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(54) Title: STABILIZED HEAT TRANSFER COMPOSITIONS, METHODS AND SYSTEMS

(57) Abstract: The present invention relates to heat transfer compositions comprising refrigerant, lubricant and stabilizer, wherein the refrigerant comprises from about 10% by weight to 100% by weight of trifluoriodomethane (CF₃I), and wherein said lubricant comprises polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and wherein said stabilizer comprises an alkylated naphthalene and optionally but preferably an acid depleting moiety.



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STABILIZED HEAT TRANSFER COMPOSITIONS, METHODS AND SYSTEMS

Field of the Invention

5 The present invention relates to compositions, methods and systems having utility in heat exchange applications, including in air conditioning and refrigeration applications. In particular aspects the invention relates to compositions useful in heat transfer systems of the type in which the refrigerant R-410A would have been used. The compositions of the invention are useful in particular as a replacement of the refrigerant R-410A for heating and
10 cooling applications and to retrofitting heat exchange systems, including systems designed for use with R-410A.

Background

 Mechanical refrigeration systems, and related heat transfer devices, such as heat pumps and air conditioners are well known in the art for industrial, commercial and domestic
15 uses. Chlorofluorocarbons (CFCs) were developed in the 1930s as refrigerants for such systems. However, since the 1980s, the effect of CFCs on the stratospheric ozone layer has become the focus of much attention. In 1987, a number of governments signed the Montreal Protocol to protect the global environment, setting forth a timetable for phasing out the CFC products. CFCs were replaced with more environmentally acceptable materials
20 that contain hydrogen, namely the hydrochlorofluorocarbons (HCFCs).

 One of the most commonly used hydrochlorofluorocarbon refrigerants was chlorodifluoromethane (HCFC-22). However, subsequent amendments to the Montreal protocol accelerated the phase out of the CFCs and scheduled the phase-out of HCFCs, including HCFC-22.

25 In response to the need for a non-flammable, non-toxic alternative to the CFCs and HCFCs, industry has developed a number of hydrofluorocarbons (HFCs) which have zero ozone depletion potential. R-410A (a 50:50 w/w blend of difluoromethane (HFC-32) and pentafluoroethane (HFC-125)) was adopted as the industry replacement for HCFC-22 in air conditioning and chiller applications as it does not contribute to ozone depletion. However,
30 R-410A is not a drop-in replacement for R-22. Thus, the replacement of R-22 with R-410A required the redesign of major components within heat exchange systems, including the replacement and redesign of the compressor to accommodate the substantially higher operating pressure and volumetric capacity of R-410A, when compared with R-22.

 While R-410A has a more acceptable Ozone Depleting Potential (ODP) than R-22,
35 the continued use of R-410A is problematic since it has a high Global Warming Potential of

2088. There is therefore a need in the art for the replacement of R-410A with a more environmentally acceptable alternative.

The EU implemented the F-gas regulation to limit HFCs which can be placed on the market in the EU from 2015 onwards, as shown in Table 1. By 2030, only 21% of the quantity of HFCs that were sold in 2015 will be available. Therefore, it is desired to limit GWP below 427 as a long term solution.

Table 1: F-Gas Regulation

Year	Phasedown Percentage	GWP Level
2015	100%	2034*
2016 – 2017	93%	1891
2018 – 2020	63%	1281
2021 – 2023	67%	915
2024 – 2026	31%	630
2027 – 2029	24%	488
After 2030	21%	427

*2015 GWP level is based on UNEP 2012 Use Study with no growth rate.

It is understood in the art that it is highly desirable for a replacement heat transfer fluid to possess a difficult to achieve mosaic of properties including excellent heat transfer properties (and in particular heat transfer properties that are well matched to the needs of the particular application), chemical stability, low or no toxicity, non-flammability, lubricant miscibility and/or lubricant compatibility amongst others. In addition, any replacement for R-410A would ideally be a good match for the operating conditions of R-410A in order to avoid modification or redesign of the system. The development of a heat transfer fluid meeting all of these requirements, many of which are unpredictable, is a significant challenge.

With regard to efficiency in use, it is important to note that a loss of refrigerant thermodynamic performance or energy efficiency may result in an increase in fossil fuel usage as a result of the increased demand for electrical energy. The use of such a refrigerant will therefore have a negative secondary environmental impact.

Flammability is considered to be an important property for many heat transfer applications. As used herein, the term "non-flammable" refers to compounds or compositions which are determined to be non-flammable in accordance with ASTM standard E-681-2009 Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases) at conditions described in ASHRAE Standard 34-2016 Designation and Safety Classification of Refrigerants and described in Appendix B1 to ASHRAE Standard 34-2016, which is incorporated herein by reference and referred to herein for convenience as "Non-Flammability Test".

It is very important for maintenance of system efficiency and proper and reliable functioning of the compressor, that lubricant circulating in a vapour compression heat

transfer system is returned to the compressor to perform its intended lubricating function. Otherwise, lubricant might accumulate and become lodged in the coils and piping of the system, including in the heat transfer components. Furthermore, when lubricant accumulates on the inner surfaces of the evaporator, it lowers the heat exchange efficiency of the evaporator, and thereby reduces the efficiency of the system.

R-410A is currently commonly used with polyol ester (POE) lubricating oil in air conditioning applications, as R-410A is miscible with POE at temperatures experienced during use of such systems. However, R-410A is immiscible with POE at temperatures typically experienced during operation of low temperature refrigeration systems, and heat pump systems. Therefore, unless steps are taken to mitigate against this immiscibility, POE and R-410A cannot be used in low temperature refrigeration or heat pump systems.

Applicants have come to appreciate that it is desirable to be able to provide compositions which are capable of being used as a replacement for R-410A in air conditioning applications, and in particular in residential air conditioning and commercial air conditioning applications, which include, rooftop air conditioning, variable refrigerant flow (VRF) air conditioning and chiller air conditioning applications. Applicants have also come to appreciate that the compositions, methods and systems of the invention have advantage in, for example, heat pump and low temperature refrigeration systems, wherein the drawback of immiscibility with POE at temperatures experienced during operation of these systems is eliminated.

Summary

The present invention provides refrigerant compositions which can be used as a replacements for R-410A and which exhibit in preferred embodiments the desired mosaic of properties of excellent heat transfer properties, chemical stability, low or no toxicity, non-flammability, lubricant miscibility and lubricant compatibility in combination with low Global Warming Potential (GWP) and near zero ODP.

The present invention includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant comprising from about 5% by weight to 100% by weight of trifluoriodomethane (CF_3I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene, wherein said alkylated naphthalene is present in the composition in an amount of from 1% to less than 10% by weight by weight based on the weight of the alkylated naphthalene and the lubricant. The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 1**.

As used herein with respect to percentages based on a list of identified compounds, the term "relative percentage" means the percentage of the identified compound based on the total weight of the listed compounds.

As used herein with respect to weight percentages, the term "about" with respect to
5 an amount of an identified component means the amount of the identified component can vary by an amount of +/- 2% by weight.

In connection with the use of stabilizers comprising alkylated naphthalene in heat transfer compositions comprising CF₃I refrigerants and lubricant that comprises POE and/or PVE, applicants have found that a critical range exists in which the stabilizing effect of the
10 alkylated naphthalene is beneficially and unexpectedly enhanced relative to the stabilizing effect outside of the range of from 1% to less than 10% by weight based on the alkylated naphthalene and the lubricant, or preferably from 1.5% to less than 8%, or preferably from 1.5% to about 6%, or preferably from 1.5 to 5%. The reason for the enhanced performance within this critical range derives from the discovery that stabilizing performance
15 of the alkylated naphthalene can, in the absence of other solutions described hereinafter, be deteriorate to an undesirable extent for some applications when used in amounts above about 10%. Furthermore, applicants believe that the stabilizing performance of alkylated naphthalene also is less than desirable for some applications when used in amounts of less than 1%. The existence of this critical range is unexpected.

20 The present invention includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant comprising from about 10% by weight to about 75% by weight of trifluoroiodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene, wherein said alkylated naphthalene is present in the composition in an amount
25 of from 1% to less than 10% by weight based on the weight of the alkylated naphthalene and the lubricant. The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 2**.

The present invention includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant comprising from about 5% by weight to about 50%
30 by weight by weight difluoromethane (HFC-32) and from about 35% by weight to about 70% by weight of trifluoroiodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene, wherein said alkylated naphthalene is present in the composition in an amount of from 1% to less than 10% by weight based on the weight of the alkylated naphthalene

and the lubricant. The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 3**.

The present invention includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant consisting essentially of from about 30% by weight
5 to about 50% by weight by weight difluoromethane (HFC-32), from 3 to 15% by weight pentafluoroethane (HFC-125) and from about 35% by weight to about 70% by weight of trifluoriodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene, wherein said alkylated naphthalene is present in the composition in an amount of from 1%
10 to less than 10% by weight based on the weight of the alkylated naphthalene and the lubricant. The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 4**.

The present invention includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant comprising from about 5% by weight to 100% by
15 weight of trifluoriodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene, wherein said alkylated naphthalene is present in the composition in an amount of from 1% to 8% by weight by weight based on the weight of the alkylated naphthalene and the lubricant. The heat transfer composition according to this paragraph is sometimes referred
20 to herein for convenience as **Heat Transfer Composition 5**.

The present invention includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant comprising from about 10% by weight to about 75%
by weight of trifluoriodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated
25 naphthalene, wherein said alkylated naphthalene is present in the composition in an amount of from 1% to 8% by weight based on the weight of the alkylated naphthalene and the lubricant. The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 6**.

The present invention includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant comprising from about 5% by weight to about 50%
30 by weight by weight difluoromethane (HFC-32) and from about 35% by weight to about 70% by weight of trifluoriodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene, wherein said alkylated naphthalene is present in the composition in an amount
35 of from 1% to 8% by weight based on the weight of the alkylated naphthalene and the

lubricant. The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 7**.

The present invention includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant consisting essentially of from about 30% by weight
5 to about 50% by weight by weight difluoromethane (HFC-32), from 3 to 15% by weight pentafluoroethane (HFC-125) and from about 35% by weight to about 70% by weight of trifluoriodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene, wherein said alkylated naphthalene is present in the composition in an amount of from 1%
10 to 8% by weight based on the weight of the alkylated naphthalene and the lubricant. The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 8**.

The present invention includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant comprising from about 5% by weight to 100% by
15 weight of trifluoriodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene, wherein said alkylated naphthalene is present in the composition in an amount of from 1.5% to 8% by weight by weight based on the weight of the alkylated naphthalene and the lubricant. The heat transfer composition according to this paragraph is sometimes referred
20 to herein for convenience as **Heat Transfer Composition 9**.

The present invention includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant comprising from about 10% by weight to about 75%
by weight of trifluoriodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated
25 naphthalene, wherein said alkylated naphthalene is present in the composition in an amount of from 1.5% to 8% by weight based on the weight of the alkylated naphthalene and the lubricant. The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 10**.

The present invention includes heat transfer compositions comprising refrigerant,
30 lubricant and stabilizer, said refrigerant comprising from about 10% by weight to about 75% by weight of trifluoriodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene, wherein said alkylated naphthalene is present in the composition in an amount of from 1.5% to 6% by weight based on the weight of the alkylated naphthalene and the

lubricant. The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 11**.

The present invention includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant comprising from about 30% by weight to about 50%
5 by weight by weight difluoromethane (HFC-32) and from about 35% by weight to about 70% by weight of trifluoriodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene, wherein said alkylated naphthalene is present in the composition in an amount of from 1.5% to 6% by weight based on the weight of the alkylated naphthalene and the
10 lubricant. The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 12**.

The present invention includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant consisting essentially of from about 30% by weight to about 50% by weight by weight difluoromethane (HFC-32), from 3 to 15% by weight
15 pentafluoroethane (HFC-125) and from about 35% by weight to about 70% by weight of trifluoriodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene, wherein said alkylated naphthalene is present in the composition in an amount of from 1.5% to 6% by weight based on the weight of the alkylated naphthalene and the lubricant. The
20 heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 13**.

The present invention also includes any of Heat Transfer Compositions 1 – 13 wherein said stabilizer is essentially free of an ADM as defined hereinafter. The heat transfer composition according to this paragraph is sometimes referred to herein for
25 convenience as **Heat Transfer Composition 13A**.

The present invention also includes any of Heat Transfer Compositions 1 – 13 wherein said stabilizer is essentially free of an ADM as defined hereinafter and wherein said stabilizer further comprises BHT. The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 13B**.

30 The present invention also includes heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant comprising from about 5% by weight to 100% by weight of trifluoriodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene and an acid depleting moiety. The heat transfer composition according to this

paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 14**.

As used herein, the term “acid depleting moiety” (which is sometimes referred to herein for convenience as “ADM”) means a compound or radical which when present in a heat transfer composition comprising a refrigerant that contains about 10% by weight or greater of CF₃I (said percentage being based in the weight of all the refrigerants in the heat transfer composition), has the effect of substantially reducing the acid moieties that would otherwise be present in the heat transfer composition. As used herein, the term “substantially reducing” as used with respect to the acid moieties in the heat transfer composition means that acid moieties are reduced sufficiently to result in a reduction in TAN value (as defined hereinafter) of at least about 10 relative percent.

In connection with the use of stabilizers comprising alkylated naphthalene and an ADM, applicants have found that certain materials are able to substantially and unexpectedly enhance the performance of stabilizers which comprise or consist essentially of alkylated naphthalene stabilizer(s). In particular, applicants have found that certain materials are able to aid in the depletion of acidic moieties in heat transfer compositions containing CF₃I, including any heat transfer compositions of the present invention. Applicants have found that formulating heat transfer compositions to have an ADM provides an unexpected and synergistic enhancement to the stability function of at least the alkylated naphthalene stabilizers according to the present invention. The reason for this synergistic effect is not understood with certainty, but without being bound by or to any theory of operation, it is believed that the alkylated naphthalene stabilizers of the present invention function in large part by stabilizing free radicals formed from the CF₃I of the present refrigerants, but that this stabilizing effect is at least somewhat diminished in the presence of acid moieties. As a result, the presence of the ADM of the present invention allows the alkylated naphthalene stabilizers to perform with an unexpected and synergistically enhanced effect. Furthermore, applicants have found that the deterioration in performance which applicants have observed at relatively high concentrations of alkylated naphthalene (i.e., about about 10%) can be counteracted by the incorporation into the heat transfer composition (or into a stabilized lubricant) of an ADM. The present invention therefore includes stabilizer comprising an alkylated naphthalene and an ADM. The stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 1**.

The present invention also includes stabilizer comprising from about 40% by weight to about 99.9% of alkylated naphthalenes and from 0.05% to about 50% by weight of ADM

based on the weight of the stabilizer. The stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 2**.

The present invention also includes stabilizer comprising from about 50% by weight to about 99.9% of alkylated naphthalenes and from 0.1% to about 50% by weight of ADM
5 based on the weight of the stabilizer. The stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 3**.

The present invention also includes stabilizer comprising from about 40% by weight to about 95% of alkylated naphthalenes and from 5% to about 30% by weight of ADM based on the weight of the alkylated naphthalenes and ADM in the stabilizer. The stabilizer
10 according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 4**.

The present invention also includes stabilizer comprising from about 40% by weight to about 95% of alkylated naphthalenes and from 5% to about 20% by weight of ADM based on the weight of the alkylated naphthalenes and ADM in the stabilizer. The stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 5**.

15 The present invention also includes heat transfer compositions comprising refrigerant, lubricant comprising POE lubricant and/or polyvinyl ether (PVE) lubricant and Stabilizer 1, said refrigerant comprising from about 5% by weight to 100% by weight of trifluoroiodomethane (CF_3I). The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 15**.

20 The present invention also includes heat transfer compositions comprising refrigerant, lubricant comprising POE lubricant and/or polyvinyl ether (PVE) lubricant and Stabilizer 2, said refrigerant comprising from about 5% by weight to 100% by weight of trifluoroiodomethane (CF_3I). The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 16**.

25 The present invention also includes heat transfer compositions comprising refrigerant, lubricant comprising POE lubricant and/or polyvinyl ether (PVE) lubricant and Stabilizer 4, said refrigerant comprising from about 5% by weight to 100% by weight of trifluoroiodomethane (CF_3I). The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 17**.

30 The present invention also includes heat transfer compositions comprising refrigerant, lubricant comprising POE lubricant and/or polyvinyl ether (PVE) lubricant and Stabilizer 1, said refrigerant comprising from about 20% by weight to about 75% by weight of trifluoroiodomethane (CF_3I). The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 18**.

The present invention also includes heat transfer compositions comprising refrigerant, lubricant comprising POE lubricant and/or polyvinyl ether (PVE) lubricant and Stabilizer 2, said refrigerant comprising from about 20% by weight to about 75% by weight of trifluoriodomethane (CF_3I). The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 19**.

The present invention also includes heat transfer compositions comprising refrigerant, lubricant comprising POE lubricant and/or polyvinyl ether (PVE) lubricant and Stabilizer 4, said refrigerant comprising from about 20% by weight to about 75% by weight of trifluoriodomethane (CF_3I). The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 20**.

The present invention also includes heat transfer compositions comprising refrigerant, lubricant comprising POE lubricant and/or polyvinyl ether (PVE) lubricant and Stabilizer 1, said refrigerant comprising from about 5% by weight to about 50% by weight by weight difluoromethane (HFC-32) and from about 35% by weight to about 70% by weight of trifluoriodomethane (CF_3I). The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 21**.

The present invention also includes heat transfer compositions comprising refrigerant, lubricant comprising POE lubricant and/or polyvinyl ether (PVE) lubricant and Stabilizer 2, said refrigerant comprising from about 5% by weight to about 50% by weight by weight difluoromethane (HFC-32) and from about 35% by weight to about 70% by weight of trifluoriodomethane (CF_3I). The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 22**.

The present invention also includes heat transfer compositions comprising refrigerant, lubricant comprising POE lubricant and/or polyvinyl ether (PVE) lubricant and Stabilizer 4, said refrigerant comprising from about 5% by weight to about 50% by weight by weight difluoromethane (HFC-32) and from about 35% by weight to about 70% by weight of trifluoriodomethane (CF_3I). The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 23**.

refrigerant, lubricant comprising POE lubricant and/or polyvinyl ether (PVE) lubricant and Stabilizer 1, said refrigerant comprising from about 30% by weight to about 50% by weight by weight difluoromethane (HFC-32), from 3 to 15% by weight pentafluoroethane (HFC-125) and from about 35% by weight to about 70% by weight of trifluoriodomethane (CF_3I). The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 24**.

The present invention also includes heat transfer compositions comprising refrigerant, lubricant comprising POE lubricant and/or polyvinyl ether (PVE) lubricant and Stabilizer 2, said refrigerant comprising from about 30% by weight to about 50% by weight by weight difluoromethane (HFC-32), from 3 to 15% by weight pentafluoroethane (HFC-125) and from about 35% by weight to about 70% by weight of trifluoroiodomethane (CF₃I). The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 25**.

The present invention also includes heat transfer compositions comprising refrigerant, lubricant comprising POE lubricant and/or polyvinyl ether (PVE) lubricant and Stabilizer 3, said refrigerant comprising from about 30% by weight to about 50% by weight by weight difluoromethane (HFC-32), from 3 to 15% by weight pentafluoroethane (HFC-125) and from about 35% by weight to about 70% by weight of trifluoroiodomethane (CF₃I). The heat transfer composition according to this paragraph is sometimes referred to herein for convenience as **Heat Transfer Composition 26**.

The present invention also includes stabilized lubricants comprising: (a) POE lubricant and/or polyvinyl ether (PVE) lubricant; and (b) a stabilizer of the present invention, including each of Stabilizers 1 - 5.

Description

Definitions:

For the purposes of this invention, the term "about" in relation to temperatures in degrees centigrade (°C) means that the stated temperature can vary by an amount of +/- 5°C. In preferred embodiments, temperature specified as being about is preferably +/- 2°C, more preferably +/- 1°C, and even more preferably +/- 0.5°C of the identified temperature.

The term "capacity" is the amount of cooling provided, in BTUs/hr, by the refrigerant in the refrigeration system. This is experimentally determined by multiplying the change in enthalpy in BTU/lb, of the refrigerant as it passes through the evaporator by the mass flow rate of the refrigerant. The enthalpy can be determined from the measurement of the pressure and temperature of the refrigerant. The capacity of the refrigeration system relates to the ability to maintain an area to be cooled at a specific temperature. The capacity of a refrigerant represents the amount of cooling or heating that 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.

The phrase “coefficient of performance” (hereinafter “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
5 expresses the ratio of useful refrigeration or cooling capacity to the energy applied by the compressor in compressing the vapor and therefore expresses the capability of a given compressor to pump quantities of heat for a given volumetric flow rate of a heat transfer fluid, such as a refrigerant. In other words, given a specific compressor, a refrigerant with a higher COP will deliver more cooling or heating power. One means for estimating COP of a
10 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 which is incorporated herein by reference in its entirety).

The phrase “discharge temperature” refers to the temperature of the refrigerant at
15 the outlet of the compressor. The advantage of a low discharge temperature 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 and avoids the use of costly controls such as liquid injection to reduce discharge temperature.

The phrase “Global Warming Potential” (hereinafter “GWP”) was developed to allow
20 comparisons of the global warming impact of different gases. Specifically, it is a measure of how much energy the emission of one ton of a gas will absorb over a given period of time, relative to the emission of one ton of carbon dioxide. The larger the GWP, the more that a given gas warms the Earth compared to CO₂ over that time period. The time period usually used for GWP is 100 years. GWP provides a common measure, which allows analysts to
25 add up emission estimates of different gases. See www.epa.gov.

The phrase “Life Cycle Climate Performance” (hereinafter “LCCP”) is a method by which air conditioning and refrigeration systems can be evaluated for their global warming impact over the course of their lifetime. LCCP includes the direct impacts of refrigerant emissions and the indirect impacts of energy consumption used to operate the system,
30 energy to manufacture the system, and transport and safely dispose of the system. The direct impacts of refrigerant emissions are obtained from the refrigerant’s GWP value. For the indirect emissions, the measured refrigerant properties are used to obtain the system performance and energy consumption. LCCP is determined by using Equations 1 and 2 as follows. Equation 1 is Direct Emissions = Refrigerant Charge (kg) x (Annual Loss Rate x
35 Lifetime + End-of-Life Loss) x GWP. Equation 2 is Indirect Emissions = Annual Power

Consumption x Lifetime x CO₂ per kW-hr of electrical production. The Direct Emissions as determined by Equation 1 and the Indirect Emissions as determined by Equation 2 are added together to provide the LCCP. TMY2 and TMY3 data produced by the National Renewable Laboratory and available in BinMaker® Pro Version 4 Software is used for the analysis. The GWP values reported in the Intergovernmental Panel on Climate Change (IPCC)'s Assessment Report 4 (AR4) 2007 are used for the calculations. LCCP is expressed as carbon dioxide mass (kg-CO_{2eq}) over the lifetime of the air conditioning or refrigeration systems.

The term "mass flow rate" is the mass of refrigerant passing through a conduit per unit of time.

The term "Occupational Exposure Limit (OEL)" is determined in accordance with ASHRAE Standard 34-2016 Designation and Safety Classification of Refrigerants.

As the term is used herein, "replacement for" with respect to a particular heat transfer composition or refrigerant of the present invention as a "replacement for" a particular prior refrigerant means the use of the indicated composition of the present invention in a heat transfer system that heretofore had been commonly used with that prior refrigerant. By way of example, when a refrigerant or heat transfer composition of the present invention is used in a heat transfer system that has heretofore been designed for and/or commonly used with R410A, such as residential air conditioning and commercial air conditioning (including roof top systems, variable refrigerant flow (VRF) systems and chiller systems) then the present refrigerant is a replacement for R410A in such systems. The phrase "thermodynamic glide" applies to zeotropic refrigerant mixtures that have varying temperatures during phase change processes in the evaporator or condenser at constant pressure.

The phrase "thermodynamic glide" applies to zeotropic refrigerant mixtures that have varying temperatures during phase change processes in the evaporator or condenser at constant pressure.

As the term is used herein, "TAN value" refers to the total acid number as determined in accordance with ASHRAE Standard 97 - "Sealed Glass Tube Method to Test the Chemical Stability of Materials for Use within Refrigerant Systems" to simulate long-term stability of the heat transfer compositions by accelerated aging.

Heat Transfer Compositions

Applicants have found that the heat transfer compositions of the present invention, including each of Heat Transfer Compositions 1 – 26 as described herein, are capable of providing exceptionally advantageous properties and in particular stability in use and non-

flammability, especially with the use of the heat transfer compositions as a replacement for R-410A and especially in prior 410A residential air conditioning systems, and prior R-410A commercial air conditioning systems (including prior R-410A roof top systems, prior R-410A variable refrigerant flow (VRF) systems and prior R-410A chiller systems).

5 As used herein, the reference Heat Transfer Compositions 1 – 26 refers to each of Heat Transfer Compositions 1 through 26, including Heat Transfer Compositions 13A and 13B.

A particular advantage of the refrigerants included in the heat transfer compositions of the present invention is that they are non-flammable when tested in accordance with the
10 Non-Flammability Test, and as mentioned above there has been a desire in the art to provide refrigerants and heat transfer compositions which can be used as a replacement for R-410A in various systems, and which has excellent heat transfer properties, low environmental impact (including particularly low GWP and near zero ODP), excellent chemical stability, low or no toxicity, and/or lubricant compatibility and which maintains non-
15 flammability in use. This desirable advantage can be achieved by refrigerants and heat transfer compositions of the present invention.

Preferably, the heat transfer compositions of the present invention, including each of Heat Transfer Compositions 1 – 26, include refrigerant in an amount of greater than 40% by weight, or greater than 70% by weight, or greater than 80% by weight, or greater than 90%
20 of the heat transfer composition.

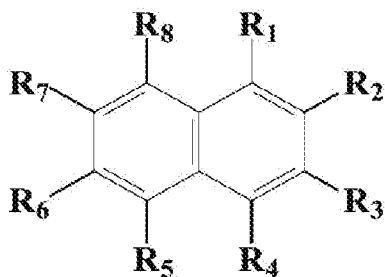
Preferably, the heat transfer compositions of the present invention, including each of Heat Transfer Compositions 1 – 26, consist essentially of the refrigerant, the lubricant and stabilizer.

The heat transfer compositions of the invention may include other components for
25 the purpose of enhancing or providing certain functionality to the compositions, preferably without negating the enhanced stability provided in accordance with present invention. Such other components or additives may include, dyes, solubilizing agents, compatibilizers, auxiliary stabilizers, antioxidants, corrosion inhibitors, extreme pressure additives and anti-wear additives.

30 **Stabilizers:**

Alkylated Naphthalenes

Applicants have surprisingly and unexpectedly found that alkylated naphthalenes are highly effective as stabilizers for the heat transfer compositions of the present invention. As used herein, the term “alkylated naphthalene” refers to compounds having the following
35 structure:



where each $R_1 - R_8$ is independently selected from linear alkyl group, a branched alkyl group and hydrogen. The particular length of the alkyl chains and the mixtures or branched and straight chains and hydrogens can vary within the scope of the present invention, and it will be appreciated and understood by those skilled in the art that such variation is reflected the physical properties of the alkylated naphthalene, including in particular the viscosity of the alkylated compound, and producers of such materials frequently define the materials by reference to one or more of such properties as an alternative the specification of the particular R groups.

Applicants have found unexpected, surprising and advantageous results are associated the use of alkylated naphthalene as a stabilizer according to the present invention having the following properties, and alkylated naphthalene compounds having the indicated properties are referred to for convenience herein as Alkylated Naphthalene 1 (or AN1) – Alkylated Naphthalene 5 (or AN5) as indicated respectively in rows 1 – 5 in the Table below:

ALKYLATED NAPHTHALENE TABLE 1

Property	AN1	AN2	AN3	AN4	AN5
Viscosity @ 40°C (ASTM D467), cSt	20 – 200	20 – 100	20 – 50	30 - 40	about 36
Viscosity @ 100°C (ASTM D467), cSt	3 – 20	3 – 10	3 – 8	5 - 7	about 5.6
Pour Point (ASTM D97), °C	-50 to -20	-67 to -25	-40 to -30	-67 to -30	about -33

As used herein in connection with viscosity at 40°C measured according to ASTM D467, the term “about” means +/- 4 cSt.

As used herein in connection with viscosity at 100°C measured according to ASTM D467, the term “about” means +/- 0.4 cSt.

As used herein in connection with pour point as measured according to ASTM D97, the term “about” means +/- 5°C.

- Applicants have also found that unexpected, surprising and advantageous results are associated the use of alkylated naphthalene as a stabilizer according to the present invention having the following properties, and alkylated naphthalene compounds having the indicated properties are referred to for convenience herein as Alkylated Naphthalene 6 (or AN6) – Alkylated Naphthalene 10 (or AN10) as indicated respectively in rows 6 – 10 in the Table below:

ALKYLATED NAPHTHALENE TABLE 2

Property	AN6	AN7	AN 8	AN 9	AN10
Viscosity @ 40°C (ASTM D467), cSt	20 – 200	20 – 100	20 – 50	30 – 40	about 36
Viscosity @ 100°C (ASTM D467), cSt	3 – 20	3 – 10	3 – 8	5 – 7	about 5.6
Aniline Point (ASTM D611), °C	40 – 110	50 – 90	50 – 80	60 - 70	about 36
NoackVolatility CEC L40 (ASTM D6375), wt%	1 – 50	5 – 30	5 – 15	10 - 15	about 12
Pour Point (ASTM D97), °C	-50 to -20	-67 to - 25	-40 to - 30	-67 to - 30	about -33
Flash Point (ASTM D92)), °C	200 – 300	200 – 270	220 – 250	230 - 240	about 236

10

Examples of alkylated naphthalenes within the meaning of Alkylated Naphthalene 1 and Alkylated Naphthalene 6 include those sold by King Industries under the trade designations NA-LUBE KR-007A; KR- 008; KR-009; KR-015; KR-019; KR-005FG; KR-015FG; and KR-029FG.

15

Examples of alkylated naphthalenes within the meaning of Alkylated Naphthalene 2 and Alkylated Naphthalene 7 include those sold by King Industries under the trade designations NA-LUBE KR-007A; KR- 008; KR-009; and KR-005FG.

An example of an alkylated naphthylene that is within the meaning of Alkylated Naphthalene 5 and Alkylated Naphthalene 10 includes the product sold by King Industries

under the trade designation NA-LUBE KR-008.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, wherein the alkylated naphthalene is AN1.

5 The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, wherein the alkylated naphthalene is AN2.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, wherein the alkylated naphthalene is AN3

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, wherein the alkylated naphthalene is AN4.

10 The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, wherein the alkylated naphthalene is AN5.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, wherein the alkylated naphthalene is AN6.

15 The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, wherein the alkylated naphthalene is AN7.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, wherein the alkylated naphthalene is AN8.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, wherein the alkylated naphthalene is AN9.

20 The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, wherein the alkylated naphthalene is AN10.

Acid Depleting Moieties (ADM)

Those skilled in the art will be able to determine, without undo experimentation, a variety of ADMs that are useful in accordance with the present invention, and all such ADMs
25 are within the scope hereof.

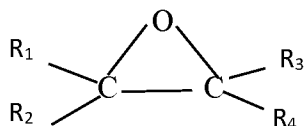
Epoxides

Applicants have found that epoxides, and particularly alkylated epoxides, are effective at producing the enhanced stability discussed herein when used in combination with alkylated naphthalene stabilizers, and while applicants are not necessarily bound by theory
30 it is believed that this synergistic enhancement stems at least in part due to its effective functioning as an ADM in the heat transfer compositions of the present invention.

In preferred embodiments the epoxide is selected from the group consisting of epoxides that undergo ring-opening reactions with acids, thereby depleting the system of acid while not otherwise deleteriously affecting the system.

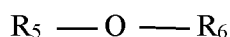
35 Useful epoxides include aromatic epoxides, alkyl epoxides, and alkenyl epoxides.

Preferred epoxides include epoxides of the following Formula I:



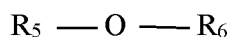
where at least one of said $R_1 - R_4$ is selected from a two to fifteen carbon (C2 – C15) acyclic group, a C2 – C15 aliphatic group and a C2 – C15 ethers. An epoxide according to Formula 1 is sometimes referred to herein for convenience as **ADM1**.

In a preferred embodiment, at least one of $R_1 - R_4$ of Formula I is an ether having the following structure:



where each of R_5 and R_6 is independently a C1 – C14 straight chain or branched chain, preferably unsubstituted, alkyl group. An epoxide according to the paragraph is sometimes referred to herein for convenience as **ADM2**.

In a preferred embodiment, one of $R_1 - R_4$ of Formula I is an ether having the following structure:



where each of R_5 and R_6 is independently a C1 – C14 straight chain or branched chain, preferably unsubstituted, alkyl group, and the remaining three of $R_1 - R_4$ are H. An epoxide according to the paragraph is sometimes referred to herein for convenience as **ADM3**.

In preferred embodiments the epoxide comprises, consists essentially of or consists of 2-ethylhexyl glycidyl ether. An epoxide according to this paragraph is sometimes referred to herein for convenience as **ADM4**.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 13 and 14 - 26, wherein the composition comprises AN1 and ADM1.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 13 and 14 - 26, wherein the composition comprises AN5 and ADM1.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 13 and 14 - 26, wherein the composition comprises AN10 and ADM1.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 13 and 14 - 26, wherein the composition comprises AN1 and

ADM4.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 13 and 14 - 26, wherein the composition comprises AN5 and ADM4.

5 The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 13 and 14 - 26, wherein the composition comprises AN10 and ADM4.

10 The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 13 and 14 – 26 hereof, comprising each of AN2 or AN3 or AN4 or AN6 or AN7 or AN8 or AN 9 and ADM1.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 13 and 14 – 26 hereof, comprising each of AN2 or AN3 or AN4 or AN5 or AN6 or AN7 or AN8 or AN 9 or AN10 and ADM2.

15 The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 13 and 14 – 26 hereof, comprising each of AN2 or AN3 or AN4 or AN5 or AN6 or AN7 or AN8 or AN 9 or AN10 and ADM3.

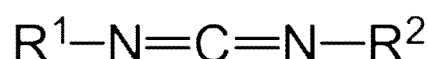
The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 13 and 14 – 26 hereof, comprising each of AN2 or AN3 or AN4 or AN6 or AN7 or AN8 or AN 9 and ADM4.

20 When the ADM is present in the Heat Transfer Compositions of the present invention, including each of Heat Transfer Compositions 1 – 13 and 14 - 26, the alkylated naphthalene is preferably present in an amount of from 0.01% to about 10%, or from about 1.5% to about 4.5%, or from about 2.5% to about 3.5%, where amounts are in percent by weight based on the amount of alkylated naphthalene plus refrigerant in the system.

25 When the ADM is present in the Heat Transfer Compositions of the present invention, including each of Heat Transfer Compositions 1 – 13 and 14 - 26, the alkylated naphthalene is preferably present in an amount of from 0.1% to about 20%, or from 1,5% to about 10%, or from 1,5% to about 8%, where amounts are in percent by weight based on the amount of alkylated naphthalene plus lubricant in the system.

30 **Carbodiimides**

The ADM can include carbodiimides. In preferred embodiments the carbodiimides include compounds having the following structure:



Other Stabilizers

It is contemplated that stabilizers other than the alkylated naphthalenes and ADM may be included in the heat transfer compositions of the present invention, including each of Heat Transfer Compositions 1 – 26. Examples of such other stabilizers are described hereinafter.

Phenol-based Compounds

In preferred embodiments, the stabilizer further includes a phenol based compound.

The phenol-based compound can be one or more compounds selected from 4,4'-methylenebis(2,6-di-tert-butylphenol); 4,4'-bis(2,6-di-tert-butylphenol); 2,2- or 4,4-biphenyldiols, including 4,4'-bis(2-methyl-6-tert-butylphenol); derivatives of 2,2- or 4,4-biphenyldiols; 2,2'-methylenebis(4-ethyl-6-tert-butylphenol); 2,2'-methylenebis(4-methyl-6-tert-butylphenol); 4,4-butylenedibis(3-methyl-6-tert-butylphenol); 4,4-isopropylidenebis(2,6-di-tert-butylphenol); 2,2'-methylenebis(4-methyl-6-nonylphenol); 2,2'-isobutylenedibis(4,6-dimethylphenol); 2,2'-methylenebis(4-methyl-6-cyclohexylphenol); 2,6-di-tert-butyl-4-methylphenol (BHT); 2,6-di-tert-butyl-4-ethylphenol; 2,4-dimethyl-6-tert-butylphenol; 2,6-di-tert-alpha-dimethylamino-p-cresol; 2,6-di-tert-butyl-4(N,N'-dimethylaminomethylphenol); 4,4'-thiobis(2-methyl-6-tert-butylphenol); 4,4'-thiobis(3-methyl-6-tert-butylphenol); 2,2'-thiobis(4-methyl-6-tert-butylphenol); bis(3-methyl-4-hydroxy-5-tert-butylbenzyl) sulfide; bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, tocopherol, hydroquinone, 2,2',6,6'-tetra-tert-butyl-4,4'-methylenediphenol and t-butyl hydroquinone, and preferably BHT.

The phenol compounds, and in particular BHT, can be provided in the heat transfer composition in an amount of greater than 0 and preferably from 0.0001% by weight to about 5% by weight, preferably 0.001% by weight to about 2.5% by weight, and more preferably from 0.01% to about 1% by weight. In each case, percentage by weight refers to the weight of the heat transfer composition.

The phenol compounds, and in particular BHT, can be provided in the heat transfer composition in an amount of greater than 0 and preferably from 0.0001% by weight to about 5% by weight, preferably 0.001% by weight to about 2.5% by weight, and more preferably from 0.01% to about 1% by weight. In each case, percentage by weight refers to the weight based on the weight of the lubricant in the heat transfer composition.

The present invention also includes stabilizer comprising from about 40% to about 95% by weight of alkylated naphthalenes, including each of AN1 – AN10, and from 0.1 to about 10% by weight of BHT, based on the weight of the all the stabilizer components in the composition. The stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 6**.

The present invention also includes stabilizer comprising from about 40% to about 95% by weight of alkylated naphthalenes, including each of AN1 – AN10, from 5% to about 30% by weight of ADM, including each of ADM1 – ADM4, and from 0.1 to about 10% by weight of BHT, based on the weight of the all the stabilizer components in the composition.

5 The stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 7**.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, wherein the heat transfer composition comprises Stabilizer 6. The present invention includes heat transfer compositions, including each of
10 Heat Transfer Compositions 1 – 13 and 14 – 26 hereof, wherein the heat transfer compositions comprises Stabilizer 7.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, comprising AN1 and BHT. The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26
15 hereof, comprising AN5 and BHT.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 26 hereof, comprising AN10 and BHT.

The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 13 and 14 - 26 hereof, comprising AN5, ADM4 and BHT.

20 The present invention includes heat transfer compositions, including each of Heat Transfer Compositions 1 – 13 and 14 - 26 hereof, comprising AN10, ADM4 and BHT.

Diene-based Compounds

The diene-based compounds include C3 to C15 dienes and to compounds formed by reaction of any two or more C3 to C4 dienes. Preferably, the diene based compounds
25 are selected from the group consisting of allyl ethers, propadiene, butadiene, isoprene, and terpenes. The diene-based compounds are preferably terpenes, which include but are not limited to terebene, retinal, geraniol, terpinene, delta-3 carene, terpinolene, phellandrene, fenchene, myrcene, farnesene, pinene, nerol, citral, camphor, menthol, limonene, nerolidol, phytol, carnosic acid, and vitamin A1. Preferably, the stabilizer is farnesene. Preferred
30 terpene stabilizers are disclosed in US Provisional Patent Application No. 60/638,003 filed on December 12, 2004, published as US 2006/0167044A1, which is incorporated herein by reference.

In addition, the diene based compounds can be provided in the heat transfer composition in an amount greater than 0 and preferably from 0.0001% by weight to about
35 5% by weight, preferably 0.001% by weight to about 2.5% by weight, and more preferably

from 0.01% to about 1% by weight. In each case, percentage by weight refers to the weight of the heat transfer composition.

Phosphorus-based Compounds

The phosphorus compound can be a phosphite or a phosphate compound. For the purposes of this invention, the phosphite compound can be a diaryl, dialkyl, triaryl and/or trialkyl phosphite, and/or a mixed aryl/alkyl di- or tri-substituted phosphite, in particular one or more compounds selected from hindered phosphites, tris-(di-tert-butylphenyl)phosphite, di-n-octyl phosphite, iso-octyl diphenyl phosphite, iso-decyl diphenyl phosphite, tri-iso-decyl phosphate, triphenyl phosphite and diphenyl phosphite, particularly diphenyl phosphite.

The phosphate compounds can be a triaryl phosphate, trialkyl phosphate, alkyl mono acid phosphate, aryl diacid phosphate, amine phosphate, preferably triaryl phosphate and/or a trialkyl phosphate, particularly tri-n-butyl phosphate.

The phosphorus compounds can be provided in the heat transfer composition in an amount of greater than 0 and preferably from 0.0001% by weight to about 5% by weight, preferably 0.001% by weight to about 2.5% by weight, and more preferably from 0.01% to about 1% by weight. In each case, by weight refers to weight of the heat transfer composition.

Nitrogen Compounds

When the stabilizer is a nitrogen compound, the stabilizer may comprise an amine based compound such as one or more secondary or tertiary amines selected from diphenylamine, p-phenylenediamine, triethylamine, tributylamine, diisopropylamine, triisopropylamine and triisobutylamine. The amine based compound can be an amine antioxidant such as a substituted piperidine compound, i.e. a derivative of an alkyl substituted piperidyl, piperidinyl, piperazinone, or alkyoxypiperidinyl, particularly one or more amine antioxidants selected from 2,2,6,6-tetramethyl-4-piperidone, 2,2,6,6-tetramethyl-4-piperidinol; bis-(1,2,2,6,6-pentamethylpiperidyl)sebacate; di(2,2,6,6-tetramethyl-4-piperidyl)sebacate, poly(N-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidyl succinate; alkylated paraphenylenediamines such as N-phenyl-N'-(1,3-dimethyl-butyl)-p-phenylenediamine or N,N'-di-sec-butyl-p-phenylenediamine and hydroxylamines such as tallow amines, methyl bis tallow amine and bis tallow amine, or phenol-alpha-naphthylamine or Tinuvin®765 (Ciba), BLS®1944 (Mayzo Inc) and BLS® 1770 (Mayzo Inc). For the purposes of this invention, the amine based compound also can be an alkyldiphenyl amine such as bis (nonylphenyl amine), dialkylamine such as (N-(1-methylethyl)-2-propylamine, or one or more of phenyl-alpha-naphthyl amine (PANA), alkyl-phenyl-alpha-naphthyl-amine (APANA), and bis (nonylphenyl) amine. Preferably the amine

based compound is one or more of phenyl-alpha-naphthyl amine (PANA), alkyl-phenyl-alpha-naphthyl-amine (APANA) and bis (nonylphenyl) amine, and more preferably phenyl-alpha-naphthyl amine (PANA).

Alternatively, or in addition to the nitrogen compounds identified above, one or more
5 compounds selected from dinitrobenzene, nitrobenzene, nitromethane, nitrosobenzene, and TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] may be used as the stabilizer.

The nitrogen compounds can be provided in the heat transfer composition in an amount of greater than 0 and from 0.0001% by weight to about 5% by weight, preferably 0.001% by weight to about 2.5% by weight, and more preferably from 0.01% to about 1% by weight. In
10 each case, percentage by weight refers to the weight of the heat transfer composition.

Isobutylene

Isobutylene may also be used as a stabilizer according to the present invention.

Additional Stabilizer Compositions

The present invention also provides a stabilizer consisting essentially of alkylated
15 naphthalene, including each of AN1 – AN10 and an ADM, including each of ADM1 – ADM4 and a phenol. A stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 8**.

The present invention also provides a stabilizer consisting of alkylated naphthalene, including each of AN1 – AN10 and an ADM, including each of ADM1 – ADM4 and a
20 phosphate. A stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 9**.

The present invention also provides stabilizer comprising alkylated naphthalene, including each of AN1 – AN10 and an ADM, including each of ADM1 – ADM4 and a combination of a phosphate and a phenol. A stabilizer according to this paragraph is
25 sometimes referred to herein for convenience as **Stabilizer 10**.

The present invention also provides a stabilizer comprising alkylated naphthalene, including each of AN1 – AN10, in an amount of from about 40% by weight to about 95% by weight, an ADM, including each of ADM1 – ADM4, in an amount of from about 0.5% by weight to about 25% by weight, and an additional stabilizer selected from a phosphate, a
30 phenol and combinations of these in an amount of from about 0.1% by weight to about 50% by weight, wherein said weight percentages are based on the total weight of the stabilizer. A stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 11**.

The present invention also provides a stabilizer comprising alkylated naphthalene,
35 including each of AN1 – AN10, in an amount of from about 70% by weight to about 95% by

weight, an ADM, including each of ADM1 – ADM4, in an amount of from about 0.5% by weight to about 15% by weight, and an additional stabilizer selected from a phosphate, a phenol and combinations of these in an amount of from about 0.1% by weight to about 25% by weight, wherein said weight percentages are based on the total weight of the stabilizer.

5 A stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 12**.

The present invention also provides a stabilizer consisting essentially of alkylated naphthalene, including each of AN1 – AN10 and an ADM, including each of ADM1 – ADM4 and BHT. A stabilizer according to this paragraph is sometimes referred to herein for
10 convenience as **Stabilizer 13**.

The present invention also provides a stabilizer consisting of alkylated naphthalene, including each of AN1 – AN10 and an ADM, including each of ADM1 – ADM4 and BHT. A stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 14**.

15 The present invention also provides a stabilizer consisting essentially of alkylated naphthalene, including each of AN1 – AN10 and an ADM, including each of ADM1 – ADM4, BHT and a phosphate. A stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 15**.

The present invention also provides a stabilizer consisting of alkylated naphthalene, including each of AN1 – AN10 and an ADM, including each of ADM1 – ADM4, BHT and a
20 phosphate. A stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 16**.

The present invention also provides a stabilizer comprising alkylated naphthalene, including each of AN1 – AN10, in an amount of from about 40% by weight to about 95% by
25 weight, an ADM, including each of ADM1 – ADM4, in an amount of from about 0.5% by weight to about 10% by weight, and BHT, in an amount of from about 0.1% by weight to about 50% by weight, wherein said weight percentages are based on the total weight of the stabilizer. A stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 17**.

30 The present invention also provides a stabilizer comprising alkylated naphthalene, including each of AN1 – AN10, in an amount of from about 70% by weight to about 95% by weight, an ADM, including each of ADM1 – ADM4, in an amount of from about 0.5% by weight to about 10% by weight, and BHT, in an amount of from about 0.1% by weight to about 25% by weight, wherein said weight percentages are based on the total weight of the
35 stabilizer. A stabilizer according to this paragraph is sometimes referred to herein for

convenience as **Stabilizer 18**.

The present invention also provides a stabilizer comprising alkylated naphthalene, including each of AN1 – AN10, in an amount of from about 40% by weight to about 95% by weight, an ADM, including each of ADM1 – ADM4, in an amount of from about 5% by weight to about 25% by weight, and a third stabilizer compound selected from BHT, a phosphate and combinations of these in an amount of from 1% by weight to about 55% by weight, wherein said weight percentages are based on the total weight of the stabilizer. A stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 19**.

The present invention also provides a stabilizer comprising alkylated naphthalene, including each of AN1 – AN10, in an amount of from about 40% by weight to about 95% by weight, an ADM, including each of ADM1 – ADM4, in an amount of from about 5% by weight to about 25% by weight, and BHT, in an amount of from about 0.1% by weight to about 5% by weight, wherein said weight percentages are based on the total weight of the stabilizer. A stabilizer according to this paragraph is sometimes referred to herein for convenience as **Stabilizer 20**.

The stabilizers of the present invention, including each of Stabilizers 1 – 20, can be used in any of the heat transfer compositions of the present invention, including any of Heat Transfer compositions 1 - 13 and 14 -26.

The stabilizers of the present invention, including each of Stabilizers 1 – 6, can also be used in any of Heat Transfer compositions 13A and 13B.

LUBRICANTS

In general, the heat transfer composition of the present invention, including each of Heat Transfer Compositions 1 – 26, comprises a POE lubricant and/or a PVE lubricant wherein the lubricant is present in amounts preferably of from about 0.1% by weight to about 5%, or from 0.1% by weight to about 1% by weight, or from 0.1% by weight to about 0.5% by weight, based on the weight of the heat transfer composition.

POE Lubricants

The POE lubricant of the present invention includes in preferred embodiments a neopentyl POE lubricant. As used herein, the term neopentyl POE lubricant refers to polyol esters (POEs) derived from a reaction between a neopentyl polyol (preferably pentaerythritol, trimethylolpropane, or neopentyl glycol, and in embodiments where higher viscosities are preferred, dipentaerythritol) and a linear or branched carboxylic acid.

Commercially available POEs include neopentyl glycol dipelargonate which is available as Emery 2917 (registered trademark) and Hatcol 2370 (registered trademark) and

pentaerythritol derivatives including those sold under the trade designations Emkarate RL32-3MAF and Emkarate RL68H by CPI Fluid Engineering. Emkarate RL32-3MAF and Emkarate RL68H are preferred neopentyl POE lubricants having the properties identified below:

Property	RL32-3MAF	RL68H
Viscosity @ 40°C (ASTM D467), cSt	about 31	about 67
Viscosity @ 100°C (ASTM D467), cSt	about 5.6	about 9.4
Pour Point (ASTM D97), °C	about -40	about -40

5

Other useful esters include phosphate esters, di-basic acid esters and fluoro esters.

A lubricant consisting essentially of a POE having a viscosity at 40°C measured in accordance with ASTM D445 of from about 30 cSt to about 70 cSt and a viscosity Measured @ 100°C in accordance with ASTM D445 of from about 5 cSt to about 10 cSt is referred to herein as **Lubricant 1**.

10

A lubricant consisting essentially of a neopentyl POE having a viscosity at 40°C measured in accordance with ASTM D467 of from about 30 cSt to about 70 cSt is referred to for convenience as **Lubricant 2**.

15

In preferred embodiments, the present Heat Transfer Compositions, including each of Heat Transfer Compositions 1 – 26, comprise a POE lubricant.

In preferred embodiments, the present Heat Transfer Compositions, including each of Heat Transfer Compositions 1 – 26, comprise lubricant consisting essentially of a POE lubricant.

20

In preferred embodiments, the present Heat Transfer Compositions, including each of Heat Transfer Compositions 1 – 26, comprise lubricant consisting of a POE lubricant.

A preferred heat transfer composition comprises Heat Transfer Composition 1 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 2 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

25

A preferred heat transfer composition comprises Heat Transfer Composition 3 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 4 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 5 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 6 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

5 A preferred heat transfer composition comprises Heat Transfer Composition 7 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 8 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

10 A preferred heat transfer composition comprises Heat Transfer Composition 9 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 10 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 11 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

15 A preferred heat transfer composition comprises Heat Transfer Composition 12 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 13 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

20 A preferred heat transfer composition comprises Heat Transfer Composition 13A wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 13B wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 14 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

25 A preferred heat transfer composition comprises Heat Transfer Composition 15 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 16 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

30 A preferred heat transfer composition comprises Heat Transfer Composition 17 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 18 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 19 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 20 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 21 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

5 A preferred heat transfer composition comprises Heat Transfer Composition 22 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 23 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

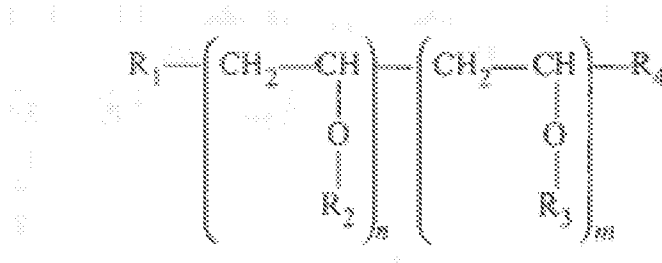
10 A preferred heat transfer composition comprises Heat Transfer Composition 24 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 25 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

A preferred heat transfer composition comprises Heat Transfer Composition 26 wherein the lubricant is Lubricant 1 and/or Lubricant 2.

15 **PVE Lubricants**

The lubricant of the present invention can include PVE lubricants generally. In preferred embodiments the PVE lubricant is as PVE according to Formula II below:



Formula II

20 where R_2 and R_3 are each independently C1 – C10 hydrocarbons, preferably C2 - C8 hydrocarbons, and R_1 and R_4 are each independently alkyl, alkylene glycol, or polyoxyalkylene glycol units and n and m are selected preferably according to the needs of those skilled in the art to obtain a lubricant with the desired properties, and preferable n and m are selected to obtain a lubricant with a viscosity at 40°C measured in accordance with
 25 ASTM D467 of from about 30 to about 70 cSt. A PVE lubricant according to the description immediately above is referred to for convenience as **Lubricant 3**. Commercially available polyvinyl ethers include those lubricants sold under the trade designations FVC32D and FVC68D, from Idemitsu.

30 In preferred embodiments, the present Heat Transfer Compositions, including each of Heat Transfer Compositions 1 – 26, comprise a PVE lubricant.

In preferred embodiments, the present Heat Transfer Compositions, including each of Heat Transfer Compositions 1 – 26, comprise lubricant consist essentially of a PVE lubricant.

5 In preferred embodiments, the present Heat Transfer Compositions, including each of Heat Transfer Compositions 1 – 26, comprise lubricant consisting of a PVE lubricant.

In preferred embodiments, the PVE in the present Heat Transfer Compositions, including each of Heat Transfer Compositions 1 – 26, is a PVE according to Formula II.

10 In preferred embodiments, the present Heat Transfer Compositions, including each of Heat Transfer Compositions 1 – 26, comprise lubricant consist essentially of Lubricant 3.

STABILIZED LUBRICANTS

The present invention also provides stabilized lubricants comprising: (a) POE lubricant; and (b) a stabilizer of the present invention, including each of Stabilizers 1 - 20.
15 The stabilized lubricant according to this paragraph is sometimes referred to herein for convenience as **Stabilized Lubricant 1**.

The present invention also provides stabilized lubricants comprising: (a) neo pentyl POE lubricant; and (b) a stabilizer of the present invention, including each of Stabilizers 1 - 20. The stabilized lubricant according to this paragraph is sometimes referred to herein for
20 convenience as **Stabilized Lubricant 2**.

The present invention also provides stabilized lubricants comprising: (a) Lubricant 1 or Lubricant 2; and (b) a stabilizer of the present invention, including each of Stabilizers 1 - 20. The stabilized lubricant according to this paragraph is sometimes referred to herein for convenience as **Stabilized Lubricant 3**.

25 The present invention also provides stabilized lubricants comprising: (a) Lubricant 3; and (b) a stabilizer of the present invention, including each of Stabilizers 1 - 20. The stabilized lubricant according to this paragraph is sometimes referred to herein for convenience as **Stabilized Lubricant 4**.

The present invention also includes stabilized lubricants comprising: (a) POE lubricant and/or polyvinyl ether (PVE) lubricant; and (b) Stabilizer 1. The stabilized lubricant according to this paragraph is sometimes referred to herein for convenience as **Stabilized Lubricant 5**.

The present invention also includes stabilized lubricants comprising: (a) POE lubricant and/or polyvinyl ether (PVE) lubricant; and (b) Stabilizer 2. The stabilized lubricant

according to this paragraph is sometimes referred to herein for convenience as **Stabilized Lubricant 6**.

The present invention also includes stabilized lubricants comprising: (a) POE lubricant and/or polyvinyl ether (PVE) lubricant; and (b) Stabilizer 3. The stabilized lubricant according to this paragraph is sometimes referred to herein for convenience as **Stabilized Lubricant 7**.

The present invention also includes stabilized lubricants comprising: (a) POE lubricant and/or polyvinyl ether (PVE) lubricant; and (b) Stabilizer 4. The stabilized lubricant according to this paragraph is sometimes referred to herein for convenience as **Stabilized Lubricant 8**.

The present invention also includes stabilized lubricants comprising: (a) POE lubricant and/or polyvinyl ether (PVE) lubricant; and (b) Stabilizer 5. The stabilized lubricant according to this paragraph is sometimes referred to herein for convenience as **Stabilized Lubricant 9**.

The present invention also includes stabilized lubricants comprising: (a) POE lubricant and/or a PVE lubricant; and (b) from 1% to less than 10% by weight of alkylated naphthalene based on the weight of the lubricant and alkylated naphthalene. The stabilized lubricant according to this paragraph is sometimes referred to herein for convenience as **Stabilized Lubricant 10**.

The present invention also includes stabilized lubricants comprising: (a) POE lubricant and/or a PVE lubricant; and (b) from 1% to 8% by weight of alkylated naphthalene based on the weight of the lubricant and alkylated naphthalene. The stabilized lubricant according to this paragraph is sometimes referred to herein for convenience as **Stabilized Lubricant 11**.

The present invention also includes stabilized lubricants comprising: (a) POE lubricant and/or a PVE lubricant; and (b) from 1.5% to 8% by weight of alkylated naphthalene based on the weight of the lubricant and alkylated naphthalene. The stabilized lubricant according to this paragraph is sometimes referred to herein for convenience as **Stabilized Lubricant 12**.

The present invention also includes stabilized lubricants comprising: (a) POE lubricant and/or a PVE lubricant; and (b) from 1.5% to 6% by weight of alkylated naphthalene based on the weight of the lubricant and alkylated naphthalene. The stabilized lubricant according to this paragraph is sometimes referred to herein for convenience as **Stabilized Lubricant 13**.

The present invention includes heat transfer compositions of the invention, including each of Heat Transfer Compositions 1 – 26, in which the lubricant and stabilizer are a stabilized lubricant of the present invention, including each of Stabilized Lubricants 1 – 13.

Methods, Uses and Systems

5 The heat transfer compositions disclosed herein are provided for use in heat transfer applications, including air conditioning applications, with highly preferred air conditioning applications including residential air conditioning, commercial air conditioning applications (such as roof top applications, VRF applications and chillers).

10 The present invention also includes methods for providing heat transfer including methods of air conditioning, with highly preferred air conditioning methods including providing residential air conditioning, providing commercial air conditioning (such as methods of providing roof top air conditioning, methods of providing VRF air conditioning and methods of providing air conditioning using chillers).

15 The present invention also includes heat transfer systems, including air conditioning systems, with highly preferred air conditioning systems including residential air conditioning, commercial air conditioning systems (such as roof top air conditioning systems, VRF air conditioning systems and air conditioning chiller systems).

20 The invention also provides uses of the heat transfer compositions, methods using the heat transfer compositions and systems containing the heat transfer compositions in connection with refrigeration, heat pumps and chillers (including portable water chillers and central water chillers).

25 Any reference to the heat transfer composition of the invention refers to each and any of the heat transfer compositions as described herein. Thus, for the following discussion of the uses, methods, systems or applications of the composition of the invention, the heat transfer composition may comprise or consist essentially of any of Heat Transfer Compositions 1 – 26.

30 For heat transfer systems of the present invention that include a compressor and lubricant for the compressor in the system, the system can comprises a loading of refrigerant and lubricant such that the lubricant loading in the system is from about 5% to 60% by weight, or from about 10% to about 60% by weight, or from about 20% to about 50% by weight, or from about 20% to about 40% by weight, or from about 20% to about 30% by weight, or from about 30% to about 50% by weight, or from about 30% to about 40% by weight. As used herein, the term “lubricant loading” refers to the total weight of lubricant contained in the system as a percentage of total of lubricant and refrigerant
35 contained in the system. Such systems may also include a lubricant loading of from about

5% to about 10% by weight, or about 8 % by weight of the heat transfer composition.

The heat transfer systems according to the present invention can comprise a compressor, an evaporator, a condenser and an expansion device, in fluid communication with each other, a Heat Transfer Compositions 1 - 26 and a sequestration material in the system, wherein said sequestration material preferably comprises: i. copper or a copper alloy, or ii. activated alumina, or iii. a zeolite molecular sieve comprising copper, silver, lead or a combination thereof, or iv. an anion exchange resin, or v. a moisture-removing material, preferably a moisture-removing molecular sieve, or vi. a combination of two or more of the above.

The present invention also includes methods for transferring heat of the type comprising evaporating refrigerant liquid to produce a refrigerant vapor, compressing in a compressor at least a portion of the refrigerant vapor and condensing refrigerant vapor in a plurality of repeating cycles, said method comprising:

(a) providing a heat transfer composition according to the present invention, including each of Heat Transfer Compositions 1 - 26;

(b) optionally but preferably providing lubricant for said compressor; and

(b) exposing at least a portion of said refrigerant and/or at least a portion of said lubricant to a sequestration material.

Uses, Equipment and Systems

In preferred embodiments, residential air conditioning systems and methods have refrigerant evaporating temperatures in the range of from about 0°C to about 10°C and the condensing temperature is in the range of about 40°C to about 70°C.

In preferred embodiments, residential air conditioning systems and methods used in a heating mode have refrigerant evaporating temperatures in the range of from about -20°C to about 3°C and the condensing temperature is in the range of about 35°C to about 50°C.

In preferred embodiments, commercial air conditioning systems and methods have refrigerant evaporating temperatures in the range of from about 0°C to about 10°C and the condensing temperature is in the range of about 40°C to about 70°C.

In preferred embodiments, hydronic system systems and methods have refrigerant evaporating temperatures in the range of from about -20°C to about 3°C and the condensing temperature is in the range of about 50°C to about 90°C.

In preferred embodiments, medium temperature systems and methods have refrigerant evaporating temperatures in the range of from about -12°C to about 0°C and the condensing temperature is in the range of about 40°C to about 70°C.

5 In preferred embodiments, low temperature systems and methods have refrigerant evaporating temperatures in the range of from about -40°C to about -12°C and the condensing temperature is in the range of about 40°C to about 70°C

In preferred embodiments, rooftop air conditioning systems and methods have refrigerant evaporating temperatures in the range of from about 0°C to about 10°C and the condensing temperature is in the range of about 40°C to about 70°C.

10 In preferred embodiments, VRF systems and methods have refrigerant evaporating temperatures in the range of from about 0°C to about 10°C and the condensing temperature is in the range of about 40°C to about 70°C.

The present invention includes the use of Heat Transfer Composition 1, in a residential air conditioning system.

15 The present invention therefore includes the use of Heat Transfer Composition 2, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 3, in a residential air conditioning system.

20 The present invention therefore includes the use of Heat Transfer Composition 4, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 5, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 6, in a residential air conditioning system.

25 The present invention therefore includes the use of Heat Transfer Composition 7, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 8, in a residential air conditioning system.

30 The present invention therefore includes the use of Heat Transfer Composition 9, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 10, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 11, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 12, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 13, in a residential air conditioning system.

5 The present invention therefore includes the use of Heat Transfer Composition 13A, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 13B, in a residential air conditioning system.

10 The present invention therefore includes the use of Heat Transfer Composition 14, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 15, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 16, in a residential air conditioning system.

15 The present invention therefore includes the use of Heat Transfer Composition 17, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 18, in a residential air conditioning system.

20 The present invention therefore includes the use of Heat Transfer Composition 19, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 20, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 21, in a residential air conditioning system.

25 The present invention therefore includes the use of Heat Transfer Composition 22, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 23, in a residential air conditioning system.

30 The present invention therefore includes the use of Heat Transfer Composition 24, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 25, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 26, in a residential air conditioning system.

The present invention therefore includes the use of Heat Transfer Composition 1, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 2, in a chiller system.

5 The present invention therefore includes the use of Heat Transfer Composition 3, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 4, in a chiller system.

10 The present invention therefore includes the use of Heat Transfer Composition 5, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 6, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 7, in a chiller system.

15 The present invention therefore includes the use of Heat Transfer Composition 8, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 9, in a chiller system.

20 The present invention therefore includes the use of Heat Transfer Composition 10, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 11, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 12, in a chiller system.

25 The present invention therefore includes the use of Heat Transfer Composition 13, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 13A, in a chiller system.

30 The present invention therefore includes the use of Heat Transfer Composition 13B, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 14, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 15, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 16, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 17, in a chiller system.

5 The present invention therefore includes the use of Heat Transfer Composition 18, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 19, in a chiller system.

10 The present invention therefore includes the use of Heat Transfer Composition 20, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 21, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 22, in a chiller system.

15 The present invention therefore includes the use of Heat Transfer Composition 23, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 24, in a chiller system.

20 The present invention therefore includes the use of Heat Transfer Composition 25, in a chiller system.

The present invention therefore includes the use of Heat Transfer Composition 26, in a chiller system.

25 Examples of commonly used compressors, for the purposes of this invention include reciprocating, rotary (including rolling piston and rotary vane), scroll, screw, and centrifugal compressors. Thus, the present invention provides each and any of the refrigerants and/or heat transfer compositions as described herein for use in a heat transfer system comprising a reciprocating, rotary (including rolling piston and rotary vane), scroll, screw, or centrifugal compressor.

30 Examples of commonly used expansion devices, for the purposes of this invention include a capillary tube, a fixed orifice, a thermal expansion valve and an electronic expansion valve. Thus, the present invention provides each and any of the refrigerants and/or heat transfer compositions as described herein for use in a heat transfer system comprising a capillary tube, a fixed orifice, a thermal expansion valve or an electronic expansion valve.

For the purposes of this invention, the evaporator and the condenser can each be in the form a heat exchanger, preferably selected from a finned tube heat exchanger, a microchannel heat exchanger, a shell and tube, a plate heat exchanger, and a tube-in-tube heat exchanger. Thus, the present invention provides each and any of the refrigerants and/or heat transfer compositions as described herein for use in a heat transfer system wherein the evaporator and condenser together form a finned tube heat exchanger, a microchannel heat exchanger, a shell and tube, a plate heat exchanger, or a tube-in-tube heat exchanger.

The systems of the present invention thus preferably include a sequestration material in contact with at least a portion of a refrigerant and/or at least a portion of a the lubricant according to the present invention wherein the temperature of said sequestration material and/or the temperature of said refrigerant and/or the temperature of said lubricant when in said contact are at a temperature that is preferably at least about 10C wherein the sequestration material preferably comprises a combination of: an anion exchange resin, activated alumina, a zeolite molecular sieve comprising silver, and a moisture-removing material, preferably a moisture-removing molecular sieve.

As used in this application, the term "in contact with at least a portion" is intended in its broad sense to include each of said sequestration materials and any combination of sequestration materials being in contact with the same or separate portions of the refrigerant and/or the lubricant in the system and is intended to include but not necessarily limited to embodiments in which each type or specific sequestration material is: (i) located physically together with each other type or specific material, if present; (ii) is located physically separate from each other type or specific material, if present, and (iii) combinations in which two or more materials are physically together and at least one sequestration material is physically separate from at least one other sequestration material.

The heat transfer composition of the invention can be used in heating and cooling applications.

In a particular feature of the invention, the heat transfer composition can be used in a method of cooling comprising condensing a heat transfer composition and

subsequently evaporating said composition in the vicinity of an article or body to be cooled.

Thus, the invention relates to a method of cooling in a heat transfer system comprising an evaporator, a condenser and a compressor, the process comprising i) condensing a heat transfer composition as described herein; and
5 ii) evaporating the composition in the vicinity of body or article to be cooled; wherein the evaporator temperature of the heat transfer system is in the range of from about -40°C to about $+10^{\circ}\text{C}$.

Alternatively, or in addition, the heat transfer composition can be used in a
10 method of heating comprising condensing the heat transfer composition in the vicinity of an article or body to be heated and subsequently evaporating said composition.

Thus, the invention relates to a method of heating in a heat transfer system comprising an evaporator, a condenser and a compressor, the process comprising
15 i) condensing a heat transfer composition as described herein, in the vicinity of a body or article to be heated and
ii) evaporating the composition; wherein the evaporator temperature of the heat transfer system is in the range of about -30°C to about 5°C .

The heat transfer composition of the invention is provided for use in air
20 conditioning applications including both transport and stationary air conditioning applications. Thus, any of the heat transfer compositions described herein can be used in any one of:

- an air conditioning application including mobile air conditioning, particularly in trains and buses conditioning,
- 25 - a mobile heat pump, particularly an electric vehicle heat pump;
- a chiller, particularly a positive displacement chiller, more particularly an air cooled or water cooled direct expansion chiller, which is either modular or conventionally singularly packaged,
- a residential air conditioning system, particularly a ducted split or a ductless
30 split air conditioning system,
- a residential heat pump,
- a residential air to water heat pump/hydronic system,

- an industrial air conditioning system
- a commercial air conditioning system, particularly a packaged rooftop unit and a variable refrigerant flow (VRF) system;
- a commercial air source, water source or ground source heat pump system.

5 The heat transfer composition of the invention is provided for use in a refrigeration system. The term “refrigeration system” refers to any system or apparatus or any part or portion of such a system or apparatus which employs a refrigerant to provide cooling. Thus, any of the heat transfer compositions described herein can be used in any one of:

- 10 - a low temperature refrigeration system,
- a medium temperature refrigeration system,
- a commercial refrigerator,
- a commercial freezer,
- an ice machine,
- 15 - a vending machine,
- a transport refrigeration system,
- a domestic freezer,
- a domestic refrigerator,
- an industrial freezer,
- 20 - an industrial refrigerator and
- a chiller.

Each of the heat transfer compositions described herein, including Heat Transfer Compositions 1 – 26, is particularly provided for use in a residential air-conditioning system (with an evaporator temperature in the range of about 0 to
25 about 10°C, particularly about 7°C for cooling and/or in the range of about -20 to about 3°C, particularly about 0.5°C for heating). Alternatively, or additionally, each of the heat transfer compositions described herein, including each of Heat Transfer Compositions 1 – 26, is particularly provided for use in a residential air conditioning system with a reciprocating, rotary (rolling-piston or rotary vane) or scroll
30 compressor.

Each of the heat transfer compositions described, including Heat Transfer Compositions 1 – 26, is particularly provided for use in an air cooled chiller (with an

evaporator temperature in the range of about 0 to about 10°C, particularly about 4.5°C), particularly an air cooled chiller with a positive displacement compressor, more particular an air cooled chiller with a reciprocating scroll compressor.

Each of the heat transfer compositions described herein, including Heat Transfer Compositions 1 – 26, is particularly provided for use in a residential air to water heat pump hydronic system (with an evaporator temperature in the range of about -20 to about 3°C, particularly about 0.5°C or with an evaporator temperature in the range of about -30 to about 5°C, particularly about 0.5°C).

Each of the heat transfer compositions described herein, including Heat Transfer Compositions 1 – 26, is particularly provided for use in a medium temperature refrigeration system (with an evaporator temperature in the range of about -12 to about 0°C, particularly about -8°C).

Each of the heat transfer compositions described herein, including Heat Transfer Compositions 1 – 26, is particularly provided for use in a low temperature refrigeration system (with an evaporator temperature in the range of about -40 °C to about -12°C, particularly about from about -40°C to about -23°C or preferably about -32°C).

The heat transfer composition of the invention, including Heat Transfer Compositions 1 – 26, is provided for use in a residential air conditioning system, wherein the residential air-conditioning system is used to supply cool air (said air having a temperature of for example, about 10°C to about 17°C, particularly about 12°C) to buildings for example, in the summer.

The heat transfer composition of the invention, including Heat Transfer Compositions 1 – 26, is thus provided for use in a split residential air conditioning system, wherein the residential air-conditioning system is used to supply cool air (said air having a temperature of for example, about 10°C to about 17°C, particularly about 12°C).

The heat transfer composition of the invention, including Heat Transfer Compositions 1 – 26, is thus provided for use in a ducted split residential air conditioning system, wherein the residential air-conditioning system is used to supply cool air (said air having a temperature of for example, about 10°C to about 17°C, particularly about 12°C).

The heat transfer composition of the invention, including Heat Transfer Compositions 1 – 26, is thus provided for use in a window residential air conditioning system, wherein the residential air-conditioning system is used to supply cool air (said air having a temperature of for example, about 10°C to about 17°C, particularly about 12°C).

The heat transfer composition of the invention, including Heat Transfer Compositions 1 – 26, is thus provided for use in a portable residential air conditioning system, wherein the residential air-conditioning system is used to supply cool air (said air having a temperature of for example, about 10°C to about 17°C, particularly about 12°C).

The residential air conditions systems as described herein, including in the immediately preceeding paragraphs, preferably have an air-to-refrigerant evaporator (indoor coil), a compressor, an air-to-refrigerant condenser (outdoor coil), and an expansion valve. The evaporator and condenser can be round tube plate fin, a finned tube or microchannel heat exchanger. The compressor can be a reciprocating or rotary (rolling-piston or rotary vane) or scroll compressor. The expansion valve can be a capillary tube, thermal or electronic expansion valve. The refrigerant evaporating temperature is preferably in the range of 0 °C to 10°C. The condensing temperature is preferably in the range of 40 °C to 70 °C.

The heat transfer composition of the invention, including Heat Transfer Compositions 1 – 26, is provided for use in a residential heat pump system, wherein the residential heat pump system is used to supply warm air (said air having a temperature of for example, about 18°C to about 24°C, particularly about 21°C) to buildings in the winter. It can be the same system as the residential air-conditioning system, while in the heat pump mode the refrigerant flow is reversed and the indoor coil becomes condenser and the outdoor coil becomes evaporator. Typical system types are split and mini-split heat pump system. The evaporator and condenser are usually a round tube plate fin, a finned or microchannel heat exchanger. The compressor is usually a reciprocating or rotary (rolling-piston or rotary vane) or scroll compressor. The expansion valve is usually a thermal or electronic expansion valve. The refrigerant evaporating temperature is preferably in the range of about -20 °C to

about 3°C or about -30 °C to about 5°C. The condensing temperature is preferably in the range of about 35 °C to about 50 °C.

The heat transfer composition of the invention, including Heat Transfer Compositions 1 – 26, is provided for use in a commercial air-conditioning system wherein the commercial air conditioning system can be a chiller which is used to supply chilled water (said water having a temperature of for example about 7°C) to large buildings such as offices and hospitals, etc. Depending on the application, the chiller system may be running all year long. The chiller system may be air-cooled or water-cooled. The air-cooled chiller usually has a plate, tube-in-tube or shell-and-tube evaporator to supply chilled water, a reciprocating or scroll compressor, a round tube plate fin, a finned tube or microchannel condenser to exchange heat with ambient air, and a thermal or electronic expansion valve. The water-cooled system usually has a shell-and-tube evaporator to supply chilled water, a reciprocating, scroll, screw or centrifugal compressor, a shell-and-tube condenser to exchange heat with water from cooling tower or lake, sea and other natural recourses, and a thermal or electronic expansion valve. The refrigerant evaporating temperature is preferably in the range of about 0 °C to about 10°C. The condensing temperature is preferably in the range of about 40 °C to about 70 °C.

The heat transfer composition of the invention, including Heat Transfer Compositions 1 – 26, is provided for use in a residential air-to-water heat pump hydronic system, wherein the residential air-to-water heat pump hydronic system is used to supply hot water (said water having a temperature of for example about 50°C or about 55°C) to buildings for floor heating or similar applications in the winter. The hydronic system usually has a round tube plate fin, a finned tube or microchannel evaporator to exchange heat with ambient air, a reciprocating, scroll or rotary compressor, a plate, tube-in-tube or shell-in-tube condenser to heat the water, and a thermal or electronic expansion valve. The refrigerant evaporating temperature is preferably in the range of about -20 to about 3°C, or -30 to about 5°C. The condensing temperature is preferably in the range of about 50 °C to about 90 °C.

The heat transfer composition of the invention, including Heat Transfer Compositions 1 – 26, is provided for use in a medium temperature refrigeration

system, wherein the refrigerant has an evaporating temperature preferably in the range of about -12 °C to about 0°C, and in such systems the refrigerant has a condensing temperature preferably in the range of about 40 °C to about 70 °C, or about 20 °C to about 70 °C.

5 The present invention thus provides a medium temperature refrigeration system used to chill food or beverages, such as in a refrigerator or a bottle cooler, wherein the refrigerant has an evaporating temperature preferably in the range of about -12 °C to about 0°C, and in such systems the refrigerant has a condensing temperature preferably in the range of about 40 °C to about 70 °C, or about 20 °C to
10 about 70 °C.

 The medium temperature systems of the present invention, including the systems as described in the immediately preceding paragraphs, preferably have an air-to-refrigerant evaporator to provide chilling, for example to the food or beverage contained therein, a reciprocating, scroll or screw or rotary compressor, an air-to-
15 refrigerant condenser to exchange heat with the ambient air, and a thermal or electronic expansion valve. The heat transfer composition of the invention, including Heat Transfer Compositions 1 – 26, is provided for use in a low temperature refrigeration system, wherein the refrigerant has an evaporating temperature that is preferably in the range of about -40 °C to about -12°C and the refrigerant has a
20 condensing temperature that is preferably in the range of about 40 °C to about 70 °C, or about 20 °C to about 70 °C.

 The present invention thus provides a low temperature refrigeration system used to provide cooling in a freezer wherein the refrigerant has an evaporating temperature that is preferably in the range of about -40 °C to about -12°C and the
25 refrigerant has a condensing temperature that is preferably in the range of about 40 °C to about 70 °C, or about 20 to about 70 °C.

 The present invention thus also provides a low temperature refrigeration system used to provide cooling in an ice cream machine wherein the refrigerant has an evaporating temperature that is preferably in the range of about -40 °C to about -12°C and the
30 refrigerant has a condensing temperature that is preferably in the range of about 40 °C to about 70 °C, or about 20 °C to about 70 °C.

The low temperature systems of the present invention, including the systems as described in the immediately preceeding paragraphs, preferably have an air-to-refrigerant evaporator to chill the food or beverage, a reciprocating, scroll or rotary compressor, an air-to-refrigerant condenser to exchange heat with the ambient air, and a thermal or electronic expansion valve.

The present invention therefore provides the use in a chiller of a heat transfer composition of the present invention, including each of Heat Transfer Compositions 1 - 26 wherein said alkylated naphthalene is AN5 wherein said heat transfer composition further comprises BHT, wherein the AN 5 is present in an amount of from about 0.001% by weight to about 5% by weight based on the weight of the lubricant and the BHT is present in an amount of from about 0.001% by weight to about 5 % by weight based on the weight of the lubricant .

The present invention therefore provides the use use in a chiller of a heat transfer composition of the present invention, including each of Heat Transfer Compositions 1 - 26 wherein said heat transfer composition further comprises BHT, wherein the AN5 is present in an amount of from about 0.001% by weight to about 5% by weight based on the weight of the heat transfer composition and the BHT is present in an amount of from about 0.001% by weight to about 5 % by weight based on the weight of heat transfer composition.

For the purposes of this invention, each heat transfer composition in accordance with the present invention, including each of Heat Transfer Compositions 1 – 26, is provided for use in a chiller with an evaporating temperature in the range of about 0 °C to about 10°C and a condensing temperature in the range of about 40 °C to about 70 °C. The chiller is provided for use in air conditioning or refrigeration, and preferably for commercial air conditioning. The chiller is preferably a positive displacement chiller, more particularly an air cooled or water cooled direct expansion chiller, which is either modular or conventionally singularly packaged.

The present invention therefore provides the use of each heat transfer composition in accordance with the present invention, including each of Heat Transfer Compositions 1 – 26, in stationary air conditioning, particularly residential air conditioning, industrial air conditioning or commercial air conditioning.

The present invention therefore provides the use in stationary air conditioning, particularly residential air conditioning, industrial air conditioning or commercial air conditioning , of a heat transfer composition of the present invention, including each of Heat Transfer Compositions 1 - 26 wherein said alkylated naphthalene is AN5 and wherein said heat transfer composition further comprises BHT, wherein the AN5 is present in an amount

of from about 0.001% by weight to about 5% by weight based on the weight of the lubricant and the BHT is present in an amount of from about 0.001% by weight to about 5 % by weight based on the weight of the lubricant .

The present invention therefore provides the use in stationary air conditioning,
5 particularly residential air conditioning, industrial air conditioning or commercial air conditioning ,of a heat transfer composition of the present invention, including each of Heat Transfer Compositions 1 - 26 wherein said alkylated naphthalene is AN5 and wherein said heat transfer composition further comprises BHT, wherein the AN5 is present in an amount
10 of from about 0.001% by weight to about 5% by weight based on the weight of the heat transfer composition and the BHT is present in an amount of from about 0.001% by weight to about 5 % by weight based on the weight of heat transfer composition.

Each heat transfer composition in accordance with the present invention, including each of Heat Transfer Compositions 1 – 26, is provided as a low GWP replacement for the refrigerant R-410A.

15 Each heat transfer composition in accordance with the present invention, including each of Heat Transfer Compositions 1 – 26, is provided as a low GWP retrofit for the refrigerant R-410A.

The heat transfer compositions and the refrigerants of the present invention, including each of Heat Transfer Compositions 1 – 26, therefore can be used as a retrofit
20 refrigerant/heat transfer composition or as a replacement refrigerant/heat transfer composition.

The present invention thus includes methods of retrofitting existing heat transfer system designed for and containing R-410A refrigerant, without requiring substantial engineering modification of the existing system, particularly without modification of the
25 condenser, the evaporator and/or the expansion valve.

The present invention thus also includes methods of using a refrigerant or heat transfer composition of the present invention as a replacement for R-410A, and in particular as a replacement for R-410A in residential air conditioning refrigerant, without requiring substantial engineering modification of the existing system, particularly without modification
30 of the condenser, the evaporator and/or the expansion valve.

The present invention thus also includes methods of using a refrigerant or heat transfer composition of the present invention as a replacement for R-410A, and in particular as a replacement for R-410A in a residential air conditioning system.

The present invention thus also includes methods of using a refrigerant or heat transfer composition of the present invention as a replacement for R-410A, and in particular as a replacement for R-410A in a chiller system.

There is therefore provided a method of retrofitting an existing heat transfer system
5 that contains R-410A refrigerant, said method comprising replacing at least a portion of the existing R-410A refrigerant with a heat transfer composition of the present invention, including each of Heat Transfer Compositions 1 – 26.

The step of replacing preferably comprises removing at least a substantial portion of, and preferably substantially all of, the existing refrigerant (which can be but is not limited to
10 R-410A) and introducing a heat transfer composition, including each of Heat Transfer Compositions 1 – 26, without any substantial modification of the system to accommodate the refrigerant of the present invention. Preferably, the method comprises removing at least about 5%, about 10%, about 25%, about 50%, or about 75% by weight of the R-410A from the system and replacing it with the heat transfer compositions of the invention.

15 Alternatively, the heat transfer composition can be used in a method of retrofitting an existing heat transfer system designed to contain or containing R410A refrigerant, wherein the system is modified for use with a Heat Transfer Composition of the present invention.

Alternatively, the heat transfer composition can be used as a replacement in a heat transfer system which is designed to contain or is suitable for use with R-410A refrigerant.

20 It will be appreciated that the invention encompasses the use of the heat transfer compositions of the invention, including each of Heat Transfer Compositions 1 – 17, as a low Global Warming replacement for R-410A or is used in a method of retrofitting an existing heat transfer system or is used in a heat transfer system which is suitable for use with R-410A refrigerant as described herein.

25 It will be appreciated by the skilled person that when the heat transfer composition is provided for use in a method of retrofitting an existing heat transfer system as described above, the method preferably comprises removing at least a portion of the existing R-410A refrigerant from the system. Preferably, the method comprises removing at least about 5%, about 10%, about 25%, about 50% or about 75% by weight of the R-410A from the system
30 and replacing it with the heat transfer compositions of the invention, including each of Heat Transfer Compositions 1 – 17.

The heat transfer compositions of the invention may be employed as a replacement in systems which are used or are suitable for use with R-410A refrigerant, such as existing or new heat transfer systems.

The compositions of the present invention exhibit many of the desirable characteristics of R-410A but have a GWP that is substantially lower than that of R-410A while at the same time having operating characteristics i.e. capacity and/or efficiency (COP) that are substantially similar to or substantially match, and preferably are as high as or
5 higher than R-410A. This allows the claimed compositions to replace R-410A in existing heat transfer systems without requiring any significant system modification for example of the condenser, the evaporator and/or the expansion valve. The composition can therefore be used as a direct replacement for R-410A in heat transfer systems.

10 The heat transfer compositions of the invention therefore preferably exhibits operating characteristics compared with R-410A wherein the efficiency (COP) of the composition is greater than 90% of the efficiency of R-410A in the heat transfer system.

The heat transfer composition of the invention therefore preferably exhibits operating characteristics compared with R-410A wherein the capacity is from 95 to 105% of the capacity of R-410A in the heat transfer system.

15 It will be appreciated that R-410A is an azeotrope-like composition. Thus, in order for the claimed compositions to be a good match for the operating characteristics of R-410A, the any of the refrigerants included in the heat transfer compositions of the invention, including each of Heat Transfer Compositions 1 – 26, desirably show a low level of glide. Thus, the refrigerants included in the heat transfer compositions of the invention, including
20 each of Heat Transfer Compositions 1 – 26, according to invention as described herein may provide an evaporator glide of less than 2°C, preferably less than 1.5 °C.

The heat transfer composition of the invention therefore preferably exhibits operating characteristics compared with R-410A wherein the efficiency (COP) of the composition is from 100 to 102% of the efficiency of R-410A in the heat transfer system and wherein the
25 capacity is from 92 to 102% of the capacity of R-410A in the heat transfer system.

Preferably, the heat transfer composition of the invention preferably exhibit operating characteristics compared with R-410A wherein:

- the efficiency (COP) of the composition is from 100 to 105% of the efficiency of R-410A; and/or
 - 30 - the capacity is from 92 to 102% of the capacity of R-410A,
- in heat transfer systems, in which the compositions of the invention are to replace the R-410A refrigerant.

In order to enhance the reliability of the heat transfer system, it is preferred that the heat transfer composition of the invention further exhibit the following characteristics compared
35 with R-410A:

- the discharge temperature is not greater than 10°C higher than that of R-410A;
and/or
- the compressor pressure ratio is from 98 to 102% of the compressor pressure ratio of R-410A,

5 in heat transfer systems, in which the composition of the invention is used to replace the R-410A refrigerant.

The existing heat transfer compositions used to replace R-410A are preferably used in air conditioning heat transfer systems including both mobile and stationary air conditioning systems. As used here, the term mobile air conditioning systems means mobile, non-
10 passenger car air conditioning systems, such as air conditioning systems in trucks, buses and trains. Thus, each of the heat transfer compositions as described herein, including each of Heat Transfer Compositions 1 – 26, can be used to replace R-410A in any one of:

- an air conditioning system including a mobile air conditioning system, particularly air conditioning systems in trucks, buses and trains,
- 15 - a mobile heat pump, particularly an electric vehicle heat pump;
- a chiller, particularly a positive displacement chiller, more particularly an air cooled or water cooled direct expansion chiller, which is either modular or conventionally singularly packaged,
- a residential air conditioning system, particularly a ducted split or a ductless split air
20 conditioning system,
- a residential heat pump,
- a residential air to water heat pump/hydronic system,
- an industrial air conditioning system and
- a commercial air conditioning system particularly a packaged rooftop unit and a
25 variable refrigerant flow (VRF) system;
- a commercial air source, water source or ground source heat pump system.

The heat transfer composition of the invention is alternatively provided to replace R410A in refrigeration systems. Thus, each of the heat transfer compositions as described herein, including each of Heat Transfer Compositions 1 – 26, can be used to
30 replace R10A in in any one of:

- a low temperature refrigeration system,
- a medium temperature refrigeration system,
- a commercial refrigerator,
- a commercial freezer,
- 35 - an ice machine,

- a vending machine,
- a transport refrigeration system,
- a domestic freezer,
- a domestic refrigerator,
- 5 - an industrial freezer,
- an industrial refrigerator and
- a chiller.

Each of the heat transfer compositions described herein, , including each of Heat Transfer Compositions 1 – 26, is particularly provided to replace R-410A in a residential air-
10 conditioning system (with an evaporator temperature in the range of about 0 to about 10°C, particularly about 7°C for cooling and/or in the range of about -20 to about 3°C or 30 to about 5°C, particularly about 0.5°C for heating). Alternatively, or additionally, each of the heat transfer compositions described herein, including each of Heat Transfer Compositions 1 – 26, is particularly provided to replace R-410A in a residential air conditioning system
15 with a reciprocating, rotary (rolling-piston or rotary vane) or scroll compressor.

Each of the heat transfer compositions described herein, including each of Heat Transfer Compositions 1 – 26, is particularly provided to replace R-410A in an air cooled chiller (with an evaporator temperature in the range of about 0 to about 10°C, particularly about 4.5°C), particularly an air cooled chiller with a positive displacement compressor,
20 more particular an air cooled chiller with a reciprocating scroll compressor.

Each of the heat transfer compositions described herein, including each of Heat Transfer Compositions 1 – 26, is particularly provided to replace R-410A in a residential air to water heat pump hydronic system (with an evaporator temperature in the range of about -20 to about 3°C or about -30 to about 5°C, particularly about 0.5°C).

25 Each of the heat transfer compositions described herein, including each of Heat Transfer Compositions 1 – 26, is particularly provided to replace R-410A in a medium temperature refrigeration system (with an evaporator temperature in the range of about -12 to about 0°C, particularly about -8°C).

Each of the heat transfer compositions described herein, including each of Heat
30 Transfer Compositions 1 – 26, is particularly provided to replace R-410A in a low temperature refrigeration system (with an evaporator temperature in the range of about -40 to about -12°C, particularly from about -40°C to about -23°C or preferably about -32°C).

There is therefore provided a method of retrofitting an existing heat transfer system designed to contain or containing R-410A refrigerant or which is suitable for use with R-
35 410A refrigerant, said method comprising replacing at least a portion of the existing R-410A

refrigerant with a heat transfer composition of the present invention, including each of Heat Transfer Compositions 1 – 26.

There is therefore provided a method of retrofitting an existing heat transfer system designed to contain or containing R-410A refrigerant or which is suitable for use with R-410A refrigerant, said method comprising replacing at least a portion of the existing R-410A refrigerant with a heat transfer composition according to the present invention, including each of Heat Transfer Compositions 1 – 26.

The invention further provides 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 according to the present invention, including each of Heat Transfer Compositions 1 – 26.

Particularly, the heat transfer system is a residential air-conditioning system (with an evaporator temperature in the range of about 0 to about 10°C, particularly about 7°C for cooling and/or in the range of about -20 to about 3°C or about -30 to about 5°C, particularly about 0.5°C for heating).

Particularly, the heat transfer system is an air cooled chiller (with an evaporator temperature in the range of about 0°C to about 10°C, particularly about 4.5°C), particularly an air cooled chiller with a positive displacement compressor, more particular an air cooled chiller with a reciprocating or scroll compressor.

Particularly, the heat transfer system is a residential air to water heat pump hydronic system (with an evaporator temperature in the range of about -20 °C to about 3°C or about -30 °C to about 5°C, particularly about 0.5°C).

The heat transfer system can be a refrigeration system, such as a low temperature refrigeration system, a medium temperature refrigeration system, a commercial refrigerator, a commercial freezer, an ice machine, a vending machine, a transport refrigeration system, a domestic freezer, a domestic refrigerator, an industrial freezer, an industrial refrigerator and a chiller.

EXAMPLES

The refrigerant compositions identified in Table 2 below as Refrigerants A1, A2 and A3 are refrigerants within the scope of the present invention as described herein. Each of the refrigerants was subjected to thermodynamic analysis to determine its ability to match the operating characteristics of R-4104A in various refrigeration systems. The analysis was performed using experimental data collected for properties of various binary pairs of components used in the composition. The vapor/liquid equilibrium behavior of CF₃I was determined and studied in a series of binary pairs with each of HFC-32 and R125. The

composition of each binary pair was varied over a series of relative percentages in the experimental evaluation and the mixture parameters for each binary pair were regressed to the experimentally obtained data. Vapor/liquid equilibrium behavior data for the binary pair HFC-32 and HFC-125 available in the National Institute of Science and Technology (NIST) Reference Fluid Thermodynamic and Transport Properties Database software (Refprop 9.1 NIST Standard Database 2013) were used for the Examples. The parameters selected for conducting the analysis were: same compressor displacement for all refrigerants, same operating conditions for all refrigerants, same compressor isentropic and volumetric efficiency for all refrigerants. In each Example, simulations were conducted using the measured vapor liquid equilibrium data. The simulation results are reported for each Example.

Table 2: Refrigerants evaluated for Performance Examples

Refrigerant	HFC-32 (wt%)	HFC-125 (wt%)	CF ₃ I (wt%)	GWP (100 years)	Flammability
A1	40%	3.5%	56.5%	393	Non Flammable
A2	41%	3.5%	55.5%	400	Non-Flammable
A3	44%	3.5%	52.5%	420	Non-Flammable

Refrigerant A1 comprises 100% by weight of the three compounds listed in Table 2 in their relative percentages and is non-flammable. **Refrigerant A1** consists of the three compounds listed in Table 2 in their relative percentages and is non-flammable. **Refrigerant A2** comprises 100% by weight of the three compounds listed in Table 2 in their relative percentages and is non-flammable. **Refrigerant A2** consists of the three compounds listed in Table 2 in their relative percentages and is non-flammable. **Refrigerant A3** comprises 100% by weight of the three compounds listed in Table 2 in their relative percentages and is non-flammable. **Refrigerant A3** consists of the three compounds listed in Table 2 in their relative percentages and is non-flammable.

Example 1 - Environment/GWP

LCCP was determined for R410, other known refrigerants, and a refrigerant of the present invention and reported in Table 3. In Table 3, the refrigerant having a GWP of 400 is a refrigerant of the present invention. Known refrigerants were used for the GWPs of 1, 150, 250, 750, and 2088. The known refrigerant having a GWP of 2088 is R410A.

Table 3 shows LCCP results in four regions: USA, EU, China and Brazil. As GWP decreases, the direct emissions are lower. However, system efficiency is lower so it

consumes more energy and increases the indirect emissions. Therefore, the total emissions (kg-CO_{2eq}) first decreases and then increases as GWP decreases. The different energy structures in these regions show values of the optimum GWP that has the lowest total emissions. The number of AC units is also different among these regions: USA and EU have more AC units than China and Brazil. Figure 1 and the last column of Table 3 shows the total emissions considering all four regions and number of AC units. As GWP decreases, the total emissions decrease until reaching the lowest value for a refrigerant of the present invention having a GWP of 400. In the range of GWP between 250 and 750, the total emissions are very similar. However, total emission significantly increases when GWP is lower than 150 because the indirect emissions increase significantly. So the present invention demonstrates a surprising and unexpected result.

Table 3: LCCP (kg-CO_{2eq})

GWP (100 years)	USA	EU	China	Brazil	Overall
2088 (R410A)	22932	9967	44395	5648	19676
750	21572	8659	42907	4376	18326
400 (refrigerant of present invention)	21523	8673	43112	4121	18238
250	21700	8404	43662	3997	18358
150	22541	8622	67552	4001	19044
1	22552	8534	67727	3880	19030

Example 2A - Residential Air-Conditioning System (Cooling)

Residential air-conditioning system is used to supply cool air (26.7°C) to buildings in the summer. Refrigerants A1, A2, and A3 were used in a simulation of a residential air-conditioning system as described above and the performance results are in Table 4 below. The operating conditions are: condensing temperature= 46°C; condenser sub-cooling= 5.5°C; evaporating temperature= 7°C; evaporator superheat= 5.5°C; isentropic Efficiency= 70%; volumetric efficiency= 100%; and temperature rise in Suction Line=5.5°C.

Table 4. Performance in Residential Air-Conditioning System (Cooling)

Refrigerant	Capacity (% of R410A)	Efficiency (% of R410A)	Pressure ratio (% of R410A)	Evaporator glide (°C)
R410A	100%	100%	100%	0.1
A1	92%	102%	100%	4.1
A2	93%	102%	100%	3.8
A3	95%	102%	100%	3.0

Table 4 shows the thermodynamic performance of a residential air-conditioning system compared to R410A system. Refrigerants A1 to A3 show 92% or higher capacity and higher efficiency than R410A. It indicates the system performance is similar to R410A. Refrigerants A1 to A3 show 100% pressure ratio compared to R410A. It indicates the compressor efficiencies are similar to R410A, and no changes on R410A compressor are needed.

Example 2B. - Residential Air-Conditioning System (Cooling)

A residential air-conditioning system configured to supply cool air in accordance with Example 2A in which POE lubricant is included in the system and is stabilized with alkylated naphthalene according to the present invention (AN4 in an amount of from about 6% to about 10% based on the weight of the lubricant) and ADM according to the present invention (ADM4 in an amount of about 0.05 – 0.5 % by weight based on the weight of the lubricant). The system so configured operates continuously for an extended period of days, and after such operation the lubricant is tested and is found to have remained stable during such actual operation.

Example 3A - Residential Heat pump System (Heating)

Residential heat pump system is used to supply warm air (21.1°C) to buildings in the winter. Refrigerants A1, A2, and A3 were used in a simulation of a residential heat pump system as described above and the performance results are in Table 5 below. The operating conditions are: condensing temperature= 41°C; condenser sub-cooling= 5.5°C; evaporating temperature= 0.5°C; evaporator superheat= 5.5°C; isentropic efficiency= 70%; volumetric efficiency= 100%; and temperature rise in suction line=5.5°C.

Table 5. Performance in Residential Heat pump System (Heating)

Refrigerant	Capacity (% of R410A)	Efficiency (% of R410A)	Pressure ratio (% of R410A)	Evaporator glide (°C)
R410A	100%	100%	100%	0.1
A1	89%	101%	100%	4.2
A2	90%	101%	100%	3.9
A3	92%	101%	100%	3.0

Table 5 shows the thermodynamic performance of a residential heat pump system compared to R410A system. The capacity of Refrigerant A1 can be recovered with a larger compressor. Refrigerants A2 and A3 show 90% or higher capacity and higher efficiency than R410A. It indicates the system performance is similar to R410A. Refrigerants A1 to A3 show 100% pressure ratio compared to R410A. It indicates the compressor efficiencies are similar to R410A, and no changes on R410A compressor are needed.

Example 3B. - Residential Heat Pump System (Heating)

A heat pump system is configured in accordance with Example 3A in which POE lubricant was included in the system and which is stabilized with alkylated naphthalene according to the present invention (AN4 in an amount of from about 6% to about 10% based on the weight of the lubricant) and ADM according to the present invention (ADM4 in an amount of about 0.05 – 0.5 % by weight based on the weight of the lubricant). The system so configured operates continuously for an extended period of days, and after such operation the lubricant is tested and was found to have remained stable during such actual operation.

Example 4A - Commercial Air-Conditioning System – Chiller

Commercial air-conditioning system (chiller) is used to supply chilled water (7°C) to large buildings such as office and hospital, etc. Refrigerants A1, A2, and A3 were used in a simulation of a commercial air-conditioning system as described above and the performance results are in Table 6 below. The operating conditions are: condensing temperature=46°C; condenser sub-cooling=5.5°C; evaporating temperature=4.5°C; evaporator superheat=5.5°C; isentropic efficiency= 70%; volumetric efficiency= 100%; and temperature rise in suction line=2°C.

Table 6. Performance in Commercial Air-Conditioning System – Air-Cooled Chiller

Refrigerant	Capacity (% of R410A)	Efficiency (% of R410A)	Pressure ratio (% of R410A)	Evaporator glide (°C)
R410A	100%	100%	100%	0.1
A1	92%	102%	100%	4.1
A2	93%	102%	100%	3.8
A3	95%	102%	100%	3.0

Table 6 shows the thermodynamic performance of a commercial air-conditioning system compared to R410A system. Refrigerants A1 to A3 show 92% or higher capacity and higher efficiency than R410A. It indicates the system performance is similar to R410A. Refrigerants A1 to A3 show 100% pressure ratio compared to R410A. It indicates the compressor efficiencies are similar to R410A, and no changes on R410A compressor are needed.

Example 4B. Commercial Air-Conditioning System – Chiller

A commercial air conditioning is configured in accordance with Example 4A in which POE lubricant is included in the system and is stabilized with alkylated naphthalene according to the present invention (AN4 in an amount of from about 6% to about 10% based on the weight of the lubricant) and ADM according to the present invention (ADM4 in an amount of about 0.05 – 0.5 % by weight based on the weight of the lubricant). The system so configured operates continuously for an extended period of days, and after such

operation the lubricant is tested and was found to have remained stable during such actual operation.

Example 5A - Residential Air-to-Water Heat Pump Hydronic System

Residential air-to-water heat pump hydronic system is used to supply hot water (50°C) to buildings for floor heating or similar applications in the winter. Refrigerants A1, A2, and A3 were used in a simulation of a residential heat pumpsystem as described above and the performance results are in Table 7 below. The operating conditions are: condensing temperature= 60°C; condenser sub-cooling= 5.5°C; evaporating temperature= 0.5°C; evaporator superheat= 5.5°C; isentropic efficiency= 70%; volumetric Efficiency= 100%; and temperature rise in suction line=2°C.

Table 7. Performance in Residential Air-to-Water Heat Pump Hydronic System

Refrigerant	Capacity (% of R410A)	Efficiency (% of R410A)	Pressure ratio (% of R410A)	Evaporator glide (°C)
R410A	100%	100%	100%	0.1
A1	93%	103%	100%	3.9
A2	94%	103%	100%	3.6
A3	96%	103%	99%	2.8

Table 7 shows the thermodynamic performance of a residential heat pump system compared to R410A system. Refrigerants A1 to A3 show 93% or higher capacity and higher efficiency than R410A. It indicates the system performance is similar to R410A. Refrigerants A1 to A2 show 100% pressure ratio compared to R410A. It indicates the compressor efficiencies are similar to R410A, and no changes on R410A compressor are needed.

Example 5B. - Residential Air-to-Water Heat Pump Hydronic System

A residential air-to-water heat pump hydronic system is configured in accordance with Example 5A in which POE lubricant is included in the system and is stabilized with alkylated naphthalene according to the present invention (AN4 in an amount of from about 6% to about 10% based on the weight of the lubricant) and ADM according to the present invention (ADM4 in an amount of about 0.05 – 0.5 % by weight based on the weight of the lubricant). The system so configured operates continuously for an extended period of days, and after such operation the lubricant is tested and was found to have remained stable during such actual operation.

Example 6A - Medium Temperature Refrigeration System

Medium temperature refrigeration system is used to chill the food or beverage such as in refrigerator and bottle cooler. Refrigerants A1, A2, and A3 were used in a simulation of a medium temperature refrigeration system as described above and the performance results are in Table 8 below. The operating conditions: condensing temperature= 40.6°C;

condenser sub-cooling= 0°C (system with receiver); evaporating temperature= -6.7°C; evaporator superheat= 5.5°C; isentropic efficiency= 70%; volumetric efficiency= 100%; and degree of superheat in the suction line = 19.5°C.

Table 8. Performance in Medium Temperature Refrigeration System

Refrigerant	Capacity (% of R410A)	Efficiency (% of R410A)	Pressure ratio (% of R410A)	Evaporator glide (°C)
R410A	100%	100%	100%	0.1
A1	94%	104%	100%	4.1
A2	94%	104%	100%	3.7
A3	97%	104%	99%	2.9

5 Table 8 shows the thermodynamic performance of a medium temperature refrigeration system compared to R410A system. Refrigerants A1 to A3 show 94% or higher capacity and higher efficiency than R410A. It indicates the system performance is similar to R410A. Refrigerants A1 to A2 show 100% pressure ratio compared to R410A. It indicates the compressor efficiencies are similar to R410A, and no changes on R410A
10 compressor are needed.

Example 6B. Medium Temperature Refrigeration System

A medium temperature refrigeration system is configured to chill food or beverages such as in a refrigerator and bottle cooler is configured in accordance with Example 6A in which POE lubricant is included in the system and is stabilized with alkylated naphthalene
15 according to the present invention (AN4 in an amount of from about 6% to about 10% based on the weight of the lubricant) and ADM according to the present invention (ADM4 in an amount of about 0.05 – 0.5 % by weight based on the weight of the lubricant). The system so configured operates continuously for an extended period of days, and after such operation the lubricant is tested and was found to have remained stable during such actual
20 operation.

Example 7A - Low Temperature Refrigeration System

Low temperature refrigeration system is used to freeze the food such as in ice cream machine and freezer. Refrigerants A1, A2, and A3 were used in a simulation of a low temperature refrigeration system as described above and the performance results are in
25 Table 9 below. The operating conditions: condensing temperature= 40.6°C; condenser sub-cooling= 0°C (system with receiver); evaporating temperature= -28.9°C; degree of superheat at evaporator outlet = 5.5°C; isentropic efficiency= 65%; volumetric efficiency= 100%; and degree of superheat in the suction line = 44.4°C.

Table 9. Performance in Low Temperature Refrigeration System

Refrigerant	Capacity (% of R410A)	Efficiency (% of R410A)	Pressure ratio (% of R410A)	Evaporator glide (°C)
R410A	100%	100%	100%	0.1
A1	96%	105%	100%	4.0

A2	97%	105%	99%	3.7
A3	99%	105%	99%	2.7

Table 9 shows the thermodynamic performance of a low temperature refrigeration system compared to R410A system. Refrigerants A1 to A3 show 96% or higher capacity and higher efficiency than R410A. It indicates the system performance is similar to R410A.

- 5 Refrigerants A1 to A3 show 99% or 100% pressure ratio compared to R410A. It indicates the compressor efficiencies are similar to R410A, and no changes on R410A compressor are needed.

Example 7B. Low Temperature Refrigeration System

- 10 A low temperature refrigeration system is configured to freeze food such as in an ice cream machine and a freezer is configured in accordance with Example 7A in which POE lubricant is included in the system and is stabilized with alkylated naphthalene according to the present invention (AN4 in an amount of from about 6% to about 10% based on the weight of the lubricant) and ADM according to the present invention (ADM4 in an amount of about 0.05 – 0.5 % by weight based on the weight of the lubricant). The system so
- 15 configured operates continuously for an extended period of days, and after such operation the lubricant is tested and was found to have remained stable during such actual operation.

Example 8A. Commercial Air-Conditioning System – Packaged Rooftops

- A packaged rooftop commercial air conditioning system configured to supply cooled or heated air to buildings is tested. The experimental system includes a packaged rooftop
- 20 air-conditioning/heat pump systems and has an air-to-refrigerant evaporator (indoor coil), a compressor, an air-to-refrigerant condenser (outdoor coil), and an expansion valve. The testing described herein is representative of the results from such systems. The operating conditions for the test are:

1. Condensing temperature = about 46°C (corresponding outdoor ambient temperature = about 67°C)
2. Condenser sub-cooling = about 5.5°C
3. Evaporating temperature = about 7°C (corresponding indoor ambient temperature = 26.7°C)
4. Evaporator Superheat = about 5.5°C
- 30 5. Isentropic Efficiency = 70%
6. Volumetric Efficiency= 100%
7. Temperature Rise in Suction Line = 5.5°C

The performance with each of refrigerants A1 – A3 is found to be acceptable

Example 8A. Commercial Air-Conditioning System – Packaged Rooftops

A packaged rooftop commercial air conditioning system is configured to supply cooled or heated air to buildings in accordance with Example 8A in which POE lubricant is included in the system and is stabilized with alkylated naphthalene according to the present invention (AN4 in an amount of from about 6% to about 10% based on the weight of the lubricant) and ADM according to the present invention (ADM4 in an amount of about 0.05 – 0.5 % by weight based on the weight of the lubricant). The system so configured operates continuously for an extended period of days, and after such operation the lubricant is tested and is found to have remained stable during such actual operation.

Example 9A - Commercial Air-Conditioning System – Variable Refrigerant Flow

Systems

A commercial air-conditioning system with variable refrigerant flow is configured to supply cooled or heated air to buildings is tested. The experimental system includes multiple (4 or more) air-to-refrigerant evaporators (indoor coils), a compressor, an air-to-refrigerant condenser (outdoor coil), and an expansion valve. The testing described herein is representative of the results from such systems. The operating conditions for the test are:

1. Condensing temperature = about 46°C, Corresponding outdoor ambient temperature= 67°C
2. Condenser sub-cooling = about 5.5°C
3. Evaporating temperature = about 7°C (corresponding indoor ambient temperature= 26.7°C)
4. Evaporator Superheat = about 5.5°C
5. Isentropic Efficiency = 70%
6. Volumetric Efficiency = 100%
7. Temperature Rise in Suction Line = 5.5°C. The performance with each of refrigerants A1 – A3 is found to be acceptable.

Example 9B. Commercial Air-Conditioning System – Variable Flow Refrigerant

A commercial air-conditioning system with variable refrigerant flow is configured to supply cooled or heated air to buildings is configured in accordance with Example 9A in which POE lubricant is included in the system and is stabilized with alkylated naphthalene according to the present invention (AN4 in an amount of from about 6% to about 10% based on the weight of the lubricant) and ADM according to the present invention (ADM4 in an amount of about 0.05 – 0.5 % by weight based on the weight of the lubricant). The system so configured operates continuously for an extended period of days, and after such operation the lubricant is tested and was found to have remained stable during such actual operation.

Comparative Example 1 - Heat Transfer Compositions Comprising Refrigerant and Lubricant and BHT

A heat transfer compositions of the present invention is tested in accordance with ASHRAE Standard 97 - "Sealed Glass Tube Method to Test the Chemical Stability of Materials for Use within Refrigerant Systems" to simulate long-term stability of the heat transfer compositions by accelerated aging. The tested refrigerant consists of 41% by weight R-32, 3.5% by weight of R-125 and 55.5% by weight of CF3I, with 1.7 volume % air in the refrigerant. The POE lubricant tested was an ISO 32 POE having a viscosity at 40°C of about 32 cSt and having a moisture content of 300 ppm or less (Lubricant A). Included with the lubricant is the stabilizer BHT, but no alkylated naphthalene and no ADM were included. After testing, the fluid is observed for clarity and total acid number (TAN) is determined. The TAN value is considered to reflect the stability of the lubricant in the fluid under conditions of use in the heat transfer composition. The fluid is also tested for the presence of trifluoromethane (R-23), which is considered to reflect refrigerant stability since this compound is believed to be a product of the breakdown of CF3I.

The experiment is carried out by preparing sealed tubes containing 50% by weight of the R-466a refrigerant and 50% by weight of the indicated lubricant, each of which has been degassed. Each tube contains a coupon of steel, copper, aluminum and bronze. The stability is tested by placing the sealed tube in an oven maintained at about 175°C for 14 days. The results were as follows:

Lubricant Visual – yellow to brown

TAN - >2 mgKOH/g

R-23 – >1 wt%

Example 10 - Stabilizers for Heat Transfer Compositions Comprising Refrigerant and Lubricant

The test of Comparative Example 1 is repeated except that 2% by weight of alkylated naphthalene (AN4) based on the weight of the lubricant is added. The results (designated E10) are reported in Table 10 below, together with the results from Comparative Example 1 (designated CE1).

Table 10

	CE1 (no AN)	E10 (2% AN)
Lubricant Visual	yellow to brown	Clear
TAN mgKOH/g	>2	<0.2
R-23 –wt%	>1	<0.2

As can be seen from the data above, the refrigerant/lubricant fluid without the alkylate naphthalene stabilizer according to the present invention exhibits a less than ideal visual appearance, and relatively high TAN and R-23 values. This results are achieved notwithstanding that BHT stabilizer is included. In contrast, the addition of 2% alkylated naphthalene according to the present invention produces a dramatic and unexpected improvement in all tested stability results, including a dramatic, order of magnitude improvement in both TAN and R-23 concentration.

Example 11 - Stabilizers for Heat Transfer Compositions Comprising Refrigerant and Lubricant

The test of Example 10 is repeated except that 4% by weight of alkylated naphthalene (AN4) based on the weight of the lubricant is added. The results are similar to the results of Example 10.

Example 12 - Stabilizers for Heat Transfer Compositions Comprising Refrigerant and Lubricant

The test of Example 10 is repeated except that 6% by weight of alkylated naphthalene (AN4) based on the weight of the lubricant is added. The results are similar to the results of Example 10.

Example 13 - Stabilizers for Heat Transfer Compositions Comprising Refrigerant and Lubricant

The test of Example 10 is repeated except that 8% by weight of alkylated naphthalene (AN4) based on the weight of the lubricant is added. The results are similar to the results of Example 10.

Example 14 - Stabilizers for Heat Transfer Compositions Comprising Refrigerant and Lubricant

The test of Comparative Example 1 is repeated except that 10% by weight of alkylated naphthalene (AN4) based on the weight of the lubricant is added. The results (designated E14) are reported in Table 11 below, together with the results from Comparative Example 1 (designated CE1) and Example 10 (designated E10).

Table 11

	CE1 (No AN)	E10 (2% AN)	E14 (10% AN)
Lubricant Visual	yellow to brown	Clear	Dark Brown to Black
TAN mgKOH/g	>2	<0.2	>5

R-23 –wt%	>1	<0.2	>1
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As can be seen from the data above, the refrigerant/lubricant fluid with 10% alkylated naphthalene stabilizer (and no ADM) unexpectedly exhibits a substantial deterioration in stabilizing performance for each criteria tested compared to the fluid with the AN level of 2%.

5 **Example 15 - Stabilizers for Heat Transfer Compositions Comprising Refrigerant and Lubricant**

The test of Example 14 is repeated except that in addition to the 10% by weight of alkylated naphthalene (AN4) based on the weight of the lubricant being added, 1000 ppm by weight (0.1 % by weight) of ADM (ADM4) is also added. The results (designated E15) are reported in Table 12 below, together with the results from Comparative Example 1 (designated CE1), Example 10 (designated E10) and Example 14 (designated E14)..

Table 12

	CE1 (No AN)	E10 (2% AN)	E14 (10% AN)	E15 (10% AN + 0.1% ADM)
Lubricant Visual	yellow to brown	Clear	Dark Brown to Black	Crysal clear
TAN mgKOH/g	>2	<0.2	>5	<.1
R-23 –wt%	>1	<0.2	>1	<0.01

As can be seen from the data above, the refrigerant/lubricant fluid with 10% alkylated naphthalene stabilizer and 0.1% by weight (1000 ppm) ADM unexpectedly exhibits the best performance, with an R-23 value that is even better than the excellent results from Example 10.

15 **Example 16 - Stabilizers for Heat Transfer Compositions Comprising Refrigerant and Lubricant**

The test of Example 15 is repeated except that the lubricant was an ISO 74 POE having a viscosity at 40°C of about 74 cSt and having a moisture content of 300 ppm or less (Lubricant B). The results were as follows:

Lubricant Visual – clear to slight yellow

TAN - <0.1 mgKOH/g

R-23 – <0.05 wt%

25 **Example 17 - Stabilizers for Heat Transfer Compositions Comprising Refrigerant and Lubricant**

The test of Example 15 is repeated except that the lubricant is an ISO 68 PVE having a viscosity at 40°C of about 68 cSt and having a moisture content of 300 ppm or less (Lubricant c). The results were as follows:

Lubricant Visual – crystal clear

5 TAN - <0.1 mgKOH/g

R-23 – 0.028 wt%

Example 18 - Stabilizers for Heat Transfer Compositions Comprising Refrigerant and Lubricant

10 The test of Example 15 is repeated except that the lubricant was an ISO 32 PVE having a viscosity at 40°C of about 32 cSt and having a moisture content of 300 ppm or less (Lubricant c). The results were similar to the results from Example 17.

Example 19 — Miscibility with POE oil

15 Miscibility of ISO POE-32 oil (having a viscosity at about 32 cSt at a temperature of 40°C) is tested for different weight ratios of lubricant and refrigerant and different temperatures for R-410A refrigerant and for each of Refrigerants A1 and A3 as specified in Table 1 for Example 1 above. The results of this testing are reported in Table 11 below:

TABLE 13

Liquid Refrigerant Mass Percentage in the Refrigerant and Lubricant Mixture, %	R-410A Miscibility Temperature Range		Refrigerant A of the present invention
	Lower Limit, °C	Upper Limit, °C	
60	about -26	NA	Fully miscible
70	about -23	about 55	Fully miscible
80	about -22	about 48	Fully miscible
90	about -31	about 50	Fully miscible

20 As can be seen from the table above, R-410A is immiscible with POE oil below about -22 °C, and R-410A cannot therefore be used in low temperature refrigeration applications without make provisions to overcome the accumulation of POE oil in the evaporator. Furthermore, R-410A is immiscible with POE oil above 50°C, which will cause problems in the condenser and liquid line (e.g. the separated POE oil will be trapped and accumulated) when R-410A is used in high ambient conditions. Conversely, applicants have surprisingly
25 and unexpectedly found that refrigerants of the present invention are fully

miscible with POE oil across a temperature range of -40°C to 80°C, thus providing a substantial and unexpected advantage when used in such systems.

The invention will now be illustrated by reference to the following numbered embodiments. The subject matter of the numbered embodiments may be additionally combined with subject matter from the description or from one or more of the claims.

Numbered Embodiment 1. A heat transfer compositions comprising refrigerant
5 comprising from about 10% by weight to about 75% by weight of trifluoroiodomethane (CF₃I), lubricant comprising POE and/or PVE lubricant and stabilizer comprising alkylated naphthalene.

Numbered Embodiment 2. A heat transfer composition according to Number Embodiment
1 wherein said alkylated naphthalene is present in the heat transfer composition in an
10 amount of from 1% to less than 10% by weight based on the weight of the alkylated naphthalene and the lubricant.

Numbered Embodiment 3. A heat transfer composition according to Number Embodiment
1 wherein said alkylated naphthalene is present in the composition in an amount of from
1.5% to less than 10%.

15 **Numbered Embodiment 4.** A heat transfer composition according to Number Embodiment
1 wherein said alkylated naphthalene is present in the composition in an amount of from
1.5% to less than 8%.

Numbered Embodiment 5. A heat transfer composition according to Number Embodiment
1 wherein said alkylated naphthalene is present in the composition in an amount of from
20 1.5% to less than 6%.

Numbered Embodiment 6. A heat transfer composition according to Number Embodiment
1 wherein said alkylated naphthalene is present in the composition in an amount of from
1.5% to less than 5%.

Numbered Embodiment 7. A heat transfer composition according to any of Number
25 Embodiments 1 – 6 wherein said alkylated naphthalene is selected from AN1, or AN2, or
AN3, or AN4, or AN5, or AN6, or AN7, or AN8, or AN9 or AN10.

Numbered Embodiment 8. A heat transfer composition according to any of Number
Embodiments 1 – 7 wherein said alkylated naphthalene comprises AN5.

Numbered Embodiment 9. A heat transfer composition according to any of Number
30 Embodiments 1 – 7 wherein said alkylated naphthalene consists essentially of AN5.

Numbered Embodiment 10. A heat transfer composition according to any of Number
Embodiments 1 – 7 wherein said alkylated naphthalene consists of AN5.

Numbered Embodiment 11. A heat transfer composition according to any of Number
Embodiments 1 – 7 wherein said alkylated naphthalene comprises AN10.

Numbered Embodiment 12. A heat transfer composition according to any of Number Embodiments 1 – 7 wherein said alkylated naphthalene consists essentially of AN10.

Numbered Embodiment 13. A heat transfer composition according to any of Number Embodiments 1 – 7 wherein said alkylated naphthalene consists of AN10.

5 **Numbered Embodiment 14.** A heat transfer composition according to any of Number Embodiments 1 – 13 wherein said stabilizer further comprises an ADM.

Numbered Embodiment 15. A heat transfer composition according to any of Number Embodiments 1 – 14 wherein said ADM comprises ADM4.

10 **Numbered Embodiment 16.** A heat transfer composition according to any of Number Embodiments 1 – 15 wherein said ADM consists essentially of ADM4.

Numbered Embodiment 17. A heat transfer composition according to any of Number Embodiments 1 – 15 wherein said ADM naphthalene consists of ADM4.

15 **Numbered Embodiment 18.** A heat transfer composition according to any of Number Embodiments 1 – 7 wherein said stabilizer is selected from Stabilizer 1, Stabilizer 2, Stabilizer 3, Stabilizer 4, Stabilizer 5, Stabilizer 6, Stabilizer 7, Stabilizer 8, Stabilizer 9, Stabilizer 10, Stabilizer 11, Stabilizer 12, Stabilizer 13, Stabilizer 14, Stabilizer 15, Stabilizer 16, Stabilizer 17, Stabilizer 18, Stabilizer 19, Stabilizer 20.

Numbered Embodiment 19. A heat transfer composition according to any of Number Embodiments 1 – 18 wherein said lubricant comprises POE.

20 **Numbered Embodiment 20.** A heat transfer composition according to any of Number Embodiments 1 – 19 wherein said lubricant consists essentially of POE.

Numbered Embodiment 21. A heat transfer composition according to any of Number Embodiments 1 – 19 wherein said lubricant consists of POE.

25 **Numbered Embodiment 22.** A heat transfer composition according to any of Number Embodiments 1 – 21 wherein said lubricant comprises Lubricant 1.

Numbered Embodiment 23. A heat transfer composition according to any of Number Embodiments 1 – 21 wherein said lubricant consists essentially of Lubricant 1.

Numbered Embodiment 24. A heat transfer composition according to any of Number Embodiments 1 – 21 wherein said lubricant consists of Lubricant 1.

30 **Numbered Embodiment 25.** A heat transfer composition according to any of Number Embodiments 1 – 19 wherein said lubricant comprises PVE.

Numbered Embodiment 26. A heat transfer composition according to any of Number Embodiments 1 – 20 wherein said lubricant consists essentially of PVE.

35 **Numbered Embodiment 27.** A heat transfer composition according to any of Number Embodiments 1 – 21 wherein said lubricant consists of PVE.

Numbered Embodiment 28. The heat transfer compositions of any one of Numbered Embodiments 1 to 27, wherein the composition further comprises one or more component selected from the group consisting of a dye, a solubilizing agent, a compatibilizer, a corrosion inhibitor, an extreme pressure additive and an anti-wear additive.

- 5 **Numbered Embodiment 29.** The heat transfer composition of Numbered Embodiments 1 - 28, wherein the stabilizer further comprises a phenol-based compound.

Numbered Embodiment 30. The heat transfer composition of Numbered Embodiments 1 - 30 wherein the stabilizer further comprises a phosphorus compound.

- 10 **Numbered Embodiment 31.** The heat transfer composition of any one of Numbered Embodiments 1 to 6 and 13 to 30, wherein the alkylated naphthalene is one or more of NA-LUBE KR-007A; KR-008, KR-009; KR-0105, KR-019 and KR-005FG.

Numbered Embodiment 32. The heat transfer composition of any one of Numbered Embodiments 1 to 6 and 13 to 30, wherein the alkylated naphthalene is one or more of NA-LUBE KR-007A, KR-008, KR-009 and KR-005FG.

- 15 **Numbered Embodiment 33.** The heat transfer composition of any one of Numbered Embodiments 1 to 32 wherein the alkylated naphthalene is NA-LUBE KR-008.

- Numbered Embodiment 34.** The heat transfer composition of any one of Numbered Embodiments 1 - 33, wherein the stabilizer comprises a phenol based compound selected from 4,4'-methylenebis(2,6-di-tert-butylphenol); 4,4'-bis(2,6-di-tert-butylphenol); 2,2- or 4,4-biphenyldiols, including 4,4'-bis(2-methyl-6-tert-butylphenol); derivatives of 2,2- or 4,4-biphenyldiols; 2,2'-methylenebis(4-ethyl-6-tert-butylphenol); 2,2'-methylenebis(4-methyl-6-tert-butylphenol); 4,4-butyldienebis(3-methyl-6-tert-butylphenol); 4,4-isopropylidenebis(2,6-di-tert-butylphenol); 2,2'-methylenebis(4-methyl-6-nonylphenol); 2,2'-isobutyldienebis(4,6-dimethylphenol); 2,2'-methylenebis(4-methyl-6-cyclohexylphenol); 2,6-di-tert-butyl-4-methylphenol (BHT); 2,6-di-tert-butyl-4-ethylphenol; 2,4-dimethyl-6-tert-butylphenol; 2,6-di-tert-alpha-dimethylamino-p-cresol; 2,6-di-tert-butyl-4(N,N'-dimethylaminomethylphenol); 4,4'-thiobis(2-methyl-6-tert-butylphenol); 4,4'-thiobis(3-methyl-6-tert-butylphenol); 2,2'-thiobis(4-methyl-6-tert-butylphenol); bis(3-methyl-4-hydroxy-5-tert-butylbenzyl) sulfide; bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, tocopherol, hydroquinone, 2,2',6,6'-tetra-tert-butyl-4,4'-methylenediphenol and t-butyl hydroquinone.
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Numbered Embodiment 35. The heat transfer composition of any one of Numbered Embodiments 30 to 34, wherein the stabilizer comprises BHT.

Numbered Embodiment 36. The heat transfer composition of any one of Numbered Embodiments 30 to 34, wherein the phenol consists essentially of BHT.

Numbered Embodiment 37. The heat transfer composition of any one of Numbered Embodiments 30 to 34, wherein the phenol consists of BHT.

Numbered Embodiment 38. The heat transfer composition of Numbered Embodiment 30 to 34 wherein said phenol is present in the heat transfer composition in an amount of
5 greater than 0 and preferably from 0.0001% by weight to about 5% by weight, preferably 0.001% by weight to about 2.5% by weight, and more preferably from 0.01% to about 1% by weight, where percentage by weight refers to the weight of the heat transfer composition.

Numbered Embodiment 39. The heat transfer composition of Numbered Embodiment 30 to 34 wherein said phenol is present in the heat transfer composition in an amount of
10 greater than 0 and preferably from 0.0001% by weight to about 5% by weight, preferably 0.001% by weight to about 4% by weight, and more preferably from 1% to 4% by weight, where percentage by weight refers to the weight of the lubricant eat transfer composition.

CLAIMS

1. A heat transfer compositions comprising refrigerant, lubricant and stabilizer, said refrigerant comprising from about 5% by weight to 100% by weight of trifluoriodomethane (CF₃I), said lubricant comprising polyol ester (POE) lubricant and/or polyvinyl ether (PVE) lubricant, and said stabilizer comprising alkylated naphthalene, wherein said alkylated naphthalene is present in the composition in an amount of from 1% to less than 10% by weight based on the weight of the alkylated naphthalene and the lubricant.
2. The heat transfer composition of claim 1 wherein said alkylated naphthalene is present in the composition in an amount of from 1% to 8% by weight based on the weight of the alkylated naphthalene and the lubricant.
3. The heat transfer composition of claim 1 wherein said alkylated naphthalene is present in the composition in an amount of from 1.5% to 6% by weight based on the weight of the alkylated naphthalene and the lubricant.
4. The heat transfer composition of claim 3 wherein said stabilizer further comprises an acid depleting moiety (ADM).
5. The heat transfer composition of claim 4 wherein said stabilizer comprises from about 40% by weight to about 99.9% of alkylated naphthalenes and from 0.05% to about 50% by weight of ADM based on the weight of the stabilizer.
6. The heat transfer composition of claim 5 wherein said stabilizer comprises from about 40% by weight to about 95% of alkylated naphthalenes and from 1% to about 20% by weight of ADM based on the weight of the stabilizer.
7. The heat transfer composition of claim 6 wherein said alkylated naphthalene comprises AN5 and where said ADM comprises ADM4.
8. The heat transfer composition of claim 7 wherein said alkylated naphthalenes consists essentially of AN5 and where said ADM consists essentially of ADM4.
9. The heat transfer composition of claim 8 wherein said stabilizer further comprises BHT.
10. A stabilized heat transfer composition comprising: (a) a lubricant selected from POE lubricant and PVE lubricant; and (b) a stabilizer comprising from about 50% by weight to about 99.9% of alkylated naphthalene based on the weight of the stabilizer.

11. The stabilized heat transfer composition of claim 10 wherein said lubricant comprises neopentyl POE lubricant having a viscosity at 40°C measured in accordance with ASTM D445 of from about 30 cSt to about 70 cSt.

12. The stabilized heat transfer composition of claim 11 wherein said stabilizer further comprises from 0.05% to about 50% by weight of ADM based on the weight of the stabilizer.

13. The stabilized heat transfer composition of claim 12 wherein said alkylated naphthalenes consists essentially of AN5 and where said ADM consists essentially of ADM4.

14. The stabilized heat transfer composition of claim 13 wherein said stabilizer further comprises BHT.

15. The stabilized heat transfer composition of claim 12 wherein said alkylated naphthalenes consists essentially of AN10 and where said ADM consists essentially of ADM4 and further comprising BHT.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/068931**A. CLASSIFICATION OF SUBJECT MATTER****C09K 5/04(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; C07C 211/58; C10M 105/64; F25B 9/00

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, refrigerant, lubricant, stabilizer, alkylated naphthalene

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2018-022943 A1 (HONEYWELL INTERNATIONAL INC.) 01 February 2018 claims 1, 11, 13, 24, 29, 34; paragraphs [0168]-[0170]	1-15
Y	US 5198134 A (STEINBERG, D. H. et al.) 30 March 1993 abstract	1-15
Y	HOURLANI, M. J. et al. "Alkylated Naphthalenes as High-Performance Synthetic Lubricating Fluids", Tribology Transactions, 2007, Vol. 50, pages 82-87 pages 83, 84	1-15
A	WO 2018-022888 A1 (HONEYWELL INTERNATIONAL INC.) 01 February 2018 the whole document	1-15
A	WO 2018-022949 A2 (HONEYWELL INTERNATIONAL INC.) 01 February 2018 the whole document	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2019/068931

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2018-022943 A1	01/02/2018	CA 3032010 A1 CN 109689832 A EP 3491094 A1 JP 2019-527281 A KR 10-2019-0038813 A US 10301521 B2 US 2018-0030324 A1 US 2019-0249055 A1	01/02/2018 26/04/2019 05/06/2019 26/09/2019 09/04/2019 28/05/2019 01/02/2018 15/08/2019
US 5198134 A	30/03/1993	EP 0512954 A1 EP 0512954 B1 JP 05-170709 A	11/11/1992 08/03/1995 09/07/1993
WO 2018-022888 A1	01/02/2018	CA 3031947 A1 CN 109689830 A EP 3365408 A1 JP 2009-161730 A JP 2015-134927 A JP 2018-044169 A JP 2019-527285 A KR 10-2019-0030212 A US 10208235 B2 US 10246621 B2 US 2009-0127497 A1 US 2017-0321099 A1 US 2018-0244969 A1 US 2018-0362820 A1 US 2019-0136106 A1 US 9938442 B2	01/02/2018 26/04/2019 29/08/2018 23/07/2009 27/07/2015 22/03/2018 26/09/2019 21/03/2019 19/02/2019 02/04/2019 21/05/2009 09/11/2017 30/08/2018 20/12/2018 09/05/2019 10/04/2018
WO 2018-022949 A2	01/02/2018	CA 3031948 A1 CN 109715758 A EP 3491095 A2 JP 2019-527286 A KR 10-2019-0039499 A US 2018-0030325 A1 WO 2018-022949 A3	01/02/2018 03/05/2019 05/06/2019 26/09/2019 12/04/2019 01/02/2018 08/03/2018