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REFRIGERATION

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The present invention relates to refrigeration, and more particularly to refrigeration by means of the absorption principle.

One of the objects of the present invention is to provide a new and improved working fluid or medium for an absorption refrigerating system, which is especially adapted for air conditioning purposes.

A further object is a working fluid of the character described which requires a minimum amount of power per unit of refrigeration to effect transfer of the solution from the low side to the high side of the system.

Another object is to provide an absorption refrigeration machine which may be operated with a slight differential between those pressures prevailing within the machine and atmospheric pressure, thereby permitting the fabrication of the machine from lighter construction materials.

A still further object is to provide a working fluid such that the pressure differential between the low side and the high side of the absorption refrigerating system is relatively small, thereby minimizing the possibility of pump failures, as well as reducing the power requirements per ton of refrigeration for effecting the circulation of the solution.

Another object is to provide a novel refrigerant-absorbent combination wherein the refrigerant forms a thermally unstable, loose molecular compound with the absorbent, by intermolecular hydrogen bonding.

The foregoing and other objects may be accomplished in accordance with the present invention, one aspect of which includes a novel refrigerant-absorbent combination in which the refrigerant comprises a member selected from the group consisting of water and alcohols boiling below approximately 212° F., and the absorbent comprises a member selected from the group consisting of relatively nonvolatile aliphatic amines and relatively nonvolatile aliphatic amides.

The refrigerant component of the present invention comprises either water or a volatile alcohol having a boiling point below approximately 212° F. As specific examples of the refrigerant, mention may be made of the following compounds: water, methyl alcohol, ethyl alcohol, isopropyl alcohol, normal propyl alcohol, tertiary butyl alcohol, secondary butyl alcohol and the like. The foregoing compounds are mentioned merely by way of example and serve to indicate the type of refrigerant embraced within the scope of the present invention.

The solvent or absorbent component of the present invention comprises either a nonvolatile aliphatic amine or a nonvolatile aliphatic amide, or mixtures thereof. Preferably the absorbent should have a boiling point above approximately 364° F., inasmuch as a solvent of lower boiling point creates fractionation difficulties in separating the refrigerant from the absorbent. From a theoretical point of view, the only requirement is that the boiling points of the refrigerant and the absorbent should differ to such an extent that the materials may be separated by suitable fractionating equipment. However, from a practical point of view, the greater the difference between the boiling points of the absorbent and the refrigerant, the less difficult will be the fractionation problem, and, in general, absorbents boiling below approximately 364° F. will be found to be impractical because of the elaborate equipment required for fractionation.

The absorbents may comprise the monoamines and/or the monoamides, as before indicated. However, the polyamines and/or polyamides in general are preferred. Of the many compounds of the class described which may be used, the following may be mentioned purely by way of example: triethylene tetramine; tetraethylene pentamine; methylated triethylene tetramine (new compound, vide infra); trimethyl triethylene tetramine, new compound, vide infra); hexamethylene diamine; decamethylene diamine; hydroxyethyl ethylene diamine; dimethyl acetamide; dimethyl valeramide; methyl acetamide; tetramethyl oxamide; triacetyl trimethyl triethylene tetramine (new compound, vide infra); and the like, either alone or in combination. The foregoing specific compounds are mentioned purely for the purpose of illustrating the nature of the absorbent contemplated by the present invention.

The physical properties of certain specific examples of the refrigerant and absorbent components preferred in accordance with the present invention are set forth in Table I. From an inspection of Table I, it will be apparent that the latent heats of vaporization of the refrigerants are relatively high and that their vapor pressures are relatively low. The low vapor pressures permit the fabrication of the machine from relatively light construction materials. The small differential in pressure between the low side and high side reduces the difficulty in pumping the solution from the low side of the system to the high side. Moreover, the low pressure used in the operation of the machine reduces the probability of loss of chemical due to leaks.

TABLE I

Physical properties of refrigerant and absorbent components

Compounds	Property						
	Boiling point, °F.	Vapor pressure				Latent heat of vaporization at 40° F.	
		At 40° F.		At 105° F.		Cal./g.	B.t.u./lb.
		mm. Hg.	in. Hg.	mm. Hg.	in. Hg.		
Refrigerants:							
H_2O	212	6.33	0.25	57.1	2.25	593	1067
CH_3OH	147	39.2	1.54	267.5	10.53	284	511
C_2H_5OH	172	16.6	0.654	140.0	5.51	219	394
i-C_3H_7OH	176-178	11.1	0.437	107.0	4.22	185	333
n-C_3H_7OH	203	4.6	0.181	51.0	2.0	196	353
s-C_4H_9OH	203	5.5	0.216			157	282
t-C_4H_9OH	176	14.1	0.555	120.0	4.73	149	268
Absorbents:				At 230° F.			
Triethylene tetramine	230 (2 mm.)			2.1	0.083		
Tetraethylene pentamine	293 (2 mm.)			0.465	0.018		
Methylated triethylene tetramine	210-217 (2 mm.)						
Trimethyl triethylene tetramine				3.0	0.118		
Hexamethylene diamine	[1] 154 (2 mm.)			10.0	0.394		
Decamethylene diamine	[2]						
Hydroxyethyl ethylene diamine	214 (2 mm.)						
Methyl acetamide	403						
Dimethyl acetamide	324						
Tetramethyl oxamide	[3]						
Dimethyl valeramide	185-189 (4 mm.)						
Triacetyl trimethyl triethylene tetramine	392-437 (2-4) with slight decomp.						
Adiponitrile	223 (2 mm.)						
Sebaconitrile	284-286 (2-3 mm.)						

[1] M. P.=102° F. [2] M. P.=142.5° F. [3] M. P.=176° F.

When the refrigerant and absorbent compounds of the present invention are mixed together, it appears that intermolecular hydrogen bonding takes place between the active hydrogen atom of the refrigerant component and the effective pair of unshared valence electrons of the donor oxygen and/or donor nitrogen atoms of the absorbent. In other words, as a result of hydrogen bonding, a loose molecular type of compound appears to be formed between the refrigerant and the solvent, and this hydrogen bonding appears to account for the extraordinary properties of the working media contemplated by the present invention.

From the foregoing specific examples of the components of the present working fluid, it will be apparent that a large number of individual combinations may be devised. A description of each combination theoretically possible would, of course, be superfluous, and it will be sufficient for the purpose of disclosing the present invention to describe merely a few specific embodiments of the refrigerant-absorbent combination, which are characteristic of the type of working fluid embraced within the scope of the appended claims. Accordingly, in the following detailed description it should be borne in mind that the invention is by no means restricted to the specific embodiments, and that the examples are cited merely for the purpose of illustrating the properties of the combination and the advantages of the present working medium over those heretofore proposed.

The solubility characteristics of several specific embodiments of the present working fluid, using typical amines as the absorbents, are given in Table II.

TABLE II

Amines

Solvent	Refrigerant	Solubility of refrigerant in solvent		
		Grams/gram [1]	Mol fractions	
			Calcd. [3]	Observed [4]
Triethylene tetramine				
$NH_2(CH_2CH_2NH)_2CH_2CH_2NH_2$	H_2O	0.174	0.177	0.588
Do	CH_3OH	0.344	0.223	0.605
Do	C_2H_5OH	0.326	0.200	0.508
Do	i-C_3H_7OH	0.228	0.164	0.357
Do	n-C_3H_7OH	0.247	0.148	0.362
Do	t-C_4H_9OH	0.306	0.183	0.376
Do	s-C_4H_9OH	0.312	0.178	0.360
Tetraethylene pentamine				
$NH_2(CH_2CH_2NH)_3CH_2CH_2NH_2$	H_2O	0.157	0.177	0.622
Methylated triethylene tetramine I (new compd.-vide infra)	H_2O	[2] 0.0163	[2] 0.129	[2] 0.156
Do	CH_3OH	0.174	0.223	0.523
Do	C_2H_5OH	0.162	0.200	0.416
Trimethyl triethylene tetramine (new compd.-vide infra)	H_2O	0.0632	0.177	0.398
Do	CH_3OH	0.242	0.223	0.588
Do	C_2H_5OH	0.220	0.200	0.469
Hexamethylene diamine				
$NH_2(CH_2)_6NH_2$	H_2O	0.096	0.177	0.382
Do	CH_3OH	0.377	0.223	0.578
Do	C_2H_5OH	0.318	0.200	0.445
Do	i-C_3H_7OH	0.293	0.164	0.362
Do	n-C_3H_7OH	0.304	0.148	0.370
Do	t-C_4H_9OH	0.365	0.183	0.364
Do	s-C_4H_9OH	0.400	0.178	0.385
25% triethylene tetramine				
75% dimethyl ether of tetraethylene glycol	CH_3OH	0.126		
50% triethylene tetramine				
50% dimethyl ether of tetraethylene glycol	do	0.209		
75% triethylene tetramine				
25% dimethyl ether of tetraethylene glycol	do	0.280		

[1] [2] [3] [4] See footnote below Table III, following page.

The solubility characteristics of several embodiments of the present working fluid, wherein specific amides are employed as the absorbents, are given in Table III.

TABLE III

Amides

Solvent	Refrigerant	Solubility of refrigerant in solvent		
		Grams/gram [1]	Mol fractions	
			Calcd.[3]	Observed [4]
Dimethyl acetamide	H_2O	0.0627	0.177	0.232
	CH_3OH	0.215	0.223	0.369
	C_2H_5OH	0.242	0.200	0.314
Dimethyl valeramide	CH_3OH	0.124	0.223	0.337
Methyl acetamide	CH_3OH	0.184	0.223	0.297
Triacetyl dimethyl triethylene tetramine (new compound—vide infra)	H_2O	0.088	0.177	0.610
	CH_3OH	0.110	0.223	0.520
50% dimethyl acetamide, 50% dimethyl ether of tetraethylene glycol	CH_3OH	0.123	----------	----------

[1] Observed solubility of refrigerant in solvent at 90° F. under pressure corresponding to vapor pressure of refrigerant at 40° F. in terms of grams refrigerant per gram solvent, except as otherwise noted.
[2] Observed solubility of refrigerant in solvent at 100° F. under pressure corresponding to vapor pressure of refrigerant at 40° F. in terms of grams refrigerant per gram solvent.
[3] Calculated solubility under same conditions, in terms of mol fractions.
[4] Observed solubility under same conditions in terms of mol fractions.

Of the numerous absorbents available which may be used in accordance with the present invention, triethylene tetramine and hexamethylene diamine constitute the preferred embodiments. Accordingly, in the following description, the invention will be described with particular reference thereto, it being clearly understood, however, that these examples are merely representative of the type of solvents contemplated by the present invention.

The solubility characteristics of various refrigerants in the preferred solvents, at pressures other than those shown in Table I, are given in Table IV.

In order to show the significant improvement in the efficiency of an absorption system provided with the working fluid of the present invention, calculations were made for various working media to show the power required per ton of refrigeration to effect transfer of the solution from the low side to the high side of the system (disregarding friction), the results being given in Table V. Such calculations are made with reference to a machine designed for air conditioning, operating under the following conditions: refrigerant temperature on the low side, 40° F.; temperature of solution leaving the heater, 228° to 235° F.; temperature of solution leaving the absorber, 95° to 105° F.; and refrigerant temperature in the receiver, 95° to 110° F. It should be understood that in the following discussion, the quantitative data, where given, are to be taken in a relative sense only; in other words, the data are intended to be comparative, rather than absolute.

TABLE V

Power requirements to effect circulation

Solvent	Refrigerant	Solubility			Vapor pressures			SPPM lb./min./ton of refrigeration	PF
		S_{90-40} G./g.	$S_{230-105}$ G./g.	ΔS G./g.	P_{40} lb./in.^{2}	P_{105} lb./in.^{2}	ΔP lb./in.^{2}		
Triethylene tetramine	H_2O	0.174	0.0104	0.164	.123	1.105	0.982	1.348	1.325
	CH_3OH	3.77	.0538	.323	.758	5.175	5.417	1.799	9.735
Hexamethylene diamine	C_2H_5OH	.318	.0505	.267	.322	2.71	2.39	2.752	6.578

S_{90-40}=Solubility of refrigerant in solvent at 90° F. under pressure corresponding to vapor pressure of refrigerant at 40° F. in terms of grams refrigerant per gram solvent.
$S_{230-105}$=solubility of refrigerant in same solvent at 230° F. under pressure corresponding to vapor pressure of refrigerant at 105° F. in terms of grams refrigerant per gram solvent.
ΔS=S_{90-40} less $S_{230-105}$.
P_{40}=Vapor pressure of refrigerant at 40° F. in pounds per square inch abs.
P_{105}=vapor pressure of refrigerant at 105° F. in pounds per square inch abs.
ΔP=P_{105} less P_{40}.
SPPM=required rate of circulation of strong solution in pounds per minute to give one ton of refrigerant with saturated gaseous refrigerant temperature of 40° F. in low side, saturated gaseous refrigerant temperature of 105° F. in condenser, 100% saturated solution leaving absorber at 90° F. under pressure corresponding to vapor pressure of the refrigerant at 40° F. and 100% saturated solution leaving heater at 230° F. under pressure corresponding to vapor pressure of refrigerant at 105° F.
PF=SPPM times ΔP.

TABLE IV

Solvent	Refrigerant	Solubility with solvent at 100° F. G./g. vapor pressure corresponding to:			
		35° F.	45° F.	50° F.	55° F.
Triethylene tetramine	H_2O	.069	.127	.164	.200
	CH_3OH	.280	.409	.482	.566
	i-C_3H_7OH	.183	.295	.378	.466
Hexamethylene diamine	i-C_3H_7OH	.244	.367	.456	.552

From the data given in Table V, it will be apparent that the pressure differential between the high side and the low side of the system, in an absorption machine provided with the present working fluid, is relatively small (see "ΔP," column 8, Table V). As a result, the amount of power required to effect circulation of the solution in the system (as indicated by the value of "PF," last column, Table V) is significantly low.

In the evaluation of refrigerant-solvent com-

binations, it is convenient to express numerically the relative amount of work required to effect circulation of one refrigerant-solvent combination as compared to another. For this purpose the "relative efficiency" with respect to the work required to circulate the fluid of one combination in comparison to that of a standard or reference combination, may be defined by the equation:

$$RE = PF_r/PF_e$$

where PF_r is the PF value (SPPM times ΔP) of a standard or reference working fluid, and PF_e is the PF value of the fluid being evaluated. Table VI gives the "RE" values for the preferred embodiments of the present invention, using (*a*) methylene chloride-dimethyl ether of tetraethylene glycol (col. 3) and (*b*) methylamine-ethylene glycol (col. 4), as reference media of the prior art.

TABLE VI

Solvent	Refrigerant	RE compared to $CHCl_2$ + dimethyl ether of tetraethylene glycol	RE compared to CH_3NH_2 + ethylene glycol
Triethylene tetramine	H_2O	51.5	103.7
Hexamethylene diamine	CH_3OH	7.15	14.13
	C_2H_5OH	10.38	20.92
Dimethyl ether of tetraethylene glycol (reference)	CH_2Cl_2	1.000	2.015
Ethylene glycol (reference)	CH_3NH_2	0.495	1.000

From an inspection of Table VI, it will be apparent that the preferred embodiments of the present invention are vastly superior in respect to power requirements to the two standards selected. Thus, for example, the "RE" of triethylene tetramine plus water is 51.5, compared to methylene chloride plus dimethyl ether of tetraethylene glycol. In other words, the power requirement for the reference combination (in this case methylene chloride plus dimethyl ether of tetraethylene glycol) is nearly 52 times as great as that of the combination of triethylene tetramine plus water. The unexpected improvement in efficiency accomplished by means of the present invention will be clearly evident from the data given in Table VI.

Preparation of new absorbents

In the foregoing description of the invention, three absorbents were disclosed which are new compounds per se. The preparation of these compounds will now be described in order to enable those skilled in the art to practice the invention without the necessity of experiment. These new compounds are specifically claimed in our co-pending divisional application Serial No. 432,032, filed February 23, 1942.

Methylation of triethylene tetramine

The amine was methylated using the method of Clarke, Gillespie and Weishaus. Clarke, Gillespie and Weishaus, J. Am. Chem. Soc., 55, 457 (1933). One and one-half kilograms of 90 per cent formic acid (30 moles) was added slowly to 500 g. of triethylene tetramine (3.4 moles). Considerable heat was evolved. To this red solution 800 cc. of 40 per cent formaldehyde (12 moles) was added, the mixture refluxed on a steam bath until the evolution of carbon dioxide ceased (about twenty-four hours). One liter of concentrated hydrochloric acid was added and the mixture evaporated to dryness in vacuo on a steam-bath. The residue of amine hydrochloride was refluxed with concentrated sodium hydroxide solution (1 kg./l.) and the amine layer separated. One kilogram of solid sodium hydroxide was added, the mixture refluxed for five hours and the liquid layers decanted from the sodium chloride which was precipitated from solution. The amine layer was separated and treatment with solid sodium hydroxide repeated several times as above until all the water was removed as indicated by presence of one liquid layer over hot alkali. The amine was then dried by heating over sodium chips for ten hours and then purified by vacuum distillation to give 500 g. of a clear, non-viscous liquid, B. P. 99–103° C. at 2 mm.

Anal. Calcd. for $C_{10}H_{26}N_4$ (tetramethyl): N, 27.7. Calcd. for $C_{11}H_{28}N_4$ (pentamethyl): N, 25.9. Found: N, 26.3. Hence the amine has an average of about 4.7 methyl groups per molecule.

Trimethyl triethylene tetramine

Five hundred grams of triethylene tetramine (3.4 moles) was diluted with 200 cc. of water and the solution surrounded by an ice-bath. Then 600 g. of dimethyl sulfate (4.8 moles) was added dropwise while the cold (15–18° C.) solution was stirred vigorously with a mechanical stirrer. This addition required six hours. After all the dimethyl sulfate had been added the mixture was allowed to warm to room temperature (28° C.) and remain thus with stirring overnight. The tan reaction mixture was poured into a solution of 500 g. of sodium hydroxide dissolved in 1 l. of water and refluxed for ten hours on a steam bath to decompose the addition complex. The liquid layers were decanted from the sodium sulfate which had precipitated and the amine layer separated from the sodium hydroxide layer. The amine was refluxed with solid sodium hydroxide to remove water. This process was repeated until no separation into liquid layers occurred on refluxing the amine with solid sodium hydroxide. The amine was dried by heating overnight with sodium chips, and then purified by vacuum distillation to give 400 g. of slightly yellow, non-viscous liquid, B. P. 97–107° C. at 2–3 mm.

Anal. calcd. for $C_9H_{24}N_4$ (trimethyl): C, 57.5; H, 12.8; N, 29.8. Found: C, 57.9; H, 12.6; N, 29.6.

Acetylation of trimethyl triethylene tetramine

To 57 g. of trimethyl triethylene tetramine in an all-glass refluxing flask and condenser an excess (200 cc.) of acetic anhydride was added slowly. A vigorous reaction occurred immediately with the formation of a dark-brown solution and evolution of much heat. The mixture was refluxed overnight. The acetic anhydride was distilled from the reaction mixture leaving a dark brown tar. The tar was distilled in vacuo with slight decomposition to give 80 g. of an extremely viscous brown liquid with a green fluorescence, B. P. 200–225° C. at 2–4 mm. This amide is water soluble and alcohol soluble. Treatment of the water solution with Norite did not result in decolorizing the amide.

Anal. calcd. for $C_{15}H_{30}O_3N_4$ (trimethyl triacetyl): N, 17.8. Fond: N, 17.6.

In the foregoing detailed description of the present invention, certain aspects thereof have been illustrated with reference to an absorption refrigerating system of the two-fluid type. It should be understood, however, that this was done merely by way of example, and that the in-

vention may be used, if desired, in the Platen-Munters system by supplementing the disclosed two-fluid combination with a third fluid such as hydrogen, helium or the like. It will also be apparent that the invention is not to be restricted to the specific embodiments hereinbefore more particularly described, since these embodiments were mentioned merely for the purpose of illustrating the basic principles of the invention. The foregoing description will be sufficient to enable those skilled in the art, after a mastery of the fundamentals of the present invention, to select or provide a very large number of refrigerant-absorbent combinations which may be substituted for those hereinbefore specifically cited. Many other variations will be readily apparent to those skilled in the art. The present invention is therefore to be restricted only in accordance with the following patent claims.

We claim:

1. A working fluid for an absorption refrigerating system, which comprises a refrigerant selected from the group consisting of water and alcohols boiling below approximately 212° F. and a normally liquid absorbent having a boiling point above approximately 364° F. which is selected from the group consisting of aliphatic polyamines, N- substituted aliphatic polyamides, and N- substituted aliphatic amides.

2. A working fluid for an absorption refrigerating system, which comprises a refrigerant selected from the group consisting of water and alcohols boiling below approximately 212° F. and an absorbent having a boiling point above approximately 364° F. and comprising a compound having the formula $NH_2(CH_2CH_2NH)_nCH_2CH_2NH_2$, where n is a small whole number.

3. The working fluid of claim 2 wherein said absorbent comprises triethylene tetramine.

4. A working fluid for an absorption refrigerating system, which comprises a refrigerant selected from the group consisting of water and alcohols boiling below approximately 212° F. and an absorbent having a boiling point above approximately 364° F. and comprising a polymethylene diamine.

5. The working fluid of claim 4 wherein said polymethylene diamine comprises hexamethylene diamine.

6. The working fluid of claim 2 wherein said refrigerant comprises methyl alcohol.

7. The working fluid of claim 2 wherein said refrigerant comprises ethyl alcohol.

8. In an absorption refrigerating process wherein a refrigerant selected from the group consisting of water and alcohols boiling below approximately 212° F. is alternately absorbed in and expelled from an absorbent, the step which includes absorbing said refrigerant in a normally liquid absorbent having a boiling point above approximately 364° F. which is selected from the group consisting of aliphatic polyamines, N- substituted aliphatic polyamides, and N- substituted aliphatic amides.

9. In an absorption refrigerating process wherein a refrigerant selected from the group consisting of water and alcohols boiling below approximately 212° F. is alternately absorbed and expelled from an absorbent, the step which includes absorbing said refrigerant in an absorbent having a boiling point above approximately 364° F. and having the formula

$$NH_2(CH_2CH_2NH)_nCH_2CH_2NH_2,$$

where n is a small whole number.

10. In an absorption refrigerating process wherein a refrigerant selected from the group consisting of water and alcohols having a boiling point below approximately 212° F. is alternately absorbed in and expelled from an absorbent, the step which includes absorbing said refrigerant in an absorbent comprising a polymethylene diamine having a boiling point above approximately 364° F.

11. A working fluid for an absorption refrigerating system which comprises a refrigerant selected from the group consisting of water and alcohols boiling below approximately 212° F. and an absorbent comprising a relatively nonvolatile N- substituted aliphatic amide having a boiling point above approximately 364° F.

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