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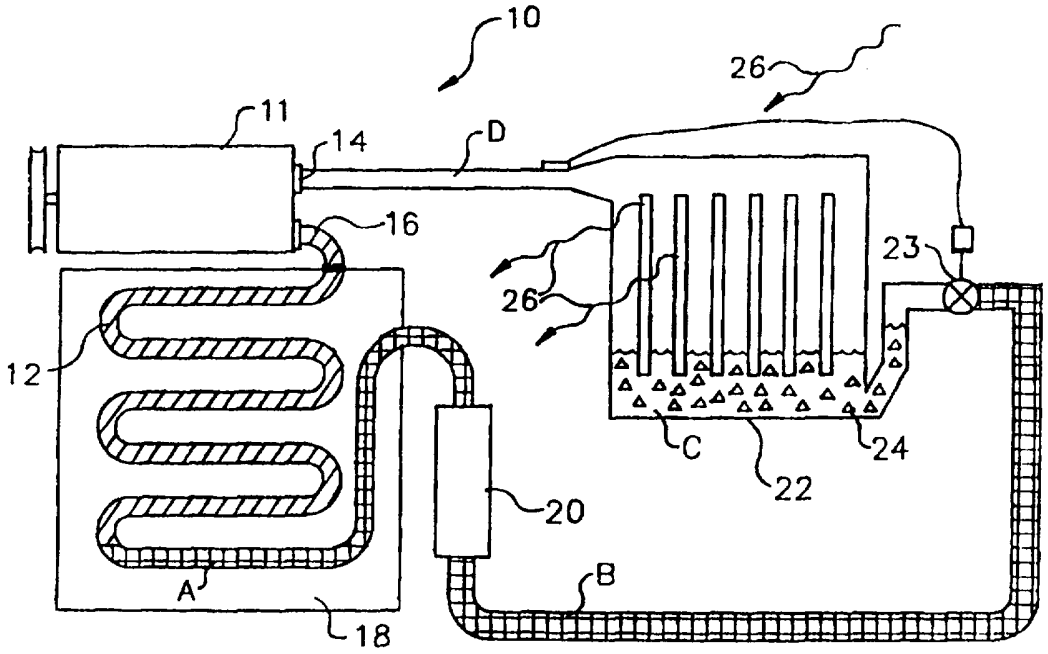

(57) Abstract

A hydrocarbon refrigerant mixture for direct substitution into systems designed for use with refrigerant R-12. The mixture of propane, butane, ethane, and friction fighting agents may be advantageously used as a substitute for R-12, thus eliminating the use of ozone depleting R-12 refrigerant. Ideally, the mixture has therein approximately fifty seven point one (57.1) percent propane, twenty three point two (23.2) percent n-butane, fifteen point one (15.1) percent iso-butane, about one point eight (1.8) percent ethane, and about two (2) percent of a petroleum based oil fortifying agent and friction fighter. Energy saving use of the refrigerant in automotive air-conditioning and in residential refrigerators is disclosed.

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IMPROVED REFRIGERANT MIXTURE

AND

METHOD OF USE IN REFRIGERATION SYSTEMS

TECHNICAL FIELD OF THE INVENTION

This invention relates to a novel, improved refrigerant mixture and its use in refrigeration systems. The refrigerant mixture is not harmful to the ozone layer, and is particularly applicable in systems such as automobile air-conditioning and home refrigeration.

BACKGROUND OF THE INVENTION

A continuing demand exists for an energy efficient "ozone friendly" refrigerant substitute which is relatively safe with respect to fire and explosion hazard, and which is substantially non-toxic in the event that the refrigerant thermally degraded, such as by way of overheating or fire. In particular, there exists a continuing need for a simple, low cost refrigerant which can be used as a direct substitute for refrigerant R-12, also commonly known as dichlorodifluoromethane. Further, it would be desirable

for such a substitute refrigerant mixture to have physical properties sufficiently comparable to R-12 so that existing refrigeration and air conditioning equipment can be used without costly mechanical or electrical modification.

In addition to the undesirable ozone depletion consequences which have been widely reported, those familiar with refrigeration systems will also recognize that R-12 and other fluorchlorocarbon refrigerants can contribute to the formation of acids under as a result of decomposition in a refrigerant system. Formation of such acids is not uncommon, and when it occurs, severe damage to metal surfaces in a refrigerant system can result. Moisture in an R-12 based refrigeration system can contribute to such acid formation, as can use of contaminated lubricating oils.

It would also be desirable for any new refrigerant useful as a direct replacement of R-12 to be useable without the need to change lubricating oils in the system. Many of the heretofore proposed refrigerant substitutes have undesirable lubrication requirements, and may require expensive cleanup of existing systems, as well as the use of more costly refrigerant types.

For the most part, the R-12 substitutes which have been proposed have been various substituted hydrocarbons, utilizing addition of bromine or other atoms, primarily in an attempt to produce a non-flammable refrigerant. Such substitutes have their own problems, such as undesirable toxicological effects on exposed individuals, particularly with respect to products (and incomplete products) of combustion.

SUMMARY OF THE INVENTION

I have now invented, and disclose herein, a novel, improved refrigerant mixture which does not have the above-discussed drawbacks common to the chlorofluorocarbon refrigerants heretofore used of which I am aware, or of the first generation of chlorofluorocarbon substitutes. Unlike the refrigerants heretofore available, my refrigerant is simple, relatively inexpensive, easy to manufacture, and otherwise superior to those heretofore used or proposed. Moreover, it may be used as a direct, "drop-in" substitute for R-12 in automotive air conditioning and in home refrigeration units. Such use results in significant energy savings, normally on the order of an ten (10) to twelve (12) percent reduction in power

consumption while delivering equivalent refrigeration capacity. In addition, the refrigerant provides a significant, demonstrated improvement with regard to protection against release of ozone depleting compounds.

Another important feature is the fact that my refrigerant is not conducive to formation of undesirable acid compounds while in use in a refrigeration system. This provides a unique safety feature when compared to many previously known refrigerants used in automotive air conditioning and home refrigeration applications.

Primary components of my novel refrigerant mixture are propane and butane. Preferably, a mixture from about forty eight and one-half (48.5) to about sixty five point seven (65.7) percent propane by liquid volume, and forty four (44) to about thirty two point six (32.6) percent butane by liquid volume, is desirable. Other components of my novel refrigerant mixture include about one and one-half (1.5) percent to about two (2.0) percent ethane by liquid volume, and about one point seven (1.7) to about two point three (2.3) percent by liquid volume of a preselected friction reducing petroleum based oil fortifying composition. Preferably, the petroleum based oil fortifying composition includes about forty to sixty (40-60) percent by liquid volume of chloro paraffin waxes and

hydrocarbon waxes, and about twenty to thirty five (20-35) percent of a chlorinated octadecanoic acid, and about five to fifteen (5-15) percent of zinc salts of phosphorodithioic acid,O,O-di-C1-14-alkyl esters, and about fifteen to twenty (15-20) percent of a hydrogenated 1-decene homopolymer.

In its simplest form, my invention is the discovery that a mixture of propane, butane, ethane, and friction fighting petroleum oil fortifiers may be directly substituted for R-12 in an existing refrigeration system at great energy saving advantage when compared to other proposed replacements. Also, my refrigerant mixture provides superior physical properties, as well as improved compatibility with lubricating oils and existing materials of construction, in R-12 replacement applications.

Thus, the advantages of my improved refrigeration mixture, including (1) protection of the ozone layer, (2) the low cost of the commonly available gases propane and butane gases, and (3) compatibility with existing lubricating oils and materials of construction, become important and self-evident in direct R-12 refrigerant substitution applications.

OBJECTS, ADVANTAGES, AND FEATURES OF THE INVENTION

From the foregoing, it will be apparent to the reader that one important and primary object of the present invention resides in the provision of an R-12 refrigerant replacement which does not contribute to the destruction of the ozone layer.

Other important but more specific objects of the invention reside in the provision of a refrigerant which may be directly and in a "drop-in" manner substituted in R-12 based refrigeration systems, and which:

reduce energy consumption, and thus improve the coefficient of performance of refrigerant systems over the use of R-12 in the same system;

can be manufactured in a simple, straightforward manner;

results in comparatively low cost refrigerant mixtures;

in conjunction with the preceding object, have the advantage that they can be widely used without cost penalty in selected refrigeration systems;

which provides a refrigerant gas mixture which is easy to install, use, and remove;

which is compatible with lubrication oils in existing refrigeration systems; and
and which is compatible with the materials of construction of existing refrigeration systems.

Other important objects, features, and additional advantages of my invention will become apparent to the reader from the foregoing and the appended claims and as the ensuing detailed description and discussion proceeds in conjunction with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

In the drawing:

Figure 1 is a process flow diagram illustrating my process of directly substituting my novel, improved refrigerant mixture in an automobile air-conditioning system.

Figure 2 is a process flow diagram illustrating my process of directly substituting my novel, improved refrigerant mixture in a residential refrigerator system.

DETAILED DESCRIPTION OF THE INVENTION

Widely utilized refrigerant systems which heretofore typically utilize R-12 include automotive and home refrigeration systems. Although the novel, improved refrigerant mixture disclosed herein may be used in other types of refrigerant circuits, my invention will be disclosed primarily with reference to direct substitution of R-12 with my novel, improved refrigerant mixture in the above types of refrigeration systems.

Turning now to Figure 1, there is shown an automotive type refrigeration system 10. That type of system is commonly utilized to cool the passenger compartment of cars and trucks. Critical components of the refrigeration system 10 include the compressor 11 which is used to raise the pressure (and the temperature) of a circulating refrigerant 12 from the cold, low pressure suction side 14 to the high temperature, high pressure discharge side 16 of the compressor 11. The pressure of refrigerant 12 is raised by compressor 11 so that the refrigerant 12 it is capable of being condensed based at a convenient temperature and pressure in the condenser 18. Actual operating temperatures and pressures will vary widely

and may be reviewed in a variety of textbooks and handbooks on refrigeration. However, for a convenient point of reference, when the outside air entering an automotive condenser is about 37.8°C (100°F), the high pressure circuit (from compressor 11 discharge to expansion valve 23) may operate at about 220 to 270 pounds per square inch gauge (about 1508 to 1851 kPA), while the low pressure circuit (from expansion valve 23 to suction side inlet 14 of compressor 11) may operate at about 20 to 30 psig (about 137 to 206 kPA). Thus, the operating conditions in the low pressure circuit correspond to a temperature of the cold, evaporating refrigerant B of roughly -6.7°C to -1.1°C (20°F to 30°F).

Low pressure refrigerant 12 vapors D are compressed by compressor 11 to form high pressure vapors A, which are then condensed in condenser 18. Condensed refrigerant B is then passed through a receiver 20, to accumulate the liquid refrigerant B. Although in R-12 systems the receiver may also include a desiccant for removal of water from the circulation refrigerant 12, so as to minimize the tendency of the refrigerant to form harmful, normally acid decomposition products, such a desiccant is not normally needed when using my refrigerant, and thus is not shown.

In order to allow the high pressure, liquid refrigerant B to enter the low pressure evaporator 22, the refrigerant is metered through a thermal expansion valve 23. The high pressure liquid refrigerant B is allowed to escape into the lower pressure evaporator 22, and most of the refrigerant 12 will enter as a liquid to a pool C at the bottom of the evaporator 22. As heat is introduced to the evaporator 22 (as via an airstream 26 passing through passageways in evaporator 22), the liquid refrigerant boils, forming bubbles 24 which rise to become a low pressure vapor stream D. That low pressure vapor stream D travels to the low pressure side suction side 14 of the compressor 11, to repeat the process.

Until recent scientific investigation recognized the dangers of chloroflurocarbon refrigerants, most automotive type refrigeration systems used dichlorodifluoromethane (R-12) as the refrigerant. Unfortunately, that compound has been found to contribute to depletion of the upper atmospheric (stratospheric) ozone layer. As a result, use of R-12 has been largely discontinued, as urged or as required by specific limitations in legislation in the United States, Europe, and elsewhere, in accord with international treaty.

I have found that a hydrocarbon refrigerant mixture, the primary components of which are propane and butane, can be directly substituted for R-12 in automotive air-conditioning and residential refrigeration systems. Preferably, a mixture from about forty eight and one-half (48.5) to about sixty five point seven (65.7) percent propane by liquid volume, and forty four point one (44.1) to about thirty two point five (32.5) percent butane by liquid volume, is desirable. Other components of my novel refrigerant mixture include about one and one-half (1.5) percent to about two (2.0) percent ethane by liquid volume, and about one point seven (1.7) to about two point three (2.3) percent by liquid volume of a preselected friction reducing petroleum based oil fortifying composition. Preferably, the petroleum based oil fortifying composition includes about forty to sixty (40-60) percent by liquid volume of chloro paraffin waxes and hydrocarbon waxes, and about twenty to thirty five (20-35) percent of a chlorinated octadecanoic acid, and about five to fifteen (5-15) percent of zinc salts of phosphorodithioic acid,O,O-di-C1-14-alkyl esters, and about fifteen to twenty (15-20) percent of a hydrogenated 1-decene homopolymer. These percentages of the said components are the liquid volume percentages of the overall mixture.

The preferred composition assumes that analysis is carried out in accord with the International Standard ISO 7941, Commercial Propane and Butane Analysis by Gas Chromotography, 1st Edition, 1988-08-01. This is the equivalent of British Standard BS7278:1990, with sample introduction of the liquid phase sample performed in accordance with the gaseous injection option of ISO 7941, Section 8.3.2.2.

I have found that by use of the preferred composition a vapor pressure curve (vapor pressure versus temperature) for my hydrocarbon refrigerant mixture very closely approximates the vapor pressure curve for R-12. Thus, the direct substitution of my novel, improved refrigerant mixture in systems designed for R-12 operation is easily accomplished. Further, my refrigerant is compatible with common materials of construction for R-12 systems, including hoses, seals, and tubing, thus eliminating concern for replacing parts in existing systems. Further, the size of the molecules in my mixture is such that leakage, primarily due to porosity of components such as hoses and seals, is minimal, when compared to other refrigerants now used, or to most other substitutes for R-12 which have been proposed.

With respect to the exact percentage of butane, I prefer to use a mixture of n-butane and iso-butane, where the iso-butane ranges from about twelve point eight (12.8) percent to about seventeen point four (17.4) percent by liquid volume of the entire refrigerant mixture, and the n-butane ranges from about nineteen point seven (19.7) to about twenty six point seven (26.7) percent by liquid volume of the entire refrigerant mixture. However, either compound may be advantageously employed in the invention as disclosed and claimed herein.

The aforementioned novel, improved refrigerant mixture is advantageous in that it does not contain appreciable amounts of halogens to cause problems such as acid formation and the resultant metal attack problems internal to the refrigeration circuit, as may be encountered in the case when moisture and/or oxygen contaminate a system using dichlorodifluoromethane (R-12). Also, both propane and butane are commonly available, at substantially lower cost than most currently available refrigerants. Particularly in automotive applications, as set forth above, the flammable properties of propane and butane should not cause particular concern, in the quantities required for small refrigeration circuits, in view of the

substantially larger quantities of flammable fuel already successfully used, for example, in propane powered and compressed natural gas powered transport vehicles.

The process of direct substitution of my novel, improved refrigerant mixture for R-12 may also be employed in residential and light commercial refrigerator systems, such as is depicted in FIG. 2. A refrigerator 40 is shown having therein a compressor 42, a condenser 44, an expansion valve 46, an evaporator 48, and a low pressure vapor line 50 which returns refrigerant vapors to the compressor 42. Operation of the system is similar to that set forth above for the automotive refrigeration system, and need not be repeated in detail as it will be quickly understood by those skilled in the art and to whom this specification is addressed. For reference, it is common for R-12 based refrigerator systems to operate in the range of about 120 psig (about 823 kPA) on the high pressure side, and at about 0 psig (about 0 kPA gauge) on the low pressure side. The novel, improved refrigerant mixture disclosed herein provides a change of state, i.e., a boiling range and a condensing range, where the refrigerant effectively mimics the boiling point of a true single component R-12 refrigerant, to within an acceptable extent.

To further elaborate on this last point, when designing a refrigeration system, it is necessary to select compressor volumetric performance and motor size which matches the condenser and evaporator capacity. In other words, the heat removed at the evaporator (to provide the desired cooling or refrigeration) must be reflected by the enthalpy change of the refrigerant as it passes through the evaporator, and the refrigerant gas carrying such heat must be compressed to a pressure where it can be condensed, and the heat rejected, at the condenser. After the components of a refrigeration system are selected, or are in place in the field, it is not easy to change refrigerants, since the desired performance must be attained at substantially the same temperatures and pressures, in order not to overload the compressor or to have an underperforming system due to lack of ability of the compressor to reach the necessary condensing pressure for a selected refrigerant.

In summary, I have now discovered that the refrigerant gas commonly used in automobile air conditioning and in home refrigerator systems, dichlorodifluoromethane (R-12) may be advantageously replaced by a novel hydrocarbon mixture which is substantially composed of propane and butane. Most

preferably, a mixture from about fifty seven point one (57.1) percent propane by liquid volume, and fifteen point one (15.1) percent iso-butane by liquid volume, and twenty three point two (23.2) percent n-butane by liquid volume, and about one point eight (1.8) percent ethane by liquid volume is desirable. Most preferably, trace hydrocarbon refrigerants are present at less than one (1.0) percent by liquid volume, and such trace hydrocarbon refrigerants most preferably comprise about point one (0.1) percent by liquid volume of iso-butene, about zero point two (0.2) percent by liquid volume of 2-transbutene, and about zero point one (0.1) percent of 2-cisbutene, and about zero point one (0.1) percent of other C-4 hydrocarbons. Also, low level trace amounts, most preferably less than zero point one (0.1) percent by liquid volume of propene may be present, and most preferably, less than zero point one (0.1) percent by liquid volume of 1,3 butadiene may be present. Other components of my novel refrigerant mixture include about two percent (2.0) percent by liquid volume of a preselected friction reducing petroleum based oil fortifying composition. Preferably, the petroleum based oil fortifying composition includes about forty to sixty (40-60) percent by liquid volume of chloro paraffin waxes and hydrocarbon waxes

(Chemical Abstracts "CAS" Registry Number 63449-39-8), and about twenty to thirty five (20-35) percent of a chlorinated octadecanoic acid (Chemical Abstracts "CAS" Registry Number 68611-20-1), and about five to fifteen (5-15) percent of zinc salts of phosphorodithioic acid,O,O-di-C1-14-alkyl esters (Chemical Abstracts "CAS" Registry Number 68649-42-3), and about fifteen to twenty (15-20) percent of a hydrogenated 1-decene homopolymer (Chemical Abstracts "CAS" Registry Number 68037-01-4). These percentages of the said components are the liquid volume percentages of the overall mixture. The petroleum based oil fortifying and friction fighting composition is available from Tri-Star Technologies Corporation of Great Falls, Montana, under the Product Name Tri-Star OZ2. However, the chlorinated paraffin waxes are available under a wide variety of commercial trade names, including Adekacizer E 410, Adekacizer E 450, Adekacizer E470, ADK Cizer E 410 ADK Cizer E 450, ADK Cizer E 470, Cereclor, Chlorez, Chlorowax, and Chloroparaffin waxes.

Also, I have discovered that by the use of the novel, improved refrigerant mixture described above, a refrigeration system designed an operated with my refrigerant mixture is more energy efficient than when

operated on R-12 refrigerant. This improvement, which can range up to ten (10) to twelve (12) percent less energy (kilowatts) usage per unit of refrigeration (kcal, BTU's, tons) in home refrigerators. The exact savings, however, will vary according to the composition of the mixture utilized and the size of the system, particularly the compressor. The energy improvements commonly seen is about four (4) to six (6) percent, with about three (3) percent due to the hydrocarbon refrigerant alone (without the aforementioned friction fighter addition) and the remainder of about one (1) to three (3) percent attributed to the friction fighter addition. The hydrocarbon refrigerant itself is a better heat conductor than R-12, which normally leads to slightly more heat dissipation by conduction to the compressor and radiation and convection cooling thereof (slightly reducing the load on the condenser). However, the friction fighter improves lubrication of the compressor, reducing wear and reducing friction loss, and lowers compressor drive motor electrical consumption.

Thus, it can be seen that I have developed and have set forth herein an exemplary process for refrigeration, using a novel, improved hydrocarbon refrigerant mixture for direct substitution in

refrigeration machinery which heretofore commonly employed R-12. My novel, improved refrigerant mixture is comprised of low cost components, and is easily prepared. Even if moisture should enter a refrigeration system using my refrigerant mixture, it does not tend to produce harmful acid breakdown products in the refrigeration system. Further, the mixture is quite compatible with refrigeration oils now used with R-12 refrigeration systems, and thus can be safely used in existing refrigeration systems with direct, "drop-in" substitution. Therefore, my novel hydrocarbon refrigerant mixture provides increased oil solubility therein, when compared to R-12, to provide distinct system operating advantanges, including better oil flow and return.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. Further, it is to be understood that minor trace compounds may be present in a refrigerant mixture as taught herein, without significantly varying the principal or affecting the practice of the invention.

The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description; and all changes which come within the meaning and range of equivalences of the claims are therefore intended to be embraced therein.

CLAIMS

I claim:

1. In a refrigeration system mechanically designed for use with refrigerant R-12, said process utilizing a refrigeration circuit comprising a compressor, a condenser, an expansion valve means, an evaporator, and a refrigerant for transport of thermal energy between the evaporator and the condenser, wherein said refrigerant is evaporated in said evaporator to produce a gas which is compressed by said compressor and thence sent to the condenser to be condensed to produce a liquid for metering into said evaporator by said expansion valve means,

the improvement comprising substitution of said R-12 refrigerant with a hydrocarbon based refrigerant mixture, wherein said substitute refrigerant mixture comprises a mixture of propane, butane, and ethane.

2. The process of claim 1, wherein said mixture of propane, butane, and ethane comprises at least about forty eight point five (48.5) percent propane by liquid volume.

3. The process of claim 1, wherein said mixture of propane, butane, and ethane comprises at least about fifty seven point one (57.1) percent propane by liquid volume.

4. The process of claim 1, wherein said mixture of propane, butane, and ethane comprises approximately sixty five point seven (65.7) percent propane by liquid volume.

5. The process of claim 1, wherein said mixture of propane, butane, and ethane comprises about two (2.0) percent ethane by liquid volume.

6. The process of claim 1, wherein said refrigeration system is employed in a motor vehicle.

7. The process of claim 6, wherein said motor vehicle comprises an automobile.

8. The process of claim 1, wherein said refrigeration system is employed in a residential refrigerator.

9. The process of using a hydrocarbon refrigerant mixture in a refrigeration system, wherein said

refrigerant mixture comprises

about forty eight point five (48.5) to about sixty five point seven (65.7) percent propane by liquid volume, and

about thirty two point six (32.6) to about forty four (44.0) butane by liquid volume, and

about one point five (1.5) to about two point zero (2.0) percent ethane by liquid volume,

with the liquid volume percentages of said components being the volume percentages of the overall refrigerant mixture.

10. A hydrocarbon refrigerant mixture, wherein said hydrocarbon refrigerant mixture comprises

about forty eight point five (48.5) to about sixty five point seven (65.7) percent propane by liquid volume, and

about thirty two point six (32.6) to about forty four (44.0) butane by liquid volume, and

about one point five (1.5) to about two point zero (2.0) percent ethane by liquid volume,

with the liquid volume percentages of said components being the volume percentages of the overall refrigerant mixture.

11. The refrigerant mixture as set forth in claim 10, wherein

propane is present in about fifty seven point one (57.1) percent liquid volume, and

butane is present in about thirty eight point three (38.3) percent by liquid volume,

ethane is present in about one point eight (1.8) percent by liquid volume,

with the liquid volume percentages of said components being the volume percentages of the overall refrigerant mixture.

12. The refrigerant mixture as set forth in any one of claims 10 or 11, wherein said butane is comprised of a mixture of iso-butane and n-butane.

13. The refrigerant mixture as set forth in claim 12, wherein said mixture of iso-butane and n-butane comprises from about twelve point eight (12.8) to about seventeen point four (17.4) percent by liquid volume of iso-butane.

14. The refrigerant mixture as set forth in claim 13, wherein said iso-butane comprises about fifteen point one (15.1) percent by liquid volume of iso-butane.

15. The refrigerant mixture as set forth in claim 12, wherein said n-butane comprises from about nineteen point seven (19.7) percent to about twenty six point seven (26.7) percent by liquid volume.

16. The refrigerant mixture as set forth in claim 15, wherein said n-butane comprises about twenty three point two (23.2) percent by liquid volume.

17. The refrigerant mixture as set forth in claim 10 or claim 11, further comprising a petroleum based oil fortifying friction fighting agent.

18. The refrigerant mixture as set forth in claim 17, wherein said petroleum based oil fortifying friction fighting agent comprises from about forty (40) percent to about sixty (60) percent of a chloro paraffin wax.

19. The refrigerant mixture as set forth in claim 17, wherein said petroleum based oil fortifying friction fighting agent comprises from about twenty (20) to about thirty five (35) percent of chlorinated octadecanoic acid.

20. The refrigerant mixture as set forth in claim 17, wherein said petroleum based oil fortifying friction fighting agent comprises from about five (5) to about fifteen (15) percent of the zinc salts of phosphorodithioic acid, O,O-di-C1-14-alkyl esters.

21. The refrigerant mixture as set forth in claim 17, wherein said petroleum based oil fortifying friction fighting agent comprises from about fifteen (15) to about twenty (20) percent of hydrogenated 1-decene homopolymer.

AMENDED CLAIMS

[received by the International Bureau on 11 June 1996 (11.06.96); original claims 1,9,10 and 17 amended; new claims 22-40 added; remaining claims unchanged (11 pages)]

1. In a refrigeration system mechanically designed for use with refrigerant R-12, said process utilizing a refrigeration circuit comprising a compressor, a condenser, an expansion valve means, an evaporator, and a refrigerant for transport of thermal energy between the evaporator and the condenser, wherein said refrigerant is evaporated in said evaporator to produce a gas which is compressed by said compressor and thence sent to the condenser to be condensed to produce a liquid for metering into said evaporator by said expansion valve means,

the improvement comprising substitution of said R-12 refrigerant with a hydrocarbon based refrigerant mixture, wherein said substitute refrigerant mixture comprises a mixture of propane, butane, and ethane,

and where said refrigerant mixture comprises about thirty two point six (32.6) percent percent propane to about sixty five point seven (65.7) percent by liquid volume.

2. The process of claim 1, wherein said mixture of propane, butane, and ethane comprises at least about forty eight point five (48.5) percent propane by liquid volume.

3. The process of claim 1, wherein said mixture of propane, butane, and ethane comprises at least about fifty seven point one (57.1) percent propane by liquid volume.

4. The process of claim 1, wherein said mixture of propane, butane, and ethane comprises approximately sixty five point seven (65.7) percent propane by liquid volume.

5. The process of claim 1, wherein said mixture of propane, butane, and ethane comprises about two (2.0) percent ethane by liquid volume.

6. The process of claim 1, wherein said refrigeration system is employed in a motor vehicle.

7. The process of claim 6, wherein said motor vehicle comprises an automobile.

8. The process of claim 1, wherein said refrigeration system is employed in a residential refrigerator.

9. In a refrigeration system mechanically designed for use with refrigerant R-12, said system utilizing a refrigeration circuit comprising a compressor, a condenser, an expansion valve means, an evaporator, and a refrigerant for transport of thermal energy between the evaporator and the condenser, wherein said refrigerant is evaporated in said evaporator to produce a gas which is compressed by said compressor and thence sent to the condenser to be condensed to produce a liquid for metering into said evaporator by said expansion valve means,

the improvement comprising the process of substitution of said R-12 refrigerant with a hydrocarbon based refrigerant mixture, wherein said substitute refrigerant mixture comprises a mixture of propane, butane, and ethane, and wherein said hydrocarbon refrigerant mixture comprises

about forty eight point five (48.5) to about sixty five point seven (65.7) percent propane by liquid volume, and

about thirty two point six (32.6) to about forty four (44.0) butane by liquid volume, and

about one point five (1.5) to about two point zero (2.0) percent ethane by liquid volume,

with the liquid volume percentages of said components being the volume percentages of the overall refrigerant mixture.

10. A hydrocarbon refrigerant mixture, wherein said hydrocarbon refrigerant mixture has a vapor pressure curve approximating that of R-12 and is suitable for use in systems mechanically designed for R-12, wherein said refrigerant mixture comprises

about forty eight point five (48.5) to about sixty five point seven (65.7) percent propane by liquid volume, and

about thirty two point six (32.6) to about forty four (44.0) butane by liquid volume, and

about one point five (1.5) to about two point zero (2.0) percent ethane by liquid volume,

with the liquid volume percentages of said components being the volume percentages of the overall refrigerant mixture.

11. The refrigerant mixture as set forth in claim 10, wherein

propane is present in about fifty seven point one (57.1) percent liquid volume, and

butane is present in about thirty eight point three (38.3) percent by liquid volume,

ethane is present in about one point eight (1.8) percent by liquid volume,

with the liquid volume percentages of said components being the volume percentages of the overall refrigerant mixture.

12. The refrigerant mixture as set forth in any one of claims 10 or 11, wherein said butane is comprised of a mixture of iso-butane and n-butane.

13. The refrigerant mixture as set forth in claim 12, wherein said mixture of iso-butane and n-butane comprises from about twelve point eight (12.8) to about seventeen point four (17.4) percent by liquid volume of iso-butane.

14. The refrigerant mixture as set forth in claim 13, wherein said iso-butane comprises about fifteen point one (15.1) percent by liquid volume of iso-butane.

15. The refrigerant mixture as set forth in claim 12, wherein said n-butane comprises from about nineteen point seven (19.7) percent to about twenty six point seven (26.7) percent by liquid volume.

16. The refrigerant mixture as set forth in claim 15, wherein said n-butane comprises about twenty three point two (23.2) percent by liquid volume.

17. The refrigerant mixture as set forth in claim 10 or claim 11, further comprising a chlorinated petroleum based oil fortifying friction fighting agent.

18. The refrigerant mixture as set forth in claim 17, wherein said petroleum based oil fortifying friction fighting agent comprises from about forty (40) percent to about sixty (60) percent of a chloro paraffin wax.

19. The refrigerant mixture as set forth in claim 17, wherein said petroleum based oil fortifying friction fighting agent comprises from about twenty (20) to about thirty five (35) percent of chlorinated octadecanoic acid.

AMENDED SHEET (ARTICLE 19)

20. The refrigerant mixture as set forth in claim 17, wherein said petroleum based oil fortifying friction fighting agent comprises from about five (5) to about fifteen (15) percent of the zinc salts of phosphorodithioic acid, O,O-di-C1-14-alkyl esters.

21. The refrigerant mixture as set forth in claim 17, wherein said petroleum based oil fortifying friction fighting agent comprises from about fifteen (15) to about twenty (20) percent of hydrogenated 1-decene homopolymer.

22. A refrigeration system mechanically designed for use with refrigerant R-12 and utilising a refrigeration circuit comprising a compressor, a condenser, an expansion valve means, an evaporator, and a refrigerant for transport of thermal energy between the evaporator and the condenser, wherein said refrigerant is evaporated in the evaporator to produce a gas which is compressed by the compressor and thence sent to the condenser to be condensed to produce a liquid for metering into said evaporator by said expansion valve means, and in which the R-12 refrigerant is substituted by a hydrocarbon based refrigerant mixture comprising

25-75% propane by liquid volume to 75-25% butane by liquid volume, the hydrocarbon based refrigerant mixture being a direct "drop-in" substitute for R-12.

23. A refrigeration system as claimed in claim 22 in which the hydrocarbon based refrigerant mixture comprises 50-60% propane by liquid volume to 50-40% butane by liquid volume.

24. A refrigeration system as claimed in claim 23 in which the hydrocarbon based refrigerant mixture comprises 50% propane by liquid volume to 50% butane by liquid volume.

25. A refrigeration system as claimed in any one of claims 22 to 24 in which the butane comprises iso-butane.

26. A refrigeration system as claimed in any of claims 22 to 24 in which the butane comprises n-butane.

27. A method of using a refrigeration system mechanically designed for use with refrigerant R-12 and utilising a refrigeration circuit comprising a compressor, a condenser, an expansion valve means, an

evaporator, and a refrigerant for transport of thermal energy between the evaporator and the condenser, wherein said refrigerant is evaporated in the evaporator to produce a gas which is compressed by the compressor and thence sent to the condenser to be condensed to produce a liquid for metering into said evaporator by said expansion valve means, the method comprising substituting the R-12 refrigerant by a hydrocarbon based refrigerant mixture comprising 25-75% propane by liquid volume to 75-25% butane by liquid volume, the hydrocarbon based refrigerant mixture being a direct "drop-in" substitute for R-12.

28. A method as claimed in claim 27 in which the hydrocarbon based refrigerant mixture comprises 50-60% propane by liquid volume to 50-40% butane by liquid volume.

29. A method as claimed in claim 28 in which the hydrocarbon based refrigerant mixture comprises 50% propane by liquid volume to 50% butane by liquid volume.

30. A method as claimed in any of claims 27 to 29 in which the butane comprises iso-butane.

31. A method as claimed in any of claims 27 to 29 in which the butane comprises n-butane.

32. A method as claimed in any of claims 27 to 31 in which the refrigeration system is employed in a motor vehicle.

33. A method as claimed in claim 32 in which the motor vehicle is an automobile.

34. A method as claimed in any of claims 27 to 31 in which the refrigeration system is employed in a residential refrigerator.

35. A refrigeration system as claimed in any of claims 22 to 26, or a method as claimed in any of claims 27 to 34 substantially as described with reference to the drawings.

36. The refrigerant mixture as set forth in claim 9, claim 22, or claim 27, further comprising a chlorinated petroleum based oil fortifying friction fighting agent.

37. The refrigerant mixture as set forth in claim 36, wherein said petroleum based oil fortifying friction fighting agent comprises from about forty (40) percent to about sixty (60) percent of a chloro paraffin wax.

38. The refrigerant mixture as set forth in claim 36, wherein said petroleum based oil fortifying friction fighting agent comprises from about twenty (20) to about thirty five (35) percent of chlorinated octadecanoic acid.

39. The refrigerant mixture as set forth in claim 36, wherein said petroleum based oil fortifying friction fighting agent comprises from about five (5) to about fifteen (15) percent of the zinc salts of phosphorodithioic acid, O,O-di-C1-14-alkyl esters.

40. The refrigerant mixture as set forth in claim 37, wherein said petroleum based oil fortifying friction fighting agent comprises from about fifteen (15) to about twenty (20) percent of hydrogenated 1-decene homopolymer.

STATEMENT UNDER ARTICLE 19(1)

1. Claims 1-21 originally were pending in the application.
2. Claims 1, 9, 10, and 17 have been amended.
3. No claims have been cancelled.
4. New claims 22-40 have been added.

Claims 1, 9, and 10 have been amended to more particularly address specific compositions which have been designed for and are capable of direct "drop-in" substitution for refrigerant R-12, in order to more clearly define the invention, for example, over Crawford, U.S. Patent No. 1,325,665, and Seaman, U.K. Patent No. 148,878.

Claim 17 has been amended to more particularly address the use of chlorinated hydrocarbon refrigeration oils as friction fighters in combination with hydrocarbon type refrigerants, to more clearly define the invention, for example, over Hustler et al, U.S. Patent 5,104,560.

FIG. 1

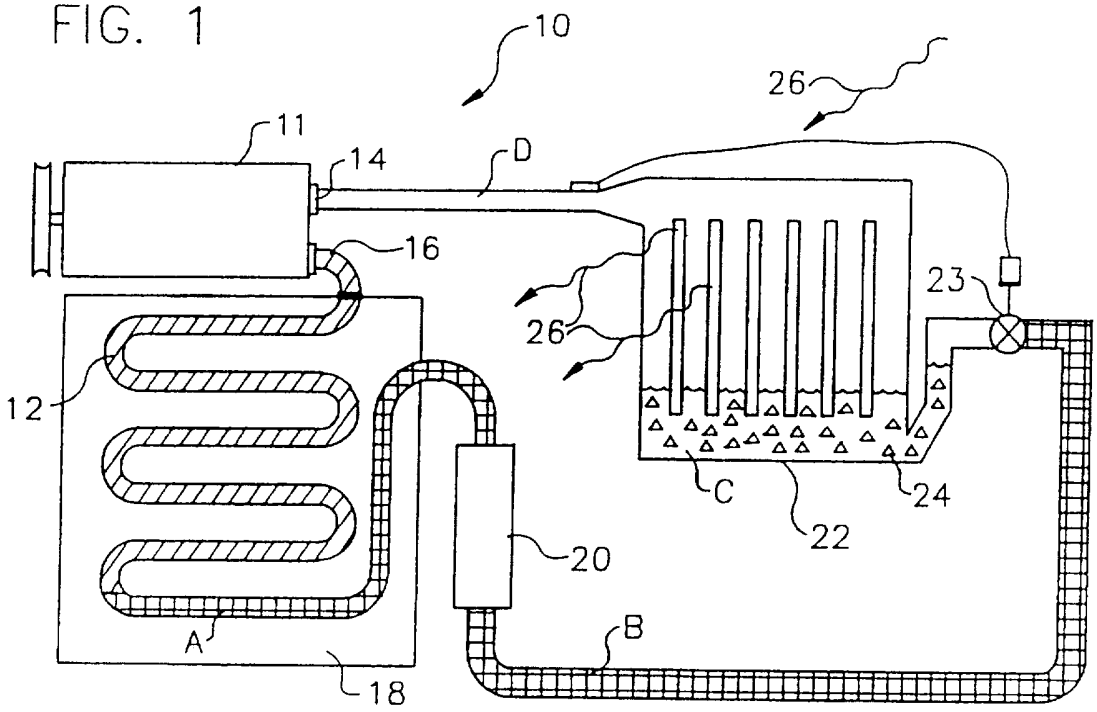
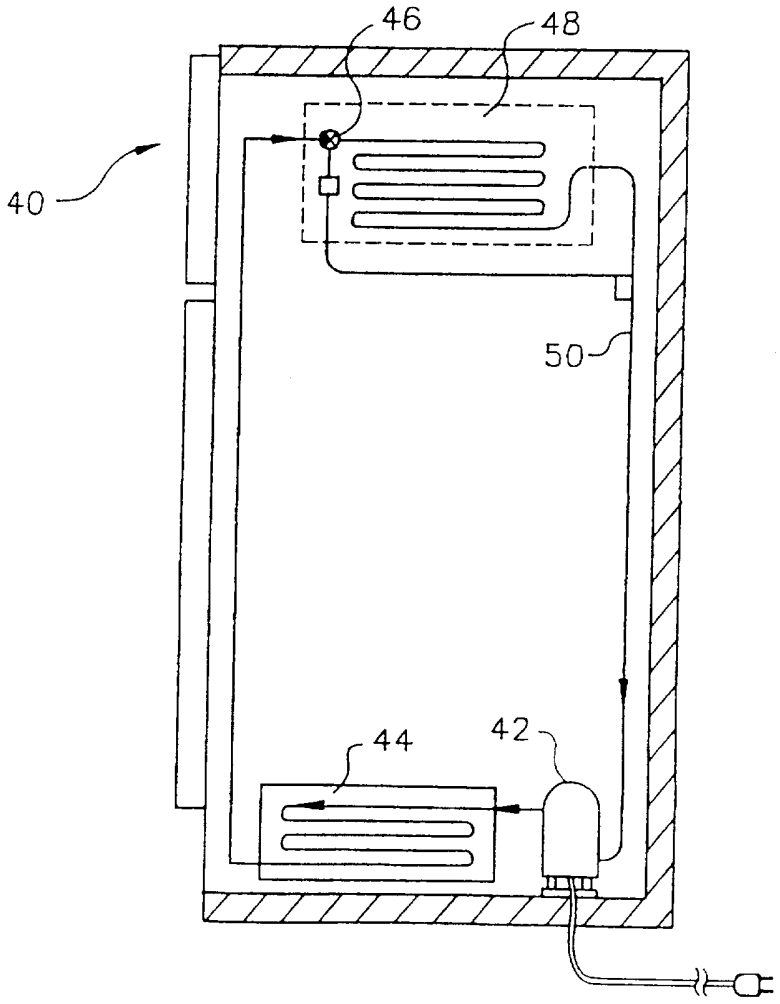


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/15643

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C09K 5/04
US CL :252/67; 62/114

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)

U.S. : 252/67; 62/114

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)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 1,325,665 (CRAWFORD) 23 December 1919, page 1, lines 39-69.	1-21
Y	US, A, 5,104,560 (HUSTER ET AL) 14 April 1992, col. 4, lines 28-58 and col. 2, lines 47-52 .	17-21
Y	US, A, 5,360,566 (STEVENSON) 01 November 1994, col. 7, lines 14-58 and col. 3, lines 8-31.	1-21
Y	GB, A, 148,878 (CRAWFORD) 10 January 1922, page 1, lines 42-70.	1-21
Y	DE, A, 4,329,477 (ROSIN) 09 March 1995, Abstract.	1-21

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier document published on or after the international filing date	"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
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search 21 MARCH 1996	Date of mailing of the international search report 11 APR 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer for CHRISTINE SKANE Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/15643

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,482,465 (GRAY) 13 November 1984, col. 1, lines 16-42 and col. 2, lines 55-60.	1-21

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/15643

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS, CAS ONLINE
search terms: propane, ethane, butane, isobutane, n-butane, refrigerant, working fluid