-404A in medium temperature refrigeration systems and/or for use in such existing systems with only minor system modification. For example, compositions A1 – A5 exhibit capacities in this medium temperature refrigeration system that are within about 8%, and even more preferably within about 5% of that of R404A. All these blends efficiencies (COP) are higher that R404A by as much as 7% which is very desirable. Especially in view of the improved GWP of compositions A1 – A5, these compositions of the present invention are excellent candidates for use as drop-in replacements for medium temperature refrigeration systems originally containing and/or designed to contain R-404A.

Since many existing medium temperature refrigeration systems have been designed for R-404A, or for other refrigerants with properties similar to R-404A, those skilled in the art will appreciate the substantial advantage of a refrigerant with low GWP and superior efficiency which can be used as replacement for R-404A or like

refrigerants with relatively minimal modifications to the system. Furthermore, those skilled in the art will appreciate that the present compositions are capable of providing substantial advantage for use in new or newly designed refrigeration systems, including preferably, medium temperature refrigeration systems.

EXAMPLE 4: Retrofit Parameters

It is contemplated that in certain embodiments the present invention provides retrofitting methods which comprise removing at least a portion of the existing refrigerant from the system and replacing at least a portion of the removed refrigerant with a composition of the present invention, preferably without substantial modification of the system and even more preferably without any change in major system components, such as compressors, condensers, evaporators, and expansion valves. Due to certain characteristics of medium temperature refrigeration systems, including particularly medium temperature refrigeration systems containing or designed to contain R404A refrigerant, it is important in certain embodiments that such systems are capable of exhibiting reliable system operating parameters with drop-in refrigerants. Such operating parameters include:

- High-Side Pressure that is within about 105%, and even more preferably within about 103% of the high side pressure of the system using R404A. This parameter is important in such embodiments because it allows the use of existing pressure components.
- Discharge Temperature that is preferably lower than about 130°C, and even more preferably lower than about 125°C. The advantage of such a characteristic is that it permits the use of existing equipment without activation of the thermal protection aspects of the system, which are preferably designed to protect compressor components. This parameter is advantageous in that it avoids the use of costly controls such as liquid injection to reduce discharge temperature.
- Lower suction pressures are acceptable if they do not cause the system to go into sub-atmospheric pressure at low evaporation temperatures. This positive pressure is required to ensure that the system has always positive pressure, avoiding any contamination with humid air in case of leak. To evaluate this

requirement, one would employ a property called “Normal Boiling Temperature” (NBT: boiling temperature at atmospheric pressure) of the fluid in question. This NBT should be as close as possible to the one of the fluid replaced (R404A) and at least lower than the lowest evaporation temperature found in typical commercial systems (example: -40ºC).

The above-noted and other operating parameters are determined for the compositions A1 – A5 identified in Table A above in accordance with the present invention, and these operating parameters is reported in Table 4 below:

TABLE 4

Name	Discharge Pressure (%)	Discharge Temp. (ºC)	Suction Pressure (%)	Normal Boiling Temp. (ºC)
R404A	100%	91.9	100%	-46.2
A1	92%	90.8	84%	-44.9
A2	97%	88.4	92%	-46.1
A3	94%	91.1	87%	-45.3
A4	91%	92.4	83%	-44.8
A5	97%	89.9	91%	-45.9

In certain preferred embodiments, the replacement step is a drop-in replacement in the sense that no substantial redesign or modification of the system is required and no major item of equipment needs to be replaced in order to accommodate the refrigerant of the present invention. That is the case with the compositions A1 – A5, which in general can be used in most retrofit procedures without any change of major components. In all compositions A1 – A5, the discharge pressure and temperature is below the limit and the Normal Boiling Temperature is similar to R404A therefore they can be used in most existent refrigeration systems.

In certain preferred embodiments, the replacement step is a drop-in replacement in the sense that no substantial redesign or modification of the system is required and no major item of equipment needs to be replaced in order to accommodate the refrigerant of the present invention. That is the case with the compositions A1 – A5, which in general can be used in most retrofit procedures without any change of major

components. In all compositions A1 – A5, the discharge pressure and temperature is below the limit and the Normal Boiling Temperature is similar to R404A therefore they can be used in most existent refrigeration systems.

Although the invention has been described with reference to preferred embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt to a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiments disclosed, but that the invention will include all embodiments falling within the scope of the appended claims or any claims later added.

CLAIMS

What is claimed is:

1. A heat transfer composition comprising: (a) from about 10% to about 35% by weight of HFC-32; (b) from about 10% to about 35% by weight of HFC-125; (c) from greater than 0% to about 30% by weight of HFO-1234ze; (d) from about 10% to about 35% by weight of HFC-134a, with the weight percent being based on the total of the components (a) – (d) in the composition.

2. The heat transfer composition of claim 1 wherein said HFO-1234ze comprises trans-HFO-1234ze.

3. The heat transfer composition of claim 1 comprising from greater than 15% to about 30% by weight of HFC-32.

4. The heat transfer composition of claim 4 comprising from greater than 20% to about 30% by weight of HFC-125.

5. The heat transfer composition of claim 1 further comprising HFO-1234yf in an amount up to about 25% by weight.

6. The heat transfer composition of claim 5 comprising from about 5% to about 30% by weight of HFO-1234ze.

7. The heat transfer composition of claim 6 having a weight ratio of HFO-1234ze:HFO-1234yf of about 5:1 to about 0.1:1.

8. The heat transfer composition of claim 1 further comprising up to about 5% by weight of HFCO-1233ze.

9. A method of replacing an existing heat transfer fluid contained in heat transfer system comprising removing at least a portion of said existing heat transfer fluid from said system, said existing heat transfer fluid being HFC-404A and replacing at least a portion of said existing heat transfer fluid by introducing into said system a heat transfer composition comprising: (a) from about 10% to about 35%

by weight of HFC-32; (b) from about 10% to about 35% by weight of HFC-125; (c) from about 0% to about 30% by weight of HFO-1234yf and from greater than 0% to about 30% by weight of HFO-1234ze; (d) from about 10% to about 35% by weight of HFC-134a, with the weight percent being based on the total of the components (a) – (d) in the composition.

10. A heat transfer system comprising a compressor, a condenser and an evaporator in fluid communication, and a heat transfer composition in said system, said heat transfer composition comprising: (a) from about 10% to about 35% by weight of HFC-32; (b) from about 10% to about 35% by weight of HFC-125; (c) from about 0% to about 30% by weight of HFO-1234yf and from greater than 0% to about 30% by weight of HFO-1234ze; (d) from about 10% to about 35% by weight of HFC-134a, with the weight percent being based on the total of the components (a) – (d) in the composition, said condenser having an operating temperature of from about 35ºC to about 45ºC.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

C09K 5/04(2006.01)i, F25B 1/00(2006.01)i, F25B 27/00(2006.01)i

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)
C09K 5/04; C09K 5/00; F25B 23/00; F25D 11/00; C11D 17/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords:heat transfer composition, HFC-32, HFC-125, HFC-134a, HFO-1234ze

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010-129920 A1 (HONEYWELL INTERNATIONAL INC. et al.) 11 November 2010 See page 3; claims 1-3,6,7 and 9; and table A.	1-10
A	US 2010-0122545 A1 (MINOR, BARBARA HAVILAND et al.) 20 May 2010 See paragraphs 1-226; and claims 1-14.	1-10
A	US 2010-0038583 A1 (SHIMOMURA, YUJI et al.) 18 February 2010 See paragraphs 1-90; and claims 1-7.	1-10
A	US 2006-0019857 A1 (WILSON, DAVID P. et al.) 26 January 2006 See paragraphs 1-86; and claims 1-49.	1-10
A	US 2011-0162410 A1 (LOW, ROBERT E.) 07 July 2011 See paragraphs 1-29; and claims 1-66.	1-10

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

☒ See patent family annex.

* 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
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"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
31 May 2013 (31.05.2013)	**02 June 2013 (02.06.2013)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer HONG, Sung Ran Telephone No. 82-42-481-5405

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/025509

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010-129920 A1	11.11.2010	AU 2003-284352 A1	13.05.2004
		AU 2003-284352 A8	13.05.2004
		AU 2003-286685 A1	13.05.2004
		AU 2005-238537 A1	10.11.2005
		AU 2006-261816 A1	04.01.2007
		AU 2006-261816 B2	19.05.2011
		AU 2010-245671 A1	01.12.2011
		AU 2010-246160 A1	11.11.2010
		CA 2503421 A1	06.05.2004
		CA 2557873 A1	10.11.2005
		CA 2564897 A1	17.11.2005
		CA 2564897 C	27.11.2012
		CA 2564903 A1	17.11.2005
		CA 2564903 C	04.12.2012
		CA 2564991 A1	17.11.2005
		CA 2608327 A1	27.04.2008
		CA 2608675 A1	27.04.2008
		CA 2612986 A1	04.01.2007
		CA 2613090 A1	04.01.2007
		CA 2628463 A1	18.05.2007
		CA 2635917 A1	12.07.2007
		CA 2646990 A1	27.09.2007
		CA 2674256 A1	30.01.2010
		CA 2706774 A1	28.05.2009
		CA 2711861 A1	16.07.2009
		CA 2745762 A1	10.06.2010
		CA 2761418 A1	11.11.2010
		CA 2761478 A1	11.11.2010
		CA 2776375 A1	07.04.2011
		CA 2798620 A1	10.11.2011
		CN 101014680 A	08.08.2007
		CN 101177378 A	14.05.2008
		CN 101182280 A	21.05.2008
		CN 101248153 A	20.08.2008
		CN 101260021 A	10.09.2008
		CN 101283071 A0	08.10.2008
		CN 101351426 A	21.01.2009
		CN 101351427 A	21.01.2009
		CN 101351430 A	21.01.2009
		CN 101395108 A	25.03.2009
		CN 101448913 A	03.06.2009
		CN 101492342 A	29.07.2009
		CN 101495431 A	29.07.2009
		CN 101553453 A	07.10.2009
		CN 101653946 A	24.02.2010
		CN 101665405 A	10.03.2010
		CN 101665681 A	10.03.2010
		CN 101796155 A	04.08.2010
		CN 101925644 A	22.12.2010

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/025509

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		CN 102015050 A	13.04.2011
		CN 102112421 A	29.06.2011
		CN 102140329 A	03.08.2011
		CN 102264860 A	30.11.2011
		CN 102281932 A	14.12.2011
		CN 102307965 A	04.01.2012
		CN 102439108 A	02.05.2012
		CN 102596869 A	18.07.2012
		CN 1732243 A	08.02.2006
		CN 1852880 A	25.10.2006
		CN 1852880 B	15.06.2011
		CN 1898353 A	17.01.2007
		CN 1902152 A	24.01.2007
		CN 1902152 B	13.10.2010
		CN 1968915 A	23.05.2007
		CN 1968915 B	03.08.2011
		CN 1972887 A	30.05.2007
		CN 1972887 B	13.10.2010
		EP 1563032 A2	17.08.2005
		EP 1563032 B1	02.05.2012
		EP 1578883 A2	28.09.2005
		EP 1658252 A2	24.05.2006
		EP 1658252 B1	04.01.2012
		EP 1678106 A2	12.07.2006
		EP 1678106 B1	04.01.2012
		EP 1716216 A2	02.11.2006
		EP 1716216 B1	18.11.2009
		EP 1716216 B9	10.03.2010
		EP 1725628 A1	29.11.2006
		EP 1725628 B1	30.05.2012
		EP 1740518 A1	10.01.2007
		EP 1740520 A1	10.01.2007
		EP 1740521 A1	10.01.2007
		EP 1893714 A2	05.03.2008
		EP 1893715 A2	05.03.2008
		EP 1916231 A2	30.04.2008
		EP 1916231 A3	23.12.2009
		EP 1916232 A1	30.04.2008
		EP 1918269 A1	07.05.2008
		EP 1918269 B1	03.11.2010
		EP 1943202 A1	16.07.2008
		EP 1943203 A1	16.07.2008
		EP 1943203 B1	19.12.2012
		EP 1943204 A1	16.07.2008
		EP 1943204 B1	02.01.2013
		EP 1954663 A1	13.08.2008
		EP 1996668 A2	03.12.2008
		EP 2009075 A2	31.12.2008
		EP 2009075 A3	11.03.2009
		EP 2036943 A2	18.03.2009

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/025509

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		EP 2036943 A3	22.07.2009
		EP 2036943 B1	13.07.2011
		EP 2076478 A1	08.07.2009
		EP 2076478 B1	03.10.2012
		EP 2080748 A2	22.07.2009
		EP 2080748 A3	21.09.2011
		EP 2085422 A2	05.08.2009
		EP 2085422 A3	06.03.2013
		EP 2098581 A2	09.09.2009
		EP 2098581 A3	04.11.2009
		EP 2146945 A1	27.01.2010
		EP 2149543 A1	03.02.2010
		EP 2154223 A1	17.02.2010
		EP 2154223 B1	09.01.2013
		EP 2163591 A2	17.03.2010
		EP 2163591 A3	16.11.2011
		EP 2163592 A2	17.03.2010
		EP 2163592 A3	16.11.2011
		EP 2167602 A2	31.03.2010
		EP 2215152 A2	11.08.2010
		EP 2228421 A2	15.09.2010
		EP 2228421 A3	02.03.2011
		EP 2228421 B1	19.10.2011
		EP 2234685 A2	06.10.2010
		EP 2238213 A2	13.10.2010
		EP 2258404 A2	08.12.2010
		EP 2258755 A2	08.12.2010
		EP 2258784 A2	08.12.2010
		EP 2258802 A2	08.12.2010
		EP 2258802 A3	24.10.2012
		EP 2258819 A2	08.12.2010
		EP 2275509 A2	19.01.2011
		EP 2277602 A2	26.01.2011
		EP 2277942 A2	26.01.2011
		EP 2277943 A2	26.01.2011
		EP 2277968 A2	26.01.2011
		EP 2277969 A2	26.01.2011
		EP 2277969 A3	10.10.2012
		EP 2277970 A2	26.01.2011
		EP 2277971 A2	26.01.2011
		EP 2277972 A2	26.01.2011
		EP 2277974 A2	26.01.2011
		EP 2277975 A2	26.01.2011
		EP 2277976 A2	26.01.2011
		EP 2277977 A2	26.01.2011
		EP 2277983 A2	26.01.2011
		EP 2277984 A2	26.01.2011
		EP 2279670 A2	02.02.2011
		EP 2280049 A2	02.02.2011
		EP 2284143 A2	16.02.2011

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/025509

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		EP 2287282 A2	23.02.2011
		EP 2287282 A3	25.05.2011
		EP 2308942 A2	13.04.2011
		EP 2311904 A2	20.04.2011
		EP 2311923 A2	20.04.2011
		EP 2314652 A2	27.04.2011
		EP 2314653 A2	27.04.2011
		EP 2314654 A2	27.04.2011
		EP 2314655 A2	27.04.2011
		EP 2327593 A2	01.06.2011
		EP 2327754 A2	01.06.2011
		EP 2327755 A2	01.06.2011
		EP 2335740 A2	22.06.2011
		EP 2335782 A2	22.06.2011
		EP 2336102 A1	22.06.2011
		EP 2336264 A2	22.06.2011
		EP 2336265 A2	22.06.2011
		EP 2336287 A2	22.06.2011
		EP 2338866 A1	29.06.2011
		EP 2338932 A2	29.06.2011
		EP 2338945 A2	29.06.2011
		EP 2338946 A2	29.06.2011
		EP 2338959 A2	29.06.2011
		EP 2338967 A2	29.06.2011
		EP 2349519 A1	03.08.2011
		EP 2364340 A1	14.09.2011
		EP 2427527 A1	14.03.2012
		EP 2427528 A2	14.03.2012
		EP 2475632 A2	18.07.2012
		EP 2483362 A2	08.08.2012
		EP 2543655 A2	09.01.2013
		EP 2546220 A2	16.01.2013
		EP 2546221 A2	16.01.2013
		EP 2546222 A2	16.01.2013
		EP 2546223 A2	16.01.2013
		EP 2546224 A2	16.01.2013
		EP 2546225 A2	16.01.2013
		JP 2006-503961 A	02.02.2006
		JP 2006-512426 A	13.04.2006
		JP 2007-500127 A	11.01.2007
		JP 2007-509942 A	19.04.2007
		JP 2007-510039 A	19.04.2007
		JP 2007-535561 A	06.12.2007
		JP 2007-535570 A	06.12.2007
		JP 2007-535571 A	06.12.2007
		JP 2007-535611 A	06.12.2007
		JP 2008-110979 A	15.05.2008
		JP 2008-110980 A	15.05.2008
		JP 2008-162999 A	17.07.2008
		JP 2008-544072 A	04.12.2008

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/025509

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		JP 2008-546892 A	25.12.2008
		JP 2009-167187 A	30.07.2009
		JP 2009-514955 A	09.04.2009
		JP 2009-514956 A	09.04.2009
		JP 2009-514957 A	09.04.2009
		JP 2009-515876 A	16.04.2009
		JP 2009-522365 A	11.06.2009
		JP 2009-530489 A	27.08.2009
		JP 2010-037343 A	18.02.2010
		JP 2010-047754 A	04.03.2010
		JP 2010-215659 A	30.09.2010
		JP 2010-235950 A	21.10.2010
		JP 2010-265471 A	25.11.2010
		JP 2010-265472 A	25.11.2010
		JP 2010-508294 A	18.03.2010
		JP 2010-528043 A	19.08.2010
		JP 2011-190272 A	29.09.2011
		JP 2011-236226 A	24.11.2011
		JP 2011-236227 A	24.11.2011
		JP 2011-236228 A	24.11.2011
		JP 4571183 B2	20.08.2010
		JP 4699758 B2	15.06.2011
		JP 4864714 B2	18.11.2011
		JP 4864878 B2	01.02.2012
		JP 4864879 B2	18.11.2011
		JP 4864880 B2	01.02.2012
		JP 5118645 B2	26.10.2012
		JP 5143011 B2	30.11.2012
US 2010-0122545 A1	20.05.2010	AU 2009-316668 A1	27.05.2010
		CA 2741871 A1	27.05.2011
		CN 102215917 A	12.10.2011
		JP 2012-509390 A	19.04.2012
		KR 10-2011-0095896 A	25.08.2011
		WO 2010-059677 A2	27.05.2010
		WO 2010-059677 A3	15.07.2010
US 2010-0038583 A1	18.02.2010	AU 2008-220295 A1	04.09.2008
		AU 2008-220295 B2	16.06.2011
		CA 2678661 A1	04.09.2008
		CN 101548001 A	30.09.2009
		CN 101622332 A	06.01.2010
		EP 2119759 A1	18.11.2009
		EP 2128229 A1	02.12.2009
		JP 2009-074017 A	09.04.2009
		JP 2009-074018 A	09.04.2009
		KR 10-2009-0113817 A	02.11.2009
		KR 10-2009-0113821 A	02.11.2009
		MX 2009008933 A	28.08.2009
		RU 2009135830 A	10.04.2011

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/025509

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 2010-0038582 A1	18.02.2010
		WO 2008-105256 A1	04.09.2008
		WO 2008-105366 A1	04.09.2008
US 2006-0019857 A1	26.01.2006	AU 2005-236036 A1	03.11.2005
		AU 2005-236036 B2	02.10.2008
		AU 2005-236038 A1	03.11.2005
		AU 2005-236038 B2	02.10.2008
		AU 2005-236039 A1	03.11.2005
		AU 2005-236039 B2	21.08.2008
		BR PI0509947 A	25.09.2007
		BR PI0509948 A	25.09.2007
		CA 2564023 A1	03.11.2005
		CA 2564023 C	17.07.2012
		CN 101124288 A0	13.02.2008
		CN 101636466 A	27.01.2010
		CN 1965049 A	16.05.2007
		CN 1969027 A	23.05.2007
		CN 1969028 A	23.05.2007
		CN 1977023 A	06.06.2007
		EP 1735397 A1	27.12.2006
		EP 1735398 A1	27.12.2006
		EP 1735398 B1	27.06.2012
		EP 1735399 A1	27.12.2006
		EP 1735400 A1	27.12.2006
		EP 1735401 A1	27.12.2006
		EP 1737922 A2	03.01.2007
		EP 1737922 B1	10.12.2008
		EP 1920024 A1	14.05.2008
		EP 2017320 A1	21.01.2009
		EP 2272936 A1	12.01.2011
		EP 2292715 A1	09.03.2011
		EP 2292715 B1	22.08.2012
		EP 2336266 A1	22.06.2011
		EP 2336266 B1	22.08.2012
		ES 2318481 T3	01.05.2009
		JP 2007-532766 A	15.11.2007
		JP 2007-532767 A	15.11.2007
		JP 2008-504373 A	14.02.2008
		JP 2008-504374 A	14.02.2008
		JP 2008-505989 A	28.02.2008
		JP 2008-506793 A	06.03.2008
		JP 2012-067308 A	05.04.2012
		JP 2012-067309 A	05.04.2012
		JP 2012-067310 A	05.04.2012
		JP 5122944 B2	02.11.2012
		JP 5122945 B2	02.11.2012
		KR 10-1150177 B1	29.05.2012
		KR 10-1222878 B1	17.01.2013
		KR 10-2006-0134214 A	27.12.2006

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/025509

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		KR 10-2006-0134215 A	27.12.2006
		KR 10-2007-0002093 A	04.01.2007
		KR 10-2007-0004099 A	05.01.2007
		KR 10-2007-0007366 A	15.01.2007
		KR 10-2007-0007935 A	16.01.2007
		KR 10-2013-0018376 A	20.02.2013
		MX PA06011977 A	25.01.2007
		MX PA06011978 A	25.01.2007
		MX PA06011979 A	25.01.2007
		US 2005-0233923 A1	20.10.2005
		US 2005-0233931 A1	20.10.2005
		US 2005-0233932 A1	20.10.2005
		US 2005-0233933 A1	20.10.2005
		US 2005-0233934 A1	20.10.2005
		US 2006-0022166 A1	02.02.2006
		US 2006-0025322 A1	02.02.2006
		US 2006-0033071 A1	16.02.2006
		US 2006-0033072 A1	16.02.2006
		US 2006-0043330 A1	02.03.2006
		US 2006-0116310 A1	01.06.2006
		US 6969701 B2	29.11.2005
		US 7074751 B2	11.07.2006
		US 7098176 B2	29.08.2006
		US 7341984 B2	11.03.2008
		US 7413674 B2	19.08.2008
		US 7465698 B2	16.12.2008
		US 7479477 B2	20.01.2009
		US 7605117 B2	20.10.2009
		US 7622435 B2	24.11.2009
		WO 2005-103187 A1	03.11.2005
		WO 2005-103188 A1	03.11.2005
		WO 2005-103189 A1	03.11.2005
		WO 2005-103190 A1	03.11.2005
		WO 2005-103191 A2	03.11.2005
		WO 2005-103191 A3	22.02.2007
		WO 2005-103192 A1	03.11.2005
		WO 2006-112881 A1	26.10.2006
US 2011-0162410 A1	07.07.2011	AU 2009-323863 A1	10.06.2010
		AU 2009-323865 A1	10.06.2010
		AU 2009-323869 A1	10.06.2010
		AU 2010-238362 A1	21.10.2010
		CA 2745518 A1	10.06.2010
		CA 2745520 A1	10.06.2010
		CA 2745531 A1	10.06.2010
		CA 2758412 A1	21.10.2010
		CA 2768410 A1	25.08.2011
		CN 102191017 A	21.09.2011
		CN 102239228 A	09.11.2011
		CN 102245731 A	16.11.2011

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/025509

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		CN 102250586 A	23.11.2011
		CN 102272259 A	07.12.2011
		CN 102428129 A	25.04.2012
		EP 2367895 A1	28.09.2011
		EP 2367896 A1	28.09.2011
		EP 2367898 A1	28.09.2011
		EP 2440607 A1	18.04.2012
		EP 2440629 A1	18.04.2012
		GB 2457345 A	19.08.2009
		GB 2477835 A	17.08.2011
		GB 2480513 A	23.11.2011
		GB 2480517 A	23.11.2011
		JP 2011-168771 A	01.09.2011
		JP 2011-256361 A	22.12.2011
		JP 2012-510550 A	10.05.2012
		JP 2012-510551 A	10.05.2012
		JP 2012-510552 A	10.05.2012
		JP 2012-524137 A	11.10.2012
		JP 5021079 B2	22.06.2012
		KR 10-1229259 B1	04.02.2013
		KR 10-2011-0099253 A	07.09.2011
		KR 10-2011-0099701 A	08.09.2011
		KR 10-2011-0099702 A	08.09.2011
		KR 10-2011-0128124 A	28.11.2011
		KR 10-2012-0025472 A	15.03.2012
		KR 10-2012-0128585 A	27.11.2012
		US 2009-0158771 A1	25.06.2009
		US 2011-0173997 A1	21.07.2011
		US 2011-0184890 A1	28.07.2011
		US 2011-0191268 A1	04.08.2011
		US 2011-0258146 A1	20.10.2011
		US 2011-0258147 A1	20.10.2011
		US 2011-0260095 A1	27.10.2011
		US 2012-0126187 A1	24.05.2012
		US 7914696 B2	29.03.2011
		US 8333901 B2	18.12.2012
		WO 2009-047535 A2	16.04.2009
		WO 2009-047542 A1	16.04.2009
		WO 2010-064005 A1	10.06.2010
		WO 2010-064007 A1	10.06.2010
		WO 2010-064011 A1	10.06.2010
		WO 2010-119265 A1	21.10.2010
		WO 2011-101608 A1	25.08.2011
		WO 2011-144885 A1	24.11.2011
		WO 2011-144905 A2	24.11.2011
		WO 2011-144905 A3	08.03.2012
		WO 2011-144906 A2	24.11.2011
		WO 2011-144906 A3	01.03.2012
		WO 2011-144907 A2	24.11.2011
		WO 2011-144907 A3	08.03.2012

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/025509

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		WO 2011-144908 A2	24.11.2011
		WO 2011-144908 A3	01.03.2012
		WO 2011-144909 A2	24.11.2011
		WO 2011-144909 A3	01.03.2012