(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
3 June 2010 (03.06.2010)

PCT

(10) **International Publication Number**
WO 2010/062888 A3

(51) **International Patent Classification**:
F25B 15/02 (2006.01)

(21) **International Application Number**:
PCT/US2009/065681

(22) **International Filing Date**:
24 November 2009 (24.11.2009)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
61/118,042 26 November 2008 (26.11.2008) US

(71) **Applicant** *(for all designated States except US)*: **E. I. du Pont de Nemours and Company** [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).

(72) **Inventor; and**
(75) **Inventor/Applicant** *(for US only)*: **KONTOMARIS, Konstantinos** [US/US]; 63 Quail Hollow Drive, Hockessin, Delaware 19707 (US).

(74) **Agent**: **HAMBY, Jane, O.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(88) **Date of publication of the international search report**:
4 November 2010

WO 2010/062888 A3

(54) **Title**: ABSORPTION CYCLE SYSTEM HAVING DUAL ABSORPTION CIRCUITS

(57) **Abstract**: An absorption cycle system utilizes an additional absorption circuit in conjunction with a traditional absorption circuit. The absorbent used in the additional absorption circuit could contain an ionic compound, or any absorbent with relatively low crystallization. Mixtures of such absorbent with water remain liquid at temperatures lower than the minimum feasible operating temperature of the traditional lithium bromide water absorbent solutions of the prior art.

TITLE

ABSORPTION CYCLE SYSTEM HAVING DUAL ABSORPTION CIRCUITS

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the priority benefit of U.S. Provisional Patent Application No. 61/118,042, filed November 26, 2008.

BACKGROUND

1. Field of the Disclosure.

The present disclosure relates to an absorption cycle system which has dual absorption circuits. Such a system is useful in a wide range of absorption cycle applications including low temperature refrigeration, comfort air conditioning and space heating.

2. Description of Related Art.

Single effect absorption cycle systems with a single absorption circuit are known in the art. In a typical absorption cycle system, a refrigerant, such as water vapor, is absorbed into an absorbent mixture, such as an aqueous lithium bromide (LiBr) solution, and then is released out of the absorbent mixture. The absorber is part of a single absorption circuit, which includes a pump, a heat exchanger, an expansion or pressure reduction device and a generator, where the refrigerant is released from the absorbent mixture before it enters a condenser and an evaporator.

However, a drawback of such a standard system, which typically uses lithium bromide and water as the absorbent/refrigerant pair, is that the minimum feasible absorber operating temperature is limited by the crystallization temperature of the absorbent/refrigerant mixture.

It would be desirable to find suitable absorption cycle configurations and corresponding absorbent/refrigerant mixtures, in particular absorbent/water mixtures, which allow (for example, as a result of resisting crystallization) the refrigerant returning from the evaporator to be absorbed at a temperature lower than the minimum feasible absorber operating temperature of an absorber which uses a lithium bromide/water solution as the absorbent/refrigerant mixture.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an absorption cycle system which utilizes an additional absorption circuit in conjunction with a traditional absorption circuit. The absorbent used in the additional absorption circuit could be any absorbent whose absorbent/refrigerant mixtures are more advantageous at low temperatures (for example, as a result of resisting crystallization) compared to the absorbent used in the traditional absorption circuit. The absorbent used in the additional absorption circuit could be or could contain an ionic compound or other crystallization suppressing additives. Mixtures of such absorbent with water at compositions effective for the cycle operation resist crystallization at temperatures lower than the minimum feasible operating temperature of the traditional lithium bromide/water solutions of the prior art.

With such a system, the additional absorber can be operated at lower temperatures than a traditional absorber which circulates lithium bromide and water as the absorbent/refrigerant mixture. A lower feasible absorber operating temperature is expected to enable novel cooling and heating applications especially for low ambient temperatures. A lower feasible absorber operating temperature is expected to also enable higher cycle energy efficiency, which is expressed in the industry as a higher coefficient of performance, or COP.

In addition, the use of two absorption circuits allows the simultaneous use of thermally sensitive absorbents (such as thermally sensitive ionic compounds or absorbent formulations containing thermally sensitive crystallization suppressants or other thermally sensitive additives) in one circuit and high-temperature heat sources in the other circuit.

Therefore, in accordance with the present invention, there is provided an absorption cycle system comprising an evaporator for circulating a refrigerant therethrough, a first absorption circuit disposed in fluid communication with the evaporator for mixing the refrigerant from the evaporator with a first absorbent, thereby forming a first absorbent and refrigerant mixture, and for circulating the first absorbent and refrigerant mixture therethrough; a second absorption circuit disposed in fluid communication with the first absorption circuit for mixing a portion of the refrigerant from the first absorption circuit with a second absorbent, thereby forming a second absorbent and refrigerant mixture, and for circulating the second absorbent and refrigerant mixture therethrough, and a condenser disposed in fluid communication with the second absorption circuit and with the evaporator. The first-absorbent/refrigerant mixture resists crystallization, and therefore remains operational, at temperatures lower than the second-absorbent/refrigerant mixture that circulates in the second absorption circuit.

According to another embodiment of the present invention, some of the heat from the high pressure refrigerant vapor may be recovered and transferred to the first generator, instead of being rejected at the condenser. This results in higher energy efficiency. Thus, in accordance with this embodiment, the absorption cycle system of the present invention includes a heat recovery line extending between the second generator and through the first generator for recovering heat from the refrigerant exiting the second generator. The heat recovery line continues from the first generator to the condenser, for delivering the refrigerant vapor to the condenser.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention may be better understood with reference to the following Figures, wherein:

FIG.1 is a schematic diagram of an absorption cycle system according to one embodiment of the present invention.

FIG. 2 is a schematic diagram of an absorption cycle system according to another embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

A schematic diagram of an absorption cycle system according to the present invention is shown generally at 10 in FIG. 1. The system is first described as an absorption cooling system with respect to FIG. 1. The system includes an evaporator 10-1 for circulating a refrigerant therethrough, a first absorption circuit, shown generally at 20 in FIG. 1, disposed in fluid communication with the evaporator, for mixing the refrigerant from the evaporator with a first absorbent, thereby forming a first absorbent and refrigerant mixture, and for circulating the first absorbent and refrigerant mixture therethrough, a second absorption circuit, shown generally at 30 in FIG. 1, disposed in fluid communication with the first absorption circuit, for mixing a portion of the refrigerant from the first absorption circuit with a second absorbent, thereby forming a second absorbent and refrigerant mixture and for circulating the second absorbent and refrigerant mixture therethrough, and a condenser 10-2 disposed in fluid communication with the second absorption circuit and the evaporator.

The evaporator of the system of the present invention includes an inlet line 14 for delivering a refrigerant to the evaporator. The refrigerant in the system of the present invention as described below is water, it being understood that other refrigerants may be used in this system, as will be described below. The refrigerant is partially evaporated liquid when it enters the evaporator. The evaporator, in some embodiments, also includes tubes (not shown) through which flows chilled water or other heat transfer fluid. The partially evaporated refrigerant contacts the tubes in the evaporator, and the liquid portion of the refrigerant is evaporated, thereby absorbing heat and forming refrigerant vapor. The chilled water exits the evaporator through an outlet line 11 at a temperature lower than the temperature at which it entered the evaporator and is sent to a body to be cooled, such as a building, shown at 10-4 in FIG. 1. A body to be cooled may be any space, location, object or body which it is desirable to cool, including the interior spaces of buildings requiring air conditioning, and refrigerator or freezer spaces, in for instance hotels or restaurants, or industrial process areas for example used to process or produce food products.

The chilled water from the building is delivered back to the evaporator through a line 12, and is recirculated through the tubes in the evaporator. The refrigerant vapor, exits the evaporator through a line 13 as shown in FIG. 1, and is sent to the first absorption circuit 20 via this line.

The first absorption circuit 20 comprises a first absorber 20-1, a liquid pump 20-2, a first heat exchanger 20-3 and a first, or low temperature, generator 20-4. The first absorber has an inlet for delivering the refrigerant vapor, where it is combined with a mixture of refrigerant and a first absorbent with a low refrigerant-content delivered via line 25 to form a first-absorbent/refrigerant mixture with a high refrigerant-content. The first absorbent may be or may contain an ionic compound. The absorption of the refrigerant into the first absorbent also, in general, generates heat (heat of absorption). Cooling water or another heat transfer fluid circulates through the tube bundles (not shown) of the absorber to collect this heat of absorption from the system. The high refrigerant-content mixture collects at the bottom of the first absorber, so that the first absorption cycle can begin again.

The high refrigerant-content first-absorbent/refrigerant mixture exits from the first absorber through an outlet line 21 and is sent to the liquid pump, 20-2, which pumps the said mixture to the first heat exchanger 20-3. The first heat exchanger, which may be a shell and tube type heat exchanger, pre-heats the mixture before it enters the first or low temperature generator. After exiting the heat exchanger, the mixture flows into the first generator through a line 22. The first generator is supplied with low-temperature heat from any suitable external source. In one embodiment, within the generator is a bundle of tubes (not shown) which carry a heat transfer fluid which may be hot water, steam, or combustion gases, which are supplied to the first generator via a line 23. The heat transfer fluid transfers heat into the high refrigerant-content first-absorbent/refrigerant mixture. The heat causes the said mixture to release refrigerant vapor, which exits from the first generator through a line 26, leaving a low refrigerant-content mixture behind. The refrigerant is now a higher pressure vapor. In some instances, there is only trace refrigerant left in the liquid mixture exiting the first generator via a line 24. In other instances some non-negligible amount of refrigerant remains in the absorbent/refrigerant mixture exiting the first generator, said amount ranging from about 1 weight percent to about 80 weight percent. In any case, the amount of refrigerant in the mixture exiting the first generator via line 24 is lower than in the mixture that exited the first absorber via line 21. The exact amount of refrigerant remaining in the mixture exiting the first generator will depend on many factors including the solubility of the refrigerant in the first absorbent.

The low refrigerant-content first-absorbent/refrigerant mixture flows via line 24 back to the first heat exchanger where it is cooled by the high refrigerant-content first-absorbent/refrigerant mixture which has been pumped out of the first absorber. The low refrigerant-content first-absorbent/refrigerant mixture flows from the first heat exchanger through an expansion or pressure reduction device 20-5 to the first absorber via a line 25 and collects in the bottom of the first absorber where it started the first absorption circuit cycle, and the cycle in the first absorption circuit repeats.

The second absorption circuit includes a second absorber 30-1, a second liquid pump 30-2, a second heat exchanger 30-3 and a second, or high temperature generator 30-4. As noted above, the refrigerant vapor from the first absorption circuit exits the first generator and is delivered to the second absorption circuit via a line 26. The refrigerant vapor is delivered to second absorber 30-1, which includes tube bundles (not shown). A low refrigerant-content mixture of refrigerant and a second absorbent is also delivered to the second absorber via a line 35. The refrigerant and the second absorbent collect in the bottom of the second absorber. Lithium bromide may be used as the second absorbent in this system, it being understood that the present invention is not limited to the use of lithium bromide as the second absorbent. Again, as in the first absorber, the refrigerant vapor is absorbed into the low refrigerant-content second-absorbent/refrigerant mixture, thus forming a high refrigerant-content second-absorbent/refrigerant mixture. The absorption of the refrigerant into the second absorbent also, in general, generates heat (heat of absorption). A heat transfer fluid, for instance, cooling water, circulates through the tube bundles of the second absorber to collect this heat of absorption from the system.

Second pump 30-2 pumps the high refrigerant-content second-absorbent/refrigerant mixture via a line 31 to the second heat exchanger 30-3, which, like the first heat exchanger, may be a shell and tube type heat exchanger. The second heat exchanger pre-heats the said mixture before it enters the second generator 30-4 via a line 32. The second generator is supplied with high-temperature heat from any suitable external source. In one embodiment, within the second generator is a bundle of tubes which carry a heat transfer fluid, which may be, for instance, combustion gases, steam, or hot water, which is supplied to the second generator via a line 33. In some embodiments, the heat transfer fluid may have been heated to high temperatures through a concentrated solar thermal system. The heat transfer fluid transfers heat into the high refrigerant-content second-absorbent/refrigerant mixture. The heat causes the said mixture to release refrigerant vapor, which exits from the second generator through a line 36, leaving a low refrigerant-content mixture behind in the second generator. The refrigerant is now a high pressure vapor, which exits the generator via line 36. The low refrigerant-content, second-absorbent/refrigerant mixture flows via line 34 back to the second heat exchanger where it is cooled by the high refrigerant-content second-absorbent/refrigerant mixture, which has been pumped out of the second absorber to the second heat exchanger. The low refrigerant-content second-absorbent/refrigerant mixture flows from the second heat exchanger through an expansion or pressure reduction device 30-5 to the second absorber via a line 35 and collects in the bottom of the second absorber, where it started the second absorption circuit cycle, and the second absorption circuit cycle repeats. As in the first absorption circuit, the amount of refrigerant in the mixture exiting the second generator via line 34 is lower than in the mixture that exited the second absorber via line 31, and can range from a trace amount or more commonly from about 1 weight percent to about 80 weight percent. The exact amount of refrigerant remaining in the mixture exiting the second generator will depend on many factors including the solubility of the refrigerant in the second absorbent.

As noted above, the refrigerant, which is a high pressure vapor, exits the second generator 30-4 via line 36. The high pressure refrigerant vapor flows to the condenser 10-2 as shown in FIG. 1. In the condenser, the heat transfer fluid, such as cooling water, flows through tubes (not shown) in the condenser, and the refrigerant vapor condenses to form refrigerant liquid on the outside of the tubes that collects in a trough (not shown) at the bottom of the condenser. In other condenser designs the released heat could be supplied to building air instead of to the heat transfer fluid, it being understood that various other condenser designs are within the scope of the present invention. The refrigerant liquid exits from the condenser trough via inlet line 14 to the evaporator through an expansion or pressure reduction device 10-3 that partially evaporates the refrigerant liquid. The partially evaporated refrigerant liquid contacts the tubes of the evaporator which have water or some other heat transfer fluid flowing therethrough. The heat transfer fluid is cooled as the liquid refrigerant is evaporated forming refrigerant vapor. The cooled heat transfer fluid is circulated back to a body to be cooled, such as a building, thus providing the cooling effect as desired for instance for air conditioning. The refrigerant vapor migrates from the evaporator to the first absorber, and the overall refrigerant cycle repeats.

Instead of being run as an absorption cooling system as described above, the system of FIG. 1 may be used as a heat pump. In this case, the system is an absorption heating system in which the heat supplied by the cycle in FIG. 1 at the first absorber, the second absorber and the condenser is used to meet various heating needs such as heating building air or water. As noted above, the refrigerant, which is a high pressure vapor, exits the second generator 30-4 via line 36. The high pressure refrigerant vapor flows to the condenser 10-2 as shown in FIG. 1. In the condenser, cooling water or other heat transfer fluid flows through tubes (not shown) in the condenser, and the refrigerant vapor condenses to form refrigerant liquid on the outside of the tubes that collects in a trough (not shown) at the bottom of the condenser. Upon condensation of the refrigerant vapor heat is released. In other condenser designs the released heat could be supplied to building air instead of to the cooling water, it being understood that various other condenser designs are within the scope of the present invention. The refrigerant liquid exits from the condenser trough via inlet line 14 to the evaporator through an expansion or pressure reduction device 10-3 that partially evaporates the refrigerant liquid. The refrigerant is partially evaporated liquid when it enters the evaporator. In some embodiments, the evaporator also includes tubes (not shown) through which flows water or other heat transfer fluid supplying the evaporator with heat harvested from a source external to the cycle system such as water at the bottom of a lake or a pond or the ground at depths below the earth's surface where temperatures remain moderate throughout the year or low temperature waste process heat. The evaporator may receive heat from the ambient air. The partially evaporated refrigerant contacts the tubes in the evaporator, and the liquid portion of the refrigerant is evaporated, thereby absorbing heat and forming refrigerant vapor. The heat transfer fluid exits the evaporator through an outlet line 11 at a temperature lower than the temperature at which it entered the evaporator and is sent back to the external heat source, which in this embodiment is in place of the building shown at 10-4 in FIG. 1. In this embodiment, there is no longer exchange of heat between chilled water and a building to be cooled, but rather between the water or heat transfer fluid that supplies heat to the evaporator and the external heat source. In this case, the heat transfer fluid from the external heat source is delivered back to the evaporator through a line 12.

FIG. 2 shows a second embodiment of an absorption cooling system of the present invention. Such a system is generally shown at 110. The system includes an evaporator 110-1 disposed in fluid communication with a first absorption circuit, shown generally at 120 in FIG. 2, a second absorption circuit, shown generally at 130 in FIG. 2, disposed in fluid communication with the first absorption circuit, and a condenser 110-2 disposed in fluid communication with the second absorption circuit and the evaporator.

The evaporator of the system of the present invention includes an inlet line 114 for delivering a refrigerant to the evaporator. Again, the refrigerant in the system of the second embodiment of the present invention is water, it being understood that other refrigerants may be used in this system. The evaporator of the second embodiment operates in the same way that the evaporator of FIG. 1 does. Thus, refrigerant is partially evaporated liquid when it enters the evaporator. The evaporator also includes tubes (not shown) through which flows chilled water or other heat transfer fluid. The partially evaporated refrigerant contacts the tubes in the evaporator, and the liquid portion of the refrigerant is evaporated, thereby absorbing heat and forming refrigerant vapor. The chilled water exits the evaporator through an outlet line 111 at a temperature lower than the temperature at which it entered the evaporator and is sent to a body to be cooled, such as a building, shown at 110-4 in FIG. 2.

The chilled water from the building is delivered back to the evaporator through a line 112, and is recirculated through the tubes in the evaporator. The refrigerant vapor exits the evaporator through a line 113 as shown in FIG. 2, and is sent to the first absorption circuit 120 via this line.

The first absorption circuit 120 comprises a first absorber 120-1, a liquid pump 120-2, a first heat exchanger 120-3 and a first, or low temperature, generator 120-4. The first absorber has an inlet for delivering the refrigerant vapor, where it is combined with a mixture of refrigerant and a first absorbent with a low refrigerant-content delivered via line 125, to form a first-absorbent/refrigerant mixture with a high refrigerant-content. The first absorbent may be or may contain an ionic compound. The absorption of the refrigerant into the absorbent also, in general, generates heat (heat of absorption). Cooling water moves through the tube bundles (not shown) of the absorber to remove this heat of absorption from the system. The high refrigerant-content mixture collects at the bottom of the first absorber, so that the first absorption circuit cycle can begin again.

The high refrigerant-content first-absorbent/refrigerant mixture exits from the first absorber through an outlet line 121 and is sent to the liquid pump, 120-2, which pumps the said mixture to the first heat exchanger 120-3. The first heat exchanger 120-3, which may be a shell and tube type heat exchanger, pre-heats the said mixture before it enters the first (or low temperature) generator 120-4. After exiting the heat exchanger, the said mixture flows into the first generator through a line 122. The first generator is supplied with low-temperature heat from any suitable external source. In one embodiment, within the generator is a bundle of tubes (not shown) which carry hot water, steam, or combustion gases, which are supplied to the first generator via a line 123. The hot water, steam or combustion gases transfer heat into the high refrigerant-content first-absorbent/refrigerant mixture. The heat causes the said mixture to release refrigerant vapor, which exits from the first generator through a line 126, leaving a low refrigerant-content mixture behind. The refrigerant is now a higher pressure vapor. In some instances, there is only trace refrigerant left in the liquid mixture exiting the first generator via line 124. In other instances some non-negligible amount of refrigerant remains in the first-absorbent/refrigerant mixture exiting the first generator, said amount ranging from about 1 weight percent to about 80 weight percent. In any case, the amount of refrigerant in the mixture exiting the first generator via line 124 is lower than in the mixture that exited the first absorber via line 121. The exact amount of refrigerant remaining in the mixture exiting the first generator will depend on many factors including the solubility of the refrigerant in the first absorbent.

The low refrigerant-content first-absorbent/refrigerant mixture flows via line 124 back to the first heat exchanger where it is cooled by the high refrigerant-content first-absorbent/refrigerant mixture, which has been pumped out of the first absorber. The low refrigerant-content first-absorbent/refrigerant mixture flows from the first heat exchanger through an expansion or pressure reduction device 120-5 to the first absorber via a line 125 and collects in the bottom of the first absorber where it started the first absorption circuit cycle, and the cycle in the first absorption circuit repeats.

The second absorption circuit includes a second absorber 130-1, a second liquid pump 130-2, a second heat exchanger 130-3 and a second, or high temperature generator 130-4. As noted above, the refrigerant vapor from the first absorption circuit exits the first generator and is delivered to the second absorption circuit via a line 126. The refrigerant vapor is delivered to second absorber 130-1, which includes tube bundles (not shown). A low refrigerant-content mixture of refrigerant and a second absorbent is also delivered to the second absorber via line 135. The refrigerant and the second absorbent collect in the bottom of the second absorber. Lithium bromide may be used as the second absorbent in this system, it being understood that the present invention is not limited to the use of lithium bromide as the second absorbent. Again, as in the first absorber the refrigerant vapor is absorbed into the low refrigerant-content second-absorbent/refrigerant mixture, thus forming a high refrigerant-content second-absorbent/refrigerant mixture. The absorption of the refrigerant into the absorbent also, in general, generates heat (heat of absorption). Cooling water moves through the tube bundles of the second absorber to remove this heat of absorption from the system.

Second pump 130-2 pumps the high refrigerant-content second-absorbent/refrigerant mixture via a line 131 to the second heat exchanger 130-3, which, like the first heat exchanger, may be a shell and tube type heat exchanger. The second heat exchanger pre-heats the said mixture before it enters the second generator 130-4 via a line132. The second generator is supplied with high-temperature heat from any suitable external source. In one embodiment, within the second generator is a bundle of tubes (not shown) which carry combustion gases, steam, or hot water which are supplied to the generator via a line 133. The combustion gases, steam or hot water transfer heat into the high refrigerant-content second-absorbent/refrigerant mixture. The heat causes the mixture to release refrigerant vapor, which exits from the second generator through a heat recovery line 136a, leaving a low refrigerant-content mixture behind in the second generator. The refrigerant is now a high pressure vapor, which exits the second generator via line 136a. The heat recovery line extends between the second generator and through the first generator, and recovers heat from the refrigerant exiting the second generator. In this embodiment, all of the high pressure refrigerant vapor is sent back to the first, or low temperature generator 120-4, instead of to the condenser. Some of the heat from the high pressure refrigerant vapor is recovered and transferred to the first generator, instead of being rejected at the condenser, as in the first embodiment. This results in higher energy efficiency. The heat recovery line continues from the first generator to the condenser for delivering the refrigerant vapor to the condenser. The high pressure refrigerant vapor is thus sent to the condenser via a line 136b.

The low refrigerant-content second-absorbent/refrigerant mixture flows via line 134 back to the second heat exchanger where it is cooled by the high refrigerant-content second-absorbent/refrigerant mixture, which has been pumped out of the second absorber to the second heat exchanger. The low refrigerant-content second-absorbent/refrigerant mixture flows from the second heat exchanger through an expansion or pressure reduction device to the second absorber via a line 135 and collects in the bottom of the second absorber, where it started the second absorption circuit cycle, and the second absorption circuit cycle repeats.

The high pressure refrigerant vapor flows to the condenser 110-2 as shown in FIG. 2. In the condenser, cooling water flows through tubes (not shown) in the condenser, and the refrigerant vapor condenses to form refrigerant liquid on the outside of the tubes that collects in a trough (not shown) at the bottom of the condenser. The refrigerant liquid exits from the condenser trough via inlet line 114 to the evaporator through an expansion or pressure reduction device 110-3 that partially evaporates the refrigerant liquid. The partially evaporated refrigerant liquid contacts the tubes of the evaporator which have water or some other heat transfer fluid flowing therethrough. The heat transfer fluid is cooled as the liquid portion of the refrigerant is evaporated forming refrigerant vapor. The cooled heat transfer fluid is circulated back to a body to be cooled, such as a building, thus providing the cooling effect as desired for instance for air conditioning. The refrigerant vapor migrates to the first absorber from the evaporator, and the overall refrigerant cycle repeats.

The use of the configuration in FIG.2 for heating is also within the scope of the present invention. The only difference in FIG. 2 relative to FIG. 1 is the line that leads the working fluid vapor exiting the high-temperature Generator II (130-4) to the lower temperature Generator I (120-4) where the working fluid provides some of its heat to the lower temperature Generator I (120-4) before it condenses in the condenser (110-2). The heat released upon condensation in the condenser 110-2 is now used for heating rather than being rejected to the ambient (which was the case in the cooling mode of cycle operation). In the heating mode of cycle operation, an external heat source is used in place of a building 110-4 as shown in FIG. 2. Again, in this embodiment, there is no longer exchange of heat between chilled water and a building to be cooled, but rather between the water or heat transfer fluid that supplies heat to the evaporator and the external heat source. In general, the option of redistributing heat from the high temperature generator to the low temperature generator in the embodiment of FIG. 2 may allow more optimum use of available heat sources in some cases.

In either the embodiment of FIG. 1 or of FIG. 2 where the absorption cycle is an absorption heating system as discussed above, the use of absorbent solutions in the first (low-temperature) absorber that resist crystallization at low temperatures and, therefore, allow operation of the first absorber at temperatures closer to the cold ambient temperatures during the heating season, could enable dramatically higher energy efficiencies. Such absorbent solutions that resist crystallization at low temperatures are disclosed in U.S. Provisional Patent Application Serial Numbers 61/112,415 and 61/112,428 both filed November 7, 2008 and 61/165,089, 61/165,093, 61/165,147, 61/165,155, 61/165,161, 61/165,160, 61/165,166, and 61/165,173, all of which were filed March 31, 2009. They include compositions containing LiBr, water and inorganic salts, wherein the inorganic salts have been shown to lower the temperature at which LiBr crystallization produces system failures. The LiBr crystallization temperature suppressants include but are not limited to cesium formate, and other Group I metal salts, phosphonic acid salts, and ionic liquids comprising fluorinated anions, cations or both.

These crystallization resistant compositions were based primarily on using water as the refrigerant. It should be noted that the phase diagram of the working fluid used in the absorption cycle of this invention should allow the coexistence of vapor and liquid phases in equilibrium in the evaporator at temperatures lower than the temperatures at which heat is extracted from the external sources. In other words, the triple point temperature of the working fluid should be lower than the temperature at which external heat is supplied to the evaporator.

The triple point temperature of water is 0.0098°C. Therefore, when water is used as the refrigerant and the absorption cycle is to be used for heating when the temperature of ambient air drops below 0.0098°C, or more practically, below, say, 4°C, the heat supplied to the evaporator must be harvested from sources external to the system other than ambient air. External heat sources available at temperatures higher than the water triple point temperature include, the ground below the earth's surface, natural bodies of water (e.g. water at the bottom of a nearby lake or pond), and low temperature process waste heat.

Refrigerant/Absorbent Pairs:

Refrigerants:

The present invention provides refrigerant pair compositions for use in an absorption cycle, which can be used for cooling, or for transferring heat from outside to inside, depending on the application. In one embodiment, water is used as a refrigerant in this invention. In another embodiment, the refrigerant may be a hydrofluorocarbon, a hydrochlorofluorocarbon, a chlorofluorocarbon, a fluorocarbon, a chlorocarbon, nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), ammonia (NH_3), nitrous oxide (N_2O), argon (Ar), hydrogen (H_2), a non-fluorinated hydrocarbon, or mixtures thereof, meaning mixtures of any of the foregoing refrigerants in this paragraph. The non-fluorinated hydrocarbons are selected from the group consisting of C_1 to C_7 straight-chain, branched or cyclic alkanes and C_1 to C_7 straight-chain, branched or cyclic alkenes, are within the scope of this invention as well.

Hydrofluorocarbon refrigerants may include compounds having any combination of hydrogen and fluorine with carbon and include compounds with at least one carbon-carbon double bond. Examples of hydrofluorocarbon refrigerants useful for the invention include but are not limited to difluoromethane (HFC-32), fluoromethane (HFC-41), pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1-trifluoroethane (HFC-143a), 1,1-difluoroethane (HFC-152a), fluoroethane (HFC-161), 1,1,1,3,3-pentafluoropropane (HFC-245fa), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,3,3-pentafluorobutane (HFC-365mfc), 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-43-10mee), 1,1,1,2,2,3,4,5,5,6,6,7,7,7-tetradecafluoroheptane (HFC-63-14mcee), 1,2-difluoroethene (HFO-1132), 2,3,3,3-tetrafluoropropene (HFO-1234yf), 1,3,3,3-tetrafluoropropene (HFO-1234ze), 1,2,3,3-tetrafluoropropene (HFO-1234ye), 3,3,3-trifluoropropene (HFO-1243zf), 1,2,3,3,3-pentafluoropropene (HFO-1225ye), 1,1,1,3,3-pentafluoropropene (HFO-1225zc), 1,1,1,4,4,4-hexafluoro-2-butene (HFO-1336mzz), 1,1,1,2,2,5,5,5-octafluoro-2-pentene (HFO-1438mczz), 1,1,1,2,2,4,5,5,6,6,7,7,7-tridecafluoro-3-heptene (HFO-162-13mczy) and 1,1,1,2,2,3,5,5,6,6,7,7,7-tridecafluoro-3-heptene (HFO-162-13mcyz), and mixtures thereof. In one embodiment of the invention, the hydrofluorocarbon refrigerants are selected from the group consisting of difluoromethane (HFC-32), pentafluoroethane (HFC-125), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1-trifluoroethane (HFC-143a), 1,1-difluoroethane (HFC-152a), 2,3,3,3-tetrafluoropropene (HFO-1234yf), and mixtures thereof.

Additionally, in another embodiment, hydrofluorocarbon refrigerants may include 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf, $CF_3CCl=CH_2$), cis- or trans-1-chloro-3,3,3-trifluoropropene (HCFO-1233zd, $CF_3CH=CHCl$), 3,4,4,4-tetrafluoro-3-trifluoromethyl-1-butene ($(CF_3)_2CFCH=CH_2$, HFO-1447fzy), cis- or trans-1,1,1,4,4,5,5,5-octafluoro-

2-pentene ($CF_3CF_2CH{=}CHCF_3$, HFO-1438mzz), and combinations thereof.

Chlorofluorocarbon refrigerants may include compounds having any combination of chlorine and fluorine with carbon and include compounds with carbon-carbon double bonds. Representative chlorofluorocarbon refrigerants useful for the invention include but are not limited to dichlorodifluoromethane (CFC-12), fluorotrichloromethane (CFC-11), 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113), 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114) and mixtures thereof.

Hydrochlorofluorocarbon refrigerants may include compounds with any combination of hydrogen, chlorine and fluorine with carbon and include compounds with carbon-carbon double bonds. Representative hydrochlorofluorocarbon refrigerants useful for the invention include but are not limited to chlorodifluoromethane (HCFC-22), 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd), and mixtures thereof.

Fluorocarbon refrigerants may include compounds with any combination of fluorine and carbon and include compounds with carbon-carbon double bonds, as well as cyclic compounds. Examples of fluorocarbon refrigerants useful for the invention include but are not limited to perfluoromethane (FC-14), perfluoroethane (FC-116), perfluoropropane (FC-218, perfluorocyclobutane (FC-C318), octafluoro-2-butene (FO-1318my), and mixtures thereof.

Chlorocarbon refrigerants may include compounds with only chlorine, carbon and optionally hydrogen. Examples of chlorocarbon refrigerants include but are not limited to 1,2-dichloroethylene, methylene chloride, trichloroethylene, perchloroethylene, and mixtures thereof.

Non-fluorinated hydrocarbon refrigerants useful for the invention may include but are not limited to methane, ethane, ethylene, propane, cyclopropane, propylene, n-butane, butane, isobutane, cyclobutane, n-pentane, isopentane, n-hexane, cyclohexane, n-heptane, and mixtures thereof.

In some embodiments, mixtures of the various classes of refrigerants are intended to be included in the scope of the present invention. Additionally, azeotrope and azeotrope-like compositions formed by 2 or more of the many refrigerants disclosed herein may be particularly useful in the present absorption cycle systems.

In another embodiment, the hydrofluorocarbon working fluids may comprise mixtures or blends of hydrofluorocarbons with other compounds such as hydrofluorocarbons, hydrochlorofluorocarbons, hydrocarbons or other compounds. Such working fluid blends include the following compositions:

HFO-1447fzy with at least one compound selected from the group consisting of cis- or trans-HFO-1438mzz, cis- or trans-HFO-1336mzz, HCFO-1233xf, and cis- or trans-HCFO-1233zd;

cis-HFO-1438mzz with at least one compound selected from the group consisting of trans-HFO-1438mzz, cis- or trans-HFO-1336mzz, HCFO-1233xf, and cis- or trans-HCFO-1233zd;

trans-HFO-1438mzz with at least one compound selected from the group consisting of cis- or trans-HFO-1336mzz, HCFO-1233xf, cis- or trans-HCFO-1233zd, and isopentane;

cis-HFO-1336mzz with at least one compound selected from the group consisting of trans-HFO-1336mzz, HCFO-1233xf, cis- or trans-HCFO-1233zd, isopentane, n-pentane, cyclopentane, methyl formate, 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123), and trans-1,2-dichloroethylene; trans-HFO-1336mzz with at least one compound selected from the group consisting of HCFO-1233xf, and cis- or trans-HCFO-1233zd;

HCFO-1233xf with at least one compound selected from the group consisting of cis- and trans-HCFO-1233zd.

In another embodiment, working fluids that are mixtures may be azeotrope or azeotrope-like compositions such as the following:

about 51 weight percent to about 70 weight percent cis-HFO-1336mzz and about 49 weight percent to about 30 weight percent isopentane;

about 62 weight percent to about 78 weight percent cis-HFO-1336mzz and about 38 weight percent to about 22 weight percent n-pentane;

about 75 weight percent to about 88 weight percent cis-HFO-1336mzz and about 25 weight percent to about 12 weight percent cyclopentane;

about 25 weight percent to about 35 weight percent cis-HFO-1336mzz and about 75 weight percent to about 65 weight percent HCFC-123;

about 67 weight percent to about 87 weight percent cis-HFO-1336mzz and about 33 weight percent to about 13 weight percent trans-1,2-dichloroethylene; and

about 61 weight percent to about 78 weight percent trans-HFO-1438mzz and about 39 weight percent to about 22 weight percent isopentane.

In one embodiment, a refrigerant as used herein may also be selected from the group consisting water, and mixtures of water with HFC-32, HFC-125, HFC-134, HFC-134a, HFC-143a, HFC-152a, HFC-161, HCFC-22, FC-14, FC-116, CFC-12, NH_3, CO_2, N_2, O_2, H_2, Ar, methane, ethane, propane, cyclopropane, propylene, butane, butene, and isobutane.

Although certain refrigerants are specified above, the inventive absorption cycle of this invention could, in general, be advantageous for any refrigerant or mixture of refrigerants for which two absorbents are available such that the first-absorbent/refrigerant mixture is preferable at low temperatures and the second-absorbent/refrigerant mixture is preferable at high temperatures. Preference for an absorbent/refrigerant mixture for the low temperature absorption circuit could be the result of various properties of the absorbent/refrigerant mixture over the preferred operating concentration and temperature ranges for the intended application including reduced crystallization temperature, advantageous refrigerant absorption/desorption properties at low temperatures, reduced viscosity and enhanced heat and mass transfer in the absorber. Preference for an absorbent/refrigerant mixture for the high temperature absorption circuit could be the result of various properties of the absorbent/refrigerant mixture over the preferred operating concentration and temperature ranges for the intended application including higher thermal stability, reduced corrosivity toward materials of equipment construction, advantageous refrigerant absorption/desorption properties at high temperatures and enhanced heat and mass transfer properties.

Mixtures of refrigerants are also useful for achieving proper boiling temperature or pressure appropriate for absorption equipment. In particular, mixtures that form azeotropes, azeotrope-like mixtures, or constant boiling mixtures are sometimes preferred because minimal to no fractionation of the mixture will occur if the refrigerant leaks from the absorption cooling system.

Absorbents:

In a preferred embodiment of the absorption cycle of this invention, the absorbent used is an ionic compound, which can in principle be any ionic compound that absorbs water. A suitable ionic compound that absorbs water is an ionic compound with which at least to some extent water is miscible, or in which at least to some extent water is soluble or dispersible so as to form an adequately stable emulsion. The energy efficiency of the absorption cycle will, generally, increase with increased absorptivity of the ionic compound for water (i.e. water has high miscibility therewith or water is soluble therein to a large extent). One such ionic compound is lithium bromide (LiBr).

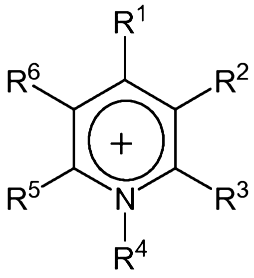
Many ionic compounds are formed by reacting a nitrogen-containing heterocyclic ring, preferably a heteroaromatic ring, with an alkylating agent (for example, an alkyl halide) to form a quaternary ammonium salt, and performing ion exchange or other suitable reactions with various Lewis acids or their conjugate bases to form the ionic compound. Examples of suitable heteroaromatic rings include substituted pyridines, imidazole, substituted imidazole, pyrrole and substituted pyrroles. These rings can be alkylated with virtually any straight, branched or cyclic C_{1-20} alkyl group, but preferably, the alkyl groups are C_{1-16} groups. Various triarylphosphines, thioethers and cyclic and non-cyclic quaternary ammonium salts may also been used for this purpose. Counterions that may be used include chloroaluminate, bromoaluminate, gallium chloride, tetrafluoroborate, tetrachloroborate, hexafluorophosphate, nitrate, trifluoromethane sulfonate, methylsulfonate, p-toluenesulfonate, hexafluoroantimonate, hexafluoroarsenate, tetrachloroaluminate, tetrabromoaluminate, perchlorate, hydroxide anion, copper dichloride anion, iron trichloride anion, zinc trichloride anion, as well as various lanthanum, potassium, lithium, nickel, cobalt, manganese, and other metal-containing anions.

Ionic compounds may also be synthesized by salt metathesis, by an acid-base neutralization reaction or by quaternizing a selected nitrogen-containing compound; or they may be obtained commercially from several companies such as Merck (Darmstadt, Germany) or BASF (Mount Olive, New Jersey).

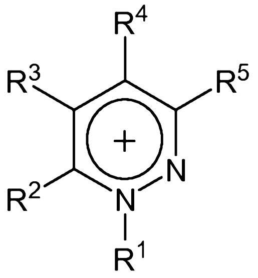
Representative examples of ionic compounds useful herein included among those that are described in sources such as *J. Chem. Tech. Biotechnol.,* 68:351-356 (1997); *Chem. Ind.,* 68:249-263 (1996); *J. Phys. Condensed Matter,* 5: (supp 34B):B99-B106 (1993); *Chemical and Engineering News,* Mar. 30, 1998, 32-37; *J. Mater. Chem.,* 8:2627-2636 (1998); Chem. *Rev.,* 99:2071-2084 (1999); and WO 05/113,702 (and references therein cited). In one embodiment, a library, *i.e.* a combinatorial library, of ionic compounds may be prepared, for example, by preparing various alkyl derivatives of a quaternary ammonium cation, and varying the associated anions. The acidity of the ionic compounds can be adjusted by varying the molar equivalents and type and combinations of Lewis acids.

Ionic compounds that are suitable for use as absorbents include those having cations selected from the following, and mixtures thereof:

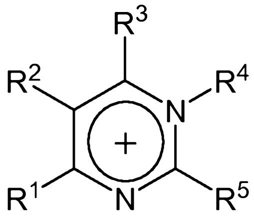
Lithium, Sodium, Potassium, Cesium, and the following Formulae:



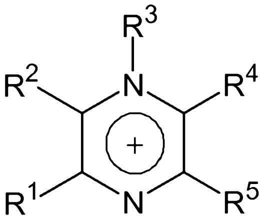
Pyridinium



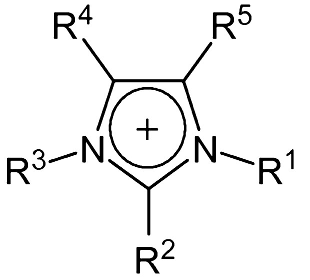
Pyridazinium



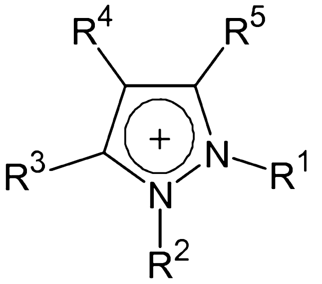
Pyrimidinium



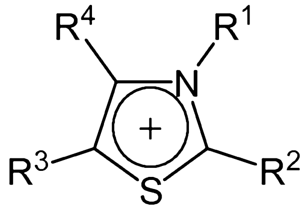
Pyrazinium



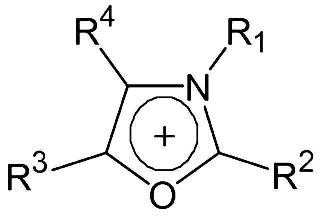
Imidazolium



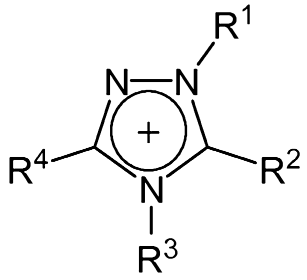
Pyrazolium



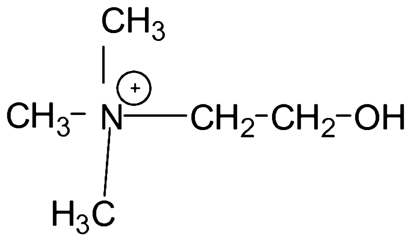
Thiazolium



Oxazolium

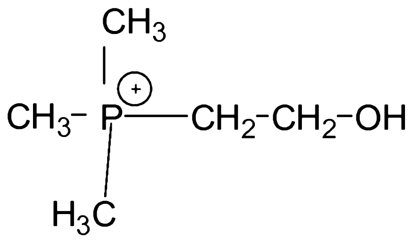


Triazolium



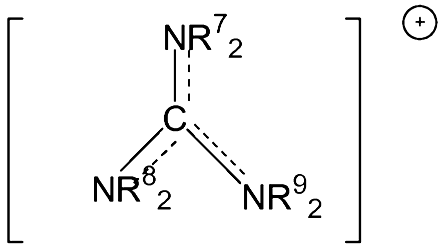
$$CH_3\!-\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H_3C}{|}}{N^{\oplus}}}\!-\!CH_2\!-\!CH_2\!-\!OH$$

Choline

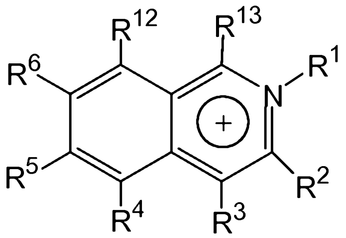


$$CH_3\!-\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H_3C}{|}}{P^{\oplus}}}\!-\!CH_2\!-\!CH_2\!-\!OH$$

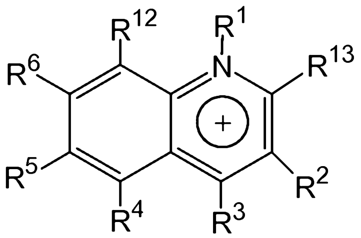
Phosphonium Choline



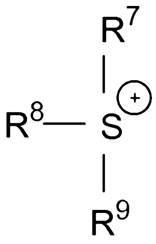
Guanidinium



Isoquinolinium

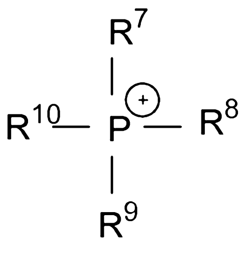


Quinolinium



$R^8\text{—}\overset{R^7}{\underset{R^9}{S^{+}}}$

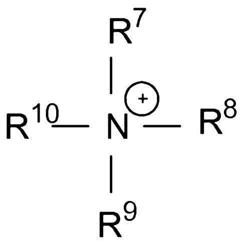
Sulfonium



$R^{10}\text{—}\overset{R^7}{\underset{R^9}{P^{+}}}\text{—}R^8$

Phosphonium

and



$R^{10}\text{—}\overset{R^7}{\underset{R^9}{N^{+}}}\text{—}R^8$

Ammonium

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^{12} and R^{13} are independently selected from the group consisting of:

(i) H

(ii) halogen

(iii) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(iv) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(v) C_6 to C_{20} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and

(vi) C_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(1) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F I, OH, NH_2 and SH,
(2) OH,
(3) NH_2, and
(4) SH;

R^7, R^8, R^9, and R^{10} are independently selected from the group consisting of:

(i) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic

(ii) alkane or alkene, optionally substituted with at least one

(iii) member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(iv) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic

(v) alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

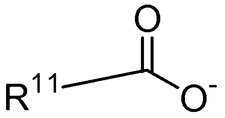
(vi) C_6 to C_{25} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and

(vii) C_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(1) -CH_3, -C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH,
(2) OH,
(3) NH_2, and
(4) SH; and

wherein optionally at least two of R^1, R^2, R^3, R^4, R^5, $R^{6,}$ R^7, R^8, R^9, and R^{10} can together form a cyclic or bicyclic alkanyl or alkenyl group.

Ionic compounds suitable for use as absorbents include those having anions selected from the following, and mixtures thereof: $[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[HCO_2]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_3]^{3-}$, $[HPO_3]^{2-}$, $[H_2PO_3]^{1-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CuCl_2]^-$, Cl^-, Br^-, I^-, SCN^-; $BR^1R^2R^3R^4$, $BOR^1OR^2OR^3OR^4$, carborates (1-carbadodecaborate(1-)), optionally substituted with alkyl or substituted alkyl, carboranes (dicarbadodecaborate(1-)) optionally substituted with alkylamine, substituted alkylamine, alkyl or substituted alkyl, and preferably any fluorinated anion. Fluorinated anions useful herein include $[BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$, $[CF_3SO_3]^-$, $[HCF_2CF_2SO_3]^-$, $[CF_3HFCCF_2SO_3]^-$, $[HCClFCF_2SO_3]^-$, $[(CF_3SO_2)_2N]^-$, $[(CF_3CF_2SO_2)_2N]^-$, $[(CF_3SO_2)_3C]^-$, $[CF_3CO_2]^-$, $[CF_3OCFHCF_2SO_3]^-$, $[CF_3CF_2OCFHCF_2SO_3]^-$, $[CF_3CFHOCF_2CF_2SO_3]^-$, $[CF_2HCF_2OCF_2CF_2SO_3]^-$, $[CF_2ICF_2OCF_2CF_2SO_3]^-$, $[CF_3CF_2OCF_2CF_2SO_3]^-$, $[(CF_2HCF_2SO_2)_2N]^-$, $[(CF_3CFHCF_2SO_2)_2N]^-$; and F^-. Other suitable anions include those of the Formula:



wherein R^{11} is selected from the group consisting of:

(i) -CH_3, -C_2H_5, or C_3 to C_{10} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(ii) $-CH_3$, $-C_2H_5$, or C_3 to C_{10} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(iii) C_6 to C_{10} unsubstituted aryl, or C_3 to C_{10} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and

(iv) C_6 to C_{10} substituted aryl, or C_3 to C_{10} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(1) $-CH_3$, $-C_2H_5$, or C_3 to C_{10} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F I, OH, NH_2 and SH,

(2) OH,

(3) NH_2, and

(4) SH.

In another embodiment, ionic compounds suitable for use herein may have a cation selected from the group consisting of pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, triazolium, phosphonium, ammonium, benzyltrimethylammonium, cesium, choline, dimethylimidazolium, guanidinium, lithium, phosphonium choline (hydroxyethyl trimethylphosphonium), potassium, sodium, tetramethylammonium, tetramethylphosphonium, and anions selected from the group consisting of, aminoacetate (glycine), ascorbate, benzoate, catecholate, citrate, dimethylphosphate, formate, fumarate, gallate, glycolate, glyoxylate, iminodiacetate, isobutyrate, kojate (5-hydroxy-2-hydroxymethyl-4-pyrone ion), lactate, levulinate, oxalate, pivalate, propionate, pyruvate, salicylate, succinamate, succinate, tiglate ($CH_3CH=C(CH_3)COO^-$); , tetrafluoroborate, tetrafluoroethanesulfonate, and tropolonate (2-hydroxy-2,4,6-cycloheptatrien-1-one ion), $[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CuCl_2]^-$, Cl^-, Br^-, I^-, SCN^-, $[BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$, $[CF_3SO_3]^-$, $[HCF_2CF_2SO_3]^-$, $[CF_3HFCCF_2SO_3]^-$, $[HCClFCF_2SO_3]^-$, $[(CF_3SO_2)_2N]^-$, $[(CF_3CF_2SO_2)_2N]^-$, $[(CF_3SO_2)_3C]^-$, $[CF_3CO_2]^-$, $[CF_3OCFHCF_2SO_3]^-$, $[CF_3CF_2OCFHCF_2SO_3]^-$, $[CF_3CFHOCF_2CF_2SO_3]^-$, $[CF_2HCF_2OCF_2CF_2SO_3]^-$, $[CF_2ICF_2OCF_2CF_2SO_3]^-$, $[CF_3CF_2OCF_2CF_2SO_3]^-$, $[(CF_2HCF_2SO_2)_2N]_-$, $[(CF_3CFHCF_2SO_2)_2N]^-$, F^-, and any fluorinated anion. Do we cover the various Gen0.5 crystallization suppression additives we filed on over the past several months?

In general, water would be expected to be more miscible with or soluble in ionic compounds that are hydrophilic to some extent, and ionic compounds having cations having at least one alcohol side chain, or those comprising anions having at least one acetate or sulfate group, would thus be desirable choices for use in various embodiments of this invention. Water will also preferably be miscible with or soluble in an ionic compound as used herein over the temperature range of the operation of the absorption system, particularly from that of the evaporator to that of the generator. Evaporator temperatures can be as low as about 5°C. Single effect generator temperatures can be as high as about 150°C, while double effect generator temperatures can be as high as about 200°C. As a consequence, over a temperature range of from about 5°C to about 200°C, a variety of different levels of the relative content of the refrigerant and absorbent in an absorption cycle are suitable, and the concentration of either water or an ionic compound in a composition formed therefrom may be in the range of from about 1% to about 99% by weight of the combined weight of the ionic compound and water therein.

In various embodiments of this invention, an ionic compound formed by selecting any of the individual cations described or disclosed herein, and by selecting any of the individual anions described or disclosed herein with which to pair the cation, may be used as an absorbent in an absorption heating or cooling cycle. Correspondingly, in yet other embodiments, a subgroup of ionic compounds formed by selecting (i) a subgroup of any size of cations, taken from the total group of cations described and disclosed herein in all the various different combinations of the individual members of that total group, and (ii) a subgroup of any size of anions, taken from the total group of anions described and disclosed herein in all the various different combinations of the individual members of that total group, may be used as an absorbent. In forming an ionic compound, or a subgroup of ionic compounds, by making selections as aforesaid, the ionic compound or subgroup will be used in the absence of the members of the group of cations and/or anions that are omitted from the total group thereof to make the selection, and, if desirable, the selection may thus be made in terms of the members of the total group that are omitted from use rather than the members of the group that are included for use.

An absorbent as used in an absorption heating or cooling cycle is desirably a compound that has high solubility for a refrigerant (*e.g.,* water) and also a very high boiling point relative to the refrigerant.

Although certain absorbents are described above, in general, any two absorbents could be used as the first and second absorbents of the present invention, as long as the first absorbent is more advantageous at low temperatures (*e.g.*, more resistant to crystallization, or less viscous), and the second absorbent is more advantageous at high temperatures (e.g. thermally stable). Either absorbent could (but does not have to) contain or consist essentially of an ionic compound, that is, it could contain or consist essentially of a non-ionic compound. Suitable non-ionic compound absorbents include, but are not limited to ethers, esters, amides and ketones.

Mixtures of ionic compounds may also be used herein as the absorbent, and such mixtures may be desirable, for example, for achieving proper absorption behavior, in particular if water is mixed with other components such as alcohols, esters or ethers which maybe used in combination with absorption equipment.

Additives, such as lubricants, corrosion inhibitors, stabilizers, dyes, crystallization inhibitors (such as cesium formate etc.), and other appropriate materials may be added to the refrigerant pair compositions useful for the invention for a variety of purposes provided they do not have an undesirable influence on the extent to which water is soluble in an ionic compound absorbent. The refrigerant pair compositions of the invention may be prepared by any convenient method, including mixing or combining the desired amounts of each component in an appropriate container using, for example, known types of stirrers having rotating mixing elements.

Cooling water is used in both the absorbers and condenser in the embodiments as described above. For sake of simplicity, the cooling water streams through the two absorbers and the condenser are not shown. In one embodiment, the cooling water will flow into the first and the second absorbers, where it warms due to the heat of absorption of the refrigerant absorbing into the first or second absorbent. From the first absorber, the cooling water will flow to the second absorber. From the second absorber, the cooling water will flow to the condenser tube bundle, wherein it will provide the cooling to condense the refrigerant vapor to refrigerant liquid. The cooling water is thus heated further and flows out of the condenser via a line, not shown, to a cooling tower or other device intended to release the heat picked up in the system to the surrounding environment and provide cooled water again to the system.

The present invention allows for various configurations and approaches for removing the heat of refrigerant absorption from the two absorbers and removing the heat of refrigerant condensation (and possibly, sub-cooling) from the condenser, and should not be limited to those configurations specifically described herein.

The present invention allows for various configurations for optimizing energy management, in general, thereby increasing cycle energy efficiency, and heat recovery, in particular, from the high-temperature, high-pressure refrigerant before said refrigerant rejects heat at the condenser, it being understood that various configurations with heat recovery before the condenser are within the scope of the present invention.

The present invention allows for various designs for the various equipment components required for a specific implementation of an absorption cycle, especially for the absorbers, generators, heat exchangers, and condensers effecting the required heat and mass transfer operations and should not be limited to those designs specifically described herein.

The hot water, steam, or combustion gases supplied to either the first or the second generator in order to release refrigerant vapor from the first- or the second-absorbent/refrigerant mixture may be supplied by any number of sources, including water heated with waste heat from a combustion engine (combustion gases) and solar heated water, among others.

In one embodiment, disclosed herein is a process for producing cooling comprising forming a first- absorbent/refrigerant mixture at a first absorber, heating said first-absorbent/refrigerant mixture to release refrigerant vapor, sending the refrigerant vapor to a second absorber, forming a second- absorbent/refrigerant mixture, heating the second-absorbent/refrigerant mixture to release refrigerant vapor, condensing said refrigerant vapor to form liquid refrigerant, evaporating said liquid refrigerant at a lower pressure in the vicinity of a heat transfer fluid, transferring said heat transfer fluid to the vicinity of a body to be cooled, and reforming the heated first- and second-absorbent/refrigerant mixture.

By reforming is meant re-diluting the concentrated first- and second-absorbent/refrigerant mixtures through the absorption of refrigerant vapor to restore the ability of the said mixtures to transfer refrigerant to the first and second generators, respectively.

In another embodiment, in a similar manner to the process described above to produce cooling, an absorption cycle may be used to generate heat with for instance an absorption heat pump. In this process the heat of absorption generated by absorbing the refrigerant into the absorbents in the absorbers and, primarily, the heat of condensation generated by condensing the refrigerant vapor to refrigerant liquid in the condenser can be transferred to water or some other heat transfer fluid, which is used to heat any space, location, object or body.

In addition, the present invention is not limited to only those embodiments shown or described herein. For instance, the extension of the present invention to cycles where the refrigerant is transferred successively through three absorption circuits connected in series is also within the scope of the present invention and could be advantageous for the optimum utilization of heat sources available at three different temperatures.

CLAIMS

What is claimed is:

1. An absorption cycle system, comprising:
   (a) an evaporator for circulating a refrigerant therethrough;
   (b) a first absorption circuit disposed in fluid communication with the evaporator for mixing the refrigerant from the evaporator with a first absorbent, thereby forming a first absorbent and refrigerant mixture and for circulating the first absorbent and refrigerant mixture therethrough;
   (c) a second absorption circuit disposed in fluid communication with the first absorption circuit for mixing a portion of the refrigerant from the first absorption circuit with a second absorbent, thereby forming a second absorbent and refrigerant mixture and for circulating the second absorbent and refrigerant mixture therethrough; and
   (d) a condenser disposed in fluid communication with the second absorption circuit and with the evaporator.

2. The system of claim 1, wherein the first absorption circuit comprises:
   (a) a first absorber disposed in fluid communication with the evaporator for absorbing the refrigerant from the evaporator into the first absorbent and refrigerant mixture
   (b) a first heat exchanger disposed in fluid communication with the first absorber for receiving and pre-heating the first absorbent and refrigerant mixture from the first absorber,
   (c) a first liquid pump for pumping the first absorbent and refrigerant mixture from the first absorber to the first heat exchanger, and
   (d) a first generator disposed in fluid communication with the first heat exchanger for receiving the pre-heated mixture from the

first heat exchanger and transferring additional heat into the pre-heated mixture.

3. The system of claim 2, wherein the second absorption circuit comprises:

   (a) a second absorber disposed in fluid communication with the first generator for absorbing a portion of the refrigerant from the first generator into a second mixture comprising the refrigerant and a second absorbent in the second absorber;

   (b) a second heat exchanger disposed in fluid communication with the second absorber for pre-heating the second absorbent and refrigerant mixture from the second absorber,

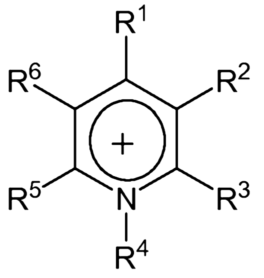
   (c) a second liquid pump for pumping the second absorbent and refrigerant mixture from the second absorber to the second heat exchanger, and

   (d) a second generator disposed in fluid communication with the second heat exchanger for receiving the pre-heated mixture from the second heat exchanger and transferring additional heat into the second mixture.

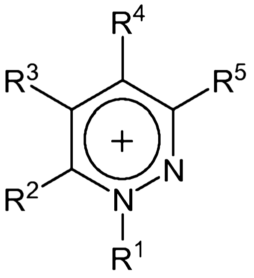
4. The absorption cycle system of claim 1, wherein the first absorbent and the second absorbent are each an ionic compound.

5. The absorption cycle system of claim 4, wherein the ionic compound comprises a cation and an anion, wherein the cation is selected from the group consisting of:

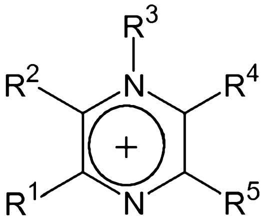
lithium, sodium, potassium, cesium,



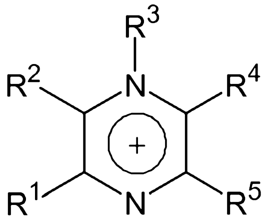
Pyridinium



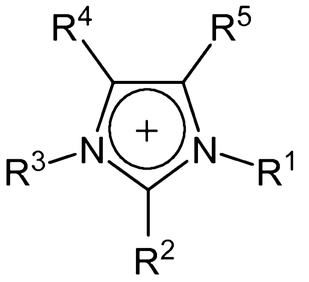
Pyridazinium



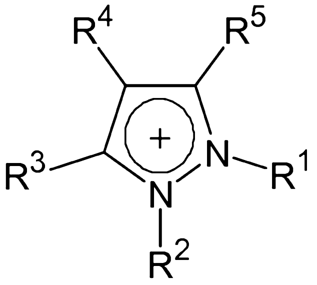
Pyrimidinium



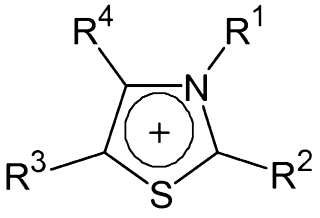
Pyrazinium



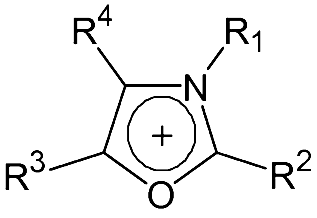
Imidazolium



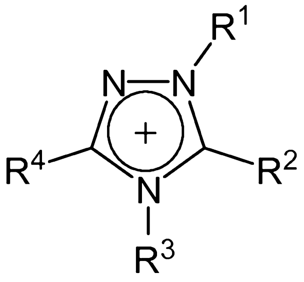
Pyrazolium



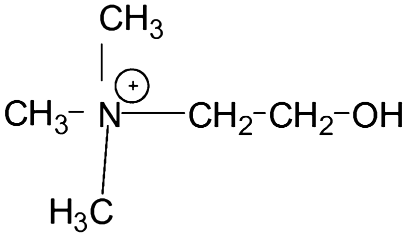
Thiazolium



Oxazolium

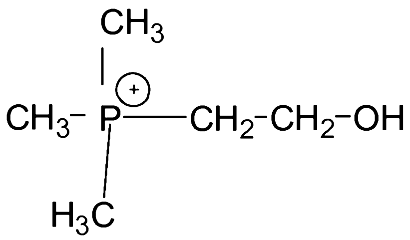


Triazolium



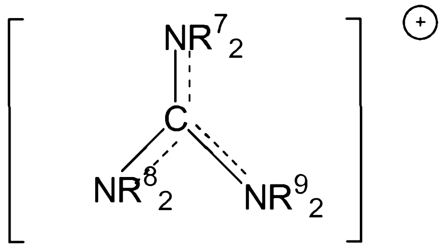
$$CH_3-\overset{+}{N}(CH_3)(H_3C)-CH_2-CH_2-OH$$

Choline

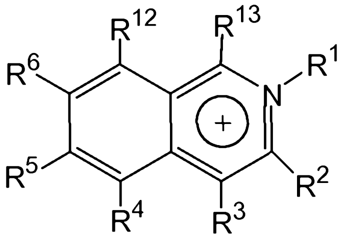


$$CH_3-\underset{H_3C}{\overset{CH_3}{P^{\oplus}}}-CH_2-CH_2-OH$$

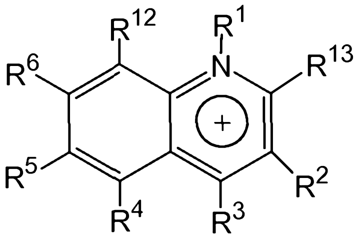
Phosphonium Choline



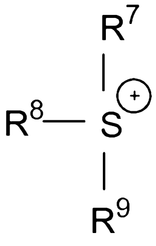
Guanidinium



Isoquinolinium

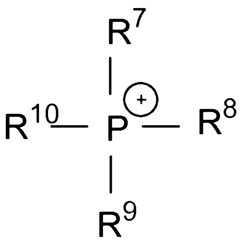


Quinolinium



$$R^8-\underset{R^9}{\overset{R^7}{S^{\oplus}}}$$

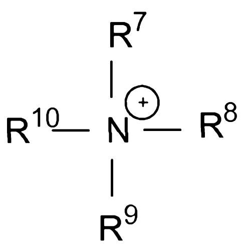
Sulfonium



$$R^{10}-\underset{R^9}{\overset{R^7}{P^{\oplus}}}-R^8$$

Phosphonium

and



$$R^{10}-\underset{R^9}{\overset{R^7}{N^{\oplus}}}-R^8$$

Ammonium

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^{12} and R^{13} are independently selected from the group consisting of:

(a) H

(b) halogen

(c) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(d) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(e) C_6 to C_{20} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and

(f) C_6 to C_{25} substituted aryl or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

  (1) -CH3, -C2H5, or C3 to C25 straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F I, OH, NH2 and SH,

  (2) OH,

  (3) NH2, and

  (4) SH;

R^7, R^8, R^9, and R^{10} are independently selected from the group consisting of:

(a) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(b) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(c) C_6 to C_{25} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; andC_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

  (1) $-CH_3$, $-C_2H_5$, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH,
  (2) OH,
  (3) NH_2, and
  (4) SH; and

wherein optionally at least two of R^1, R^2, R^3, R^4, R^5, $R^{6,}$ R^7, R^8, R^9, and R^{10} can together form a cyclic or bicyclic alkanyl or alkenyl group;

and an anion selected from the group consisting of:

$[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_3]^{3-}$, $[HPO_3]^{2-}$, $[H_2PO_3]^{1-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CuCl_2]^-$, Cl^-, Br^-, I^-, SCN^-; $BR^1R^2R^3R^4$, $BOR^1OR^2OR^3OR^4$, carborates optionally substituted with alkyl or substituted alkyl, carboranes optionally substituted with alkylamine, substituted alkylamine, alkyl or substituted alkyl, and a fluorinated anion.

6. The absorption cycle system of claim 4, wherein the refrigerant comprises water.

7. The absorption cycle system of claim 4, wherein the refrigerant is selected from the group consisting of hydrofluorocarbons, hydrochlorofluorocarbons, chlorofluorocarbons, fluorocarbons, chlorocarbons, nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), ammonia (NH_3), nitrous oxide (N_2O), argon (Ar), hydrogen (H_2), non-fluorinated hydrocarbons, and mixtures thereof.

8. The absorption cycle system of claim 7, wherein the non-fluorinated hydrocarbon is selected from the group consisting of C_1 to C_7 straight-chain, branched or cyclic alkanes and C_1 to C_7 straight-chain, branched or cyclic alkenes.

9. The absorption cycle system of claim 7 wherein the refrigerant comprises at least one refrigerant selected from the group consisting of difluoromethane (HFC-32), fluoromethane (HFC-41), pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1-trifluoroethane (HFC-143a), 1,1-difluoroethane (HFC-152a), fluoroethane (HFC-161), 1,1,1,3,3-pentafluoropropane (HFC-245fa), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,3,3-pentafluorobutane (HFC-365mfc), 1,1,1,2,3,4,4,5,5,5-

decafluoropentane (HFC-43-10mee), 1,1,1,2,2,3,4,5,5,6,6,7,7,7-tetradecafluoroheptane (HFC-63-14mcee), 2,3,3,3-tetrafluoropropene (HFO-1234yf), 1,2-difluoroethene (HFO-1132), 1,3,3,3-tetrafluoropropene (HFO-1234ze), 1,2,3,3-tetrafluoropropene (HFO-1234ye), 3,3,3-trifluoropropene (HFO-1243zf), 1,2,3,3,3-pentafluoropropene (HFO-1225ye), 1,1,1,3,3-pentafluoropropene (HFO-1225zc), 1,1,1,4,4,4-hexafluoro-2-butene (HFO-1336mzz), 1,1,1,2,2,5,5,5-octafluoro-2-pentene (HFO-1438mczz), 1,1,1,2,2,4,5,5,6,6,7,7,7-tridecafluoro-3-heptene (HFO-162-13mczy) and 1,1,1,2,2,3,5,5,6,6,7,7,7-tridecafluoro-3-heptene (HFO-162-13mcyz), dichlorodifluoromethane (CFC-12), fluorotrichloromethane (CFC-11), 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113), 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114), chlorodifluoromethane (HCFC-22), 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd), perfluoromethane (FC-14), perfluoroethane (FC-116), perfluoropropane (FC-218, perfluorocyclobutane (FC-C318), octafluoro-2-butene (FO-1318my), 1,2-dichloroethylene, methylene chloride, trichloroethylene, perchloroethylene, methane, ethane, ethylene, propane, cyclopropane, propylene, n-butane, butane, isobutane, cyclobutane, n-pentane, isopentane, n-hexane, cyclohexane, n-heptane, nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), ammonia (NH_3), nitrous oxide (N_2O), argon (Ar), hydrogen (H_2), and mixtures thereof.

10. The absorption cycle system of claim 2, further including a first recirculation line between the first generator and the first heat exchanger, and between the first heat exchanger and the first absorber, for recirculating the first absorbent and refrigerant mixture back to the first absorber.

11. The absorption cycle system of claim 3, further including a second recirculation line between the second generator and the second absorber for recirculating the second absorbent and refrigerant mixture back to the second absorber.

12. The absorption cycle system of claim 3, further including a heat recovery line extending between the second generator and through the first generator for recovering heat from the refrigerant exiting the second generator, said heat recovery line continuing from the first generator to the condenser, for delivering the refrigerant vapor to the condenser.

13. The system of claim 1, wherein the system is an absorption cooling system.

14. The system of claim 1, wherein the system is a heat pump.