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Refrigerants and Absorbents*

Part I

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In this informal survey, Dr. Hainsworth, past president of The American Society of Refrigerating Engineers, reviews some of the more important refrigerant and absorbent developments. In the second part of the paper, to be published next month, he continues the discussion of absorbents and presents some interesting speculations as to new refrigerants of the future.

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OCCASIONALLY it is good for one's perspective and peace of mind to rediscover some of the fundamentals underlying the pursuit of our daily bread—the refrigeration industry. It was in such a contemplative mood that I was reminded that Mr. Carnot is the author of a cycle which has been a goal post in our game for a good many years. With the aid of thermodynamics (the word must be used at least once in this paper to give it character) it can be shown that the upper limits of performance when converting heat into work is a function of the absolute temperature at which the changes occur within the cycle. The device used for this conversion is a heat engine. To convert work into useful refrigeration effect a heat pump is used. Its theoretical performance may also be defined as a function of absolute temperatures.

In the refrigeration industry the heat engine and heat pump may be separated or combined. When separated the heat engine is the power plant and the heat pump is the compression refrigerating machine. When combined the system is generally an absorption refrigeration unit. The generator and absorber may be likened to the heat engine, the condenser and evaporator to the heat pump.

The working tools which we have available to convert our paper work into actual accomplishment have many limitations which in the aggregate for many applications may cut the overall performance to some 15 per cent of the Carnot Cycle performance. Our working tools are various power plant and refrigeration cycles; equipment of different types such as centrifugal, rotary and reciprocating compressors, absorption and ejector units; and finally, a variegated assortment of refrigerants and absorbents. As time goes on certain economically practical combinations of cycle, equipment, and refrigerant characteristics have been made in our efforts to advance the performance front in relation to Carnot's ideal. We seek new combinations. Based on experience, it has been found advisible to specialize, as no one combination can be equally suitable for two or more applications having such varied requirements as air conditioning, domestic refrigeration, low temperature refrigeration, industrial, commercial and residential installations, etc.

The study of refrigerants and absorbents constitutes a part of the search, and must also be specialized. Unfortunately for us, nature has camouflaged its store of refrigerants with a great variety of properties. New refrigerants suitable for use in a heat pump are extremely hard to discover. Other fluids such as water or mercury are used in the heat engine or power plant, to make available the necessary work. When the heat engine and heat pump are combined as in the absorption refrigeration unit, the problems of the research worker seeking new fluid combinations, as well as new cycles and equipment, are multiplied many fold. It is apparent that a study of refrigerants and absorbents cannot be isolated from consideration of the cycle and equipment available. Keeping this rather rambling background in mind, the purpose of this paper is to review some of the more important refrigerant and absorbent developments, and indulge in just a trace of speculation as to the future.

Early Developments

THE first refrigerant used in a continuous compression refrigeration machine was ether. Its use was based on a better understanding, reached about 1820, of the principles involved in the vaporization and liquefaction of a gas. The machine is described in British Patent 6662, issued to Jacob Perkins in 1834. One object was to save the refrigerant by using it over and over. He used a manually operated pump to compress the gas with a condenser worm, reduction valve, and purge, and an immersed evap-

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orator to cool brine. It was not until 1857 that Perkins' machine was used commercially, at which time refrigeration started on its time honored career in breweries and meat storage warehouses. Dr. Linde, in 1873, first introduced the ammonia compression machine. This was followed three years later by the use of sulfur dioxide in Pictet's refrigeration machine.

The first absorption refrigeration system which we would recognize as such was produced by Edmund Carre's brother Ferdinand, about 1815. This was an intermittent machine, using ammonia as the refrigerant and water absorbent. The modern counterpart is the Crosley Icy Ball, with its two balls connected by a piece of pipe. In its simplest form all that is necessary to obtain refrigeration is to place one of the balls on a stove for a while—then pick up the unit and place the other ball in a refrigerator, thereby producing part-time refrigeration. It was natural that the first refrigerant to be used in a practical absorption refrigeration machine to produce continuous refrigeration was ammonia. Ferdinand Carre was the inventor and his U. S. Patent No. 30201 was filed in 1858 and granted October 2, 1860. Its commercial importance was established when two of the units were brought from France to the Southern States during the Civil War emergency, when the ice supply was cut off from the North. Carre's basic idea was to use the affinity of water for ammonia by absorbing the gas as it comes from the evaporator, then using a suction pump to transfer the liquid to another vessel where the application of heat causes the liberation of ammonia gas at higher pressures. Thus this absorption machine created a suction and discharge condition of the refrigerant ammonia corresponding to the high and low side of Perkins' compressor, and the remaining components of the system were basically the same. Since the system was continuous in operation the need for manual labor was eliminated. It was recognized early in the game that the ammonia absorption machine was particularly well adapted to the production of low temperatures and required low-cost energy.

As soon as the several types of vapor refrigeration systems attained some commercial success, many refrigerant variations were tried. Pictet's mixture of SO_2 and CO_2 was first used in 1884. Another mixture, ethyl ether sulfur dioxide, was tried. Methyl chloride, ethyl chloride and straight hydrocarbons such as propane and isobutane were shortly added to the list. It soon became apparent that many properties other than the vapor pressure temperature relationship and latent heats were of importance in the selection of a refrigerant. After some years of experience one after another of the fluids was eliminated from the long list until there were only four outstanding refrigerants left, namely, ammonia, carbon dioxide, methyl chloride and sulfur dioxide. These four horsemen of the industry carried the load during a relatively long period of healthy growth.

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During this period basic refrigeration equipment was improved. The compression systems with their high side and low side floats and improved expansion valves and hermetic sealing evolved along one line into the household units which first appeared in volume about 1923, and along other lines into many commercial and industrial applications. The large ammonia absorption systems went into a decline, although there remained special applications which continued to justify new installations. Evolution of the absorption machine was along the line of smaller units with many ingenious devices tried in an effort to eliminate the mechanical solution pump. During this period there was very little progress in the refrigerant art.

The seed of a new system was planted in 1900 by Geppert when he proposed the use of air as an agent for equalizing the pressure between the refrigerant on the high side and low side, with a fan to promote gas circulation within the system. It was not until 1925, when Platen and Munters invented other internal means for producing circulation of the fluids, that the system became practical. They used a coffee percolator type of pump to circulate the solution and used hydrogen as an agent for causing circulation of the gas by gravity and for equalizing the pressure. The Electrolux domestic refrigerators, operated by gas, kerosene or electric heat, attained industrial success based on these inventions.

Other systems using solid absorbents and adsorbents in an intermittent cycle were tried with varying degrees of success. The refrigerant was mainly ammonia, as in the Ice-O-Later, wherein calcium chloride was the absorbing agent, and in the Faraday with strontium chloride absorbent. As in the case of absorption of ammonia by water, these solid absorbents form weak, thermally reversible chemical compounds with ammonia. Some refrigerated car installations using silica gel as an adsorbent for sulfur dioxide were made. Here the refrigant is used in combination with a material having pores which are almost molecular in size, thereby creating an enormous surface on which the refrigerant is adsorbed, as contrasted with the chemical absorption.

Refrigerants

THE story of refrigerants is so intimately associated with the scientific and industrial progress that it is impossible to divorce one from the other. Creation of the refrigerant depends on science. Its commercial life depends on industry. New industry cycles are continually in the making. Fundamental scientific studies of the behavior of matter within a few tenths of absolute zero have revealed such strange phenomena as practically zero electrical resistance in metals; a current induced in a metallic ring can still be detected long after the inductive source is removed; furthermore, specific heats approach zero. Determination of such facts is the scientific objective.

To attain these temperatures scientists have used cascade systems wherein liquid air, liquid hydrogen and liquid helium (B.P. —452°F.) are the refrigerants used in series. It is interesting to note that the latent heat of evaporation also approaches zero at these low temperatures, therefore vaporization of liquid helium becomes less effective as absolute zero is approached. There is one property that increases as the temperature is lowered in this range. The final stage of refrigeration depends on the magnetic susceptibility of gado-

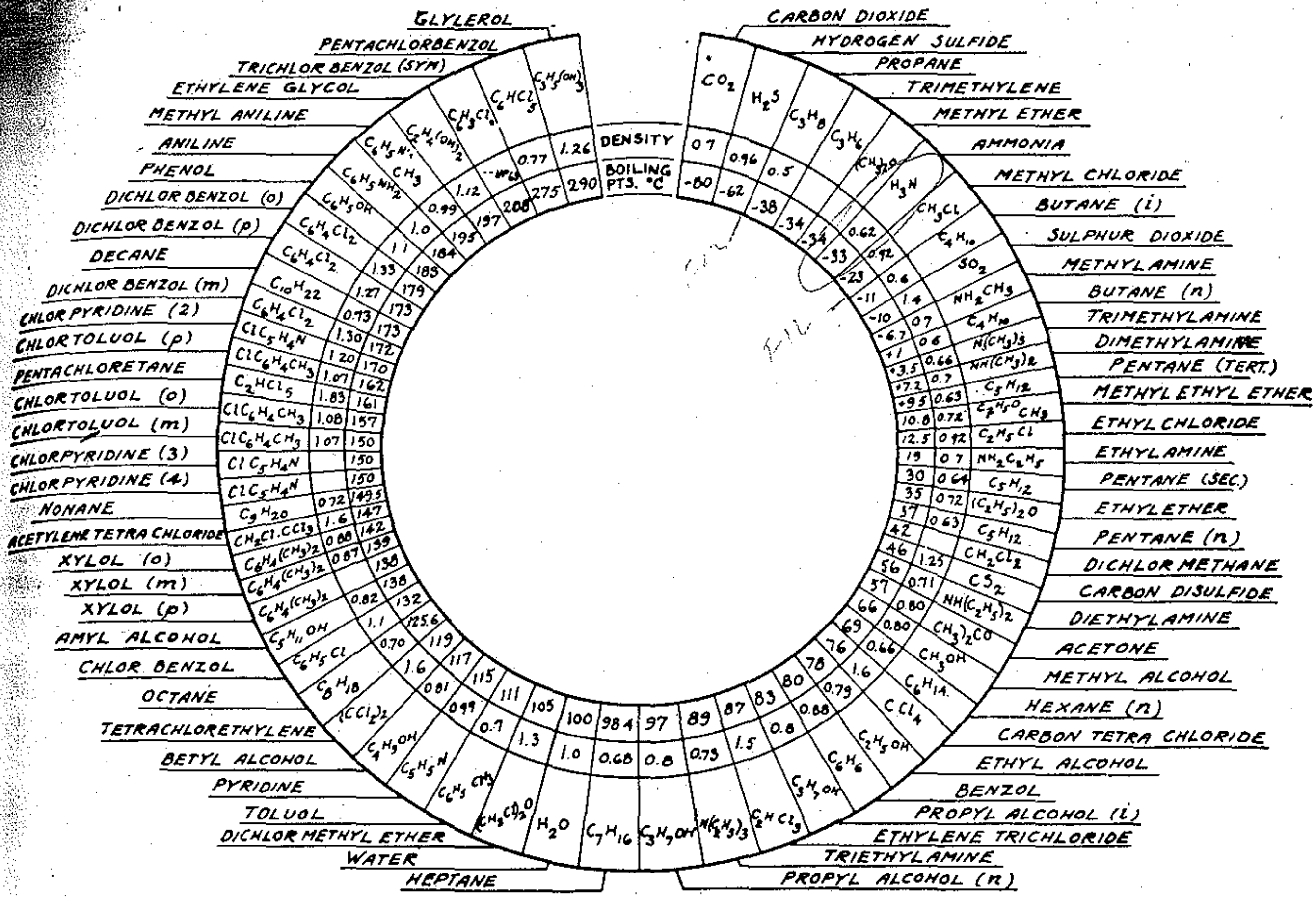

Fig. 1. Refrigerant-absorbent chart.

linium sulfate. This substance or one having similar properties may, therefore, be called a refrigerant when its "heat of demagnetization" is used to produce lower temperatures than are attainable by vaporizing liquid helium under reduced pressures. This low temperature research and development of special techniques is the forerunner of wide commercial usage which has already been extended to temperatures lower than —100°F. in many fields, as well as the commercial production of liquid air and liquid oxygen at temperatures in the neighborhood of —300°F. In the latter case, the air being liquefied is its own refrigerant. It is interesting to note that hydrocarbon refrigerants, which have been used extensively in the oil industry for some time, are again coming into their own for a variety of special extremely low temperature applications. These include ethane, ethylene, propane, and even nitrous oxide, with its very low triple point, is being considered for this work. The pressure level is one important factor. For example, the vapor pressure of ethylene is a little above atmospheric at —150°F., thereby avoiding infiltration of air in case of small leaks. But we are getting ahead of our story, let's go back to the early days of air conditioning.

About 1919, Mr. Willis Carrier decided to see what could be done with centrifugal compressors for air conditioning work. No available refrigerants were suitable. It was desirable to have the boiling point of the refrigerant above normal atmospheric temperatures with fairly large volumetric displacement per ton of refrigeration. Ethyl chloride was considered but was found unsuitable.

The first refrigerant selected was dichlorethylene, $C_2H_2Cl_2$. This was the best fluid found after a search through the chemical dictionary for a non-toxic, non-corrosive liquid with a boiling point slightly above atmospheric pressure. The next difficulty he ran into was that it was not manufactured in this country, but it was finally located abroad where it was produced as a cleaning fluid. The general trade name was "Dielene."

The next refrigerant investigated was methylene chloride. By 1926, sufficient market had been developed through the introduction of centrifugal machines to warrant the building of a plant in America for the production of this substitute for Dielene. In 1927, after suitable arrangements had been made for its commercial production, methylene chloride was substituted for Dielene. Carrier later called this Carrene. The boiling point of methylene chloride, or Carrene #1, was about 20° lower than that of Dielene and was better suited for machines of larger capacity. At the same time it could be used in the Dielene machines without redesign. Patent No. 1,781,051, dated November 11, 1930, was granted to Willis Carrier for his use of methylene chloride as a refrigerant.

A few years later a new series of refrigerants became available and the Carrier machines were redesigned for use with one of the new fluids which Carrier called Carrene #2. This new series is the Freon group.

Freon is a registered trademark which somewhere in its history was influenced by the Latin word *frio*, meaning cold. The Freon refrigerants were first described in detail in the May, 1930 issue of *Industrial and Engineering Chemistry* and later in reissue Patent No. 19,265, granted August 7, 1934, to Thomas Midgley, Albert Henne and Robert McNary. This is but one of a number of patents on the Freon series. These refrigerants are based on chlorine and fluorine substitutions for hydrogen in low molecular aliphatic hydrocarbons such as methane and ethane.

The story goes that in a somewhat casual telephone conversation Dr. Kettering mentioned to Dr. Midgley that the refrigeration industry needed a low boiling refrigerant which is non-toxic and noninflammable. Midgley picked up the problem and after exhausting the Critical Tables tried a different approach through Langmuir's Periodic Tables where the elements are systematically arranged and related properties are more readily apparent. It became evident that certain fluorine compounds should have characteristics similar to other refrigerants in use with the added desirable properties of less toxicity and flammability.

One of the compounds Midgley had in mind was dichlorodifluoromethane. The compound had been made in an organic chemistry laboratory some time earlier, but its properties were unknown, except as predicted, so it was decided that it should be synthesized. A few cubic centimeters were obtained from antimony trifluoride and carbon tetrachloride and it was not long before an unconcerned guinea pig demonstrated that the hoped-for non-toxic properties were a reality. Other hydrocarbon combinations of chlorine and fluorine were made. In general, the boiling point increases with the complexity of the molecule. In the Freon series the inflammability decreases with the increase in the number of halogen atoms and the toxicity, ranging from non-toxic to moderate toxicity, is affected by both the complexity and number of halogen substitutions. These relationships are clearly set forth in the patents. Here and there an outstanding molecular combination is obtained, and this is in part the reason for the Freon series (see Table 1). Other compounds in this chemical series may be added to the list as the demand in new refrigeration fields increases.

The orderly change in properties within the series makes it possible to select refrigerants well adapted to a wide variety of mechanical and temperature conditions. F-22 with its boiling point of —41.4°F. has just recently been added to the commercially available list. It is well adapted to use in frozen food cabinets which are so prominent in our postwar discussions.

Table 1. The Freons

	B.P., °F.		
Freon-113	117.5	$C_2Cl_3F_3$	Trichlorotrifluoroethane
Freon-11	74.7	CCl_3F	Trichloromonofluoromethane
Freon-21	48.1	$CHCl_2F$	Dichloromonofluoromethane
Freon-114	38.4	$C_2Cl_2F_4$	Dichlorotetrafluoroethane
Freon-12	—21.6	CCl_2F_2	Dichlorodifluoromethane
Freon-22	—41.4	$CHClF_2$	Monochlorodifluoromethane

In contrast to the seemingly casual manner in which the search for the new Freon refrigerants was started, the results have been of vast importance to the expansion of the refrigeration industry during the past decade.

Absorbents

GRADUALLY the search for new refrigerants extended deeper into the field of organic chemistry, especially in the endeavor to find cuitable combinations for absorption systems. A paper presented at the Annual Meeting of The American Society of Refrigerating Engineers, December 5, 1928, by Dr. R. S. Taylor, contains a notable summary of one phase of this work. The refrigerant-absorbent chart, as given in the paper, is reproduced in Fig. 1.

In selecting favorable combinations the refrigerants are naturally the low boiling compounds and the absorbents the high boiling compounds. The differential should be as great as possible, although this is by no means the determining characteristic.

A notable contribution to the refrigerant and absorbent art is the work of G. F. Zellhoeffer, M. J. Copley and C. S. Marvel, which was started in 1930. As a prelude to a discussion of their work on the theory of organic solutions let it be said that organic chemistry suffers from the mixed blessing of a tongue twisting nomenclature for the layman, including some of the longest names ever invented by man, which are at the same time surprisingly lucid to the chemist. As a refrigerating engineer my only reason for following the nomenclature in this paper is that I know of no alternative.

In an absorption refrigeration system a high degree of solubility of the refrigerant in the absorbent or solvent is desired. Any theory which sheds light on the reasons for some solvents being more effective than others is a helpful tool in the mind of the research chemist. Zellhoefer and his co-workers' scientific approach to the problem resulted in a practical working theory. In part it was concluded that in some fluids (refrigerants and absorbents) there were residual charges which tend to combine. The presence of the strongly electron-attracting halogen atoms on the carbon of one of the Freon refrigerants, for example, loosens the hydrogen and makes it available for coordination with an atom in the solvent. The solvent should contain a "donor" atom in the form of oxygen or nitrogen which becomes loosely bonded to the hydrogen of the refrigerant.

Applying this theory, many new compounds were synthesized and several thousand combinations investigated. The greater part of the investigation, as disclosed in numerous patents and articles in the American Chemical Society publications and REFRIGERATING ENGINEERING, dealt with organic absorbents for water, methylene chloride and the Freon refrigerants, especially dichloromonofluoromethane.

(The conclusion of Dr. Hainsworth's paper, continuing his discussion of absorbents, will appear in the September issue.)

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