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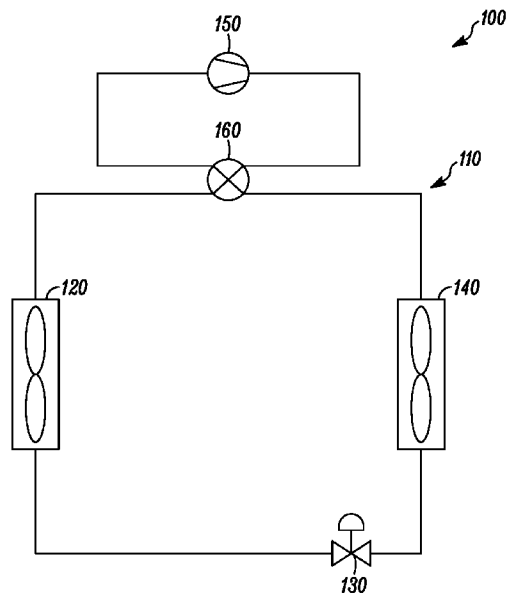


FIG. 1

(57) Abstract: Environmentally friendly refrigerant blends utilizing re-  
frigerants including 2,3,3,3-tetrafluoropropene (HFO-1234yf), difluo-  
romethane (HFC-32), and 1,1-difluoroethane (HFC-152a). The blends  
have low GWP, low toxicity, and low flammability with low tempera-  
ture glide for use in a hybrid, mild hybrid, plug-in hybrid, or full electric  
vehicles for thermal management (transferring heat from one part of the  
vehicle to the other) of the passenger compartment providing air condi-  
tioning (A/C) or heating to the passenger cabin.

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**TITLE**

COMPOSITIONS OF HFO-1234YF, HFC-152A, AND HFC-32, AND  
SYSTEMS FOR USING THE COMPOSITIONS

**FIELD**

**[0001]** The present invention is directed to compositions comprising HFO-1234yf, HFC-152a, and HFC-32 and use as refrigerant in air conditioning and heat pump systems.

**BACKGROUND**

**[0002]** The automotive industry is going through an architecture platform rejuvenation from using an internal combustion engine (ICE) for propulsion to using electric motors for propulsion. This platform rejuvenation is severely limiting the size of the internal combustion engine (ICE) in hybrid, plug-in hybrid vehicles or possibly eliminating the ICE altogether in pure electric vehicles. Some vehicles still maintain an ICE and are noted as hybrid electric vehicles (HEV) or plug-in hybrid electric vehicles (PHEV) or mild hybrid electric vehicles (MHEV). Vehicles which are fully electric and have no ICE are denoted as full electric vehicles (EV), including battery electric vehicles (BEV). All HEV, PHEV, MHEV and EVs use at least one electric motor, where the electric motor provides some form of propulsion for the vehicles normally provided by the internal combustion engine (ICE) found in gasoline/diesel powered vehicles.

**[0003]** In electrified vehicles, the ICE is typically reduced in size (HEV, PHEV, or MHEV) or eliminated (EV) to reduce vehicle weight thereby increasing the electric drive-cycle. While the ICE's primary function is to provide vehicle propulsion, it also provides heat to the passenger cabin as its secondary function. Typically, heating is required when ambient conditions are 10°C or lower. In a non-electrified vehicle, there is excess heat from the ICE, which can be scavenged and used to heat the passenger cabin. It should be noted that while the ICE may take some time (several minutes) to heat up and generate heat, it functions well down to temperatures as low as -30°C. Therefore, in electrified vehicles, ICE size reduction or elimination is creating a demand for effective heating of the passenger cabin. In current EVs, with

no ICE, positive temperature coefficient (PTC) heaters are being used. Use of a heat pump for cooling and heating can replace the PTC heater along with the air conditioning system and allow more efficient cooling and heating.

**[0004]** Due to environmental pressures, R-134a, a hydrofluorocarbon or HFC, has been phased out for automobile air conditioning in favor of lower global warming potential (GWP) refrigerants with GWP < 150. While HFO-1234yf, a hydrofluoro-olefin, meets the low GWP requirement (GWP =4 per Pappadimitriou and GWP <1 per AR5), it has lower refrigeration capacity compared to R-134a and may not fully meet the heating requirements at low (-10°C) to very low (-30°C) ambient temperatures in current system designs. Refrigerant blends commonly used in stationary refrigerant applications are another option for automotive heat pumps. Examples of compositions comprising HFO-1234yf are disclosed in WO2007/126414; the disclosure of which is hereby incorporated by reference.

**[0005]** Similarly, the heating and cooling of stationary residential and commercial structures also suffers from a lack of suitable low GWP refrigerants to replace the older high GWP refrigerants currently in use.

**[0006]** Therefore, there is a need for low GWP heat pump type fluids to meet the ever-increasing needs of hybrid, mild hybrid, plug-in hybrid and electric vehicles, electrified mass transit, and residential and commercial structures for thermal management which can provide both cooling and heating.

### **SUMMARY**

**[0007]** The present invention relates to compositions of environmentally friendly refrigerant blends with low GWP, (GWP less than or equal to 100) low toxicity (class A per ANSI/ASHRAE standard 34 or ISO standard 817) ), and low flammability (class 2 or class 2L per ASHRAE 34 or ISO 817) with low temperature glide for use in a hybrid, mild hybrid, plug-in hybrid, or full electric vehicles for complete vehicle thermal management (transferring heat from one part of the vehicle to another). The thermal management system may operate to provide cooling and/or heating of the power electronics, battery, motor and provide air conditioning (A/C) or heating to the passenger cabin. These refrigerants can also be used for mass transit mobile applications which benefit from a heat pump type system enabling both heating and

cooling of batteries, motors and passenger compartment areas. Mass transit mobile applications are not limited to, but can include transport vehicles such as ambulances, buses, shuttles, and trains.

**[0008]** In one aspect of the invention, the refrigerant compositions include mixtures of HFO-1234yf, HFC-152a, and HFC-32. Compositions of the present invention exhibit low temperature glide over the operating conditions of vehicle thermal management systems. Due to the manner in which automotive vehicles are repaired or serviced, having a low temperature glide fluid or no glide would be preferred. Currently, during some vehicle A/C repair or service processes, refrigerants are handled through specific automotive service machines which recover the refrigerant, recycle the refrigerant to some intermittent quality level removing gross contaminants and then recharge the refrigerant back into the vehicle after repairs or servicing have been completed. These machines are denoted as R/R/R machines since they recover, recycle, and recharge refrigerant. This on-site recovery, recycle and recharge of refrigerant during vehicle maintenance or repair, is possible because of single compound refrigerant, currently HFO-1234yf is being used. The current automotive service machines are not typically capable of handling refrigerant blends that may fractionate during use, and possibly exhibit preferential leak of the lowest boiling component(s). Thus, the refrigerant removed from a system during service may not yield the same percentages of the components as the original blend that was charged. Since the refrigerant is handled "on-site" at a vehicle repair shop, there is no opportunity to reconstitute the blend refrigerant back to the original composition concentrations as is done by a refrigerant recycler. Refrigerants with higher temperature glide can sometimes require "reconstitution" to the original formulation otherwise a loss in cycle performance can occur. Therefore, a need exists for refrigerants which have lower temperature glide for automotive applications. Since a heat pump fluid would be handled in the same manner as the air-conditioning fluid, this requirement for low temperature glide would also apply for a heat pump type fluid as it would be handled and/or serviced in the same manner as the traditional air-conditioning fluids. Additionally, current heat exchanger designs are based on use of single compound refrigerants. A new refrigerant with significant temperature glide could require a complete redesign of the heat exchangers and

other system components in order to maintain overall system performance of incumbent systems utilizing single component fluids.

**[0009]** While HFO-1234yf can be used as an air-conditioning refrigerant, it is limited in its ability to perform as a heat pump type fluid, i.e., capable of providing the capacity needed in both cooling and heating modes. Therefore, the refrigerants noted herein uniquely provide improved capacity over HFO-1234yf in the heating operating range, and/or extend the heating range capability over HFO-1234yf to evaporator temperatures as low as -30°C, provide similar or improved efficiency (COP), have low GWP and low to mild flammability, while also uniquely exhibiting low temperature glide. Hence these refrigerants are most useful in electrified vehicle applications, particularly HEV, PHEV, MHEV, EV and mass transit vehicles which require these properties over the lower end heating range. It should be noted that a heat pump fluid needs to perform well in an air-conditioning cycle, i.e., refrigerant average condensing temperatures up to 40°C, desirably providing equivalent or increased capacity versus HFO-1234yf. Therefore, the refrigerant blends noted herein perform well over a range of temperatures, particularly from about -30°C up to +40°C and can provide both heating or cooling depending upon which cycle is required by the heat pump system.

**[0010]** The present inventors have discovered refrigerant blends that provide cooling capacity higher than HFO-1234yf alone in heating mode, COP equal to or higher than the COP of HFO-1234yf alone, with average temperature glide less than 4 K, preferably less than 3 K, or even less than 2.5 K, are non-toxic and that would be classified as class 2 or 2L flammability by ASHRAE.

**[0011]** The present invention includes the following aspects and embodiments:

In one embodiment, disclosed herein are compositions useful as refrigerants and heat transfer fluids. The compositions disclosed herein comprise: 2,3,3,3-tetrafluoropropene (HFO-1234yf), difluoromethane (HFC-32), and 1,1-difluoroethane (HFC-152a).

**[0012]** According to any of the foregoing embodiments, also disclosed herein are compositions comprising a refrigerant blend comprising from 66 to 80 weight percent HFO-1234yf, from 1 to 10 weight percent HFC-32, and from 10 to 24 weight percent HFC-152a.

**[0013]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend consists essentially of from 69 to 80 weight percent HFO-1234yf, from 5 to 8 weight percent HFC-32, and from 12 to 24 weight percent HFC-152a.

**[0014]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend consists essentially of from 70 to 78 weight percent HFO-1234yf, from 6 to 8 weight percent HFC-32, and from 14 to 24 weight percent HFC-152a.

**[0015]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend consists essentially of from 70 to 78 weight percent HFO-1234yf, from 6 to 7.5 weight percent HFC-32, and from 14 to 24 weight percent HFC-152a.

**[0016]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend consists essentially of from 72 to 78 weight percent HFO-1234yf, from 6 to 7.5 weight percent HFC-32, and from 14 to 20 weight percent HFC-152a.

**[0017]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend consists essentially of from 74 to 78 weight percent HFO-1234yf, from 6 to 7.5 weight percent HFC-32, and from 14 to 18 weight percent HFC-152a.

**[0018]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend consists essentially of:

about 70 weight percent HFO-1234yf, 6 weight percent HFC-32, and about 24 weight percent HFC-152a;

about 74 weight percent HFO-1234yf, about 7 weight percent HFC-32, and about 19 weight percent HFC-152a;

about 77 weight percent HFO-1234yf, about 3 weight percent HFC-32, and about 20 weight percent HFC-152a;

about 78 weight percent HFO-1234yf, 7.5 weight percent HFC-32, and about 14.5 weight percent HFC-152a;

about 78 weight percent HFO-1234yf, 6 weight percent HFC-32, and about 16 weight percent HFC-152a;

about 79 weight percent HFO-1234yf, 3 weight percent HFC-32, and about 18 weight percent HFC-152a;

about 80 weight percent HFO-1234yf, 4 weight percent HFC-32, and about 16 weight percent HFC-152a;

about 70 weight percent HFO-1234yf, about 8 weight percent HFC-32, and about 22 weight percent HFC-152a; or

about 67 weight percent HFO-1234yf, about 10 weight percent HFC-32, and about 23 weight percent HFC-152a.

**[0019]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend provides average temperature glide of about 0.1 K to less than about 4 K.

**[0020]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend provides average temperature glide of about 0.1 K to less than about 3 K.

**[0021]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend provides average temperature glide of about 0.1 K to less than about 2.5 K.

**[0022]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend provides average temperature glide of about 0.1 K to less than about 2.0 K.

**[0023]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend has a GWP of equal to or less than about 100 based on AR5.

**[0024]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend consists essentially of has a GWP of less than about 75 based on AR5.

**[0025]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend consists essentially of has a GWP of less than about 50 based on AR5.

**[0026]** According to any of the foregoing embodiments, also disclosed herein are compositions further comprising at least one additional compound:

- a) comprising at least one compound selected from the group consisting of HCFC-244bb, HFC-245cb, HFC-254eb, CFC-12, HCFC-124, 3,3,3-trifluoropropyne, HCC-1140, HFC-1225ye, HFO-1225zc, HFC-134a, HFO-1243zf, and HCFO-1131; or
- b) comprising at least one compound selected from the group consisting of: HFC-23, HCFC-31, HFC-41, HFC-143a, HCFC-22, HCC-40, HFC-161, HFO-1141, HCO-1140, HCFC-151a, HCC-150a, HCC-160, HCFO-1130a, HCFC-141b, HFC-143a, HCFO-1122, and HCFC-142b; or
- c) combinations of a) and b);

wherein the total amount of additional compound comprises greater than 0 and less than 1 weight percent.

**[0027]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein the additional compound includes at least one of HFC-161, HFO-1141, HCO-1140, HCFC-151a, HCC-150a, or HCC-160 or combinations thereof.

**[0028]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend consists essentially of wherein the additional compounds comprise HFC-143a, HCC-40, HFC-161 and HCFC-151a.

**[0029]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein the additional compounds comprise HFO-1243zf, HFC-143a, HCC-40, HFC-161, and HCFC-151a.

**[0030]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein the additional compounds comprise HFO-1243zf, HCC-40, and HFC-161.

**[0031]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend has a burning velocity of 10 cm/s or less, when measured in accordance with ISO 817 vertical tube method.

**[0032]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend is classified as 2L for flammability as defined in ANSI/ASHRAE Standard 34.

**[0033]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said refrigerant blend has an LFL of less than 10 volume percent when measured in accordance with ASTM-E681.

**[0034]** According to any of the foregoing embodiments, also disclosed herein are compositions further comprising a lubricant.

**[0035]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said lubricant comprises at least one selected from the group consisting of polyalkylene glycol, polyol ester, poly- $\alpha$ -olefin, and polyvinyl ether.

**[0036]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein the polyol ester lubricant is obtained by reacting a carboxylic acid with a polyol comprising a neopentyl backbone selected from the group consisting of neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and mixtures thereof.

**[0037]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein the carboxylic acid has 2 to 18 carbon atoms.

**[0038]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said lubricant has volume resistivity of greater than  $10^{10}$   $\Omega$ -m at 20°C.

**[0039]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said lubricant has surface tension of from about 0.02 N/m to 0.04 N/m at 20°C.

**[0040]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said lubricant has a kinematic viscosity of from about 20 cSt to about 500 cSt at 40°C.

**[0041]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said lubricant has a breakdown voltage of at least 25 kV.

**[0042]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said lubricant has a hydroxy value of at most 0.1 mg KOH/g.

**[0043]** According to any of the foregoing embodiments, also disclosed herein are compositions further comprising from 0.1 to 200 ppm by weight of water.

**[0044]** According to any of the foregoing embodiments, also disclosed herein are compositions further comprising from about 10 ppm by volume to about 0.35 volume percent oxygen.

**[0045]** According to any of the foregoing embodiments, also disclosed herein are compositions further comprising from about 100 ppm by volume to about 1.5 volume percent air.

**[0046]** According to any of the foregoing embodiments, also disclosed herein are compositions further comprising a stabilizer.

**[0047]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein the stabilizer is selected from the group consisting of nitromethane, ascorbic acid, terephthalic acid, azoles, phenolic compounds, cyclic monoterpenes, terpenes, phosphites, phosphates, phosphonates, thiols, and lactones.

**[0048]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein the stabilizer is selected from toluotriazole, benzotriazole, tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-terbutyl-4-methylphenol, fluorinated epoxides, n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, d-limonene,  $\alpha$ -terpinene,  $\beta$ -terpinene,  $\alpha$ -pinene,  $\beta$ -pinene, or butylated hydroxytoluene.

**[0049]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein the stabilizer is present in an amount from about 0.001 to 1.0 weight percent based on the weight of the refrigerant.

**[0050]** According to any of the foregoing embodiments, also disclosed herein are compositions further comprising at least one tracer.

**[0051]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said at least one tracer is present in an amount from about 10 ppm by weight to about 1000 ppm by weight.

**[0052]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said at least one tracer is selected from the group consisting of hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons, hydrochloroolefins, chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof.

**[0053]** According to any of the foregoing embodiments, also disclosed herein are compositions wherein said at least one tracer is selected from the group consisting of HFC-23, HCFC-31, HFC-41, HFC-161, HFC-143a, HFC-134a, HFC-125, HFC-236fa, HFC-236ea, HFC-245cb, HFC-245fa, HFC-254eb, HFC-263fb, HFC-272ca, HFC-281ea, HFC-281fa, HFC-329p, HFC-329mmz, HFC338mf, HFC-338pcc, CFC-12, CFC-11, CFC-114, CFC-114a, HCFC-22, HCFC-123, HCFC-124, HCFC-124a, HCFC-141b, HCFC-142b, HCFC-151a, HCFC-244bb, HCC-40, HFO-1141, HCFO-1130, HCFO-1130a, HCFO-1131, HCFO-1122, HFO-1123, HFO-1234ye, HFO-1243zf, HFO-1225ye, HFO-1225zc, PFC-116, PFC-C216, PFC-218, PFC-C318, PFC-1216, PFC-31-10mc, PFC-31-10my, and combinations thereof.

**[0054]** In another embodiment, disclosed herein is a refrigerant storage container containing the compositions according to any of the foregoing embodiments, wherein the refrigerant comprises gaseous and liquid phases.

**[0055]** In another embodiment, also disclosed herein are systems for heating and cooling the passenger compartment of an electric vehicle comprising an evaporator, compressor, condenser and expansion device, each operably connected to perform a vapor compression cycle, the refrigerant composition of any of the foregoing embodiments being circulated through each of the evaporator, compressor, condenser and expansion device.

**[0056]** According to any of the foregoing embodiments, also disclosed herein are cooling and heating systems, wherein the average temperature glide is less than 4.0 K, 3.0 K, 2.5 K or 2.0 K.

**[0057]** According to any of the foregoing embodiments, also disclosed herein are cooling and heating systems, wherein the system does not include a PTC heater.

**[0058]** According to any of the foregoing embodiments, also disclosed herein are cooling and heating systems, wherein the system is not a reversible cooling loop.

**[0059]** According to any of the foregoing embodiments, also disclosed herein are cooling and heating systems, wherein the system further comprises a reheater operably connected between the compressor and the condenser.

**[0060]** According to any of the foregoing embodiments, also disclosed herein is a method for replacing HFO-1234yf in a heating and cooling system contained within an electric vehicle, comprising providing any of the foregoing compositions to said heating and cooling system as a heat transfer fluid.

**[0061]** According to any of the foregoing embodiments, also disclosed herein is a method for replacing HFO-1234yf, wherein the refrigerant blend produces volumetric capacity at least 7% higher, or 10% higher, or 15% higher, or even 20% higher than HFO-1234yf alone when operating under the same heating conditions.

**[0062]** According to any of the foregoing embodiments, also disclosed herein is a method for replacing HFO-1234yf, wherein the refrigerant blend produces COP equal to or greater than the COP of HFO-1234yf alone when operating under the same conditions.

**[0063]** In another embodiment, also disclosed herein is a method of servicing the heating and cooling system of an electric vehicle comprising removing all of a used refrigerant from the system and charging the system with any of the foregoing compositions.

**[0064]** In another embodiment, disclosed herein is a use of any of the foregoing compositions as a heat transfer fluid in a system for heating and cooling the passenger compartment of an electric vehicle.

**[0065]** In another embodiment, disclosed herein is a use of a composition comprising a refrigerant blend consisting essentially of:

78 weight percent HFO-1234yf, 8 weight percent HFC-32, and 14 weight percent HFC-152a; or

72 weight percent HFO-1234yf, 8 weight percent HFC-32, and 20 weight percent HFC-152a,

as a heat transfer fluid in a system for heating and cooling the passenger compartment of an electric vehicle.

**[0066]** In another embodiment, disclosed herein is a method for reducing the temperature glide in a heat exchanger operating with a refrigerant blend consisting essentially of HFC-32 and HFO-1234yf comprising adding HFC-152a to the refrigerant blend composition.

**[0067]** According to any of the foregoing embodiments, disclosed herein is a method for reducing temperature glide, wherein the HFC-152a is added in an amount of about 10 to 24 weight percent based on the weight percent of the total refrigerant blend composition.

**[0068]** According to any of the foregoing embodiments, disclosed herein is a method for reducing temperature glide, wherein the temperature glide in the heat exchanger is reduced to less than 3 K.

**[0069]** The various aspects and embodiments of the invention can be used alone or in combinations with each other. Other features and advantages of the present invention will be apparent from the following more detailed description of the preferred embodiment which illustrates, by way of example, the principles of the invention.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

**[0070]** FIG. 1 illustrates a reversible cooling or heating loop system, according to an embodiment.

**[0071]** FIG. 2 illustrates reversible cooling or heating loop system, according to an embodiment.

**[0072]** FIG. 3 illustrates a cooling or heating system, according to an embodiment.

**[0073]** FIG. 4 illustrates a cooling or heating system, according to an embodiment.

**[0074]** FIG. 5 illustrates a cooling or heating system, according to an embodiment.

**[0075]** FIG. 6 illustrates the reduction in glide for an embodiment of the present invention using a contour plot for temperature glide.

**[0076]** FIG. 7 illustrates a cooling or heating system, according to an embodiment.

**[0077]** FIG. 8 illustrates a cooling or heating system, according to an embodiment.

**[0078]** FIG. 9 illustrates a cooling or heating system, according to an embodiment.

**[0079]** FIG. 10 illustrates a cooling or heating system, according to an embodiment.

## **DETAILED DESCRIPTION**

### **DEFINITIONS**

**[0080]** As used herein, the term heat transfer composition or heat transfer fluid means a composition used to carry heat from a heat source to a heat sink.

**[0081]** A heat source is defined as any space, location, object or body from which it is desirable to add, transfer, move or remove heat. Example of a heat source in this embodiment is the vehicle passenger compartment requiring air conditioning.

**[0082]** A heat sink is defined as any space, location, object or body capable of absorbing heat. Example of a heat sink in one embodiment is the vehicle passenger compartment requiring heating.

**[0083]** A heat transfer system is the system (or apparatus) used to produce a heating or cooling effect in a particular location. A heat transfer system in this invention implies the heating or cooling system which provides heating or cooling of the passenger compartment of an automobile. Sometimes this system is called a heat pump system and may be a reversible heating system or a reversible cooling system, or simply a heating and cooling system.

**[0084]** A heat transfer fluid comprises at least one refrigerant and at least one member selected from the group consisting of lubricants, stabilizers, tracers, UV dyes, and flame suppressants.

**[0085]** Volumetric capacity is the amount of heat absorbed or rejected divided by the theoretical compressor displacement. Heat removed or absorbed is the enthalpy

difference across a heat exchanger multiplied by the refrigerant mass flowrate. Theoretical compressor displacement is the refrigerant mass flowrate divided by the density of the gas entering the compressor (i.e., compressor suction density). More simply, volumetric capacity is the suction density multiplied by the heat exchanger enthalpy difference. Higher volumetric capacity allows the use of a smaller compressor for the same heat load. Herein, cooling capacity refers to the volumetric capacity in cooling mode and heating capacity refers to the volumetric capacity in heating mode.

**[0086]** Coefficient of performance (COP) is the amount of heat absorbed or rejected divided by the required energy input to operate the cycle (approximated by the compressor power). COP is specific to the mode of operation of a heat pump, thus COP for heating or COP for cooling. COP is directly related to the energy efficiency ratio (EER).

**[0087]** Subcooling refers to the reduction of the temperature of a liquid below that liquid's saturation point for a given pressure. The liquid saturation point is the temperature at which the vapor is completely condensed to a liquid. By cooling a liquid below the saturation temperature (or bubble point temperature), the net refrigeration effect can be increased. Subcooling thereby improves refrigeration capacity and energy efficiency of a system. The subcool amount is the amount of cooling below the saturation temperature (in degrees).

**[0088]** Superheating refers to the increase of the temperature of a vapor above that vapor's saturation point for a given pressure. The vapor saturation point is the temperature at which the liquid is completely evaporated to a vapor. Superheating continues to heat the vapor to a higher temperature vapor at the given pressure. By heating the vapor above the saturation temperature (or dew point temperature), the net refrigeration effect can be increased. Superheating thereby improves refrigeration capacity and energy efficiency of a system when it occurs in the evaporator. Suction line superheat does not add to the net refrigeration effect and can reduce efficiency and capacity. The superheat amount is the amount of heating above the saturation temperature (in degrees).

**[0089]** Temperature glide (sometimes referred to simply as "glide") is the absolute value of the difference between the starting and ending temperatures of a phase-

change process by a refrigerant within a condenser of a refrigerant system, exclusive of any subcooling or superheating. For an evaporator, the glide is the difference in temperature between the dew point and the evaporator inlet. Glide may be used to describe condensation or evaporation of a near azeotrope or non-azeotropic composition. When referring to the temperature glide of an air conditioning or heat pump system, it is common to provide the average temperature glide being the average of the temperature glide in the evaporator and the temperature glide in the condenser. Glide is applicable to blend refrigerants, i.e. refrigerants that are composed of at least 2 components.

**[0090]** Low glide herein is defined as average glide which is less than 4K over operating range of interest, more preferably low glide is less than 3K over operating range of interest, more preferably being less than 2.5 K over operating range of interest, or most preferably being less than 2.0 K over operating range of interest, (e.g., a glide ranging from great than 0 to less than about 2.0 K) under conditions for heating.

**[0091]** An azeotropic composition is a constant-boiling mixture of two or more substances that behave as a single substance at given conditions of pressure and temperature. One way to characterize an azeotropic composition is that the vapor produced by partial evaporation or distillation of the liquid has the same composition as the liquid from which it is evaporated or distilled, i.e., the mixture distills/refluxes without compositional change. Constant-boiling compositions are characterized as azeotropic because they exhibit either a maximum or minimum boiling point, as compared with that of the non-azeotropic mixture of the same compounds. An azeotropic composition will not fractionate, assuming constant temperature and pressure, within an air conditioning or heating system during operation. Additionally, an azeotropic composition will not fractionate upon leakage from an air conditioning or heating system.

**[0092]** A near-azeotropic composition (also commonly referred to as an "azeotrope-like composition") is a substantially constant boiling liquid mixture of two or more substances that behaves essentially as a single substance. One way to characterize a near-azeotropic composition is that the vapor produced by partial evaporation or distillation of the liquid has substantially the same composition as the

liquid from which it was evaporated or distilled, that is, the mixture distills/refluxes without substantial composition change. Another way to characterize a near-azeotropic composition is that the bubble point vapor pressure and the dew point vapor pressure of the composition at a particular temperature are substantially the same.

**[0093]** Herein near-azeotropic compositions exhibit dew point pressure and bubble point pressure with virtually no pressure differential. That is, the difference in the dew point pressure and bubble point pressure at a given temperature will be a small value. It may be stated that compositions with a difference in dew point pressure and bubble point pressure of less than or equal to 3 percent (based upon the bubble point pressure) may be considered to be a near-azeotropic mixture.

**[0094]** As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a composition, process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, process, method, article, or apparatus. Further, unless expressly stated to the contrary, “or” refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

**[0095]** The transitional phrase "consisting of" excludes any element, step, or ingredient not specified. If in the claim such would close the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase "consists of" appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

**[0096]** The transitional phrase "consisting essentially of" is used to define a composition, method that includes materials, steps, features, components, or elements, in addition to those literally disclosed provided that these additional included materials, steps, features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention, especially the mode of

action to achieve the desired result of any of the processes of the present invention. The term 'consisting essentially of' occupies a middle ground between "comprising" and 'consisting of'.

**[0097]** Where applicants have defined an invention or a portion thereof with an open-ended term such as "comprising," it should be readily understood that (unless otherwise stated) the description should be interpreted to also include such an invention using the terms "consisting essentially of" or "consisting of" including, for example, a composition consisting essentially of or consisting of.

**[0098]** Also, use of "a" or "an" are employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

### **REFRIGERANT BLEND**

**[0099]** Global warming potential (GWP) is an index for estimating relative global warming contribution due to atmospheric emission of a kilogram of a particular greenhouse gas compared to emission of a kilogram of carbon dioxide. GWP can be calculated for different time horizons showing the effect of atmospheric lifetime for a given gas. The GWP for the 100-year time horizon is commonly the value referenced. For mixtures, a weighted average can be calculated based on the individual GWPs for each component. The United Nations Intergovernmental Panel on Climate Change (IPCC) provides vetted values for refrigerant GWPs in official assessment reports (ARs.) The fourth assessment report is denoted as AR4 and the fifth assessment report is denoted as AR5. The GWP values reported for refrigerant blends of the present invention herein refer to the AR5 values.

**[0100]** Ozone-depletion potential (ODP) is a number that refers to the amount of ozone depletion caused by a substance. The ODP is the ratio of the impact on ozone of a chemical compared to the impact of a similar mass of R-11 or trichlorofluoromethane. R-11 is a type of chlorofluorocarbon (CFC) and as such has chlorine in it which contributes to ozone depletion. Furthermore, the ODP of CFC-11 is defined to be 1.0. Other CFCs and hydrofluorochlorocarbons (HCFCs) have ODPs

that range from 0.01 to 1.0. Hydrofluorocarbons (HFCs) and the hydrofluoro-olefins (HFO's) described herein have zero ODP because they do not contain chlorine, bromine or iodine, species known to contribute to ozone breakdown and depletion.

**[0101]** The compositions comprise a refrigerant blend consisting essentially of 2,3,3,3-tetrafluoropropene (HFO-1234yf), difluoromethane (HFC-32), and 1,1-difluoroethane (HFC-152a). Suitable amounts of HFC-32 in the refrigerant blend include, but are not limited to, an amount between about 1 weight percent and 10 weight percent or between about 5 weight percent and 8 weight percent or between about 6 weight percent and 8 weight percent or between 6 weight percent and 7.5 weight percent or between 6 weight percent and 7 weight percent based on the total refrigerant blend composition. Suitable amounts of HFC-152a in the refrigerant blend include, but are not limited to, an amount between about 10 weight percent to 24 weight percent or between about 12 weight percent to 24 weight percent or between about 14 weight percent to 24 weight percent between about 14.5 weight percent to 24 weight percent or between about 14 weight percent to 18 weight percent based on the total refrigerant blend composition. Suitable amounts of HFO-1234yf in the refrigerant blend include, but are not limited to, an amount between about 66 weight percent to 80 weight percent or between about 69 weight percent to 80 weight percent or between about 70 weight percent to 78 weight percent or between about 72 weight percent to 78 weight percent based on the total refrigerant blend composition.

**[0102]** Specific compositions suitable for use in heat transfer system and methods of the present invention include:

about 70 weight percent HFO-1234yf, about 6 weight percent HFC-32, and about 24 weight percent HFC-152a;

about 74 weight percent HFO-1234yf, about 7 weight percent HFC-32, and about 19 weight percent HFC-152a;

about 77 weight percent HFO-1234yf, about 3 weight percent HFC-32, and about 20 weight percent HFC-152a;

about 78 weight percent HFO-1234yf, 7.5 weight percent HFC-32, and about 14.5 weight percent HFC-152a;

about 78 weight percent HFO-1234yf, about 6 weight percent HFC-32, and about 16 weight percent HFC-152a;

about 79 weight percent HFO-1234yf, about 3 weight percent HFC-32, and about 18 weight percent HFC-152a;

about 80 weight percent HFO-1234yf, about 4 weight percent HFC-32, and about 16 weight percent HFC-152a;

about 70 weight percent HFO-1234yf, about 8 weight percent HFC-32, and about 22 weight percent HFC-152a; and

about 67 weight percent HFO-1234yf, about 10 weight percent HFC-32, and about 23 weight percent HFC-152a.

**[0103]** In one embodiment, the composition comprises a refrigerant blend comprising from 66 to 80 weight percent HFO-1234yf, from 1 to 10 weight percent HFC-32, and from 10 to 24 weight percent HFC-152a. In another embodiment, said refrigerant blend consists essentially of from 69 to 80 weight percent HFO-1234yf, from 5 to 8 weight percent HFC-32, and from 12 to 24 weight percent HFC-152a. In another embodiment, said refrigerant blend consists essentially of from 70 to 78 weight percent HFO-1234yf, from 6 to 8 weight percent HFC-32, and from 14 to 24 weight percent HFC-152a. In another embodiment, the refrigerant blend consists essentially of from 70 to 78 weight percent HFO-1234yf, from 6 to 7.5 weight percent HFC-32, and from 14 to 24 weight percent HFC-152a. In another embodiment, the refrigerant blend consists essentially of from 70 to 78 weight percent HFO-1234yf, from 6 to 7.5 weight percent HFC-32, and from 14.5 to 24 weight percent HFC-152a. In another embodiment, the refrigerant blend consists essentially of from 72 to 78 weight percent HFO-1234yf, from 6 to 7.5 weight percent HFC-32, and from 14 to 20 weight percent HFC-152a. In another embodiment, the refrigerant blend consists essentially of from 74 to 78 weight percent HFO-1234yf, from 6 to 7.5 weight percent HFC-32, and from 14 to 18 weight percent HFC-152a.

**[0104]** In some embodiments of the compositions, the refrigerant blend excludes compositions containing:

78 weight percent HFO-1234yf, 8 weight percent HFC-32, and 14 weight percent HFC-152a; or

72 weight percent HFO-1234yf, 8 weight percent HFC-32, and 20 weight percent HFC-152a.

**[0105]** HFO-1234yf has very low GWP, having GWP = 1 (AR5). HFC-32 has GWP = 677 (AR5), and HFC-152a has GWP = 138 (AR5).

**[0106]** Therefore, the final blends have 0 ODP and low GWP, or GWP <100, or preferably GWP <75, or more preferably GWP<50 (by AR5 values). Table 1, shown below, is a summary table showing refrigerant blend and GWP per the 5<sup>th</sup> assessment report conducted by the Intergovernmental Panel on Climate Change (IPCC) for 2,3,3,3-tetrafluoropropene (HFO-1234yf), difluoromethane (HFC-32), and 1,1-difluoroethane (HFC-152a), and various combinations thereof. The inventive refrigerant blends can have a GWP ranging from greater than 0 to less than about 100, or greater than 0 to less than about 75.

**[0107]** For the refrigerant blend, GWP may be calculated as a weighted average of the individual GWP values in the blend, taking into account the mass (e.g., weight %) of each ingredient in the blend.

**TABLE 1**

Refrigerant (wt%)	GWP AR5 (IPCC)
HFO-1234yf	1
HFC-32	677
HFC-152a	138
HFO-1234yf (67%) / HFC-32 (10%) / HFC-152a (23%)	100
HFO-1234yf (70%) / HFC-32 (6%) / HFC-152a (24%)	74
HFO-1234yf (70%) / HFC-32 (8%) / HFC-152a (22%)	85
HFO-1234yf (74%) / HFC-32 (7%) / HFC-152a (19%)	74
HFO-1234yf (77%) / HFC-32 (3%) / HFC-152a (20%)	49
HFO-1234yf (78%) / HFC-32 (7.5%) / HFC-152a (14.5%)	72
HFO-1234yf (78%) / HFC-32 (8%) / HFC-152a (14%)	74
HFO-1234yf (79%) / HFC-32 (3%) / HFC-152a (18%)	46
HFO-1234yf (80%) / HFC-32 (4%) / HFC-152a (16%)	50

**[0108]** The refrigerant blends as described herein operate in heat exchangers, i.e., evaporators and/or condensers with low temperature glide. Thus, there is limited

fractionation of the composition in operation providing efficient and consistent performance for cooling and heating.

**[0109]** Refrigerant blend compositions containing only HFO-1234yf and HFC-32 are known to have higher temperature glide. By adding HFC-152a, the temperature glide of the refrigerant composition is decreased. This effect is notable, in particular when the HFO-1234yf composition is greater than 70 weight percent.

**[0110]** In some embodiments, the refrigerant blends provide average temperature glides less than 4K over operating range of interest, more preferably low glide is less than 3K over operating range of interest, more preferable being less than 2.5 K over operating range of interest, with most preferable being less than 2.0 K over operating range of interest, (e.g., a glide ranging from great than 0 to less than about 2.0K). This effect is observed, when any of the foregoing refrigerant blends are used in a heat pump operating in heating mode.

### **REFRIGERANT ADDITIVES**

**[0111]** The compositions of the present invention comprising a refrigerant blend may further comprise a lubricant and be used as a heat transfer fluid. The composition of the present invention containing the refrigerant blend of the present invention and the lubricant may contain additives such as a stabilizer, a leakage detection material, a tracer, and other beneficial additives.

**[0112]** The lubricant chosen for this composition preferably has sufficient solubility in the refrigerant blend to ensure that the lubricant can return to the compressor from the evaporator. Furthermore, the miscibility must not be so great as to reduce the effective viscosity of the lubricant for lubricating the compressor. In one preferred embodiment, the lubricant and refrigerant blend are miscible over a broad range of temperatures. For use in mobile air-conditioning and heating, miscibility over a temperature range from about -40°C to about +40°C is desirable. Lubricants of the invention may include polyalkylene glycol lubricants (PAG), polyol ester lubricants (POE), polyvinyl ether lubricants (PVE), poly- $\alpha$ -olefins (PAO), alkylbenzenes, mineral oils, fluorinated polyethers, and silicon lubricants.

**[0113]** Preferred lubricants may be one or more polyalkylene glycol type lubricants (PAG), one or more polyol ester type lubricants (POE), one or more poly- $\alpha$ -olefins

(PAO), or one or more polyvinyl ether lubricants. Additionally, lubricants for combination with the refrigerant blends of the present invention may be mixtures of any of PAG, POE, and/or PVE lubricants.

**[0114]** In one embodiment, polyalkylene glycol (PAG) oils are preferred and may be homopolymers or copolymers consisting of two or more oxypropylene groups. PAG oils can be un-capped, single-end capped, or double-end capped. Examples of commercial PAG oils include, but are not limited to ND-8, Castrol PAG 46, Castrol PAG 100, Castrol PAG 150, Daphne Hermetic PAG PL, and Daphne Hermetic PAG PR.

**[0115]** PAG lubricant properties that make them of use in the present invention include volume resistivity of greater than  $10^{10}$   $\Omega$ -m at 20°C, surface tension of from about 0.02 N/m to 0.04 N/m at 20°C, kinematic viscosity of from about 20 cSt to about 500 cSt at 40°C, breakdown voltage of at least 25 kV, and hydroxy value of at most 0.1 mg KOH/g.

**[0116]** In an aspect of this embodiment, the lubricant comprises PAG and the refrigerant consists essentially of about 66 to 80 weight percent HFO-1234yf, about 1 to 10 weight percent HFC-32, and about 10 to 24 weight percent HFC-152a. In another embodiment, the lubricant comprises PAG and the refrigerant consists essentially of about 69 to 80 weight percent HFO-1234yf, about 5 to 8 weight percent HFC-32, and about 12 to 24 weight percent HFC-152a. In another embodiment, the lubricant comprises PAG and the refrigerant consists essentially of about 70 to 78 weight percent HFO-1234yf, about 6 to 8 weight percent HFC-32, and about 14 to 24 weight percent HFC-152a. In another embodiment, the lubricant comprises PAG and the refrigerant consists essentially of about 70 to 78 weight percent HFO-1234yf, about 6 weight percent to 7.5 weight percent HFC-32, and about 14 weight percent to 24 weight percent HFC-152a. In another embodiment the lubricant comprises PAG and the refrigerant consists essentially of about 70 to 78 weight percent HFO-1234yf, about 6 to 7 weight percent HFC-32, and about 14 to 24 weight percent HFC-152a. In another embodiment the lubricant comprises PAG and the refrigerant consists essentially of about 72 to 78 weight percent HFO-1234yf, about 6 to 7 weight percent HFC-32, and about 14 to 20 weight percent HFC-152a. In another embodiment the lubricant comprises PAG and the refrigerant consists essentially of

about 74 to 78 weight percent HFO-1234yf, about 6 to 7 weight percent HFC-32, and about 14 to 18 weight percent HFC-152a. And, in a further aspect, the refrigerant composition further comprises greater than about 0 and less than 1 wt.% of additional compounds.

**[0117]** POE lubricants are typically formed by a chemical reaction (esterification) of a carboxylic acid, or a mixture of carboxylic acids, with an alcohol, or mixture of alcohols.

**[0118]** In one embodiment, the polyol esters as used herein include esters of a diol or a polyol having from about 3 to 20 hydroxyl groups and a carboxylic acid (or fatty acid) having from about 1 to 24 carbon atoms is preferably used as the polyol. An ester which can be used as the base oil is described in European Patent Application published in accordance with Art. 153(4) EP 2 727 980 A1, which is hereby incorporated by reference. Here, examples of the diol include ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,2-butanediol, 2-methyl-1,3-propanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 2-ethyl-2-methyl-1,3-propanediol, 1,7-heptanediol, 2-methyl-2-propyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, 1,12-dodecanediol, and the like.

**[0119]** Examples of the above-described polyol include a polyhydric alcohol such as trimethylolethane, trimethylolpropane, trimethylolbutane, di(trimethylolpropane), tri(trimethylolpropane), pentaerythritol, di(pentaerythritol), tri(pentaerythritol), glycerin, polyglycerin (dimer to eicosamer of glycerin), 1,3,5-pentanetriol, sorbitol, sorbitan, a sorbitol-glycerin condensate, adonitol, arabitol, xylitol, mannitol, etc.; a saccharide such as xylose, arabinose, ribose, rhamnose, glucose, fructose, galactose, mannose, sorbose, cellobiose, maltose, isomaltose, trehalose, sucrose, raffinose, gentianose, melezitose, among others; partially etherified products and methyl glucosides thereof; and the like. Among these, a hindered alcohol such as neopentyl glycol, trimethylolethane, trimethylolpropane, trimethylolbutane, di(trimethylolpropane), tri(trimethylolpropane), pentaerythritol, di(pentaerythritol), tri(pentaerythritol), etc. is preferable as the polyol.

**[0120]** Though the fatty acid is not particularly limited on its carbon number, in general, a fatty acid having from 1 to 24 carbon atoms is used. In the fatty acid

having from 1 to 24 carbon atoms, a fatty acid having 3 or more carbon atoms is preferable, a fatty acid having 4 or more carbon atoms is more preferable, a fatty acid having 5 or more carbon atoms is still more preferable, and a fatty acid having 10 or more carbon atoms is the most preferable from the standpoint of lubricating properties. In addition, a fatty acid having not more than 18 carbon atoms is preferable, a fatty acid having not more than 12 carbon atoms is more preferable, and a fatty acid having not more than 9 carbon atoms is still more preferable from the standpoint of compatibility with the refrigerant. In one embodiment the carboxylic acid has 2 to 18 carbon atoms.

**[0121]** In addition, the fatty acid may be either of a linear fatty acid and a branched fatty acid, and the fatty acid is preferably a linear fatty acid from the standpoint of lubricating properties, whereas it is preferably a branched fatty acid from the standpoint of hydrolysis stability. Furthermore, the fatty acid may be either of a saturated fatty acid and an unsaturated fatty acid. Specifically, examples of the above-described fatty acid include a linear or branched fatty acid such as pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, icosanoic acid, oleic acid, etc.; a so-called neo acid in which a carboxylic group is attached to a quaternary carbon atom; and the like. More specifically, preferred examples thereof include valeric acid (n-pentanoic acid), caproic acid (n-hexanoic acid), enanthic acid (n-heptanoic acid), caprylic acid (n-octanoic acid), pelargonic acid (n-nonanoic acid), capric acid (n-decanoic acid), oleic acid (cis-9-octadecenoic acid), isopentanoic acid (3-methylbutanoic acid), 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, 3,5,5-trimethylhexanoic acid, and the like. Incidentally, the polyol ester maybe a partial ester in which the hydroxyl groups of the polyol remain without being fully esterified; a complete ester in which all of the hydroxyl groups are esterified; or a mixture of a partial ester and a complete ester, with a complete ester being preferable.

**[0122]** In the polyol ester, an ester of a hindered alcohol such as neopentyl glycol, trimethylolethane, trimethylolpropane, trimethylolbutane, di(trimethylolpropane), tri(trimethylolpropane), pentaerythritol, di(pentaerythritol), tri(pentaerythritol), etc. is more preferable, with an ester of neopentyl glycol, trimethylolethane,

trimethylolpropane, trimethylolbutane, or pentaerythritol being still more preferable, from the standpoint of more excellent hydrolysis stability; and an ester of pentaerythritol is the most preferable from the standpoint of especially excellent compatibility with the refrigerant and hydrolysis stability.

**[0123]** Preferred specific examples of the polyol ester include a diester of neopentyl glycol with one kind or two or more kinds of fatty acids selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid; a triester of trimethylolethane with one kind or two or more kinds of fatty acids selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid; a triester of trimethylolpropane with one kind or two or more kinds of fatty acids selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid; a triester of trimethylolbutane with one kind or two or more kinds of fatty acids selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid; and a tetraester of pentaerythritol with one kind or two or more kinds of fatty acids selected from valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid. Incidentally, the ester with two or more kinds of fatty acids may be a mixture of two or more kinds of esters of one kind of a fatty acid and a polyol, and an ester of a mixed fatty acid of two or more kinds thereof and a polyol, particularly an ester of a mixed fatty acid and a polyol is excellent in low-temperature properties and compatibility with the refrigerant.

**[0124]** The POE lubricant used for electrified automotive air-conditioning and heating application may have a kinematic viscosity (measured at 40°C, according to ASTM D445) between 20-500cSt, or 75-110 cSt, and ideally about 80 cSt-100 cSt and most specifically, between 85 cSt-95 cSt. However, not wanting to limit the

invention, it should be noted that other lubricant viscosities may be included depending on the needs of the electrified vehicle heat pump compressor. Suitable characteristics of an automotive POE type lubricant for use with the inventive composition are listed below.

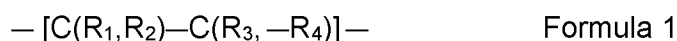
Specification Item	Units	Method	POE Properties
Viscosity at 40°C	cSt	ASTM D445	80-90
Viscosity at 100°C	cSt	ASTM D445	9.0-9.3
Viscosity Index		ASTM D2270	>80
Colour	Gardner	ASTM D1500	<1
Flash point (COC)	°C	ASTM 92	250 min
Pour point	°C	ASTM D97	-40 max
Specific Gravity (20°C)	Kg/m <sup>3</sup>	ASTM D1298	0.950-1.10
Capping Efficiency	%	ASTM E326	80-90
Total Acid Number	mgKOH/g	ASTM D974	0.1 max
Water content	ppm	ASTM E284	50 max

**[0125]** In one embodiment, the lubricant comprises POE and the POE is stable when exposed to the inventive compositions wherein the refrigeration composition has an F-ion of less than about 500 ppm and in some cases an F-ion amount of greater than 0 and less than 500 ppm, greater than 0 and less than 100 ppm and, in some cases, greater than 0 and less than 50ppm. In an aspect of this embodiment, the refrigerant consists essentially of about 66 to about 80 weight percent, preferably, about 70 weight percent to 78 weight percent or about 72 weight percent to 78 weight percent or about 74 weight percent to 78 weight percent HFO-1234yf, about 2 weight percent to 8 weight percent or 6 weight percent to 7.5 weight percent HFC-32, and about 14 weight percent to 24 weight percent or about 14.5 weight percent to 24 weight percent or about 14 weight percent to 20 weight percent or about 14 weight percent to 18 weight percent HFC-152a. And, in a further aspect, the refrigerant composition further comprises greater than about 0 and less than 1 wt.% of additional compounds.

**[0126]** In one embodiment, the lubricant comprises POE and the POE is stable when exposed to the inventive composition wherein the refrigerant blend composition has a Total Acid Number (TAN), mg KOH/g number of less than about 1, greater than 0 and less than 1, greater than 0 and less than about 0.75 and, in some cases, greater than 0 and less than about 0.4. In an aspect of this

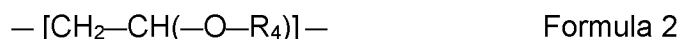
embodiment, the lubricant comprises POE and the refrigerant consists essentially of about 66 to 80 weight percent HFO-1234yf, about 1 to 10 weight percent HFC-32, and about 10 to 24 weight percent HFC-152a. In another embodiment, the lubricant comprises POE and the refrigerant consists essentially of about 69 to 80 weight percent HFO-1234yf, about 5 to 8 weight percent HFC-32, and about 12 to 24 weight percent HFC-152a. In another embodiment, the lubricant comprises POE and the refrigerant consists essentially of about 70 to 78 weight percent HFO-1234yf, about 6 to 8 weight percent HFC-32, and about 14 to 24 weight percent HFC-152a. In another embodiment, the lubricant comprises POE and the refrigerant consists essentially of about 70 to 78 weight percent HFO-1234yf, about 6 weight percent to 7.5 weight percent HFC-32, and about 14 weight percent to 24 weight percent HFC-152a. In another embodiment the lubricant comprises POE and the refrigerant consists essentially of about 70 to 78 weight percent HFO-1234yf, about 6 to 7 weight percent HFC-32, and about 14 to 24 weight percent HFC-152a. In another embodiment the lubricant comprises POE and the refrigerant consists essentially of about 72 to 78 weight percent HFO-1234yf, about 6 to 7 weight percent HFC-32, and about 14 to 20 weight percent HFC-152a. In another embodiment the lubricant comprises POE and the refrigerant consists essentially of about 74 to 78 weight percent HFO-1234yf, about 6 to 7 weight percent HFC-32, and about 14 to 18 weight percent HFC-152a. And, in a further aspect, the refrigerant composition further comprises greater than about 0 and less than 1 wt.% of additional compounds.

**[0127]** In another embodiment, PVE lubricants can be included as lubricant in the compositions of the present invention. Though not meant to limit the scope of the present invention in any way, in an embodiment of the present invention, the polyvinyl ether oil includes those taught in the literature such as described in U.S. Pat. Nos. 5,399,631 and 6,454,960. In another embodiment of the present invention, the polyvinyl ether oil is composed of structural units of the type shown by Formula 1:

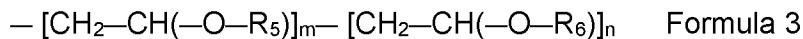


where  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are independently selected from hydrogen and hydrocarbons, where the hydrocarbons may optionally contain one or more ether

groups. In a preferred embodiment of the present invention, R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are each hydrogen, as shown in Formula 2:



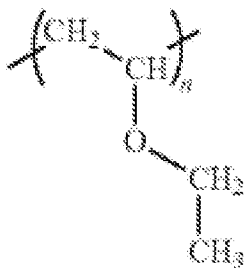
**[0128]** In another embodiment of the present invention, the polyvinyl ether oil is composed of structural units of the type shown by Formula 3:



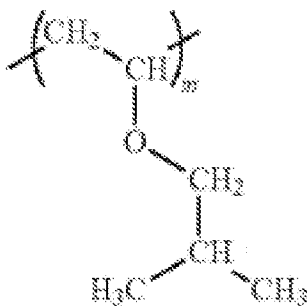
where R<sub>5</sub> and R<sub>6</sub> are independently selected from hydrogen and hydrocarbons and where m and n are integers.

**[0129]** In one embodiment, the polyvinyl ether oil comprises copolymers of the following 2 units:

Unit 1:



Unit 2:



**[0130]** The properties of the lubricant (viscosity, solubility of the refrigerant and miscibility with the refrigerant) may be adjusted by varying the n/n ratio and the sum of m+n. In another embodiment, the PVE lubricants are those that are 50-95 weight percent of unit 1.

**[0131]** In an aspect of this embodiment, the lubricant comprises PVE and the refrigerant consists essentially of about 66 to 80 weight percent HFO-1234yf, about 1 to 10 weight percent HFC-32, and about 10 to 24 weight percent HFC-152a. In another embodiment, the lubricant comprises PVE and the refrigerant consists essentially of about 69 to 80 weight percent HFO-1234yf, about 5 to 8 weight percent HFC-32, and about 12 to 24 weight percent HFC-152a. In another embodiment, the lubricant comprises PVE and the refrigerant consists essentially of about 70 to 78 weight percent HFO-1234yf, about 6 to 8 weight percent HFC-32, and about 14 to 24 weight percent HFC-152a. In another embodiment, the lubricant comprises PVE and the refrigerant consists essentially of about 70 to 78 weight percent HFO-1234yf, about 6 weight percent to 7.5 weight percent HFC-32, and about 14 weight percent to 24 weight percent HFC-152a. In another embodiment the lubricant comprises PVE and the refrigerant consists essentially of about 70 to 78 weight percent HFO-1234yf, about 6 to 7 weight percent HFC-32, and about 14 to 24 weight percent HFC-152a. In another embodiment the lubricant comprises PVE and the refrigerant consists essentially of about 72 to 78 weight percent HFO-1234yf, about 6 to 7 weight percent HFC-32, and about 14 to 20 weight percent HFC-152a. In another embodiment the lubricant comprises PVE and the refrigerant consists essentially of about 74 to 78 weight percent HFO-1234yf, about 6 to 7 weight percent HFC-32, and about 14 to 18 weight percent HFC-152a. And, in a further aspect, the refrigerant composition further comprises greater than about 0 and less than 1 wt.% of additional compounds.

**[0132]** Similar properties and characteristics may be required for use of PVE lubricants in the compositions described herein and in particular for use in automotive cooling and heating systems, as for POE lubricants.

**[0133]** In a preferred embodiment, the lubricant is soluble in the refrigerant at temperatures between about -40°C and about 80°C, and more preferably in the range of about -30°C and about 40°C, and even more specifically between -25°C and 40°C. In another embodiment, attempting to maintain the lubricant in the compressor is not a priority and thus high temperature insolubility is not preferred.

**[0134]** The amount of lubricant can range from about 1 wt% to about 20 wt%, about 1 wt% to about 7 wt%, and, in some cases, about 1 wt% to about 3 wt%.

**[0135]** To suppress the hydrolysis of the lubricating oil, it is necessary to control the moisture concentration in the heating/cooling system for electric type vehicles. Therefore, the lubricant in this embodiment needs to have low moisture, typically less than 100 ppm by weight of water.

**[0136]** In a preferred embodiment, the lubricant comprises a POE lubricant that is soluble in the vehicle heat pump system refrigerant blend at temperatures between about -35°C and about 100°C, and more preferably in the range of about -35°C and about 50°C, and even more specifically between -30°C and 40°C. In another preferred embodiment, the POE lubricant is soluble at temperatures above about 70°C, more preferably at temperatures above about 80°C, and most preferably at temperatures between 90 -95°C.

**[0137]** Of particular note are PAG, POE, PAO, and PVE lubricants having: volume resistivity of greater than  $10^{10}$   $\Omega$ -m at 20°C; surface tension of from about 0.02 N/m to 0.04 N/m at 20°C; a kinematic viscosity of from about 20 cSt to about 500 cSt, or about 50 cSt to about 200 cSt, or about 75 cSt to about 100 cSt at 40°C; a breakdown voltage of at least 25 kV; and a hydroxy value of at most 0.1 mg KOH/g.

**[0138]** HFO type refrigerants, due to the presence of a double bond, may be subject to thermal instability and decompose under extreme use, handling or storage situations. Therefore, there may be advantages to adding stabilizers to HFO type refrigerants. Stabilizers may notably include nitromethane, ascorbic acid, terephthalic acid, azoles such as toluotriazole or benzotriazole, phenolic compounds such as tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-tertbutyl-4-methylphenol, epoxides (possibly fluorinated or perfluorated alkyl epoxides or alkenyl or aromatic epoxides) such as n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, cyclic monoterpenes, terpenes, such as d-limonene,  $\alpha$ -terpinene,  $\beta$ -terpinene,  $\gamma$ -terpinene,  $\alpha$ -pinene, or  $\beta$ -pinene, phosphites, phosphates, phosphonates, thiols and lactones. Examples of suitable stabilizers are disclosed in WO2019213004, WO2020222864, and [WO2020222865](#); the disclosures of which are hereby incorporated by reference.

**[0139]** Blends may or may not include stabilizers depending on the requirements of the system being used. If the refrigerant blend does include a stabilizer, it may include any amount from 0.001 wt% up to 1 wt%, preferably from about 0.01 to about

0.5 weight percent, more preferably, from about 0.01 to about 0.3 weight percent of any of the stabilizers listed above, and, in most case, preferably d-limonene.

**[0140]** In some embodiments, the compositions as disclosed herein may contain a tracer compound or tracers. The tracer may comprise two or more tracer compounds. In some embodiments, the tracer is present in the compositions at a total concentration of about 50 parts per million by weight (ppm) to about 1000 ppm, based on the weight of the total composition. In other embodiments, the tracer is present at a total concentration of about 50 ppm to about 500 ppm. Alternatively, the tracer is present at a total concentration of about 100 ppm to about 300 ppm.

**[0141]** The tracer may be present in the compositions of the present invention in predetermined quantities to allow detection of any dilution, contamination or other alteration of the composition. The presence of certain compounds in the composition may indicate by what method or process one of the components has been produced. The tracer may also be added to the composition in a specified amount in order to identify the source of the composition. In this manner, detection of infringement on patent rights may be accomplished. The tracers may be refrigerant compounds but are present in the composition at levels that are unlikely to impact performance of the refrigerant component of the composition.

**[0142]** Tracer compounds may be hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons, hydrochloroolefins, chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof. Examples of tracer compounds include, but are not limited to HFC-23 (trifluoromethane), HCFC-31 (chlorofluoromethane), HFC-41 (fluoromethane), HFC-161 (fluoroethane), HFC-143a (1,1,1-trifluoroethane), HFC-134a (1,1,1,2-tetrafluoroethane), HFC-125 (pentafluoroethane), HFC-236fa (1,1,1,3,3,3-hexafluoropropane), HFC-236ea (1,1,1,2,3,3-hexafluoropropane), HFC-245cb (1,1,1,2,2-pentafluoropropane), HFC-245fa (1,1,1,3,3-pentafluoropropane), HFC-254eb (1,1,1,2-tetrafluoropropane), HFC-263fb (1,1,1-trifluoropropane), HFC-272ca (2,2-difluoropropane), HFC-281ea (2-fluoropropane), HFC-281fa (1-fluoropropane), HFC-329p (1,1,1,2,2,3,3,4,4-nonafluorobutane), HFC-329mmz (1,1,1-trifluoro-2-methylpropane), HFC-338mf (1,1,1,2,2,4,4,4-octafluorobutane),

HFC-338pcc (1,1,2,2,3,3,4,4-octafluorobutane), CFC-12 (dichlorodifluoromethane), CFC-11 (trichlorofluoromethane), CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane), CFC-114a (1,1-dichloro-1,2,2,2-tetrafluoroethane), HCFC-22 (chlorodifluoromethane), HCFC-123 (1,1-dichloro-2,2,2-trifluoroethane), HCFC-124 (2-chloro-1,1,1,2-tetrafluoroethane), HCFC-124a (1-chloro-1,1,2,2-tetrafluoroethane), HCFC-141b (1,1-dichloro-1-fluoroethane), HCFC-142b (1-chloro-1,1-difluoroethane), HCFC-151a (1-chloro-1-fluoroethane), HCFC-244bb (2-chloro-1,1,1,2-tetrafluoropropane), HCC-40 (chloromethane), HFO-1141 (fluoroethene), HCFO-1130 (1,2-dichloroethene), HCFO-1130a (1,1-dichloroethene), HCFO-1131 (1-chloro-2-fluoroethene), HCFO-1122 (2-chloro-1,1-difluoroethene), HFO-1123 (1,1,2-trifluoroethene), HFO-1234ye (1,2,3,3-tetrafluoropropene), HFO-1243zf (3,3,3-trifluoropropene), HFO-1225ye (1,2,3,3,3-pentafluoropropene), HFO-1225zc (1,1,3,3,3-pentafluoropropene), PFC-116 (hexafluoroethane), PFC-C216 (hexafluorocyclopropane), PFC-218 (octafluoropropane), PFC-C318 (octafluorocyclobutane), PFC-1216 (hexafluoroethane), PFC-31-10mc (1,1,1,2,2,3,3,4,4,4-decafluorobutane), PFC-31-10my (1,1,1,2,3,3,3-heptafluoro-2-trifluoromethylpropane), and combinations thereof.

### **REFRIGERANT BLEND FLAMMABILITY**

**[0143]** Flammability is a term used to mean the ability of a composition to ignite and/or propagate a flame. For refrigerants and other heat transfer compositions or working fluids, the lower flammability limit ("LFL") is the minimum concentration of the heat transfer composition in air that is capable of propagating a flame through a homogeneous mixture of the composition and air under test conditions specified in ASTM (American Society of Testing and Materials) E681. The upper flammability limit ("UFL") is the maximum concentration of the heat transfer composition in air that is capable of propagating a flame through a homogeneous mixture of the composition and air under the same test conditions.

**[0144]** In order to be classified by ANSI/ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) Standard 34 or ISO 817 ISO 817:2014(en) Refrigerants — Designation and Safety Classification as non-flammable (class 1, no flame propagation), a refrigerant must meet the conditions of ASTM E681 as formulated in both the liquid and vapor phase as well as non-

flammable in both the liquid and vapor phases that result during leakage scenarios defined by ANSI/ASHRAE standard 34-2019 or ISO 817:2014(en) Refrigerants – Designation and Safety Classification.

**[0145]** In order for a refrigerant blend to be classified by ANSI/ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) as low flammability (class 2L), the worst case of formulation (WCF) and the worst case of fractionation for flammability (WCFF) for the refrigerant blend must be determined based on manufacturing tolerances and vapor leak behavior. In order to be classified as 2L, low flammability, the WCF and WCFF must: 1) exhibit flame propagation when tested at 140°F (60°C) and 14.7 psia (101.3 kPa) and have an LFL >0.0062 lb/ft<sup>3</sup> (0.10 kg/m<sup>3</sup>) and 2) have a maximum burning velocity of ≤3.9 in./s (10 cm/s) when tested at 73.4°F (23.0°C) and 14.7 psia (101.3 kPa). Additionally, the nominal refrigerant blend must have a heat of combustion <8169 Btu/lb (19,000 kJ/kg).

**[0146]** ASHRAE Standard 34 provides a methodology to calculate the heat of combustion for refrigerant blends using a balanced stoichiometric equation based on the complete combustion of one mole of refrigerant with enough oxygen for a stoichiometric reaction.

**[0147]** When HFO-1234yf, HFC-32, and HFC-152a components are blended together in certain proportions, the resulting blend has class 2L flammability as defined by ANSI/ASHRAE standard 34 and ISO 817. Class 2L flammability is inherently less flammable (i.e., lower energy release as exemplified by the Heat of Combustion or HOC value) than both class 2 and class 3 flammability and can be managed in automotive heating/cooling systems.

**[0148]** The present inventive compositions comprising, consisting essentially of, or consisting of from 72 to 78 weight percent HFO-1234yf, from 6 to 7.5 weight percent HFC-32, and from 14 to 20 weight percent HFC-152a or from 74 to 78 weight percent HFO-1234yf, from 6 to 7.5 weight percent HFC-32, and from 14 to 18 weight percent HFC-152a are classified as Class 2L flammability by ASHRAE; an LFL of less than 10 volume percent; and a burning velocity less than 10 cm/sec. In particular, the composition consisting essentially of about 78 weight percent HFO-1234yf, about 7.5 weight percent HFC-32, and about 14.5 weight percent HFC-152a meets all the requirements and will be classified as class 2L, low flammability

by ASHRAE. In another embodiment, the composition consisting essentially of 78 weight percent HFO-1234yf (with tolerance +1.0/-1.0 wt%), about 7.5 weight percent HFC-32 (with tolerance +0.5/-1.5 wt%), and about 14.5 weight percent HFC-152a (with tolerance +0.5/-1.5 wt%) meets all the requirements and will be classified as class 2L, low flammability by ASHRAE.

**[0149]** In embodiments, the refrigerant blends include 2,3,3,3-tetrafluoropropene (HFO-1234yf), difluoromethane (HFC-32), and 1,1-difluoroethane (HFC-152a). In some embodiments, the refrigerant blends may comprise, consist essentially of, or consist of 2,3,3,3-tetrafluoropropene (HFO-1234yf), difluoromethane (HFC-32), and 1,1-difluoroethane (HFC-152a). In some embodiments, the refrigerant blends may comprise, consist essentially of, or consist of about 66 weight percent to 80 weight percent or about 69 weight percent to 80 weight percent or between about 70 weight percent to 78 weight percent or between about 72 weight percent to 78 weight percent or between about 74 weight percent to 78 weight percent HFO-1234yf; about 1 weight percent and 10 weight percent or about 5 weight percent to 8 weight percent or about 6 weight percent and 8 weight percent or 6 weight percent to 7.5 weight percent or 6 weight percent to 7 weight percent HFC-32; and about 10 weight percent to 24 weight percent or about 12 weight percent to 24 weight percent or about 14 weight percent to 24 weight percent or about 14.5 weight percent to 24 weight percent or about 14 weight percent to 20 weight percent or about 14 weight percent to 18 weight percent HFC-152a.

**[0150]** In one embodiment, any of the foregoing refrigerant compositions can further comprise at least one additional compound selected from the group consisting of HCFC-244bb, HFC-245cb, HFC-254eb, HFO-1234ze, CFC-12, HCFC-124, 3,3,3-trifluoropropyne, HCC-1140, HFC-1225ye, HFO-1225zc, HFC-134a, HFO-1243zf, and HCFO-1131.

**[0151]** In one embodiment, any of the foregoing refrigerant compositions can further comprise at least one additional compound selected from the group consisting of HFC-23, HCFC-31, HFC-41, HFC-143a, HCFC-22, HCC-40, HFC-161, HFO-1141, HCO-1140, HCFC-151a, HCFO-1130a, HCFC-141b, HFO-1132a, HFC-143a, HCFO-1122, and HCFC-142b.

**[0152]** In one embodiment, any of the foregoing refrigerant compositions can further comprise at least one additional compound selected from the group consisting of HFC-143a, HCC-40, HFC-161, and HCFC-151a. Alternatively, the composition may comprise HFC-143a, HCC-40, HFC-161, and HCFC-151a.

**[0153]** In one embodiment, any of the foregoing refrigerant compositions can further comprise at least one additional compound selected from the group consisting of HFO-1243zf, 3,3,3-trifluoropropyne, HFC-143a, HCC-40, HFC-161, and HCFC-151a. Alternatively, the composition may comprise HFO-1243zf, HFC-143a, HCC-40, HFC-161, and HCFC-151a.

**[0154]** The amount of additional compounds present in any of the foregoing refrigerant compositions can be greater than 0 ppm and less than 5,000 ppm and, in particular, can range from about 5 to about 1,000 ppm, about 5 to about 500 ppm and about 5 to about 100 ppm.

**[0155]** In one embodiment, the amount of additional compounds present in any of the foregoing refrigerant compositions can be greater than 0 and less than 1 wt% of the refrigerant composition, preferably less than 0.5 weight percent, or more preferably less than 0.1 weight percent.

**[0156]** In one embodiment, any of the foregoing refrigerant compositions can further comprise an additional compound comprising at least one of an oligomer and/or a homopolymer of HFO-1234yf. The amount can range from greater than 0 to about 100 ppm, and in some case, about 2 ppm to about 100 ppm. In an aspect of this embodiment, the refrigerant comprises about 70 to 78 weight percent HFO-1234yf, about 6 to 8 weight percent or 6-7.5 weight percent of HFC-32, and about 14 to 24 weight percent HFC-152a and, in a further aspect, the refrigerant composition further comprises greater than about 0 and less than 1 wt.% of additional compounds in addition to the oligomer and homopolymer, preferably less than 0.5 weight percent, and even more preferably less than 0.1 weight percent.

**[0157]** Another embodiment of the invention relates to storing any of the foregoing compositions in gaseous and/or liquid phases within a sealed container. The water concentration within the gas and/or liquid phase in the sealed container ranges from about 0.1 to 200 ppm by weight. The oxygen concentration within the gas and/or liquid phase in the sealed container ranges from about 10 ppm by volume to about

0.35 volume percent at about 25C. The air concentration within the gas and/or liquid phase in the sealed container ranges from about 100 ppm by volume to about 1.5 volume percent.

**[0158]** The container for storing the foregoing compositions can be constructed of any suitable material and design that is capable of sealing the compositions therein while maintaining gaseous and liquids phases. Examples of suitable containers comprise pressure resistant containers such as a tank, a filling cylinder, and a secondary filling cylinder. The container can be constructed from any suitable material such as carbon steel, manganese steel, chromium-molybdenum steel, among other low-alloy steels, stainless steel and in some cases an aluminum alloy.

**[0159]** The compositions of the present invention may be prepared by any convenient method to combine the desired amount of the individual components. A preferred method is to weigh the desired component amounts and thereafter combine the components in an appropriate vessel. Agitation may be used, if desired. In another embodiment, any of the foregoing refrigerant composition can be prepared by blending HFO-1234yf, HFC-32, and HFC-152a and, in some cases, at least one of the additional compounds.

**[0160]** In a further embodiment, the compositions may be prepared from recycled or reclaimed refrigerant. One or more of the components may be recycled or reclaimed by means of removing contaminants, such as air, water, or residue, which may include lubricant or particulate residue from system components. The means of removing the contaminants may vary widely, but can include distillation, decantation, filtration, and/or drying by use of molecular sieves or other absorbents. Then the recycled or reclaimed component(s) may be combined with the other component(s) as describe above.

**[0161]** In an embodiment of the present invention a system for heating and cooling the passenger compartment of an electric vehicle is provided. The system comprises an evaporator, compressor, condenser and expansion device, each operably connected to perform a vapor compression cycle, wherein the system contains any of the foregoing compositions comprising a refrigerant blend consisting essentially of HFO-1234yf, HFC-32, and HFC-152a. The average temperature glide in the inventive system is less than 4 K, preferably less than 3 K, or most preferably

less than 2.5 K. The system is preferably a heat pump. Due to the excellent performance of the heat pump system in both cooling and heating of the passenger compartment of an electric vehicle, the system no longer requires a positive temperature coefficient (PTC) heater.

**[0162]** The refrigerant blends may be used in a variety of heating and cooling systems. In some embodiments, a reversing valve is used and the same loop is used for cooling and heating. In other embodiments, air side bypass or refrigerant valving/system design changes can accomplish the same effect as a reversible cycle, without a reversing valve.

**[0163]** In the embodiment of FIG. 1, a refrigeration system 100 having a refrigeration loop 110 comprises a first heat exchanger 120, a pressure regulator 130, a second heat exchanger 140, a compressor 150 and a four-way valve 160. The first and second heat exchangers are of the air/refrigerant type. The first heat exchanger 120 has passing through it the refrigerant of the loop 110 and the stream of air created by a fan.

**[0164]** In cooling mode, the refrigerant set-in motion by the compressor 150 passes, via the valve 160, through the heat exchanger 120 which acts as a condenser, that is to say gives up heat energy to the outside, then through the pressure regulator 130 then through the heat exchanger 140 that is acting as an evaporator thus cooling the stream of air intended to be blown into the motor vehicle cabin interior.

**[0165]** In heat pump mode, the direction of flow of the refrigerant is reversed using the valve 160. The heat exchanger 140 acts as a condenser while the heat exchanger 120 acts as an evaporator. The heat exchanger 140 can then be used to heat up the stream of air intended for the motor vehicle cabin.

**[0166]** Additional heat transfer loops may be connected to the heat pump system and absorb or reject heat at the heat exchangers 120 and/or 140 to allow transfer of heat away from the motor or battery, and therefore serve to provide thermal management of those components of the vehicle as well as cooling and heating for the passenger cabin.

**[0167]** In the embodiment of FIG. 2, a refrigeration system 300 having a refrigeration loop 310 comprises a first heat exchanger 320, a pressure regulator 330, a second heat exchanger 340, a compressor 350 and a four-way valve 360. The first and second heat exchangers 320 and 340 are of the air/refrigerant type. The way in which the heat exchangers 320 and 340 operate is the same as in the first embodiment depicted in FIG. 1. Two fluid/liquid heat exchangers 370 and 380 are installed both on the refrigeration loop circuit 310 and on the engine cooling circuit or on a secondary glycol-water circuit. Installing fluid/liquid heat exchangers without going through an intermediate gaseous fluid (e.g. air) contributes to improving heat exchange by comparison with air/fluid heat exchangers.

**[0168]** In the embodiment of FIG. 3, a refrigeration system 400 having a refrigeration loop 410 comprises a first heat exchanger (condenser) 420, a pressure regulator 430, a second heat exchanger (evaporator) 440, a compressor 450, a three-way valve 460, and a third heat exchanger (for reheat) 470. In cooling mode, at least a portion of the discharge flow exiting the compressor 450 is directed through the three-way valve 460 and into the third heat exchanger 470. The exit stream from the third heat exchanger 470 discharges into the inlet of the first heat exchanger 420. The refrigerant is condensed by the first heat exchanger 420 using an external fan 480 and ambient air as the heat sink. The existing saturated or subcooled liquid is expanded in the pressure regulator 430 and the resulting lower pressure saturated mixture of refrigerant liquid and vapor enters the second heat exchanger 440. The refrigerant evaporates in the second heat exchanger 440 through the use of a second fan 490 that is external to the refrigeration loop. The air passing across the second heat exchanger 440 is cooled to below the air dew point temperature. This causes the moisture in the air to partially condense, thereby lowering the absolute humidity of the air. The air then passes over the third heat exchanger 470, which transfers heat into the air, increasing the air temperature to above the dew point and lowering the relative humidity of the air, which is then supplied to the passenger compartment. This process of cooling to below the dew point temperature to remove moisture and subsequently reheating to above the dew point temperature allows for cooling and relative humidity control of the vehicle cabin. In heating mode, the three-way valve 460 is modulated to prohibit the flow of refrigerant to the heat exchanger 420 and all vehicle cabin heating is accomplished

using the second heat exchanger 470 in the heat pump configuration described in FIG. 1.

**[0169]** In the embodiment of FIG. 4, an air-conditioning (AC) and heat pump (HP) system 500, heating, cooling, or both can be accomplished in a vehicle cabin or for other vehicle loads. The system 500 includes an AC circuit 510 and a HP circuit 520. In air-conditioning only mode, the HP control valve 530 upstream of the heat pump condenser 540 will be closed and the refrigerant will flow from the compressor 550 into the air-cooled AC condenser 560, through an AC expansion valve 570, and into the AC evaporator 580; providing cooling to the cabin. From the AC evaporator 580, the refrigerant will flow back to the compressor 550. In heat pump only mode, the AC control valve 535 upstream of the AC condenser 560 will be closed and the refrigerant will flow from the compressor 550 into the HP condenser 540 to provide heating to the cabin. From the HP condenser 540 the refrigerant will flow through the HP expansion valve 575 to the HP evaporator 585. A separate humidity control mode could be accomplished by sending a portion of the compressor discharge gas into the AC circuit 510 and the remaining portion into the HP circuit 520.

**[0170]** In the embodiment of FIG. 5, a system 600 for heating, cooling, or both can be accomplished for a vehicle cabin or for other vehicle loads. The system 600 includes an AC circuit 610 and a water-cooled/HP circuit 620. In AC only mode, the water loop control valve 630 upstream of the water-cooled condenser 640 will be closed and the refrigerant will flow from the compressor 650 into the AC condenser 660, through an AC expansion valve 670, and into the AC evaporator 680; providing cooling to the cabin. In HP only mode, the AC control valve 635 upstream of the AC condenser 660 will be closed and the refrigerant will flow from the compressor 650 into the water-cooled condenser 640. A heat transfer fluid (e.g., water or other heat transfer fluid) will take the heat generated in the water-cooled condenser 640 and transfer it to the cabin heater core 690; providing heat to the cabin. The heat transfer fluid may return from the cabin heater core 690 to the water-cooled condenser 640. The refrigerant will flow from the water-cooled condenser 640 through an HP expansion valve 675 into the HP evaporator 685 that cools a heat transfer fluid, which may be used to cool other components of the automobile and then back to the compressor 650. In some embodiments, there is one or more water/heat transfer fluid loop that may be used to heat and/or cool various other

components of the vehicle. A separate humidity control mode could be accomplished by sending a portion of the compressor discharge gas into the AC circuit 610 and the remaining portion into the water cooled/HP circuit 620.

**[0171]** In the embodiments of FIG. 7 through FIG. 10, the same components exist in the system, but depending on the mode of operation, only some of those components are utilized.

**[0172]** In one embodiment, in heating mode wherein specific conditions exist where both the vehicle cabin and other vehicle components require heat, the refrigerant circuit 700 operates as shown in FIG. 7. Starting at the compressor 750, discharge refrigerant vapor will take two paths. One path is through the cabin condenser 740. The cabin condenser 740 is a refrigerant-to-air heat exchanger typically of the fin-tube or microchannel type and can be single or multiple pass. A first fan 745 in the vehicle ventilation ductwork will induce a flow of either 100% outside air or a mixture of outside air and return air from the vehicle cabin across this cabin condenser 740 and the refrigerant as it condenses will heat the air. In this mode, a physical bypass 735 within the vehicle ventilation ductwork will prevent any air from flowing over the cabin evaporator 730. The second path of refrigerant out of the compressor is through valve 770 and into a liquid/heat transfer fluid heat exchanger 720, which allows heat to be transferred from the warm refrigerant to the vehicle's heat transfer fluid loop (not shown). This vehicle heat transfer loop can then be used to manage other vehicle heat loads. The heat transfer fluid of the heat transfer fluid loop may be water or a water/glycol solution. The condensed refrigerant out of exchanger 720 then combines with the condenser 740 liquid refrigerant outlet and the combined stream flows through an expansion device 775, which will drop the pressure of the liquid refrigerant and generate a liquid-vapor mixture. This liquid-vapor mixture then flows through the outdoor heat exchanger 780 (i.e. evaporator in this setup). The outdoor heat exchanger 780 will be a refrigerant-to-air heat exchanger typically of the fin-tube or microchannel type and can be single or multiple pass. A second fan 785 will induce airflow across the outdoor heat exchanger 780 and allow the liquid-vapor refrigerant mixture to pick up heat from the ambient air and vaporize completely before it flows back to the compressor 750.

**[0173]** In another embodiment, in heating mode when specific conditions exist where only cabin heating is required, the refrigerant circuit 800 operates as shown in FIG. 8. Starting at the compressor 850, discharge vapor will first flow through the cabin condenser 840. A first fan 845 in the vehicle ventilation ductwork will induce a flow of either 100% outside air or a mixture of outside air and return air from the vehicle cabin across this cabin condenser 840 and the refrigerant will exchange heat between the condenser 840 and the air. In this mode, a physical bypass 835 within the vehicle ventilation ductwork will prevent any air from flowing over the cabin evaporator 830. The refrigerant will condense in the cabin condenser 840 and flow to an expansion device 875 which will drop the pressure of the liquid refrigerant and generate a liquid-vapor mixture. This liquid-vapor mixture flows through the outdoor heat exchanger 880 (i.e., evaporator in this setup). A second fan 885 will induce airflow across the outdoor heat exchanger 880 and allow the liquid-vapor refrigerant mixture to pick up heat from the ambient air and vaporize completely before it travels back to the compressor 850.

**[0174]** In another embodiment, in cooling mode when specific conditions exist where both the vehicle cabin and the vehicle components require cooling, the refrigerant circuit 900 operates as shown in FIG. 9. Starting at the compressor 950, discharge refrigerant vapor will first flow through the cabin condenser 940, wherein there will be no heat transfer as in this mode, a physical bypass 945 within the vehicle ventilation ductwork will prevent any air from flowing over the cabin condenser 940. Vapor refrigerant will pass through the cabin condenser 940 and flow through valve 975 and into the outdoor heat exchanger 980. In this mode, the outdoor heat exchanger 980 acts as a condenser as a first fan 985 induces flow across the heat exchanger and the hot refrigerant vapor exchanges heat and condenses to a liquid. A portion of this liquid refrigerant will leave the outdoor heat exchanger 980 and enter the internal heat exchanger 990. Liquid refrigerant will be subcooled in the internal heat exchanger 990 and then flow to an expansion device 910 and into the cabin evaporator 930. This air-to-refrigerant cabin evaporator 930 will be of the fin-tube or microchannel type of heat exchanger and can be single or multiple pass. A second fan (or cabin blower fan) 935 will induce a flow of either 100% outside air or a mixture of outside air and return air from the cabin across the coil of the cabin evaporator 930 where heat will be exchanged between the air and

refrigerant. The refrigerant will vaporize and travel back to the internal heat exchanger 990 where it will be further superheated until it finally re-enters the compressor 950. The remaining portion of refrigerant exiting the condenser 980 will flow through expansion valve 915 and into the liquid/heat transfer fluid heat exchanger 920 wherein vehicle component heat is transferred via a heat transfer fluid loop (not shown) into the refrigerant. This vehicle heat transfer loop can then be used to manage other vehicle heat loads. The refrigerant vaporizes in heat exchanger 920 and joins the refrigerant exiting internal heat exchanger 990 at the suction of the compressor 950.

**[0175]** In another embodiment, in cooling mode when specific conditions exist where only vehicle cabin cooling is required, the refrigerant circuit 1000 operates as shown in FIG. 10. Starting at the compressor 1050, discharge refrigerant vapor will first flow through the cabin condenser 1040, wherein there will be no heat transfer, as in this mode, a physical bypass 1045 within the vehicle ventilation ductwork will prevent any air from flowing over the cabin condenser 1040. Vapor refrigerant will pass through the cabin condenser 1040 and flow through a valve 1075 to the outdoor heat exchanger 1080. In this mode, the outdoor heat exchanger 1080 acts as a condenser as a first fan 1085 induces flow across the heat exchanger 1080 and the hot refrigerant vapor exchanges heat and condenses to a liquid. This liquid refrigerant will leave the outdoor heat exchanger 1080 and enter the internal heat exchanger 1090. Liquid refrigerant will be subcooled in the internal heat exchanger 1090 and then flow to an expansion device 1010 and into the cabin evaporator 1030. A second fan (or cabin blower fan) 1035 will induce a flow of either 100% outside air or a mixture of outside air and return air from the cabin across the cabin evaporator 1030 where heat will be exchanged between the air and refrigerant. The refrigerant will vaporize and flow back to the internal heat exchanger 1090 where it will be further superheated until it finally returns to the compressor 1050.

**[0176]** The blends have low GWP, low toxicity, and low flammability with low temperature glide for use in a hybrid, mild hybrid, plug-in hybrid, or full electric vehicles for thermal management (transferring heat from one part of the vehicle to the other) of the passenger compartment providing air conditioning (A/C) or heating to the passenger cabin. Additionally, the refrigerant blends provide improved performance under heating mode conditions as compared to HFO-1234yf in

particular heating capacity higher than HFO-1234yf alone, at least 15% higher than HFO-1234yf alone, or more preferably at least 20% higher than HFO-1234yf alone, and COP for heating at least the same or higher than HFO-1234yf alone. The COP for heating is preferably at least 2% higher than HFO-1234yf alone, or more preferably at least 3% higher than HFO-1234yf alone.

**[0177]** In one embodiment, a method of servicing the heating and cooling system of an electric vehicle is provided. The method comprising removing all of a used refrigerant from the system and charging the system with the compositions comprising a refrigerant blend consisting essentially of HFO-1234yf, HFC-32, and HFC-152a. Due to the fractionation that may occur while operating a refrigerant with temperature glide, leakage of refrigerant may lead to a change in the composition remaining in the heating and cooling system. This change in composition makes it difficult to determine the composition remaining in the system. And therefore, if performance of the system has been deteriorating, it will be necessary to remove all the refrigerant present in the cooling and heating system and recharge the system with fresh refrigerant blend with the optimized refrigerant blend composition.

**[0178]** In one embodiment is provided a use of any of the foregoing compositions comprising a refrigerant blend consisting essentially of HFO-1234yf, HFC-32, and HFC-152a as a heat transfer fluid in a system for heating and cooling the passenger compartment of an electric vehicle. This use of the present inventive compositions has been described in detail in the foregoing description and will be demonstrated in the forthcoming examples.

**[0179]** In another embodiment, is provided a use of a composition comprising a refrigerant blend consisting essentially of:

about 78 weight percent HFO-1234yf, about 8 weight percent HFC-32, and about 14 weight percent HFC-152a; or

about 72 weight percent HFO-1234yf, about 8 weight percent HFC-32, and about 20 weight percent HFC-152a,

as a heat transfer fluid in a system for heating and cooling the passenger compartment of an electric vehicle.

**[0180]** In one embodiment is provided a method for reducing the temperature glide in a heat exchanger operating with a refrigerant blend composition consisting essentially of HFC-32 and HFO-1234yf comprising adding HFC-152a to the refrigerant blend composition, wherein the composition comprises at least about 70 weight percent HFC-1234yf. The amount of HFC-152a to be added can vary, depending on the requirements for the system in which the composition will be used. In some embodiments, the HFC-152a is added in an amount of about 10 to 24 weight percent, preferably about 14 to 24 weight percent, based on the weight percent of the total refrigerant blend composition resulting from the addition of HFC-152a. In some embodiments, the temperature glide in the heat exchanger may be reduced to less than 4 K, less than 3 K, less than 2.5 K, or even less than 2.0 K (e.g., a glide ranging from great than 0 to less than about 2.0K).

**[0181]** FIG. 6 is a contour plot showing average temperature glide for compositions containing HFO-1234yf, HFC-32 and HFC-152a. The x-axis corresponds to compositions with no HFC-152a. As HFC-152a is added to the composition, the average temperature glide is seen to decrease.

**[0182]** In other embodiments, compositions intended to replace conventional high GWP refrigerant in refrigeration, air-conditioning, and heat pump applications, it is desirable that the refrigerant composition exhibit a low GWP as well as similar or improved refrigerant properties compared to conventional refrigerants.

**[0183]** In some embodiments, the compositions as disclosed herein may be used in stationary systems, such as refrigeration, air conditioning and heat pump systems. The present inventive compositions may serve as replacements for conventional refrigerants with much higher GWP, in particular, such as R-22, R-404A, R-410A, R-407A, R-407C, or R-407F. The stationary systems may include supermarket refrigerated cases, supermarket freezer cases, chillers that provide air conditioning to large buildings, such as apartment buildings, office buildings, hospitals, and/or school buildings, residential air conditioners, residential heat pumps for heating or cooling air or for heating water or other heat transfer fluids, or residential refrigerators or freezers.

**[0184]** In one embodiment, disclosed herein is a stationary refrigeration, air conditioning or heat pump apparatus containing a refrigerant consisting essentially of

from about 70 to 78 weight percent HFO-1234yf, from about 6 to 8 weight percent HFC-32, and from about 14 to 24 weight percent HFC-152a.

**[0185]** In another embodiment, disclosed herein is a method for replacing a first refrigerant selected from R-404A, R-507A, R-507B, R-410A, R-407A, R-407C, or R-407F comprising removing at least a portion of said first refrigerant and charging a second refrigerant consisting essentially of from about 70 to 78 weight percent HFO-1234yf, from about 6 to 8 weight percent HFC-32, and from about 14 to 24 weight percent HFC-152a.

**[0186]** In another embodiment, disclosed herein is a method for replacing a first refrigerant selected from R-513A, R-448A, R-448B, R-449A, R-452A, R-454A, R-454B, R-454C, R-466A, R-1234yf, or R-1234ze comprising removing at least a portion of said first refrigerant and charging a second refrigerant consisting essentially of from about 70 to 78 weight percent HFO-1234yf, from about 6 to 8 weight percent HFC-32, and from about 14 to 24 weight percent HFC-152a.

**[0187]** The following Examples are provided to illustrate certain aspects of the invention and shall not limit the scope of the appended claims.

## **EXAMPLES**

### **EXAMPLE 1**

**[0188]** Thermodynamic Modeling Comparison for the Heat Pump Systems  
HEATING MODE: HFO-1234yf/HFC-32/HFC-152a.

**[0189]** A thermodynamic modeling program was used to model the expected performance of the blend of HFO-1234yf/HFC-32/HFC-152a compared to HFO-1234yf. Physical properties for the components were taken from NIST REFPROP Version 10. In the tables, Suct. Pres. = compressor suction pressure; Disch. Pres. = compressor discharge pressure; Disch. Temp. = compressor discharge temperature; Avg. Glide = the average of the temperature glide for heat exchanger #1 and heat exchanger #2; Heat Cap= volumetric heating capacity.

[0190] Model conditions used for the heating mode are as follows, where heat exchanger #2 was varied in 20°C increments:

Modeling Conditions	
Average Temp Heat Exchanger #1 – Inside Cabin	50°C
Average Temp Heat Exchange #2 – Inside Engine compartment	-30°C to 10°C
Evaporator superheat	10°C
Compressor Isentropic Efficiency	70%

TABLE 2

Heat Exchanger #2 = -30 C, average refrigerant temperature

Refrigerant	GWP (AR5)	Suct. Pres. (kPa)	Disc h. Pres. (kPa)	Disch Temp (C)	Avg. Glide (K)	Heat Cap (kJ/m <sup>3</sup> )	Heat Cap Rel. to R-1234yf	COP	COP Rel. to R-1234yf
1234yf	1	99	1302	73.3	0	838	100	2.19	100
1234yf/32/152a wt%									
70/6/24	74	109	1491	92.9	2.06	1021	121.7	2.30	105.1
74/7/19	74	112	1531	91.8	2.44	1040	124.0	2.29	104.4
78/7.5/14.5	72	114	1557	90.3	2.72	1049	125.1	2.27	103.7
78/8/14	74	116	1573	90.7	2.86	1059	126.3	2.27	103.6
67/10/23	100	117	1595	97.1	2.96	1100	131.2	2.31	105.2
78/6/16	63	111	1510	89.2	2.28	1017	121.3	2.28	103.8
70/8/22	85	113	1548	94.4	2.58	1061	126.5	2.30	104.9
72/8/20	82	114	1555	93.4	2.64	1061	126.5	2.29	104.6
Comparative compositions, wt%									
60/10/30	110	114	1568	100.5	2.81	1094	130.5	2.33	106.2
70/10/20	96	118	1606	95.7	3.05	1102	131.4	2.30	104.7
60/20/20	164	137	1834	106.5	4.20	1303	155.4	2.31	105.4
60/30/10	218	166	2119	111.6	4.45	1543	184.0	2.29	104.4
70/25/5	177	160	2059	104.4	4.71	1455	173.6	2.26	103.2
70/20/10	150	144	1903	101.8	4.49	1328	158.4	2.28	103.8
75/20/5	143	148	1939	99.6	4.73	1339	159.7	2.26	102.8
75/15/10	116	133	1779	96.7	4.17	1216	145.1	2.27	103.4
85/10/5	75	123	1662	89.1	3.76	1100	131.1	2.24	102.2
80/10/10	82	121	1643	91.2	3.47	1102	131.5	2.26	103.1
75/10/15	89	120	1625	93.5	3.23	1103	131.6	2.28	103.9

**TABLE 3**

**Heat Exchanger #2 = -10 C, average refrigerant temperature**

Refrigerant	GWP (AR5)	Suct. Pres. (kPa)	Disch. Pres. (kPa)	Disch. Temp. (C)	Avg. Glide (K)	Heat Cap (kJ/m <sup>3</sup> )	Heat Cap Rel. to R-1234yf	COP	COP Rel. to R-1234yf
1234yf	1	222	1302	67.3	0	1711	100	3.02	100
1234yf/32/152a wt%									
70/6/24	74	246	1491	81.3	2.24	2060	120.4	3.13	103.5
74/7/19	74	254	1531	80.6	2.66	2098	122.6	3.11	102.9
78/7.5/14.5	72	258	1557	79.7	2.98	2116	123.6	3.09	102.3
78/8/14	74	261	1573	80.0	3.13	2137	124.9	3.09	102.3
67/10/23	100	264	1595	84.4	3.22	2211	129.2	3.13	103.5
78/6/16	82	257	1555	81.8	2.88	2137	124.9	3.12	103.1
70/8/22	63	251	1510	78.8	2.49	2054	120.1	3.10	102.5
72/8/20	85	256	1548	82.4	2.81	2137	124.9	3.12	103.3
Comparative compositions, wt%									
60/10/30	110	258	1568	86.6	3.04	2199	128.5	3.15	104.3
70/10/20	96	266	1606	83.5	3.32	2215	129.4	3.12	103.1
60/20/20	164	308	1834	91.1	4.52	2582	150.9	3.12	103.3
60/30/10	218	367	2119	94.7	4.71	2997	175.2	3.08	102.0
70/25/5	177	355	2059	90.0	5.03	2851	166.6	3.06	101.1
70/20/10	150	323	1903	88.1	4.86	2630	153.7	3.08	101.9
75/20/5	143	330	1939	86.7	5.11	2652	155.0	3.06	101.1
75/15/10	116	299	1779	84.5	4.55	2430	142.0	3.08	101.8
85/10/5	75	277	1662	79.2	4.14	2219	129.7	3.05	101.0
80/10/10	82	273	1643	80.6	3.80	2221	129.8	3.08	101.7
75/10/15	89	270	1625	82.0	3.54	2219	129.7	3.10	102.4

**TABLE 4**

**Heat Exchanger #2 = +10 C, average refrigerant temperature**

Refrigerant	GWP (AR5)	Suct. Pres. (kPa)	Disch. Pres. (kPa)	Disch. Temp. (C)	Avg. Glide (K)	Heat Cap (kJ/m <sup>3</sup> )	Heat Cap Rel. to R-1234yf	COP	COP Rel. to R-1234yf
1234yf	1	438	1302	63.7	0	3193	100	4.74	100
1234yf/32/152a wt%									
70/6/24	74	491	1491	73.0	2.47	3790	118.7	4.83	101.9
74/7/19	74	505	1531	72.7	2.94	3863	121.0	4.80	101.3

Refrigerant	GWP (AR5)	Suct. Pres. (kPa)	Disch. Pres. (kPa)	Disch. Temp. (C)	Avg. Glide (K)	Heat Cap (kJ/m <sup>3</sup> )	Heat Cap Rel. to R-1234yf	COP	COP Rel. to R-1234yf
78/7.5/14.5	72	514	1557	72.3	3.30	3901	122.2	4.78	100.9
78/8/14	74	519	1573	72.5	3.46	3938	123.3	4.78	100.8
67/10/23	100	525	1595	75.2	3.52	4054	126.9	4.82	101.6
78/6/16	82	512	1555	73.5	3.18	3930	123.1	4.81	101.4
70/8/22	63	498	1510	71.6	2.76	3791	118.7	4.79	101.1
72/8/20	85	510	1548	73.8	3.09	3927	123.0	4.82	101.6
Comparative compositions, wt%									
60/10/30	110	515	1568	76.4	3.31	4027	126.1	4.85	102.2
70/10/20	96	530	1606	74.7	3.65	4064	127.3	4.80	101.3
60/20/20	164	610	1834	79.6	4.85	4670	146.2	4.79	101.0
60/30/10	218	717	2119	82.0	4.96	5334	167.0	4.71	99.4
70/25/5	177	696	2059	79.2	5.33	5115	160.2	4.69	98.9
70/20/10	150	636	1903	78.0	5.22	4760	149.1	4.73	99.8
75/20/5	143	650	1939	77.2	5.49	4805	150.5	4.70	99.2
75/15/10	116	591	1779	75.7	4.95	4440	139.0	4.74	100.1
85/10/5	75	550	1662	72.3	4.57	4099	128.4	4.73	99.7
80/10/10	82	543	1643	73.1	4.20	4090	128.1	4.75	100.3
75/10/15	89	537	1625	73.9	3.89	4078	127.7	4.78	100.8

**[0191]** Modeling results show that refrigerant blends containing HFO-1234yf, HFC-32, and HFC-152a of the present invention provide an advantage over neat HFO-1234yf. At -30°C refrigerant temperatures, HFO-1234yf has a compressor suction pressure that is sub-atmospheric and the system would be operating under vacuum. In the event of a leak, air and moisture can be pulled into the system. Therefore, HFO-1234yf is limited for use as a heat pump fluid to -20°C or higher without an upgraded system design (i.e. a hermetic system). The refrigerant blends of the present invention will function as desired at lower temperatures than HFO-1234yf alone.

**[0192]** Blends of HFO-1234yf, HFC-32, and HFC-152a are also shown to have volumetric heating capacity considerably higher than for HFO-1234yf. Many of the presently claimed refrigerant blends have 20% or higher volumetric heating capacity as compared to HFO-1234yf alone and COP also higher than that for HFO-1234yf alone. The improved heating capacity of the inventive blends shows that the new fluids can easily be used to provide adequate heat to a passenger cabin.

Additionally, the resultant inventive blends generally have a similar compressor discharge ratio versus neat HFO-1234yf over the heat pump operating range.

**[0193]** The above data demonstrates that refrigerant blends containing HFO-1234yf provide performance with low average temperature glide, being less than 4K, less than 3K, under 2.5 K, or even under 2.0 K, depending on the exact conditions. The refrigerant blends of the present invention in many cases provide lower average temperature glide than the comparative compositions from the prior art.

**EXAMPLE 2**

**COOLING MODE: HFO-1234yf/HFC-32/HFC-152a**

**Thermodynamic Modeling Comparison for the Heat Pump Systems**

**[0194]** A thermodynamic modeling program was used to model the expected performance of the blend of HFO-1234yf/HFC-32/HFC-152a compared to HFO-1234yf and comparative compositions. Physical properties for the components were taken from NIST REFPROP Version 10. In the tables, Suct. Pres. = compressor suction pressure; Disch. Pres. = compressor discharge pressure; Disch. Temp. = compressor discharge temperature; Avg. Glide = the average of the temperature glide for heat exchanger #1 and heat exchanger #2; Cool Cap= volumetric cooling capacity, where heat exchanger #2 was varied in 10 C increments:

<b>Modeling Conditions</b>	
Average Temp Heat Exchanger #1- Inside Cabin	0°C
Average Temp Heat Exchange #2- inside Engine compartment	20°C to 40°C
Evaporator Superheat	10°C
Compressor Isentropic Efficiency	70%

**TABLE 5**

**Heat Exchanger #2 = +20 C, average refrigerant temperature**

Refrigerant	GWP (AR5)	Suct Pres (kPa)	Disch Pres (kPa)	Disch Temp (C)	Avg. Glide (K)	Cool Cap (kJ/m <sup>3</sup> )	Cool Cap Rel. to R-1234yf	COP	COP Rel. to R-1234yf
1234yf	1	316	592	33.4	0	2448	100	8.6	100
1234yf/32/152a wt%									
70/6/24	74	360	681	39.7	3.18	2855	116.6	8.58	99.8
74/7/19	74	371	703	39.7	3.79	2933	119.8	8.56	99.6
78/7.5/14.5	72	379	717	39.5	4.26	2984	121.9	8.55	99.4
78/8/14	74	384	725	39.7	4.46	3016	123.2	8.55	99.4
67/10/23	100	387	732	41.2	4.47	3064	125.2	8.56	99.6
78/6/16	82	377	714	40.2	4.07	2982	121.8	8.56	99.6
70/8/22	63	366	693	39.0	3.59	2889	118.0	8.55	99.5
72/8/20	85	375	710	40.3	3.96	2971	121.3	8.56	99.6
Comparative compositions, wt%									
60/10/30	110	378	717	41.9	4.19	3015	123.2	8.58	99.8
70/10/20	96	391	739	40.9	4.63	3085	126.0	8.56	99.5
60/20/20	164	452	848	43.9	5.95	3529	144.1	8.53	99.2
60/30/10	218	532	986	45.1	5.99	4047	165.3	8.46	98.4
70/25/5	177	518	960	43.6	6.51	3930	160.5	8.47	98.5
70/20/10	150	474	884	43.0	6.43	3649	149.0	8.51	99.0
75/20/5	143	485	903	42.6	6.79	3712	151.6	8.50	98.8
75/15/10	116	440	826	41.7	6.21	3418	139.6	8.53	99.2
85/10/5	75	410	772	39.8	5.89	3191	130.3	8.52	99.2
80/10/10	82	403	761	40.1	5.37	3155	128.9	8.54	99.3
75/10/15	89	397	750	40.5	4.96	3120	127.4	8.55	99.4

**TABLE 6**

**Heat Exchanger #2 = +30 C, average refrigerant temperature**

Refrigerant	GWP (AR5)	Suct Pres (kPa)	Disch Pres (kPa)	Disch Temp (C)	Avg. Glide (K)	Cool Cap (kJ/m <sup>3</sup> )	Cool Cap Rel. to R-1234yf	COP	COP Rel. to R-1234yf
1234yf	1	316	784	44.3	0	2215	100	5.38	100
1234yf/32/152a wt%									
70/6/24	74	357	900	52.5	2.90	2601	117.4	5.41	100.7
74/7/19	74	368	927	52.4	3.46	2664	120.3	5.40	100.4

Refrigerant	GWP (AR5)	Suct Pres (kPa)	Disch Pres (kPa)	Disch Temp (C)	Avg. Glide (K)	Cool Cap (kJ/m <sup>3</sup> )	Cool Cap Rel. to R-1234yf	COP	COP Rel. to R-1234yf
78/7.5/14.5	72	376	945	52.0	3.89	2703	122.0	5.38	100.1
78/8/14	74	380	955	52.2	4.08	2730	123.3	5.38	100.0
67/10/23	100	384	966	54.5	4.11	2790	125.9	5.41	100.5
78/6/16	82	374	941	53.0	3.72	2710	122.3	5.40	100.4
70/8/22	63	363	915	51.4	3.26	2620	118.3	5.39	100.2
72/8/20	85	372	937	53.3	3.63	2702	122.0	5.40	100.5
Comparative compositions, wt%									
60/10/30	110	375	947	55.5	3.86	2754	124.4	5.42	100.9
70/10/20	96	387	974	54.0	4.26	2804	126.6	5.40	100.3
60/20/20	164	448	1115	58.2	5.58	3220	145.4	5.38	100.1
60/30/10	218	528	1294	59.9	5.68	3696	166.9	5.32	99.0
70/25/5	177	514	1259	57.6	6.14	3572	161.3	5.32	98.9
70/20/10	150	469	1161	56.7	6.03	3314	149.6	5.35	99.5
75/20/5	143	480	1185	56.1	6.37	3363	151.8	5.33	99.2
75/15/10	116	436	1085	54.9	5.77	3095	139.7	5.36	99.7
85/10/5	75	405	1014	52.1	5.40	2873	129.7	5.35	99.4
80/10/10	82	399	1000	52.7	4.94	2850	128.7	5.37	99.8
75/10/15	89	393	987	53.3	4.56	2827	127.6	5.38	100.1

**TABLE 7**

**Heat Exchanger #2 = +40 C, average refrigerant temperature**

Refrigerant	GWP (AR5)	Suct Pres (kPa)	Disch Pres (kPa)	Disch Temp (C)	Avg. Glide (K)	Cool Cap (kJ/m <sup>3</sup> )	Cool Cap Rel. to R-1234yf	COP	COP Rel. to R-1234yf
1234yf	1	316	1018	54.9	0	1974	100	3.73	100
1234yf/32/152a wt%									
70/6/24	74	355	1168	64.9	2.62	2343	118.7	3.80	101.9
74/7/19	74	365	1201	64.6	3.13	2392	121.2	3.78	101.4
78/7.5/14.5	72	372	1223	64.0	3.51	2419	122.6	3.77	101.0
78/8/14	74	376	1235	64.3	3.69	2443	123.8	3.76	100.9
67/10/23	100	380	1251	67.2	3.74	2511	127.2	3.80	101.7
78/6/16	82	371	1219	65.4	3.38	2434	123.3	3.79	101.5
70/8/22	63	361	1185	63.3	2.94	2348	119.0	3.77	101.2
72/8/20	85	369	1214	65.8	3.29	2431	123.2	3.79	101.7

Refrigerant	GWP (AR5)	Suct Pres (kPa)	Disch Pres (kPa)	Disch Temp (C)	Avg. Glide (K)	Cool Cap (kJ/m <sup>3</sup> )	Cool Cap Rel. to R-1234yf	COP	COP Rel. to R-1234yf
Comparative compositions, wt%									
60/10/30	110	372	1228	68.5	3.52	2490	126.2	3.82	102.4
70/10/20	96	384	1260	66.6	3.87	2519	127.7	3.78	101.5
60/20/20	164	444	1441	71.8	5.15	2904	147.2	3.78	101.3
60/30/10	218	524	1669	74.1	5.30	3333	168.9	3.72	99.8
70/25/5	177	509	1622	71.1	5.71	3201	162.2	3.71	99.4
70/20/10	150	464	1497	69.9	5.57	2971	150.5	3.74	100.2
75/20/5	143	475	1527	69.0	5.88	3004	152.2	3.72	99.6
75/15/10	116	431	1400	67.5	5.28	2766	140.2	3.74	100.4
85/10/5	75	400	1308	64.0	4.89	2551	129.3	3.73	99.9
80/10/10	82	395	1292	64.8	4.48	2542	128.8	3.75	100.4
75/10/15	89	389	1276	65.7	4.14	2532	128.3	3.77	101.0

**[0195]** For any heat pump fluid to be a viable candidate, it needs to also perform well in the cooling mode, i.e., in higher ambient temperatures it needs to provide adequate cooling. Modeling results show that refrigerant blends containing HFO-1234yf provide an equivalent or improved cooling advantage over neat HFO-1234yf in the cooling range from about 20°C up to 40°C average refrigerant temperature.

**[0196]** Refrigerant blends containing HFO-1234yf, HFC-32, and HFC-152a provide an advantage over neat HFO-1234yf in terms of improved cooling capacity, in some cases 20% higher than HFO-1234yf alone or more. The equivalent or improved cooling capacity of the inventive blends shows that the new fluids can easily be used to provide adequate cooling (air-conditioning) to a passenger cabin.

**[0197]** Modeling shows that refrigerant blends containing HFO-1234yf, HFC-32, and HFC-152a have similar COP or energy performance in the cooling range from average refrigerant temperature of about +20 to +40°C.

**[0198]** Additionally, refrigerant blends containing HFO-1234yf, HFC-32, and HFC-152a for the most part also exhibit lower average temperature glides than the comparative compositions from the prior art over the desired cooling range, i.e., from about +20°C to +40°C.

**EXAMPLE 3****Reduction in average temperature glide by addition of HFC-152a**

**[0199]** A thermodynamic modeling program was used to model the expected average temperature glide for blends of HFO-1234yf/HFC-32, with the addition of differing amounts of HFC-152a. Physical properties for the components were taken from NIST REFPROP Version 10.

**Modeling Conditions**

Evaporator temperature	30°C
Condenser temperature	50°C
Superheat	10°C
Subcool	0°C
Compressor Isentropic Efficiency	70%

**[0200]** The results show that addition of HFC-152a to compositions containing HFO-1234yf and HFC-32 reduces the average temperature glide. See FIG. 6 and note that the x-axis corresponds to zero HFC-152a content. As the amount of HFC-152a is increased the average temperature glide is decreasing.

**EXAMPLE 4****Flammability of a blend of HFO-1234yf, HFC-32, and HFC-152a****Flame propagation**

**[0201]** The WCF-LFL (worst case formulation for flammability) and the WCFF-LFL (worst case fractionation for flammability) were determined for a refrigerant composition containing 78 weight percent HFO-1234yf (with tolerance of +1.0/-1.0), 7.5 weight percent HFC-32 (with tolerance +0.5/-1.5), and 14.5 weight percent HFC-152a (with tolerance +0.5/-1.5). The WCF-LFL is the initial composition with the highest content of R-1234yf and R-152a based on manufacturing tolerances. The WCFF-LFL corresponds to the final liquid when a cylinder is filled with WCF-LFL at 54.4°C to 15% of the maximum full cylinder and leaked at a temperature of -26.1°C. Both the WCF-LFL and WCFF-LFL were tested according to ASTM E681-2009 test procedure as specified in ASHRAE Standard 34-2019 and described in Appendix B1 of ASHRAE Standard 34-2019. The test was run at 23°C in air, 1 atm pressure, and 50% relative humidity.

**[0202]** The test vessel was a 12-liter spherical glass flask. The ignition source was a spark from a transformer secondary rated at 15 kV/30 ma with 0.4 second spark duration. A stirrer was installed in the flask for vapor mixing. Mixture samples were prepared with concentrations determined gravimetrically and then confirmed with gas chromatographic analyses.

**[0203]** The compositions tested are as follows:

**TABLE 8**

Composition	HFO-1234yf, wt%	HFC-32, wt%	HFC-152a, wt%	Result
WCF-LFL	79.0	6.0	15.0	Flammable; LFL=5.75% v/v in air
WCFF-LFL	81.0	0.0	19.0	Flammable; LFL=5.3% v/v in air

### Burning velocity

**[0204]** The maximum burning velocity was measured for the WCF-BV and WCFF-BV of the same composition as above. The WCF-BV is the initial composition with the highest content of R-152a and R-32 based on the manufacturing tolerances. The WCFF-BV corresponds to the final liquid when a cylinder is filled with the WCF-BV at 54.4°C to 15% maximum full cylinder and leaked at a temperature of -27.54°C. The method used for testing burning velocity is the standard vertical tube method as presented in ISO 817, Appendix C. The apparatus for testing burning velocity is a Pyrex tube, 40 mm ID by 1.3 meters long. The test is run at 23°C and 101.3 kPa in dry air. The flame is observed and images of the fully developed flame front are used to measure the frontal area of the flame, from which burning velocity is calculated.

**TABLE 9**

Composition	HFO-1234yf, wt%	HFC-32, wt%	HFC-152a, wt%	Maximum burning velocity
WCF-BV	77.0	8.0	15.0	5.65 cm/s
WCFF-BV	80.4	0.1	19.5	7.46 cm/s

**Heat of Combustion**

**[0205]** The heat of combustion for a composition containing containing 78 weight percent HFO-1234yf, 7.5 weight percent HFC-32, and 14.5 weight percent HFC-152a was determined for the conditions of 25°C (77°F) and 101.3kPa (14.7 psia) The heat of combustion is calculated from a balanced stoichiometric equation of all component refrigerants. The heat of combustion was calculated to be 11.62 MJ/kg.

**[0206]** While the invention has been described with reference to a preferred embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

## CLAIMS

What is claimed is:

1. A composition comprising a refrigerant blend comprising from about 66 to 80 weight percent HFO-1234yf, from about 1 to 10 weight percent HFC-32, and from about 10 to 24 weight percent HFC-152a.
2. The composition of claim 1, wherein said refrigerant blend consists essentially of from about 69 to 80 weight percent HFO-1234yf, from about 5 to 8 weight percent HFC-32, and from about 12 to 24 weight percent HFC-152a.
3. The composition of claim 1 or 2, wherein said refrigerant blend consists essentially of from about 70 to 78 weight percent HFO-1234yf, from about 6 to 8 weight percent HFC-32, and from about 14 to 24 weight percent HFC-152a.
4. The composition of any of claims 1, 2, or 3, wherein said refrigerant blend consists essentially of from about 70 to 78 weight percent HFO-1234yf, from about 6 to 7.5 weight percent HFC-32, and from about 14 to 24 weight percent HFC-152a.
5. The composition of any of claims 1 to 4, wherein said refrigerant blend consists essentially of from about 72 to 78 weight percent HFO-1234yf, from about 6 to 7.5 weight percent HFC-32, and from about 14 to 20 weight percent HFC-152a.
6. The composition of any of claims 1 to 5, said refrigerant blend consists essentially of from about 74 to 78 weight percent HFO-1234yf, from about 6 to 7.5 weight percent HFC-32, and from about 14 to 18 weight percent HFC-152a.
7. The composition of any of claims 1 to 6, wherein said refrigerant blend consists essentially of:
  - about 70 weight percent HFO-1234yf, about 6 weight percent HFC-32, and about 24 weight percent HFC-152a;
  - about 74 weight percent HFO-1234yf, about 7 weight percent HFC-32, and about 19 weight percent HFC-152a;
  - about 77 weight percent HFO-1234yf, about 3 weight percent HFC-32, and about 20 weight percent HFC-152a;

about 78 weight percent HFO-1234yf, 7.5 weight percent HFC-32, and about 14.5 weight percent HFC-152a;

about 78 weight percent HFO-1234yf, about 6 weight percent HFC-32, and about 16 weight percent HFC-152a;

about 79 weight percent HFO-1234yf, about 3 weight percent HFC-32, and about 18 weight percent HFC-152a;

about 80 weight percent HFO-1234yf, about 4 weight percent HFC-32, and about 16 weight percent HFC-152a;

about 70 weight percent HFO-1234yf, about 8 weight percent HFC-32, and about 22 weight percent HFC-152a; or

about 67 weight percent HFO-1234yf, about 10 weight percent HFC-32, and about 23 weight percent HFC-152a.

8. The composition of any of claims 1 to 7, wherein said refrigerant provides average temperature glide of about 0.1 K to less than about 4 K.
9. The composition of any of claims 1 to 8, wherein said refrigerant provides average temperature glide of about 0.1 K to less than about 3 K.
10. The composition of any of claims 1 to 9, wherein said refrigerant provides average temperature glide of about 0.1 K to less than about 2.5 K, preferably from about 0.1K to less than about 2.0 K.
11. The composition of any of claims 1 to 10, wherein said refrigerant has a GWP of equal to or less than about 100.
12. The composition of any of claims 1 to 11, wherein said refrigerant has a GWP of less than about 75.
13. The composition of any of claims 1 to 12, wherein said refrigerant has a GWP of less than about 50.
14. The composition of any of claims 1 to 13, further comprising at least one additional compound:
  - a. comprising at least one compound selected from the group consisting of HCFC-244bb, HFC-245cb, HFC-254eb, CFC-12, HCFC-124, 3,3,3-

trifluoropropyne, HCC-1140, HFC-1225ye, HFO-1225zc, HFC-134a, HFO-1243zf, and HCFO-1131; or

- b. comprising at least one compound selected from the group consisting of: HFC-23, HCFC-31, HFC-41, HFC-143a, HCFC-22, HCC-40, HFC-161, HFO-1141, HCO-1140, HCFC-151a, HCC-150a, HCC-160, HCFO-1130a, HCFC-141b, HFC-143a, HCFO-1122, and HCFC-142b; or
- c. combinations of a) and b);

wherein the total amount of additional compound comprises greater than 0 and less than 1 weight percent.

15. The composition of any of claims 1 to 14, wherein the additional compound includes at least one of HFC-161, HFO-1141, HCO-1140, HCFC-151a, HCC-150a, or HCC-160 or combinations thereof.
16. The composition of any of claims 1 to 15, wherein the additional compounds comprise HFC-143a, HCC-40, HFC-161 and HCFC-151a.
17. The composition of any of claims 1 to 16, wherein the additional compounds comprise HFO-1243zf, HFC-143a, HCC-40, HFC-161, and HCFC-151a.
18. The composition of any of claims 1 to 17, wherein the additional compounds comprise HFO-1243zf, HCC-40, and HFC-161.
19. The composition of any of claims 1 to 18, wherein the refrigerant has a burning velocity of 10 cm/s or less, when measured in accordance with ISO 817 vertical tube method.
20. The composition of any of claims 1 to 19, wherein the refrigerant is classified as 2L for flammability as defined in ANSI/ASHRAE Standard 34.
21. The composition of any of claims 1 to 20, wherein the refrigerant has an LFL of less than 10 volume percent when measured in accordance with ASTM-E681.
22. The composition of any of claims 1 to 21, further comprising a lubricant.
23. The composition of any of claims 1 to 22, wherein said lubricant is at least one selected from the group consisting of polyalkylene glycol, polyol ester, poly- $\alpha$ -olefin, and polyvinyl ether.

24. The composition of any of claims 1 to 23, wherein the polyol ester lubricant is obtained by reacting a carboxylic acid with a polyol comprising a neopentyl backbone selected from the group consisting of neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and mixtures thereof.
25. The composition of any of claims 1 to 24, wherein the carboxylic acid has 2 to 18 carbon atoms.
26. The composition of any of claims 1 to 25, wherein said lubricant has volume resistivity of greater than  $10^{10}$   $\Omega$ -m at 20°C.
27. The composition of any of claims 1 to 26, wherein said lubricant has surface tension of from about 0.02 N/m to 0.04 N/m at 20°C.
28. The composition of any of claims 1 to 27, wherein said lubricant has a kinematic viscosity of from about 20 cSt to about 500 cSt at 40°C.
29. The composition of any of claims 1 to 28, wherein said lubricant has a breakdown voltage of at least 25 kV.
30. The composition of any of claims 1 to 29, wherein said lubricant has a hydroxy value of at most 0.1 mg KOH/g.
31. The composition of any of claims 1 to 30, further comprising from 0.1 to 200 ppm by weight of water.
32. The composition of any of claims 1 to 31, further comprising from about 10 ppm by volume to about 0.35 volume percent oxygen.
33. The composition of any of claims 1 to 32, further comprising from about 100 ppm by volume to about 1.5 volume percent air.
34. The composition of any of claims 1 to 33, further comprising a stabilizer.
35. The composition of any of claims 1 to 34, wherein the stabilizer is selected from the group consisting of nitromethane, ascorbic acid, terephthalic acid, azoles, phenolic compounds, cyclic monoterpenes, terpenes, phosphites, phosphates, phosphonates, thiols, and lactones.
36. The composition of any of claims 1 to 35, wherein the stabilizer is selected from tolutriazole, benzotriazole, tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-

di-terbutyl-4-methylphenol, fluorinated epoxides, n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenylglycidyl ether, d-limonene,  $\alpha$ -terpinene,  $\beta$ -terpinene,  $\gamma$ -terpinene,  $\alpha$ -pinene,  $\beta$ -pinene, or butylated hydroxytoluene.

37. The composition of any of claims 1 to 36, wherein the stabilizer is present in an amount from about 0.001 to 1.0 weight percent based on the weight of the refrigerant.
38. The composition of any of claims 1 to 37, further comprising at least one tracer.
39. The composition of any of claims 1 to 38, wherein said at least one tracer is present in an amount from about 10 ppm by weight to about 1000 ppm by weight.
40. The composition of any of claims 1 to 39, wherein said at least one tracer is selected from the group consisting of hydrofluorocarbons, hydrofluoroolefins, hydrochlorocarbons, hydrochloroolefins, hydrochlorofluorocarbons, hydrochlorofluoroolefins, hydrochlorocarbons, hydrochloroolefins, chlorofluorocarbons, chlorofluoroolefins, hydrocarbons, perfluorocarbons, perfluoroolefins, and combinations thereof.
41. The composition of any of claims 1 to 40, wherein said at least one tracer is selected from the group consisting of HFC-23, HCFC-31, HFC-41, HFC-161, HFC-143a, HFC-134a, HFC-125, HFC-236fa, HFC-236ea, HFC-245cb, HFC-245fa, HFC-254eb, HFC-263fb, HFC-272ca, HFC-281ea, HFC-281fa, HFC-329p, HFC-329mmz, HFC338mf, HFC-338pcc, CFC-12, CFC-11, CFC-114, CFC-114a, HCFC-22, HCFC-123, HCFC-124, HCFC-124a, HCFC-141b, HCFC-142b, HCFC-151a, HCFC-244bb, HCC-40, HFO-1141, HCFO-1130, HCFO-1130a, HCFO-1131, HCFO-1122, HFO-1123, HFO-1234ye, HFO-1243zf, HFO-1225ye, HFO-1225zc, PFC-116, PFC-C216, PFC-218, PFC-C318, PFC-1216, PFC-31-10mc, PFC-31-10my, and combinations thereof.
42. A refrigerant storage container containing the refrigerant of any of claims 1 to 41, wherein the refrigerant comprises gaseous and liquid phases.
43. A system for heating and cooling the passenger compartment of an electric vehicle, comprising an evaporator, compressor, condenser and expansion

device, each operably connected to perform a vapor compression cycle, wherein the system contains the composition of any of claims 1 to 41.

44. The system of claim 43, wherein the average temperature glide is less than 4.0 K, preferably less than 3.0 K, more preferably less than 2.5 K, or most preferably less than 2.0 K, under heating conditions.
45. The system of claim 43 or 44, wherein the system does not include a PTC heater.
46. The system of claim 43, 44, or 45, wherein the system further comprises a reheater operably connected between the compressor and the condenser.
47. The system of claim 43, 44, 45, or 46, wherein the system is not a reversible cooling loop.
48. A method for replacing HFO-1234yf in a heating and cooling system contained within an electric vehicle, comprising providing the composition of any of claims 1 to 41 as a heat transfer fluid.
49. The method of claim 48, wherein the refrigerant produces volumetric capacity at least 15% higher, preferably 20% higher than HFO-1234yf alone when operating under the same heating conditions.
50. The method of claim 48 or 49, wherein the refrigerant produces COP equal to or greater than the COP of HFO-1234yf alone when operating under the same heating conditions.
51. A method of servicing the heating and cooling system of an electric vehicle comprising removing all of a used refrigerant from the system and charging the system with the composition of any of claims 1 to 41.
52. A use of the composition of any of claims 1 to 41 as a heat transfer fluid in a system for heating and cooling the passenger compartment of an electric vehicle.
53. A use of a composition comprising a refrigerant consisting essentially of:
  - about 78 weight percent HFO-1234yf, about 8 weight percent HFC-32, and about 14 weight percent HFC-152a; or

about 72 weight percent HFO-1234yf, about 8 weight percent HFC-32, and about 20 weight percent HFC-152a,

as a heat transfer fluid in a system for heating and cooling the passenger compartment of an electric vehicle.

54. The use of claim 52 or 53 wherein the system is not a reversible cooling loop.
55. A method for reducing the temperature glide in a heat exchanger operating with a refrigerant blend composition consisting essentially of HFC-32 and HFO-1234yf comprising adding HFC-152a to the refrigerant blend composition, wherein the composition comprises at least about 70 weight percent HFO-1234yf.
56. The method of claim 55, wherein the HFC-152a is added in an amount of about 10 to 24 weight percent based on the weight percent of the total refrigerant blend composition.
57. The method of claim 55 or 56, wherein the average temperature glide in the heat exchanger is reduced to less than 4 K, preferably less than 3.0 K, more preferably less than 2.5 K, or most preferably less than 2.0 K, under heating conditions.

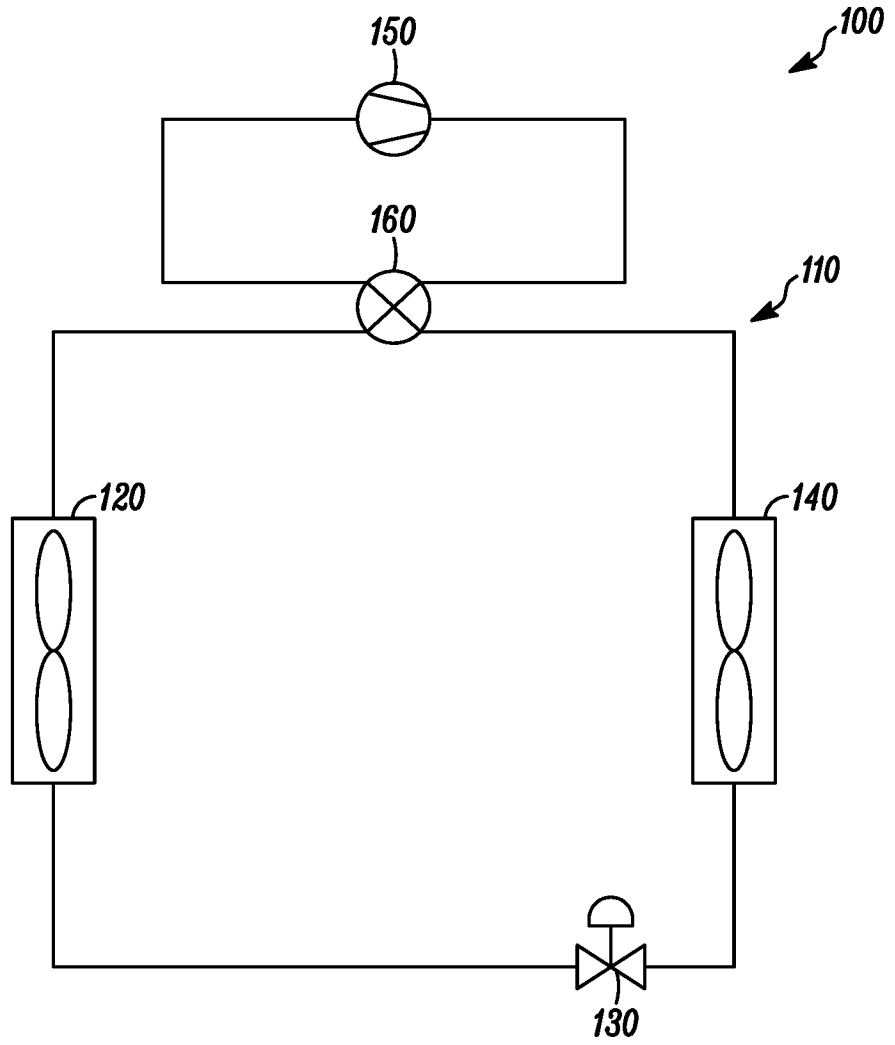


FIG. 1

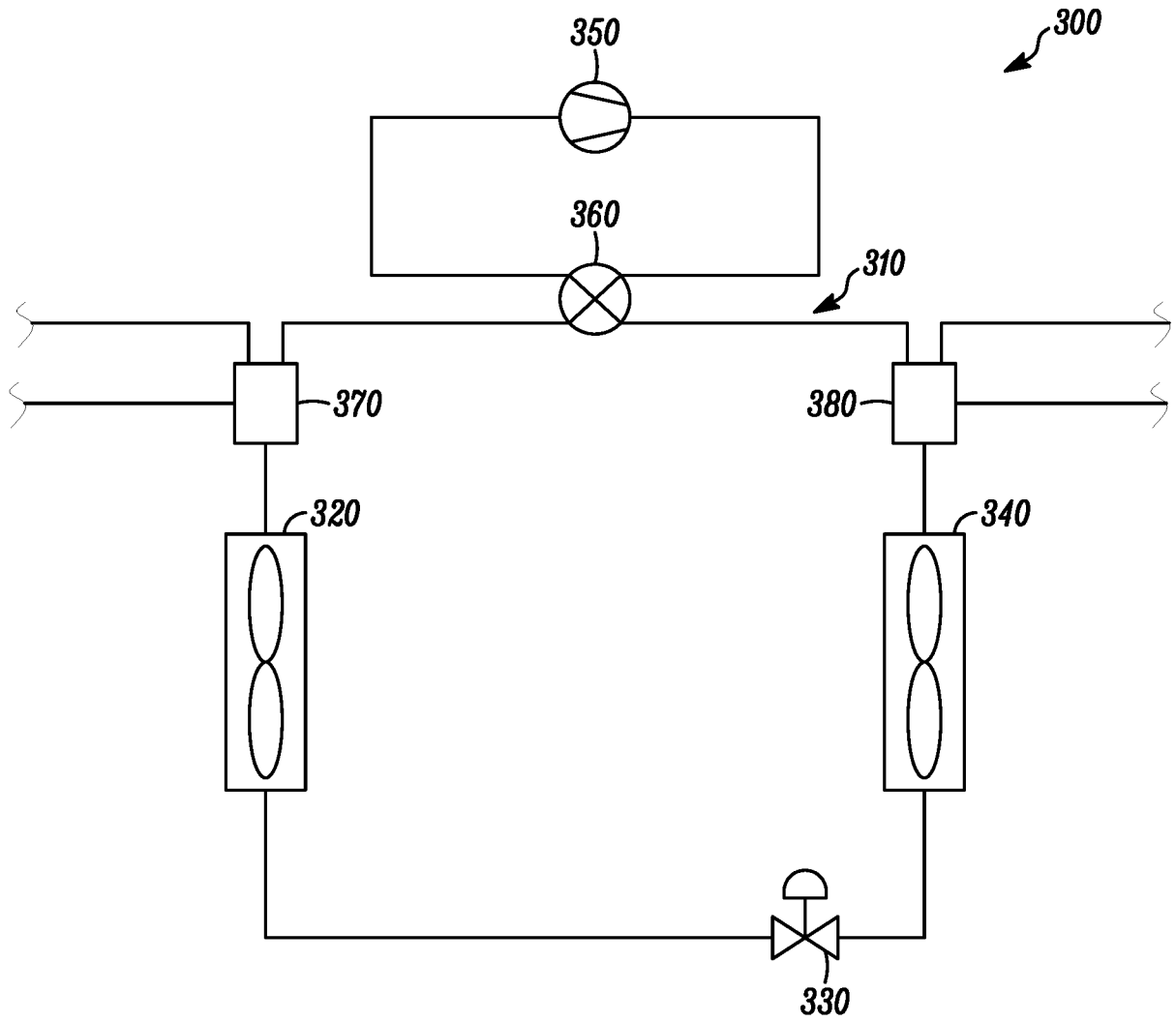


FIG. 2

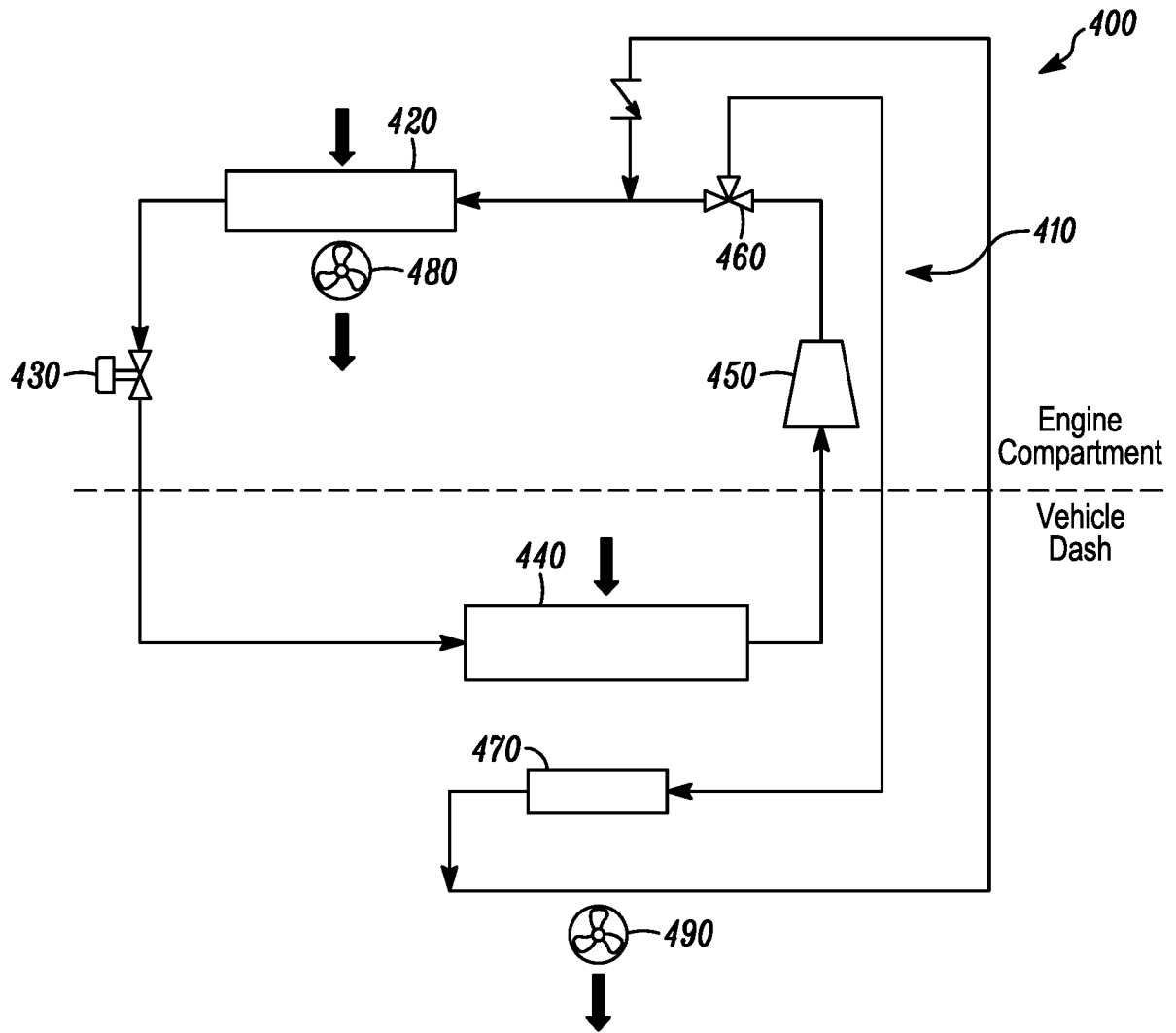


FIG. 3

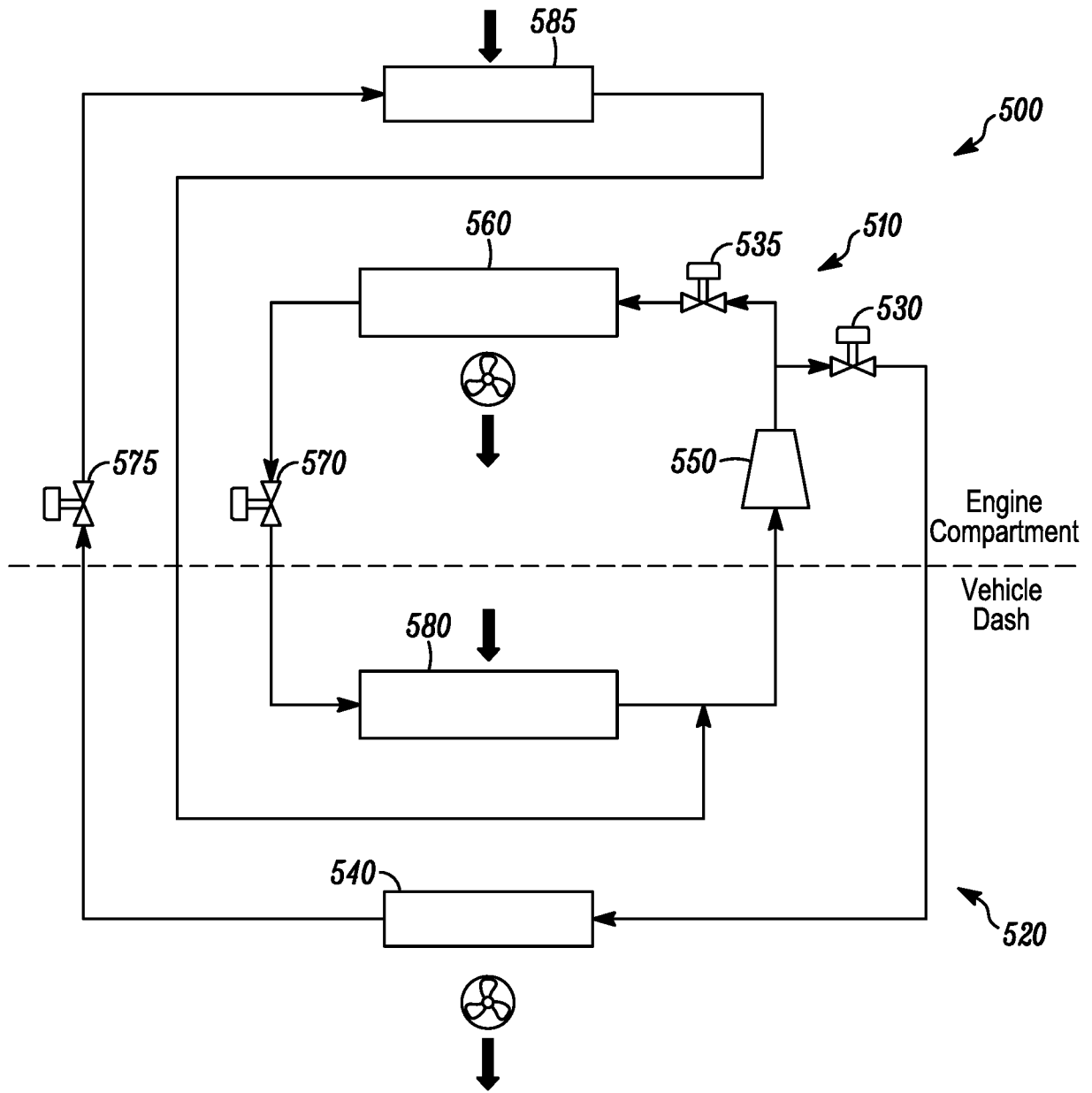


FIG. 4

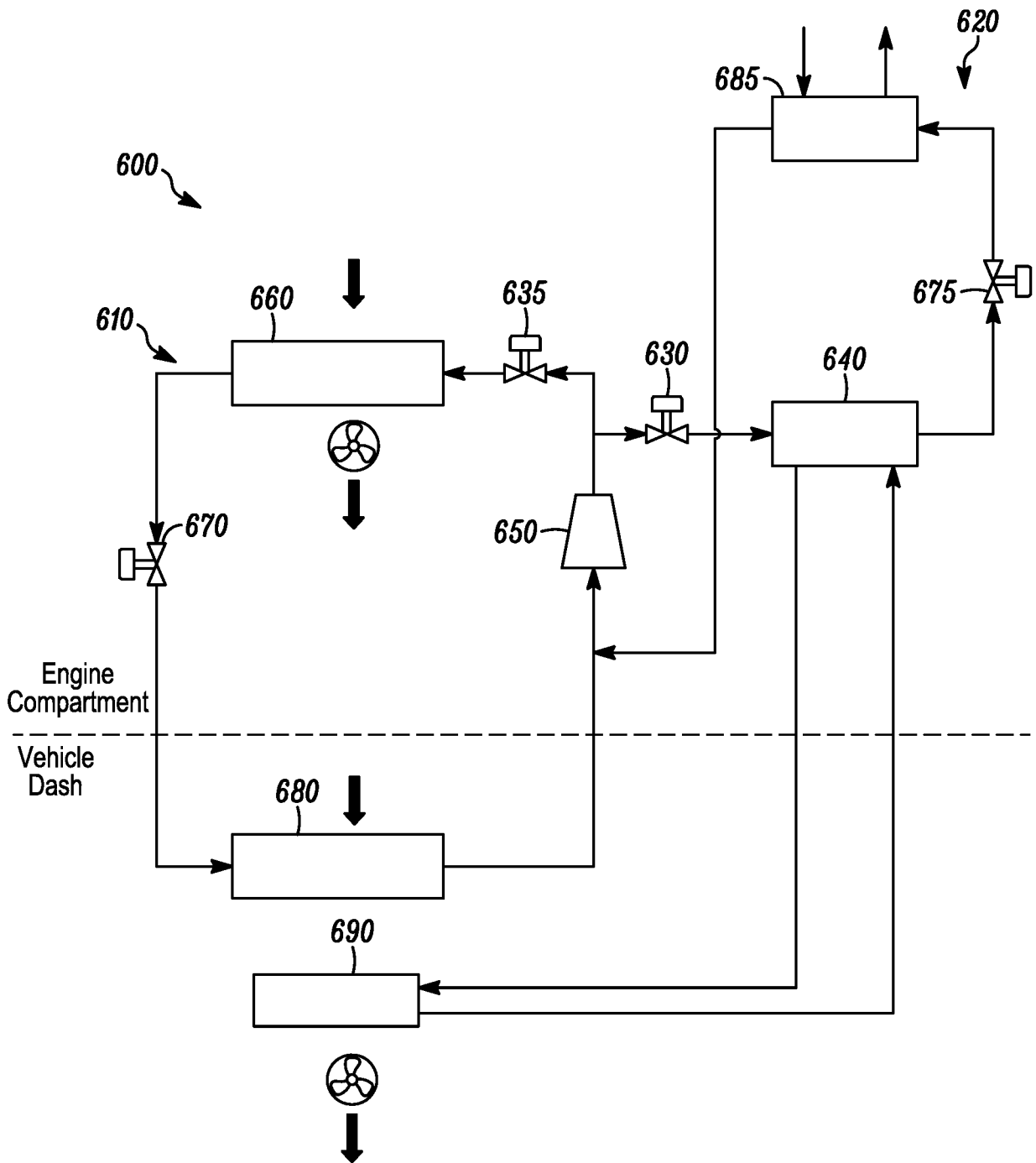


FIG. 5

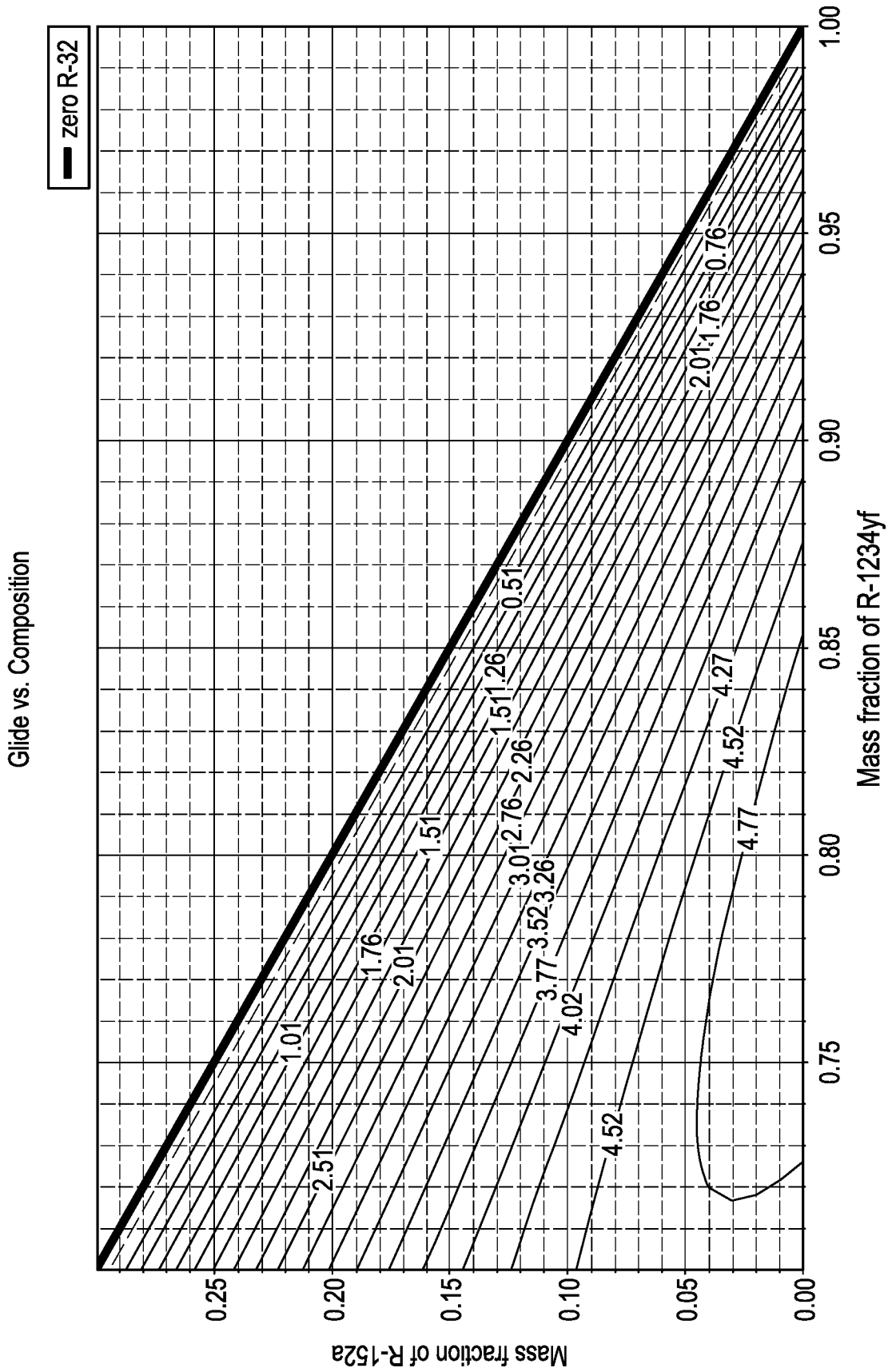


FIG. 6

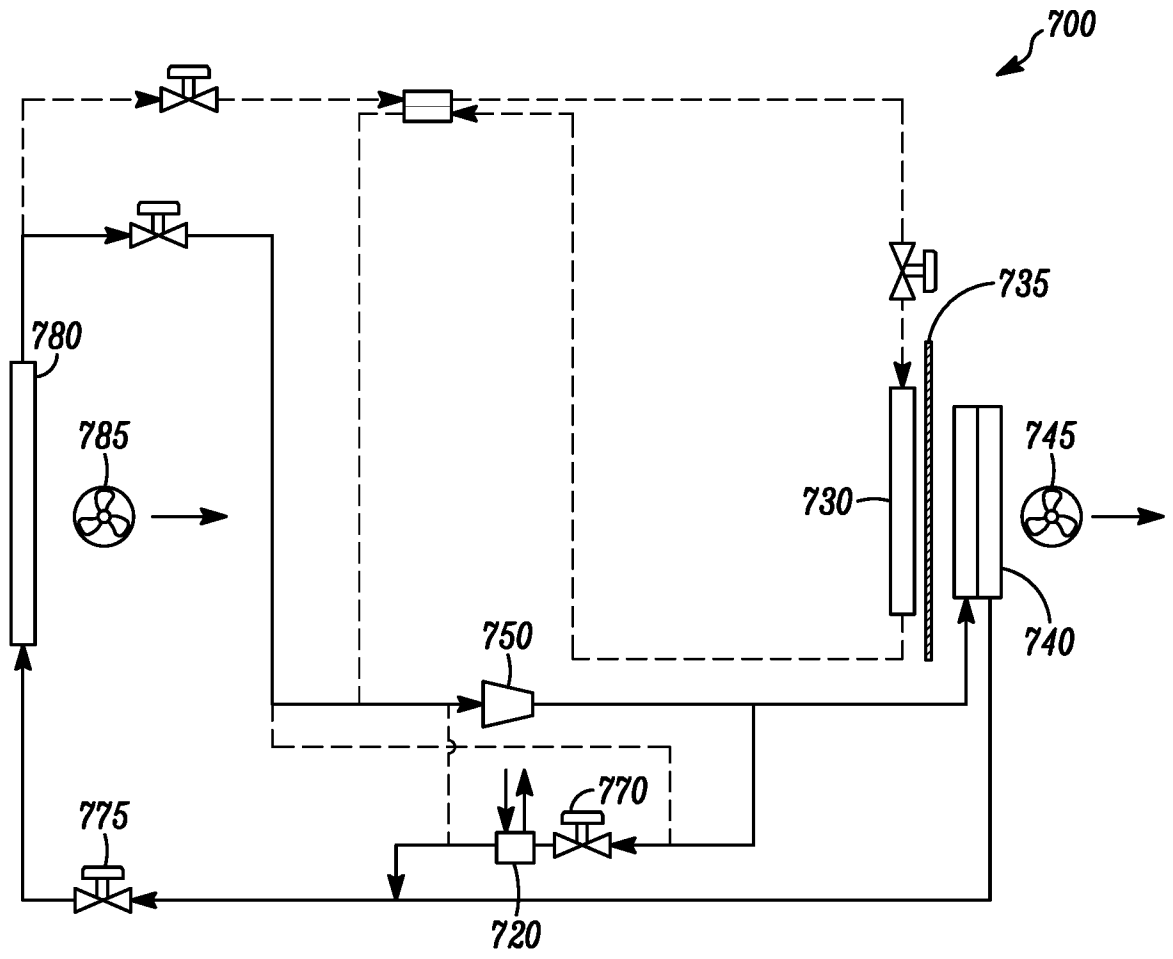


FIG. 7

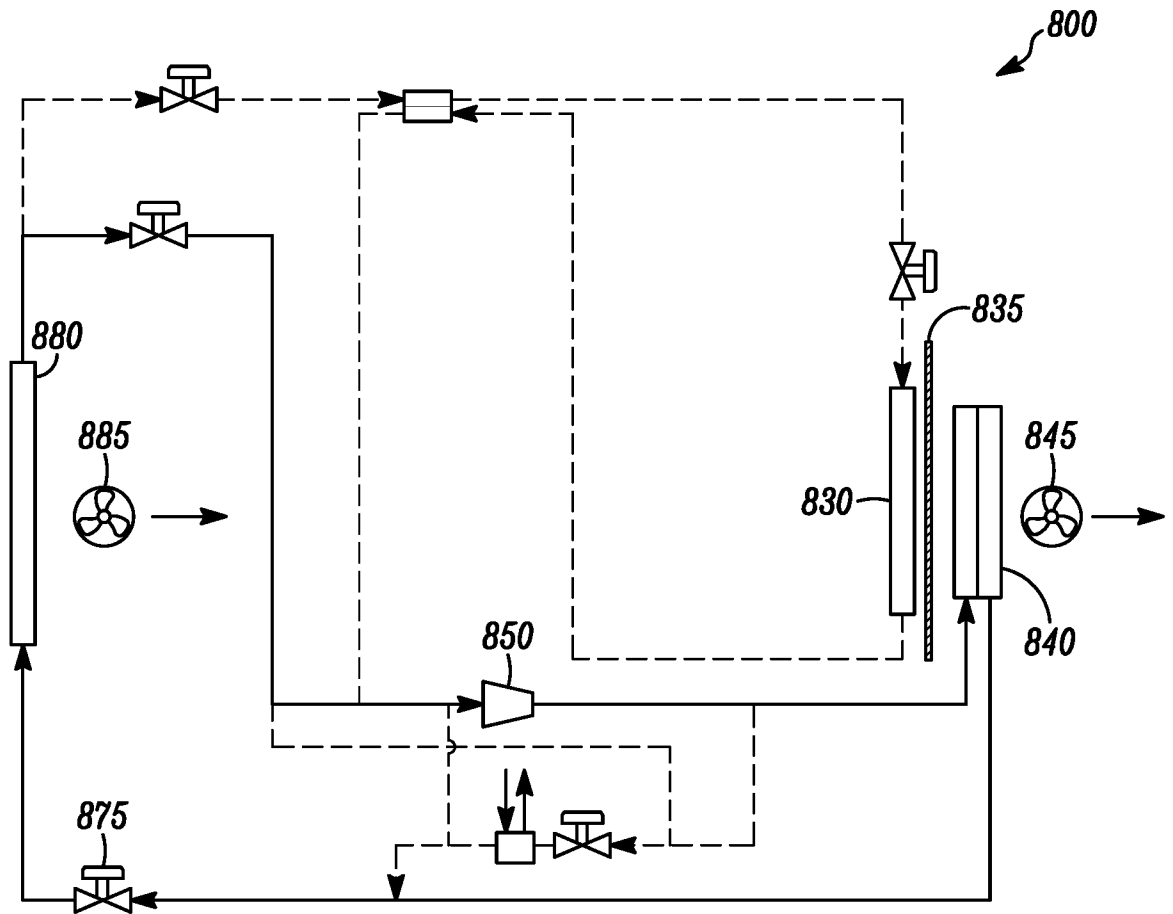


FIG. 8

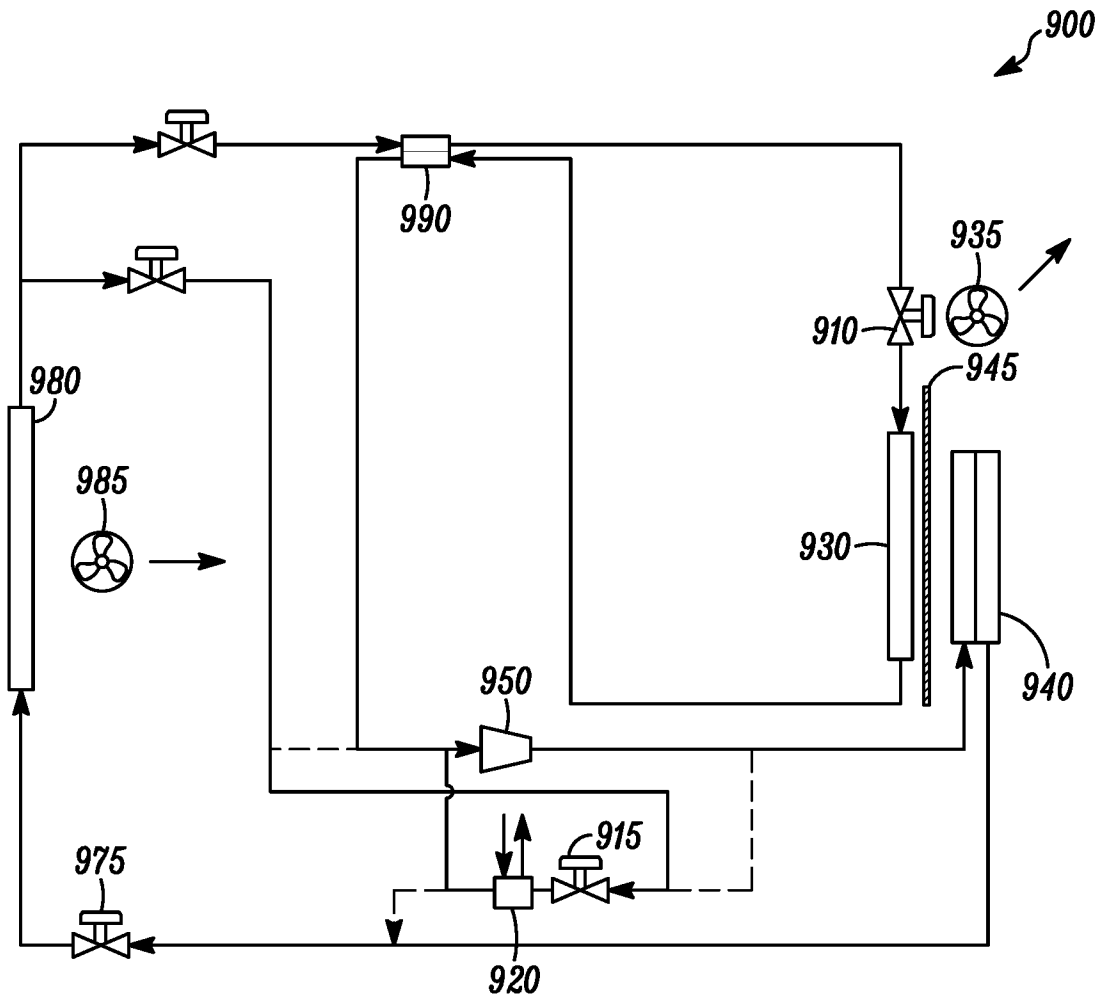


FIG. 9

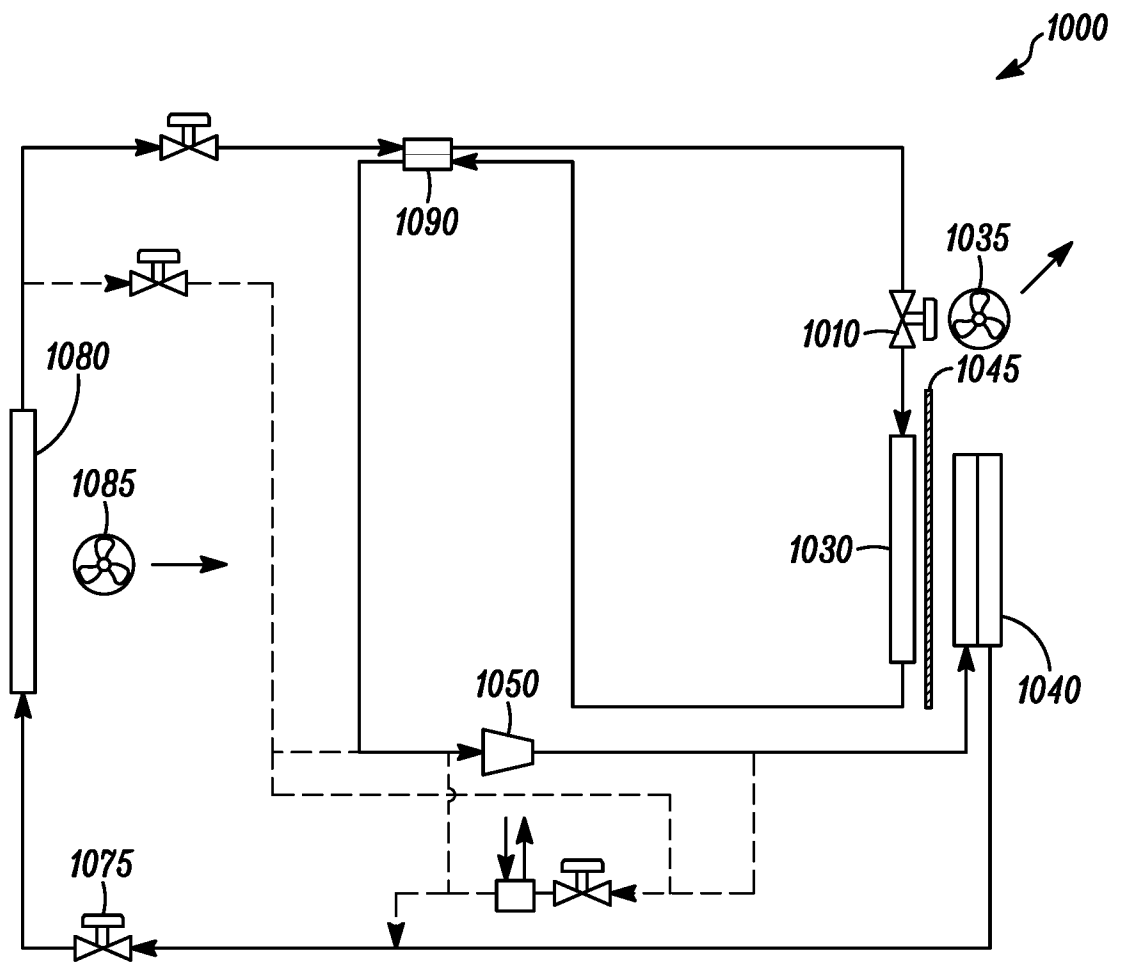


FIG. 10

**INTERNATIONAL SEARCH REPORT**

International application No  
**PCT/US2022/037055**

**A. CLASSIFICATION OF SUBJECT MATTER**  
**INV. C09K5/04**  
**ADD.**

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 G02F**

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
**EPO-Internal, CHEM ABS Data, WPI Data**

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<b>X</b>	<b>WO 2013/032908 A2 (DU PONT [US]; MINOR BARBARA HAVILAND [US]; GERSTEL JOACHIM [DE]) 7 March 2013 (2013-03-07)</b>	<b>1-47</b>
<b>Y</b>	<b>page 1, lines 6-13</b>	<b>22-30</b>
<b>A</b>	<b>page 4, line 29 - page 5, line 2 tables 1, 2</b>	<b>48-57</b>
	-----	
<b>X</b>	<b>US 2016/355718 A1 (RACHED WISSAM [FR]) 8 December 2016 (2016-12-08)</b>	<b>1-3, 8-11, 19-21, 31-33, 42-47</b>
<b>Y</b>	<b>paragraphs [0002], [0035], [0047];</b>	<b>22-30</b>
<b>A</b>	<b>claims 7-11; table 2</b>	<b>48-57</b>
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Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search  
**18 October 2022**

Date of mailing of the international search report  
**25/10/2022**

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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