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REFRIGERATION

Glenn F. Zellhoefer, Normal, Ill.

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The present invention relates to refrigeration, and more particularly to refrigeration by means of the absorption principle. The present application is in part a continuation of my copending application Serial No. 35,883 filed August 12, 1935, issued March 15, 1938, as United States Patent No. 2,111,234.

Since the disclosure of the original Carre ammonia-water absorption refrigerating system, numerous refrigerant-solvent combinations have been suggested by various investigators, with a view to increasing the efficiency of the absorption cycle. As early as 1880, Du Motay proposed to employ high-boiling organic ethers and esters as solvents in place of the aqueous media theretofore used, and within recent times, renewed interest has been evinced in these organic solvents since the commercial introduction of certain non-toxic, non-inflammable, halo-fluoro hydrocarbon refrigerants which are insoluble in aqueous absorbents. Various organic solvents were proposed for use with these new refrigerants. (See, for example, Zellhoefer Patents 2,040,894 to 2,040,904, and 2,040,906 to 2,040,912, inclusive; see also Fleischer 2,035,541.) The combinations which were suggested appeared to possess considerable merit because of the non-volatile characteristics of the solvent, the non-toxic and non-inflammable properties of the refrigerant, and the high solubility of the refrigerant in the absorbent.

As a result of a detailed study, it has been found that, although these recently proposed working fluids employing the halo-fluoro refrigerants possess merit, in actual use, they are characterized by certain rather serious disadvantages which detracted from their utility. Thus, for example, it has been found that the amount of power required per ton of refrigeration, to transfer the solution containing these halo-fluoro refrigerants from the low side of the system to the high side thereof, is undesirably high. Other disadvantages, hereinafter referred to, were discovered in the course of the investigation.

When these disadvantages were brought to light, an investigation was undertaken with a view to determining the fundamental cause of the latent defect, and this may therefore be said to constitute one of the objects of the present invention.

The ultimate object of the invention is to obviate these disadvantages, and to provide an inherently more efficient working fluid for an absorption refrigerating system.

A further object is to provide an improved working medium for an absorption refrigerating machine adapted for air-conditioning purposes.

A more particular object is to provide a working medium for an absorption refrigerating system, which medium requires a minimum amount of power per unit of refrigeration, to effect the transfer of the solution from the low side to the high side of the system.

Other objects and advantages will become apparent as the description proceeds.

Before setting out to achieve the ultimate object of the invention, it was first necessary to undertake an extended investigation, with a view to determining the fundamental cause or causes for the unsuspected disadvantages which attended the use of the prior art working media. In the course of this investigation, the surprising and altogether unexpected fact was discovered that certain of the disadvantages of the halo-fluoro refrigerant-organic solvent combinations of the prior art appeared to be correlated with the selfsame factor which was responsible for the non-toxicity of the refrigerant and its high solubility in the solvent. Contrary to all expectation, it became evident as the investigation proceeded, that the substitution of the fluorine atom for a chlorine atom in a given halogenated hydrocarbon was attended by a significant decrease in the efficiency of the refrigerant, as far as its use in an absorption refrigerating machine was concerned; and this decrease in efficiency occurred despite the fact that the molar solubility of the resulting refrigerant in the absorbent in many cases was actually increased as a result of the substitution of fluorine for chlorine.

A detailed study of the phenomenon has shown that this decrease in efficiency of the working fluid for an absorption machine was due to a number of secondary causes, practically all of which were correlated with the substitution of fluorine for chlorine in a given halogenated hydrocarbon refrigerant. Thus, it was found that the substitution of fluorine for chlorine reduced the latent heat of vaporization of the refrigerant. This effect is illustrated in Table I.

TABLE I

Substitution of F for Cl—effect on latent heat of vaporization

Series	Individual members of the series	Latent heat of vaporization at 40° F. (B. t. u. per pound)
CH ₂ X ₂	CH ₂ Cl ₂	154.4
	CH ₂ ClF.....	150.0
CHX ₃	CHCl ₃	114.0
	CHCl ₂ F.....	102.5
	CHClF ₂	87.0
CX ₄	CCl ₄ F.....	137.0
	CCl ₃ F ₂	120.0
C ₂ X ₆	C ₂ Cl ₃ F ₃	67.5
	C ₂ Cl ₂ F ₄	55*

*Latent heat at 70° F.

From an inspection of Table I, it will be evident that, when fluorine is substituted for a chlorine in a given chlorinated hydrocarbon, the latent heat of vaporization at 40° F., falls off. The practical result of this effect is that a greater weight of refrigerant must be evaporated per unit of refrigeration if a chloro-fluoro refrigerant is employed, than if the corresponding non-fluorinated refrigerant is used.

During the course of the investigation, it was also found that, in every case studied, the substitution of fluorine for chlorine greatly increased the pressure differential existing between the high and low sides of the absorption refrigerating system operating under comparable conditions. This effect is shown in Table II.

TABLE II

Substitution of F for Cl—effect on pressure differential

Series	Individual members of series	P ₁	P ₂	P ₂ —P ₁
CH ₂ X ₂	CH ₂ Cl ₂	3.38	14.8	11.42
	CH ₂ ClF.....	25.4	80.7	55.3
CHX ₃	CHCl ₃	1.48	7.09	5.51
	CHCl ₂ F.....	12.45	42.7	30.25
	CHClF ₂	82.7	227.0	145.3
CX ₄	CCl ₄	7.03	25.8	18.77
	CCl ₃ F.....	51.68	141.2	89.52
	CCl ₂ F ₂			
C ₂ X ₆	C ₂ Cl ₃ F ₃	2.67	10.4	7.73
	C ₂ Cl ₂ F ₄	15.2	49.5	34.3

P₁=vapor pressure at 40° F. in pounds per sq. in. absolute.

P₂=vapor pressure at 105° F. in pounds per sq. in. absolute.

From an inspection of Table II it will be seen that, in any given series, the value of P₂—P₁ rises very materially as the fluorine substitution proceeds. The practical result of the effect shown in Table II is that, in an absorption cycle, the pressure differential existing between the low side and high side of the system is very significantly greater where a chloro-fluoro refrigerant is used, than in the case in which the corresponding non-fluorinated refrigerant of the same series is employed. In other words, a greater amount of power is required to transfer the solution from the low side

to the high side of the system, when a fluorine-containing halogenated hydrocarbon is used, than when a non-fluorinated, halogenated hydrocarbon of the same series is employed.

At this point in the investigation, it became possible to set up the following working hypothesis: For use in an absorption refrigerating system, a non-fluorinated halogenated hydrocarbon refrigerant would be inherently more efficient than the corresponding fluorine-containing member of the same series, (1) provided, a satisfactory solvent could be found having solubility characteristics for the non-fluorinated refrigerant such that

(a) The amount of solution required to be circulated in order to transfer a given quantity of refrigerant to the high side of the system, was not materially increased;

(b) The heat of solution, and the heat absorbed by the evaporation of the refrigerant out of the solvent, did not materially increase the required heat input to the generator and the heat output from the absorber;

and (2) provided, further, that other disadvantages did not negative the reduction in power required to effect the circulation.

With this working hypothesis as a basis, the investigation was then undertaken with a view to attaining the ultimate objective: namely, the provision of a more efficient working fluid for an absorption system. This particular object was achieved with great success, and in addition, a working fluid was devised which possessed several additional, entirely unanticipated and unexpected properties which made possible an even greater improvement in efficiency than was hoped for. Before discussing these disadvantages, however, it will be convenient at this point to describe the nature of the working fluid itself, and thereafter to point out its extraordinary properties.

Briefly described, the working medium or fluid of the present invention includes a loose, molecular-type of compound formed by intermolecular hydrogen bonding between a normally liquid, relatively volatile refrigerant and a liquid, relatively non-volatile solvent. Conveniently, but not necessarily, the present working fluid may comprise the following components:

(a) As a refrigerant, a relatively volatile, chemically and thermally stable, normally liquid, non-fluorinated halogenated hydrocarbon containing at least one hydrogen atom; and

(b) As an absorbent, a relatively non-volatile, chemically and thermally stable, liquid organic solvent capable of forming a loose molecular-type of compound with the refrigerant.

In order more clearly to describe the preferred type of working fluid contemplated by the present invention, it will be convenient to discuss the nature and properties of the refrigerant separately from those of the solvent; thereafter to illustrate, by means of specific examples, the properties or characteristics of each, and finally to describe specific examples of the working fluid, and to point out its numerous advantages. It should be borne in mind, however, that the following description is illustrative rather than restrictive of the present invention as defined in the appended claims.

I. THE REFRIGERANT

As stated above, the refrigerant component of the present invention may comprise a volatile, chemically and thermally stable, non-fluorinated, halogenated aliphatic hydrocarbon, containing at

least one hydrogen atom in the molecule. Desirably, the refrigerant contains the dichloromethyl group or radical ($-\text{CHCl}_2$) within its structure. Thus, the refrigerant may have the general formula: $\text{R}-\text{CHCl}_2$. As a specific embodiment of the refrigerants embraced within the scope of the present invention, methylene chloride



the present invention, and the foregoing comments regarding stabilizers and stabilizing solvents are of particular interest in connection with other refrigerants which may, if desired, be used in place of methylene chloride.

II. THE ABSORBENT

The absorbent or solvent contemplated by the present invention comprises a relatively non-volatile, chemically and thermally stable, liquid, organic compound which preferably has a low viscosity index, and which is capable of forming a loose, molecular type of compound with the refrigerant. The absorbents may be more particularly defined by the following characteristic, fundamental or inherent properties thereof:

1. The compound contains within its molecular structure at least one effective donor atom, i. e., an atom which has, in its outer or valence electron shell or orbit, at least one pair of unshared valence electrons, which pair is capable of forming a thermally-unstable, loose molecular-type of compound with hydrogen-containing halogenated hydrocarbons.

From the foregoing statement it will be observed that the compound may contain more than one donor atom. It is important to note, however, that in all cases, regardless of whether the compound contains one or many donor atoms, at least one of these donor atoms must be an effective donor atom, i. e., it must have at least one unshared pair of valence electrons capable of forming a thermally-unstable loose, molecular-type of compound by virtue of the hydrogen bond. Thus, while it is desirable to avoid certain negative factors, such as steric-hindrance, electro-negative groups adjacent to the characteristic atom, and active hydrogen atoms within the molecule, and the like, in order to achieve maximum solubility; nevertheless, a compound may contain negative factors adjacent to one or more donor atoms, and still possess good solubility characteristics, provided it has at least one effective donor atom in addition to those which are rendered substantially non-effective by the above mentioned negative factors.

It may be pointed out in this connection that it is generally desirable to avoid increasing the molecular weight by means of large inert groups which do not contain additional donor atoms, since the gram per gram solubility usually falls off even though the mol per mol solubility remains substantially the same.

2. The absorbent should be thermally stable over a relatively wide range, for example, between about 0°F . and about 260°F .

3. The absorbent should be chemically inert with respect to the refrigerant, (and preferably also with respect to the materials normally used in the construction of the refrigerating machine) within a wide temperature range, for example, between about 0°F . and about 260°F .

4. Preferably, but not necessarily, the absorbent should be a liquid having a relatively low viscosity index, even at low temperatures, in order to obtain good heat-exchange properties. A further reason for preferring a liquid of low viscosity is that this property appears to be associated in most if not all cases with good solubility characteristics. Thus, it has been found in numerous instances that a compound of high viscosity index is characterized by poor solubility characteristics, even though the compound contains the group or linkages normally associated with high solvent capacity. Although this

is preferred. It should be understood, however, that this preferred embodiment is mentioned merely by way of example, and solely for the purpose of illustrating, by means of a specific example, the type of refrigerants which are included within the ambit of the appended claims.

It will be observed that the refrigerant, as above defined, was said to be "chemically and thermally stable." Inasmuch as this is a relative term, it is perhaps desirable at this point to indicate the significance of this defining phrase, as far as the present invention is concerned. In order to avoid any ambiguity on this point, commercial methylene chloride (such as that obtained from the R. & H. Chemicals Department of the Du Pont Company) may be cited as an example of a refrigerant which is "chemically and thermally stable" within the meaning of the present invention. Thus, it may be heated to the highest temperatures ordinarily encountered in an absorption refrigerating system, without irreversible decomposing into a different molecular species or species. Furthermore, it does not appear to enter into a non-reversible chemical action with the solvents or absorbents of the present invention. Nevertheless, it is important to observe that the foregoing statements do not preclude the formation of a thermally unstable, loose molecular type of compound between the refrigerant and the absorbent. On the contrary, this loose type of compound formation appears to take place when the refrigerant and absorbent of the present invention are brought together, and indeed it is thought that certain of the advantages of the present invention may perhaps be explained on this basis.

It is not absolutely essential, for the purpose of the present invention, that the refrigerant, in its chemically pure state, should be chemically and thermally stable. For it is well known that many halogenated hydrocarbons which are somewhat unstable in the pure state may be rendered substantially stable by adding thereto very small amounts of a suitable stabilizer such as ethanol, pinene and the like. Stabilizers for this purpose are well known to the manufacturers of halogenated hydrocarbons and in certain instances it appears that a suitable stabilizer is added, as a matter of course, by the producer of compounds of this class, regardless of whether the consumer requests a stabilized grade or not. Thus, certain manufacturers of methylene chloride customarily add a "stabilizer" to the commercial refrigerant even though the usual commercial grade appears to be stable without the addition, the "stabilizer" being added as an increased assurance that trouble will not be encountered due to inadvertent contamination of the product with water or water vapor.

Where a stabilizer is desired for any particular refrigerant, the most effective material for this purpose can readily be determined by those skilled in the art. However, in the case of the preferred embodiment of the present invention, as hereinbefore pointed out, the ordinary commercial grade is stable within the meaning of

correlation of solubility and viscosity has been frequently observed, it cannot be definitely asserted at this time that such is universally true.

5. Preferably, but not necessarily, the absorbent should have a negligible vapor pressure at about 260° F., and a freezing point below room temperature or even lower.

In the foregoing description, a suitable absorbent has been broadly defined in terms of its fundamental properties. In order to illustrate the nature of the present invention as clearly as possible, certain specific examples of the type of absorbents contemplated by the present invention will now be described. It should be borne in mind, however, that these examples are merely illustrative of the type of compounds which are above defined in terms of their inherent or fundamental characteristics or properties; and that the invention is by no means restricted to the following specific embodiments.

(A) SPECIFIC EXAMPLES OF THE ABSORBENT

A large number of organic compounds are available which possess the foregoing defining characteristics or properties.

By far the most important classes or groups of solvents contemplated by the present invention are those containing one or more oxygen atoms as the effective donor atoms. These oxygen containing compounds constitute the preferred types of solvents in accordance with the present invention.

It is perhaps well to mention at this point that the certain groups which are referred to above as negative factors may be present in the molecule for the purpose of increasing the boiling point, and although these groups may have an undesirable effect on solubility in certain instances, the net result may be a more satisfactory solvent for the purpose of the present invention.

As specific examples of the type of oxygen compounds contemplated by the present invention, the following may be mentioned:

- (a) Carboxylic esters, such as ethylene glycol diacetate, trimethylene glycol diacetate, triacetin, and the like.

(b) Ethers, such as diethylene glycol diethylether, triethylene glycol dimethylether, tetraethylene glycol dimethylether, pentaethylene glycol dimethylether, hexaethylene glycol dimethylether, diethylene glycol ditetrahydrofurfuryl ether, ethylene glycol mono-n-butyl monotetrahydrofurfuryl ether, and the like. The preparation of the higher polyglycol diethers is described and claimed in the pending applications of Glenn F. Zellhoefer, Serial No. 35,883, filed August 12, 1935, and Glenn F. Zellhoefer and Carl S. Marvel Serial Nos. 175,083, 175,084, and 175,085, filed November 17, 1937.

(c) Mixed ether—carboxylic esters, such as diethylene glycol diacetate, triethylene glycol diacetate, ethylene glycol monotetrahydrofurfuryl ether monoacetate, diethylene glycol monomethyl ether monoacetate, triethylene glycol monomethyl ether monoacetate, tetrahydrofurfuryl acetate, polyethylene glycol monoalkyl ether alkoxyacetates such as diethylene glycol monoalkyl ether alkoxyacetates, for example, diethylene glycol monoethyl ether monomethoxy- or ethoxy-acetate and the like. The preparation of the alkoxy alkanoates is described and claimed in the pending application of Glenn F. Zellhoefer and Carl S. Marvel, Serial No. 175,086, filed November 17, 1937.

(d) Ketones such as l-menthone and the like.

(e) Keto-esters such as ethyl levulinate diethyl acetonedicarboxylate and the like.

The foregoing compounds are examples of organic liquids which contain one or more oxygen atoms as effective donor atoms and which are characterized by relatively low volatility, chemical and thermal stability, relatively low viscosity, etc. A large number of examples could be cited in addition to those listed above, but the foregoing will adequately serve to illustrate the type of oxygen-containing compounds which will fulfill the above listed requirements of the absorbent in accordance with the present invention.

III. THE REFRIGERANT-ABSORBENT COMBINATION

The foregoing description has been directed largely to a description of the components or constituents of certain of the working media in accordance with the present invention, and from the details given it will be apparent that a large number of specific combinations may be devised. A description of each combination would, of course, be superfluous, and it will be sufficient to describe merely a few specific embodiments which are characteristic of the type of working fluid embraced within the scope of the present invention. In the following detailed description, however, it should be borne in mind that the invention is by no means restricted to the specific embodiments, and that these 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 three specific embodiments of the working fluid in accordance with the present invention are given in Table III.

TABLE III

Solvent		CH ₂ Cl ₂
A Diethylene glycol monoethyl ether acetate.	Gm./gm. obs. ¹ ...	0.500
	MF obs. ²	0.503
	MF calc. ³	0.311
	F. calc. ⁴	1.61
B Tetraethylene glycol dimethyl ether.	Gm./gm. obs. ¹ ...	0.580
	MF obs. ²	0.605
	MF calc. ³	0.311
	F. calc. ⁴	1.94
C Diethylene glycol diethyl ether.	Gm./gm. obs. ¹ ...	0.57
	MF obs. ²	0.520
	MF calc. ³	0.311
	F. calc. ⁴	1.67

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.

² Observed solubility under same conditions, in terms of mol fractions.

³ Calculated solubility under same conditions, in terms of mol fractions.

⁴ F = mol fraction observed ÷ mol fraction calculated.

The foregoing table gives the approximate solubility of methylene chloride in

- (A) Diethylene glycol mono ethyl ether acetate; (B) Tetraethylene glycol dimethyl ether; and (C) Diethylene glycol diethyl ether.

Solubility is expressed both in terms of "grams solute per gram solvent" and in terms of "mol fractions". In order to show the deviation of

the various solutions from Raoult's law, the theoretical solubility of the refrigerant in the solvent was calculated from the vapor pressure of the refrigerant above the solution. The deviation from the ideal is represented by the value of F , which is defined by the equation

$$F = \frac{MF \text{ (observed)}}{MF \text{ (calculated)}}$$

Where $F=1$, the calculated solubility and the observed solubility are identical and the solution is "ideal". Where, however, the value of F is greater than unity, the actual solubility is in excess of the "ideal". From an inspection of Table III, it will be evident that the solubility of methylene chloride in the three solvents is considerably in excess of the "ideal". This is generally characteristic of the refrigerant-solvent combinations in accordance with the present invention.

(A) ADVANTAGES OF THE PRESENT WORKING MEDIUM

In order to show the significant improvement in the efficiency of an absorption system as accomplished by means of the present invention, it will be convenient to compare the properties of a specific example of the present invention with one of the outstanding working media of the prior art. In the following discussion the present invention will be exemplified by a fluid comprising methylene chloride and tetraethylene glycol dimethyl ether. The prior art working media will be represented by a fluid comprising dichloromonofluoromethane and tetraethylene glycol dimethyl ether. This particular comparison is selected for the reason that the solvent in both examples is the same.

In the following direct comparison of a prior art working medium with a specific example of the present invention, the observations are made with reference to a machine designed for air conditioning. The operating conditions are as follows: refrigerant temperature on the low side, 40° to 45° 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 qualitative and comparative rather than absolute.

1. Stability

More elaborate precaution must be taken to exclude moisture from a machine which is to be used with dichloromonofluoromethane than is required for a machine to be used with methylene chloride, because of the greater corrosion of metals which takes place in the presence of dichloromonofluoromethane, and a trace of moisture under the conditions prevailing in an absorption refrigeration machine.

2. Heat transfer

The characteristics of performance of the methylene chloride solution in the absorber is such that, to afford a given temperature of outlet solution, the temperature difference between the mean temperature of the water flowing through the absorber and the solution leaving the absorber may be approximately half that required for a dichloromonofluoromethane solution where the same type and amount of heat transfer surface per ton of refrigeration capacity is used. This advantage may be used to utilize cooling water at a higher temperature to afford the same solution temperature at the outlet of the absorber, or may be used to reduce the heat transfer surface used in the absorber.

3. Heat input to still and heat output in absorber

In a machine designed for use with methylene chloride and using the same amount of total heat transfer surface per ton of refrigeration capacity as the machine designed for use with dichloromonofluoromethane, it has been observed that, per ton of refrigeration produced, appreciably less heat input to the heater is required, and appreciably less heat is dissipated in the absorber when the machines are operating under comparable operating conditions.

4. Power required to effect circulation

Calculations showing the increase in the power required per ton of refrigeration to effect the transfer of the solution from the low side to the high side of the system (disregarding friction) are shown in Table IV.

TABLE IV

Refrigerant		Solubility			Vapor pressure			SPPM	PF
Series	Member	S_1	S_2	ΔS	P_1	P_2	ΔP		
CHX ^a	CHCl ₂	0.91	0.21	0.7	1.48	7.09	5.61	5.566	31.226
	CHCl ₂ F	1.10	0.3	0.8	12.45	42.7	30.25	6.116	185.0
	CHClF ₂	1.09	0.39	0.7	82.7	227.0	144.3	8.360	1206.4
CH ₂ X ₂	CH ₂ Cl ₂	0.580	0.18	0.4	3.28	14.8	11.42	5.965	68.12
	CH ₂ ClF	0.57	0.205	0.365	25.4	80.7	55.3	6.710	371.1

S_1 =solubility of refrigerant in tetraethylene glycol dimethyl ether at 90° F. under pressure corresponding to vapor pressure of refrigerant at 40° F. in terms of grams refrigerant per gram solvent.

S_2 =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.

$\Delta S = S_1 - S_2$

P_1 =vapor pressure of refrigerant at 40° F. in lb./sq. in. abs.

P_2 =vapor pressure of refrigerant at 105° F. in lb./sq. in. abs.

$\Delta P = P_2 - P_1$

SPPM=required rate of circulation of strong solution in pounds per minute to give one ton of refrigeration 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 .

In all the examples given in Table IV it will be evident that the substitution of a fluorine atom for a chlorine atom does not appreciably affect ΔS . However, it will be recalled that the latent heat of vaporization falls off when a fluorine atom is substituted for a chlorine atom (see Table I). Therefore, a greater quantity of refrigerant must be transferred from the low side to the high side of the system to produce a unit of refrigeration where a halo-fluoro refrigerant is employed than where a non-fluorinated refrigerant of the same series is used with the same solvent.

Furthermore, the pressure differential between the high and the low sides of the system is very greatly increased by the substitution of a fluorine atom for a chlorine atom (see " ΔP "). Consequently, where a fluorine-containing refrigerant is used, a greater quantity of solution must be forced against a greater pressure head. The amount of power required to effect this circulation (indicated by the value of "PF") is therefore greater with a fluorine-containing halogenated hydrocarbon than with the corresponding non-fluorine-containing halogenated hydrocarbon of the same series.

In the evaluation of various refrigerant-solvent combinations, it has been found convenient to express numerically the relative amount of work required to effect circulation of one refrigerant-solvent combination as compared to another. Accordingly, the "relative efficiency," as regards work of circulating the fluid, of one combination in comparison to a standard combination may arbitrarily be defined by the following equation:

$$RE = \frac{PF_r}{PF_s}$$

where PF_r is the PF value (SPPM times ΔP) of a standard or reference working fluid, and PF_s is the PF value of the fluid undergoing evaluation. Where the absorbent is the same in both fluids, the value of RE will be indicative of the approximate "relative efficiencies" of the two refrigerants for use with the particular solvent as far as circulation power requirements are concerned. The values of RE for various refrigerants compared to various standard or reference refrigerants using the same solvent in all cases are shown in Table V.

TABLE V

Approximate "relative efficiencies" of various refrigerants, using tetraethylene glycol dimethyl ether as the absorbent

Refrigerant	RE (compared to CHCl_3F)	RE (compared to CHClF_2)
CH_2Cl_2	2.71625	17.710
CHCl_3F	1.0	6.5202
$\text{C}_2\text{Cl}_2\text{F}_2$	.95318	6.2149
$\text{C}_2\text{H}_2\text{Cl}_2$	.5197	3.3885
$\text{C}_2\text{Cl}_2\text{F}$	.47702	3.1104
CH_2ClF	.4987	3.2510
CH_2Cl	.21913	1.4287
CHClF_2	.15337	1.0000
$\text{C}_2\text{Cl}_2\text{F}_2$	.027782	.181145
$\text{C}_2\text{Cl}_2\text{F}_4$	.04661	.3039

From an inspection of Table V it will be immediately apparent that the preferred working fluid of the present invention is significantly

superior to various working media of the prior art. Thus, for example, the RE of methylene chloride compared to dichloromonofluoromethane as a standard is nearly 3 (column 2); in other words, the PF of methylene chloride is approximately $\frac{1}{3}$ the PF of the reference fluid under comparable conditions when the same absorbent is used. The results are even more striking when difluoromonochloromethane is the reference refrigerant. In this case the RE of methylene chloride is approximately 18; in other words, the PF of the reference refrigerant (CHClF_2) is approximately 18 times as large as that of methylene chloride under comparable conditions.

In addition to the foregoing outstanding advantages, the following additional characteristics of the working fluid in accordance with the present invention should be mentioned:

1. The preferred refrigerant (methylene chloride) is one of the most stable of the chlorinated hydrocarbons containing hydrogen. The chemical stability and chemical inertness of methylene chloride insures freedom from any undesirable chemical reactions under the conditions prevailing in an absorption machine where the heater temperatures do not exceed 260°F ., where the metals exposed to the refrigerant and solution are copper, iron, tin, or solder, and where the moisture present is held to a reasonable minimum.

2. The preferred absorbent (tetraethylene glycol dimethyl ether) is likewise characterized by an extraordinary thermal stability, and in addition, is possessed of outstanding solubility characteristics.

3. The low vapor pressure of methylene chloride permits light construction of the machine, and reduces the probability of loss of chemicals, as compared to a refrigerant of higher vapor pressure.

4. A solution of methylene chloride and the type of solvent contemplated by the present invention is characterized by very high heat transfer characteristics, thereby minimizing the amount of heat transfer surface per B. t. u. of heat transferred in the cycle of operation.

5. The low value for " ΔP " of the refrigerants of the present invention reduces the possibility of a pump failure in an absorption refrigerating machine.

6. Methylene chloride is essentially nontoxic and for commercial purposes it is rated as nontoxic.

7. Methylene chloride is essentially non-inflammable, and for commercial purposes it is rated as non-inflammable.

The term "organic compound", as employed in the present specification and in the appended claims, is to be understood in its broadest sense. It embraces the compounds of carbon, whether or not the compound also includes inorganic atoms, such as halogen phosphorus, or the like.

The term "normally liquid" as used herein is to be understood as meaning that the compound is liquid under "normal conditions"—i. e., at ordinary temperatures and pressures (e. g., room temperatures and pressures). Under other conditions, it may, of course, be liquid, solid, or gaseous.

The term "steric-hindrance" as employed herein is a loose, relative term, but as it is generally used, it denotes such a degree of hindrance that the normal reactions characteristic of the same general type of compound are either materially slowed down or, as a practical matter, effectively

prevented. It is in this sense that the term is used in the present specification. Figuratively speaking, the donor atom is "buried" within the molecule and the effect may be described as a substantial loss of ability to share electrons with hydrogen.

The term "strongly electro-negative group" refers to such groups as halogen, unsaturated carbon-carbon linkages (for example, carbon-carbon double bond), etc. Such linkages, if adjacent to a donor atom, suppress the tendency of the donor atom to share electrons with hydrogen. This is evident from a comparison of tetrahydrofurfuryl acetate and furfuryl acetate as solvents for the refrigerants of the present invention.

"Active hydrogen atom" is another loosely defined term, and may be exemplified by the hydrogen atom attached to an oxygen or nitrogen atom, as hydroxy compounds, primary or secondary amines and the like. This effect is probably due to inter-molecular association of solvent molecules by hydrogen bonding between solvent molecules.

The term "chemically inert" as used in the present application does not preclude the formation of loose, molecular-type of compounds with the refrigerant, but refers only to chemical stability in the sense that a non-reversible chemical reaction between the solvent and the refrigerant or the materials of construction should not take place. As a practical matter, the foregoing requirement of chemical inertness eliminates compounds such as the alpha halogen carbonyl compounds, alpha halo ethers and the like, as absorbents.

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 invention may be used if desired in the Platen-Munters system, by supplementing the disclosed two-fluid combination with a third fluid such as hydrogen. 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 herein mentioned basic principles of the present 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 which are to be broadly construed in view of the significant advance accomplished by means of the working fluid defined thereby.

I claim:

1. A working fluid for an absorption refrigerating system, which includes methylene chloride as a refrigerant, and an absorbent comprising a liquid disubstituted polyglycol derivative.
2. The working fluid of claim 1 wherein said polyglycol derivative is a diether.
3. The working fluid of claim 1 wherein said polyglycol derivative is a tetraethylene glycol diether.
4. The working fluid of claim 1 wherein said

polyglycol derivative is tetraethylene glycol dimethyl ether.

5. A working fluid for an absorption refrigerating system, which includes a refrigerant comprising a relatively volatile, chemically and thermally stable, non-fluorinated halogenated hydrocarbon containing within its structure the dichloromethyl group or radical ($-\text{CHCl}_2$), and an absorbent comprising a chemically stable, relatively nonvolatile, nonhalogenated liquid organic compound which contains within its structure a divalent oxygen atom both bonds of which are linked to carbon, said organic compound being capable of combining reversibly with said refrigerant to form a thermally unstable, loose molecular-type of compound.

6. The working fluid of claim 5 wherein said refrigerant is methylene chloride.

7. A working fluid for an absorption refrigerating system, which includes a refrigerant comprising methylene chloride, and an absorbent comprising a chemically stable, relatively nonvolatile, nonhalogenated liquid organic compound which contains within its structure a plurality of divalent oxygen atoms, the two bonds of each of said oxygen atoms being linked to carbon, said organic compound being capable of combining reversibly with said refrigerant to form a thermally unstable, loose molecular-type of compound.

8. A working fluid for an absorption refrigerating system, which includes a refrigerant comprising a relatively volatile, chemically and thermally stable, nonfluorinated halogenated hydrocarbon containing within its structure the dichloromethyl group or radical ($-\text{CHCl}_2$), and an absorbent comprising a nonhalogenated, thermally stable, relatively nonvolatile, liquid organic compound selected from the group consisting of ethers, esters of carboxylic acids, ether-esters, and ketones, said organic compound being capable of reversibly combining to form a thermally unstable, loose molecular compound with said refrigerant.

9. The working fluid of claim 8 wherein said ethers are polyethers.

10. The working fluid of claim 8 wherein said esters are polyesters.

11. The working fluid of claim 8 wherein said refrigerant is methylene chloride.

12. A working fluid for an absorption refrigerating system, which includes a refrigerant comprising a relatively volatile, chemically and thermally stable, nonfluorinated halogenated hydrocarbon containing within its structure the dichloromethyl group or radical ($-\text{CHCl}_2$), and an absorbent comprising a liquid disubstituted glycol derivative.

13. The process of absorbing vapors comprising a relatively volatile, chemically and thermally stable nonfluorinated halogenated hydrocarbon containing the dichloromethyl group or radical ($-\text{CHCl}_2$), which includes the step of contacting said vapors with an absorbent comprising a chemically stable, relatively nonvolatile, nonhalogenated liquid organic compound which contains within its structure a plurality of divalent oxygen atoms, the two bonds of each of said oxygen atoms being linked to carbon.

14. In an absorption refrigerating process wherein a relatively volatile, chemically and thermally stable nonfluorinated halogenated hydrocarbon containing the dichloromethyl group or radical ($-\text{CHCl}_2$) is alternately absorbed in and expelled from an absorbent, the step which in-

cludes absorbing said refrigerant in a chemically stable, relatively nonvolatile, nonhalogenated liquid organic compound which contains within its structure a divalent oxygen atom, both bonds of which are linked to carbon, said organic compound being capable of combining reversibly with said refrigerant to form a thermally unstable, loose molecular-type of compound.

15. In an absorption refrigerating process wherein a refrigerant comprising methylene chloride is alternately absorbed in and expelled from an absorbent, the step which comprises absorbing said refrigerant in a chemically stable, relatively nonvolatile, nonhalogenated liquid organic compound which contains within its structure a plurality of divalent oxygen atoms, the two bonds of each of said oxygen atoms being linked to carbon, said organic compound being capable of

combining reversibly with said refrigerant to form a thermally unstable, loose molecular-type of compound.

16. In an absorption refrigerating process wherein methylene chloride as a refrigerant is alternately absorbed in and expelled from an absorbent, the step which comprises absorbing said refrigerant in a liquid disubstituted polyglycol derivative selected from the group consisting of glycol ethers, glycol esters, and glycol ether-esters.

17. In an absorption refrigerating process wherein methylene chloride as a refrigerant is alternately absorbed in and expelled from an absorbent, the step which comprises absorbing said refrigerant in a poly ethylene glycol dialkyl ether.

GLENN F. ZELLHOEFER.

CERTIFICATE OF CORRECTION.

Patent No. 2,149,947.

March 7, 1939.

GLENN F. ZELLHOEFER.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 37, for the word "disadvantages" read advantages; page 5, second column, line 72, in the table, for "sturated" read saturated; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of April, A. D. 1939.

(Seal)

Henry Van Arsdale
Acting Commissioner of Patents.