Refrigerants and Absorbents*

Part II

By W. R. Hainsworth
Vice President, Servel, Inc., New York, N. Y.

In the first part of this interesting survey, published last month, Dr. Hainsworth traced the early developments in connection with various refrigerants. Here he outlines ideal characteristics of refrigerants and absorbents, and discusses possibilities in the way of refrigerants of the future.

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Absorbents

THE first experimental machines put out by the Williams Oil-O-Matic Heating Corporation under Zellhoefer's direction in 1934 and 1935 were charged with dichloromonofluoromethane, F-21, as refrigerant and ethyl ether of diethylene glycol acetate as solvent. In 1936 the fluids were changed and our old friend Carrene—methylene chloride—used as the refrigerant, with dimethoxytetraëthylene glycol as the solvent. According to the theory this combination may be described as a chemically stable, non-volatile, non-halogenerated liquid organic compound, with an effective donor atom which has at least one pair of unshared valence electrons which pair is capable of forming a thermally unstable loose molecular type of compound with halogenated hydrocarbons containing hydrogen. One important patent describing this refrigerant solvent combination and theory is U. S. Patent No. 2,149,947. Practical results are represented by numerous air conditioning installations made since 1935, ranging in individual capacities from 6 to 30 tons, often installed in multiple and using gas, fuel oil or steam as the main source of energy.

The work done by the research engineers of Servel, Inc., serves to illustrate another approach to the problem. It is generally agreed that the absorbent must have a greater affinity for the refrigerant than corresponds to the ordinary solubility laws. The perfect solution follows Raoult's Laws, and normally corresponds to relatively small amounts of refrigerant held in solution. The required quantities of solution circulated per unit of cooling effect becomes impractical. In this case perfection, as expressed by these laws, is a very undesirable feature.

Water has an affinity for ammonia and far greater quantities of ammonia gas can be dissolved in water than nitrogen, for example, which follows closer to the perfect solution laws. When ammonia is dissolved, heat is liberated and this constitutes a crude measure of the affinity. Very little heat is liberated when Freon is dissolved in water. One phase of the search, therefore, involves a mixing test and observation of the rise in temperature of the mixture. A rise of 15 to 20°F. indicates solubility markedly in excess of Raoult's law. Another test is the determination of the vapor pressure temperature relationships of the mixture in varying percentages as compared with the pure fluids. By far the greater number of combinations can be weeded out by these tests. The promising combinations must then be examined with respect to all the other necessary and desirable characteristics.

Table 2 illustrates the data for a series of amine compounds with water as the refrigerant.

It would appear that diethylene triamine offers some promise because of its high mixing temperature. It was therefore worth while determining the vapor pressure relationship with water, which is illustrated in Fig. 2.

One cycle which appears of interest is illustrated by the points A B C D on the chart. This corresponds to an evaporator temperature of 45° and a cooling medium capable of holding the absorber and condenser at 105°. The concentration of the strong solution is 25 per cent. The weak solution is 15 per cent when operating with a corresponding generator temperature of 175°F.

Further study of the chart soon indicates that diethylene triamine as a solvent, although suitable for an evaporative cooled unit, is not so suitable for use in a straight air-cooled air conditioning unit, nor is it practical for domestic refrigeration or low temperature applications, aside from the limitations of water as a refrigerant in these fields.

Some combinations of fluids in which both refrigerant and absorbent are organic compounds offer possibilities; others are misleading. An example is ethylene chlorhydrin for the refrigerant and diethylene

Table 2. Data for Amine Compounds with Water as the Refrigerant

	Boiling point	*Temp. rise on mixing equal vol. of water*	*Percent water in aqueous solutions having a V.P. of 10 mm. at 100°F.*	*V.P. of 10% water solution at 100°F.*
Diethanolamine	268°C.	10°C.	8.5%	11.9 mm.
Hydroxyethylethylene diamine	245	22	19	4.5
Triethylene tetramine	278	34	20	5.0
Diethylene triamine	207	38	22	5.0

triamine for the absorbent. The temperature rise on mixing in this case is over 40°C. It was soon noted that a plastic-like material formed in the mixture after standing a while. This was discouraging to the engineer seeking new fluids, but may be a lead for the chemist looking for new plastics.

Hundreds of compounds have been tested by following a similar procedure of testing for temperature rise and determining the pressure temperature concentration curves. Some of these and others which have appeared in the literature are appended.

The search continues. In the meantime and in contrast to the study of organic compounds, Servel, Inc., has developed an all year gas air conditioning system, using water as the refrigerant and lithium bromide solution as the absorbent. Thus it appears that the inorganic chemist cannot be excluded from these endeavors as long as so many of the advantages and disadvantages of organic refrigerants and absorbents are marginal in nature. Similar activities are undoubtedly being carried on by chemical and other industrial companies in the search for new refrigerants for compression systems, as well as improvements in present refrigerants by removing last traces of moisture, impurities and non-condensible gases.

Desirable Properties

It is not within the scope of this paper to present technical data on the various refrigerants or comment in more than a general way on their usage. Complete technical information on refrigerants is excellently presented in the A.S.R.E. *Data Books*, papers in REFRIGERATING ENGINEERING and many other technical publications. The present-day refrigeration industry is so complex in nature and includes such a range of applications that all the desired properties cannot be combined in any one refrigerant. In one installation the main emphasis may be on absolute safety, in another economy of operation, in another extremely low temperatures, and in another space limitations, initial cost, etc. There are now available refrigerants especially well adapted to almost any application and a wide range of mechancal equipment, but none has all the advantages. We must specialize.

A review of Table 3, listing refrigerant characteristics and their zones of influence in compression systems, illustrates the complexity of the problem. This and similar lists are included in the publications mentioned, and are repeated here to emphasize the scope of the problem when tied in with the search for new refrigerants and absorbents for absorption systems. It is obviously impossible to arrange the list in an order of importance without knowing the use, size, type and cost factors of the installation, and therefore the listing is at random.

Table 3. The Compression System: Desirable Properties and Characteristics

Refrigerant	*Influence*
1. Temperature, pressure relations	Compressor losses, weight of equipment, leakage
2. Specific vapor volume	Compactness of equipment, compressor losses
3. Density	Liquid and gas flow characteristics
4. Latent heat	Amount of refrigerant circulation
5. Critical temperature	Operating temperature limitations, power consumption
6. Toxic, flammability, explosive, injurious, irritating and odor properties	Safety
7. Inertness and stability	Service
8. Leak tendency	Detection, loss of refrigerant, service
9. Oil effect	Lubrication, heat transfer, oil return
10. Corrosiveness	Life of equipment, service
11. Heat conductivity	Heat transfer, size of surfaces
12. Freezing temperature	Operating limitation
13. Viscosity	Liquid and gas heat transfer
14. Dielectric strength	Hermetically sealed units
15. Refrigerant cost	Equipment cost, service cost

Table 4. The Absorption System: Desirable Properties and Characteristics

Solvent	*Influence*
1. Vapor pressure at generator temperature should be negligible in comparison to the vapor pressure of the refrigerant at 100°F.	Rectifier losses and operating cost
2. Temperature pressure concentration relations	Solvent should remain liquid throughout the cycle. Relations must be in confirmation with practical condenser, absorber and generator temperatures and pressures. Rate of circulation.
3. Stability	Capable of withstanding heating operation at the maximum temperature encountered in the generator
4. Low specific heat	Heat transfer requirements
5. Low surface tension	Heat transfer and absorption
6. Low viscosity	Heat transfer, power for pumping
Solvent-Refrigerant Combination	*Influence*
1. Solubility	High solubility of the refrigerant at temperatures of cooling medium (air or water) and at a pressure corresponding to the vapor pressure of the refrigerant at 40°F. Low solubility of the refrigerant in the solvent at generator temperatures and at a pressure corresponding to the vapor pressure of the refrigerant at temperature of cooling medium (air or water).
2. Stability	Solvent and refrigerant must be incapable of any non-reversible chemical action with each other within a practical temperature range (20°F. to 250°F.)
3. Super heating and super cooling	Affects operation

If the list of desirable properties and characteristics appears somewhat long for refrigerants as used in compression systems, it is then readily understandable what an enormous amount of work is involved in the search for new refrigerant and absorbent combinations suitable for absorption systems. Consider for a moment the problem of air conditioning, using a gas-operated absorption system. This is of interest to the gas industry because it tends to balance the gas house heating load and smooth out the gas load factor. The Gas Air Conditioning Committee of the American Gas Association lists the various factors involved in an "ideal" refrigerant-absorbent combination for an air conditioning absorption refrigerating machine as including solvent factors *in addi-*

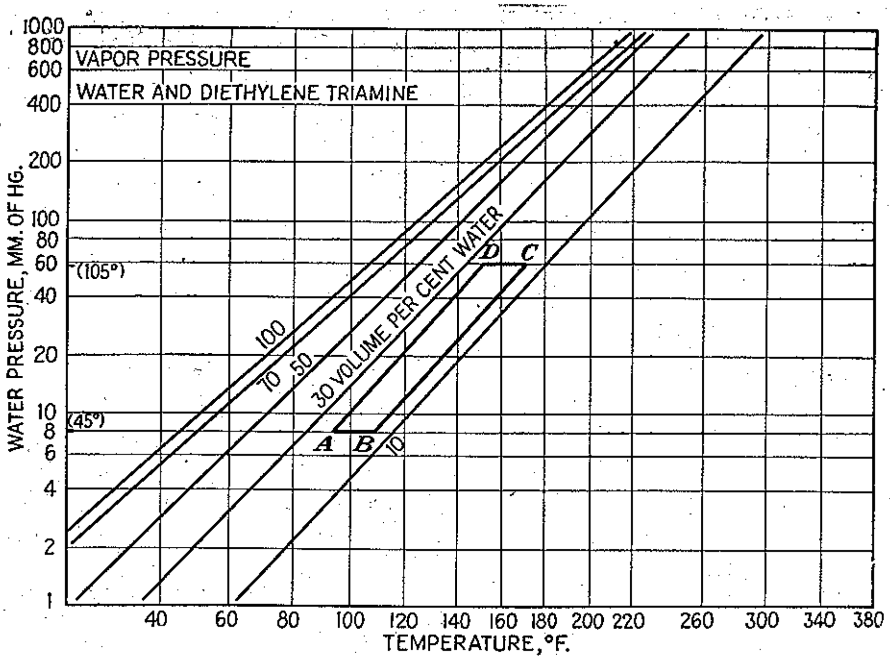

Fig. 2. Diethylene triamine—vapor pressure relationship with water.

tion to most of the refrigerant characteristics mentioned above. The list has been condensed in Table 4.

A mathematician looking at the above list of variables for refrigerants and absorbents would undoubtedly calculate extremely low chances of finding combinations of fluids having reasonably high percentages of the desirable characteristics. The problem may be further complicated by weighing the different properties in relation to their importance. In the face of these figures the research worker may be somewhat discouraged. Nevertheless, many discoveries have been made against greater odds than these. Witness the accomplishments of Midgley, Zellhoefer—and dozens of research workers in industrial laboratories.

Refrigerants to Suit Industry

WITH so many basic refrigerant variables entering the design it is understandable that ideal refrigerants for all applications do not exist. Water may be an ideal refrigerant because of its high latent heat and safety characteristics but its temperature range is limited, the displacement requirements are high and leaks are difficult to find in a high vacuum system. Ammonia has a high latent heat, good displacement characteristics and is capable of use over a wide temperature range. However, its large scale usage is mainly in industrial applications, partly because of the high cost of safety requirements in many other types of installation. Methyl chloride and sulfur dioxide have their advantages and disadvantages. The Freon refrigerants have an economic advantage in safety requirements, but the economy of operation in industrial applications is not so low as ammonia, and leaks are more difficult to find. The ideal refrigerant does not exist, but ideals are still worth working for and it would be unreasonable to assume that there will be no more new and improved refrigerants.

The road from the laboratory to acceptance by industry is long and hard and requires a great deal of courage and ability on the part of the chemical companies who undertake to produce, cooperating with the refrigerating companies, who undertake to use a new refrigerant. It is possible that when new refrigerants and absorbents do appear they will be of a type which will permit the use of smaller equipment without much change in operating efficiency. The organic chemist can synthesize almost any compound he wishes to create. He has new scientific tools to work with. Just one of these is the new infra-red spectrometer which enables him to produce an automatic recording to identify many radicals and their position within the molecule. He can tack on halogen atoms here and there, and intersperse double bonds or polarize and unbalance the molecule with side chains. He can plaster the whole carbon chain with fluorine or other components if he wishes. He may even find a thermal and pressure reversible polymerization reaction attended by heat changes larger than the latent heat of evaporation. What will be the result? Possibly a new refrigerant. Possibly a new absorbent.

Discussion: (Following the presentation of the paper by the author at the 31st Spring Meeting of The American Society of Refrigerating Engineers, Pittsburgh, Pa., June 5, 1944):

H. C. BRANDT (Carrier Corporation): After careful reading, I can find little if any controversial material in Dr. Hainsworth's paper. Yet its historical character suggests interesting phases for discussion.

It is to be hoped that the research workers, on whom our industry is dependent for future refrigerant developments, and who read this interesting paper, will not be discouraged from further endeavors by the formidable yardstick of desirable properties listed in Tables 3 and 4. Nor should they be content that progress so far has been good enough.

Those of us who have struggled to meet current refrigeration demands, running the gamut of applications from crane cab cooling and desert conditions down to —100°F. and below with the refrigerants and standard machines now available, have quickly learned that no single refrigerant is "all things to all applications." Problems confront us that are difficult to solve. Many of them are outside the realm of current experience. Often operating pressures are too high and often not high enough. It is sometimes necessary to resort to devices for quenching excessive superheat, and under extreme conditions, removal of suction valve springs is frequently practiced to reduce pressure drop through compressors when only a small amount of absolute pressure is available in the refrigerant. Our problems become more acute when refrigerants having good pressure-temperature characteristics are outlawed for a given application because of health, fire, or explosion hazards. It is obvious therefore, as pointed out by the author, that the search should continue since the reasons are many.

From a purely commercial standpoint, the aim of the industry must be to make more refrigeration available to more people. Accomplishment of this objective is not alone a matter of machine design and production. New developments in refrigerants must go hand-in-hand with progress in refrigeration machinery. Experience has shown that our industry is quick to take advantage of new developments. As proof, witness the transition from methyl chloride, carbon dioxide, sulfur dioxide, and ammonia to Freon-12 which has come to be known as the nation's No. 1 refrigerant. Freon-22, recently released commercially, may well become No. 2. In spite of a somewhat lower cycle efficiency than ammonia, methyl chloride, and Freon-12, it has compressor displacement characteristics which cannot be ignored for either high temperature work or low temperature work.

Manufacturers cannot economically supply a variety of designs each specifically for a refrigerant best suited for a given application. Those refrigerants of the future which have characteristics which will satisfy the greatest number of applications and yet are suitable for use in more or less standard machines will help our industry to grow. It is no secret that much "behind-the-scenes" research is in progress today, and our industry therefore can be confident that new and better refrigerants are a promise for the future.

H. D. Edwards (The Linde Air Products Company): I often wonder what this word "discussion" means. I found out long ago that it is very unwise to question Dr. Hainsworth's facts, because you are getting into hot water right away.

But I do think this is a wonderful resume of work that has been done in the past, but in a form that perhaps we common fellows can read and understand. I think that even if one were not interested in refrigerants and absorbents he would get a lot of pleasure out of reading Dr. Hainsworth's article.

If you are interested in refrigerants and absorbents I think one couldn't read this article without having that interest revived, and if you knew of a quick chemical you would look around and see if it would absorb something, and you might even start out looking for another.

It has been only in the last few years that the principles of design of absorbers and strippers as used in the chemical industry have been applied to the absorption refrigerating machine, and if you are laboring under the opinions that most of us gather by reading about them and hearing about them, I think you would find if you became interested in a modern design of absorption equipment that its operating

Appendix

Refrigerant	*Absorbent*
Methyl alcohol	Ethylene glycol
" "	Diethylene triamine
" "	Triethylene tetramine
" "	Hydroxyethylethylene diamine
" "	Diethylene glycol
" "	Ethylene glycol-Lithium bromide
" "	Lithium bromide
" "	Lithium chloride
" "	Zinc bromide
" "	Zinc chloride
" "	Zinc iodide
Ethyl alcohol	Ethylene glycol
" "	Diethylene triamine
" "	Triethylene tetramine
" "	Hydroxyethylethylene diamine
" "	Diethylene glycol
" "	Lithium bromide
" "	Lithium chloride
" "	Zinc bromide
" "	Zinc chloride
" "	Zinc iodide
" "	Lithium bromide & Zinc bromide
n-Propyl alcohol	Ethylene glycol
" "	Diamylamine
" "	Diethylene triamine
" "	Dipropylene triamine
" "	Triethylene tetramine
" "	Hydroxyethylethylene diamine
" "	n-Butylmonoethanol amine
" "	Dimethoxytetraethylene glycol
" "	Diethylene glycol
" "	Lithium bromide
" "	Zinc bromide
" "	Zinc chloride
" "	Zinc iodide
" "	Lithium bromide & Zinc bromide
" "	1, 2, 3—Tribromopropane
Methylene bromide	Dimethoxytetraethylene glycol
α β Dibromoethylene	" "
Ethylene dibromide	" "
Ethylene chlorobromide	" "
Ethylene dichloride	" "
Ethylene dichloride	Phorone
Trichloroethylene	Dimethoxytetraethylene glycol
1, 1, 2-Trichlorethane	Dimethoxytetraethylene glycol
"	Triglycol dichloride
"	Diethylene glycol diacetate
"	Dibutyl phthalate
"	Tributyl phosphate
"	Acetonyl acetate
Triethylamine	Dimethoxytetraethylene glycol
Acetylene tetrachloride	" "
Propylene dibromide	" "
Propylene dichloride	" "
Monochlorobutenes	" "
Methalyl chloride	" "
Ethylene chlorhydrin	" "
Ethylene chlorhydrin	Triglycol dichloride
Propylene chlorhydrin	Dimethoxytetraethylene glycol
Nitroethane	" "
1-Chloro-1-nitroethane	" "
1, 1-Dichloro-1-nitroethane	" "
1, 1-Dichloro-1-nitroethane	Dibutyl phthalate
Ethylene diamine	Ethylene glycol
n-Butylamine	Triethyl phosphate
n-Amylamine	Ethylene glycol
"	Zinc bromide
Triethylamine	n-Butylmonoethanol amine
Tetrachlorethylene	Dimethoxytetraethylene glycol
Morpholine	Ethylene glycol
Morpholine	Trimethyl phosphate
n-Methyl morpholine	Ethylene glycol
n-Methyl morpholine	Dimethoxytetraethylene glycol
Diethyl cellosolve	Acetylene tetrabromide
Diethyl cellosolve	Polychloropropane
Diethyl cellosolve	Triglycol dichloride
Methyl cellosolve	Diethylene triamine
Methyl cellosolve	Dimethoxytetraethylene glycol
Methyl cellosolve	Triglycol dichloride
Sym. dichloromethyl ether	Dimethoxytetraethylene glycol
Sym. dichloromethyl ether	Diethylene glycol diacetate
Ethyl carbonate	Dibutyl phthalate
Ethyl carbonate	Trimethyl phosphate
n-Propyl alcohol	Ethylene glycol & Zinc bromide
Ethylene diamine	Ethylene glycol & Lithium bromide
n-Amylamine	Ethylene glycol & Lithium bromide
Water	Ethylene glycol
"	Propylene glycol
"	Diethylene triamine
"	Dipropylene Triamine

"	Triethylene tetramine
"	Hydroxyethylethylene diamine
"	Triethanol amine
"	Dimethoxytetraethylene glycol
"	Diethylene glycol
"	Trimethyl phosphate
"	Triethyl phosphate
"	Ethylene glycol & Lithium bromide
"	Lithium bromide
"	Lithium chloride
"	Lithium iodide
"	Zinc bromide
"	Zinc iodide
"	Potassium acetate & Potassium formate
"	Potassium acetate & Potassium formate
"	Calcium nitrate & Calcium chloride
"	Zinc chloride & KCl & LiCl added
"	Zinc chloride & Calcium chloride
"	Phosphoric acid
"	Lithium bromide & Lithium iodide
"	Glycerol
"	2, Amino—1, Butane
"	Triethylene glycol
"	Lithium acetate
"	Tetraethylene pentamine
"	Zinc bromide
Ethyl propionate	Zinc bromide
Methyl n-butyrate	Alkazene 36
Carbon tetrachloride	Alkazene 36
Isopropyl bromide	Alkazene 36
Trichloroethylene	Alkazene 42
Carbon tetrachloride	Diphenyl
Carbon tetrachloride	Phosphen 2
Carbon tetrachloride	Ethyl acetoacetate
Methylene chloride	Dimethoxytetraethylene glycol
" "	Triacetin
" "	Benzaldehyde
" "	Bromnaphthalene
" "	o-Nitrotoluene
" "	1, 2, 4, Trichlorobenzene
" "	1, Chloronaphthalene
" "	1, Bromonaphthalene
" "	Nitrobenzene
" "	Guaiacol
" "	Safrol
" "	Eugenol
" "	Terpenial
" "	p-Chlorphenol
" "	Anethol
" "	Diphenyl ether
" "	2, 4, Dichloro anisol
" "	o-Nitroanisol
" "	Nitro cresyl ethyl ether
" "	p-Methyl hexalin
" "	1, 3, Dichlorhydrin
" "	o-Nitrophenatole
" "	Benzaldehyde
" "	Acetophenone
" "	Cinnamyl aldehyde
" "	Heptaldehyde
" "	Salicyl aldehyde
" "	Aniline
" "	Diethyl aniline
" "	p-Diethyl toluidine
" "	Benzyl aniline
" "	o-Anisidine
" "	Ethylene glycol diacetate
" "	Phenyl acetate
" "	Benzyl acetate
" "	Ethyl benzoate
" "	Triacetine
" "	Ethyl heptylate
" "	Amyl valeriate
" "	Ethyl palmitate
" "	Diethyl sulfate
" "	Triphenyl phosphite
" "	Trio-o-cresyl phosphate
" "	Sym. dichloroisopropyl acetate
" "	2, 4, Dichlorophenyl acetate
" "	Sym. trichlorophenyl acetate
" "	Methyl salicylate
" "	Benzoyl chloride
" "	Methoxytriglycol acetate
Methylene chloride	Diethylene glycol
Chloroform	" "
Ethyl iodide	" "
Propyl bromide	Dimethoxy tetraethylene glycol
Trichlorethane	Tetrachlororesorcinol
1-Methyl isopentyl amine	"
Pyradine	

difficulties would be very much less, its cost well in line with any other type of system, and its efficiency pretty high.

We are I think very much indebted to Dr. Hainsworth for this summation and presentation, particularly his verbal presentation, and it is particularly apropos at this time, because perhaps this will be one of the fields that will help in our postwar troubles just a little bit.

Predicts Large Volume Of Industrial Building

In the first three to five postwar years the United States will experience the greatest volume of industrial building and greatest employment of construction workers of any similar peacetime period, S. M. Rust, Jr., vice president of The Rust Engineering Co., of Pittsburgh, Pa., and Birmingham, Ala., predicted recently.

This building will start in large volume immediately after war restrictions are relaxed, as industries rush preparations to skim the cream from huge pent-up postwar markets, Mr. Rust said.

Thousands of inquiries and orders for designs of new plants and alterations of existing plants have been, and are being, received by engineering firms throughout the country, Mr. Rust said, providing a solid, factual basis for his assertions.

The type of designs most usually sought, he further commented, are "master plans"—not for single structures, but covering all the building and development contemplated by the firms concerned for five or more years.

"Contrary to popular belief," Mr. Rust stated, "our tremendous construction of war plants will not halt or make unnecessary extensive postwar industrial building.

"The effect will be just the opposite. The huge competitive potentialities of these plants will force industrial management to modernize to the limit and to build many entirely new plants in order to stay in the running.

"Existing plants, ranging from thousands built before or during World War I to many built for armament purposes in this war, will no more be able to compete with postwar factories specifically designed for their products than the bow and arrow with the machine gun. Such plants are doomed by the laws of economics."