Table 2 .... Thermal Stability of Fluorinated Refrigerants[21]

Refrigerant	Formula	Approx. Max. Temp for Continuous Exposure[a]	Decomposition Rate at 400 F in Steel Percent/Yr	Temp for First Trace of Decomposition in Quartz, F
113	CCl_2F-$CClF_2$	225	6	570
11	CCl_3F	225	2	840
12	CCl_2F_2	250	Less than 1	1000
114	$CClF_2$-$CClF_2$	250	1	—
22	$CHClF_2$	275-300[b]	—	550
13	$CClF_3$	Over 300	—	—

[a] In the presence of oil, steel and copper, but not including motor insulation. Based on sealed-tube test data from E. I. duPont deNemours & Co., Inc.
[b] See Reference 27.

chemical formula. In the third column are listed the approximate maximum temperatures recommended for continuous exposure in the presence of oil, steel, and copper. This condition would be representative of refrigeration equipment designed to operate for many years. The recommended temperatures are based on laboratory testing. Field experience has been in substantial agreement although there is some indication that these limits are a little conservative. It is possible that hot gas discharge temperatures higher than those shown could be tolerated, especially if the oil concentration is low.

Some actual observed decomposition rates at 400 F for the refrigerant alone in steel are shown in the fourth column. They are based on exposures of six days and disregard a higher rate indicated on initial exposure. There is considerable difference in the effect of various metals on the decomposition rate. For example, with Refrigerant 11 at 480 F in steel, the initial rate was 120 and the final rate was 36 percent per year. However, in Inconel the initial decomposition rate was 3 percent per year and in platinum it was less than 1 percent per year. The tendency of metals to promote thermal decomposition of the fluorinated refrigerants is in the following general order:

Least decomposition: Inconel < 18-8 stainless steel < nickel < copper < 1340 steel < aluminum < bronze < brass < silver: most decomposition.

This order is only approximate and exceptions may be found for individual fluorinated refrigerants or for special conditions of use. Most of the commonly used construction metals—such as steel, cast iron, brass, copper, tin, lead, aluminum—can be used satisfactorily with the fluorinated refrigerants under normal conditions of use.

Magnesium alloys and aluminum containing more than 2 percent magnesium are not recommended for use in systems containing fluorinated refrigerants where water may be present.

Zinc is not recommended for use with Refrigerant 113. Experience with zinc and the other fluorinated refrigerants has been limited and no unusual reactivity has been observed. However, zinc is somewhat more chemically reactive than other common construction metals and, therefore, it would seem wise to avoid its use with the fluorinated refrigerants unless adequate testing is carried out.

In the last column, decomposition temperatures are illustrated for moderate conditions. No metals were present in these tests and the exposure time was 30 seconds. Refrigerant 13 was not included in the tests but other evidence indicates that it is substantially more stable than Refrigerant 12. The presence of hydrogen in the Refrigerant 22 molecule in place of one of the chlorine atoms in Refrigerant 12 decreases its thermal and alkaline stability but makes it less reactive with oil.

The thermal stability of the fluorinated refrigerants will probably be between the extremes illustrated in the table for a particular application.

b. Ammonia. Ammonia is a comparatively stable gas at ordinary temperatures[22] and, therefore, thermal stability is not a problem in ordinary refrigeration usage. Under conditions of high discharge temperatures, there may be a slow decomposition to form hydrogen and nitrogen. Glass does not affect the decomposition rate. Porcelain, pumice and metals such as iron, nickel and zinc increase the decomposition markedly. The effect of pressure is to decrease the dissociation into hydrogen and nitrogen.

c. Methyl Chloride. Under ordinary conditions, dry methyl chloride is stable toward heat. Methyl chloride may be used with iron, steel, copper, brass, etc., but not with aluminum, magnesium or zinc. The use of aluminum particularly should be avoided since dangerous, spontaneously flammable methyl aluminum compounds may be formed.

d. Other Refrigerants. Sulfur dioxide is thermally stable to very high temperatures. Hydrocarbons do not present stability problems in refrigeration use. Under suitable conditions of temperature and catalysis, they are thermally decomposed to form hydrocarbons of lower molecular weight. However, these conditions are beyond the range usually encountered in refrigeration.

2. *Chemical Reactivity.* A chemical reaction is one in which the identity of the materials involved is changed. Usually, but not necessarily, more than one material enters into the reaction. In general, refrigerants do not have much chemical reactivity. Of course, it is possible for a compound to be unreactive in a refrigerant system and yet have considerable reactivity under other conditions. Reactions of most interest in refrigeration probably include hydrolysis, oxidation and reduction, thermal decomposition, reaction with oil, and direct reaction with metals.

a. Fluorinated Refrigerants. The fluorinated refrigerants are chemically inert under conditions usually found in refrigerant systems. However, some of the less highly fluorinated members of this group will take part in chemical reactions to a certain extent especially at higher temperatures.

The reaction with water may cause hydrolysis and the formation of hydrochloric and hydrofluoric acids and carbon dioxide. Obviously, the formation of these products is not desirable in a refrigerant system and in ordinary usage this reaction is negligible. In a very wet system operating at abnormally high temperatures, some hydrolysis may occur. Typical hydrolysis rates for some halogenated refrigerants are given in Table 3.

With water alone at atmospheric pressure, the rate is too low to be determined by the analytical method used. When catalyzed by the presence of steel, the hydrolysis rates are detectable but still quite low. At saturation pressures and a higher temperature, the rates are further increased. The hydrolysis is directly dependent on the amount of water present. The basis for comparison in Table 3 is one liter (more than two pounds) of water. It is clear that the amount of refrigerant hydrolyzed in a year is very small when based on the amount of water actually present in a refrigerant system. It has been proposed[22] that, so long as moisture does not appear in liquid or solid form in the system, corrosion and deterioration of the refrigerant through hydrolysis will not proceed enough to be detectable in 10 to 20 years.

Whether or not hydrolysis of the refrigerant is a significant factor, experience has shown without question that refrigerant systems operate longer and better when they are as dry as possible and every effort should be made to keep them that way.

The possibility of chemical reaction between the fluorinated refrigerant and lubricating oil is of direct concern in refrigerant systems. Direct reaction does occur between Refrigerant 12 and oil in the presence of a steel strip to form hydrochloric acid, Refrigerant 22, and other products as shown by Spauschus and Doderer.[26] Considerable differences are found with different refrigerants and different oils. Kvalnes and Parmelee[6] have studied the decomposition of Refrigerants 12 and 22 in sealed glass tubes. The amount of cleavage was measured by the amount of chloride ion found at the end of the test period. Temperature, lubricant and refrigerant type appeared to be the important controlling factors in the formation of the chloride ion. At temperatures of 250 F neither refrigerant decomposed significantly (see Fig. 1). At 300 F the decomposition of Refrigerant 12 rose

Table 3 .... Rate of Hydrolysis in Water[21]

Grams per (Liter of Water) (Year)

Refrigerant	Formula	1 Atm. Pressure 86 F		Saturation Pressure 122 F
		Water Alone	With Steel	With Steel
113	CCl_2FCClF_2	<0.005	50	40
11	CCl_3F	<0.005	10	28
12	CCl_2F_2	<0.005	1	10
21	$CHCl_2F$	<0.01	5	9
114	$CClF_2$-$CClF_2$	<0.005	1	3
22	$CHClF_2$	<0.01	0.1	

significantly while Refrigerant 22 decomposed less than 0.1% in 400 days (Figs. 1 and 2). Again, the tests showed that the amount of reaction of Refrigerant 12 was dependent upon the type of lubricant. Four times as much reaction occurred with one lubricant as with another.

The chemical reactivity of the various fluorinated refrigerants in a general way follows the same order in different types of reactions. Thus, a refrigerant with a low hydrolysis rate will probably have a low reaction rate with oil and, also, it is likely to show up well in thermal stability, if devoid of hydrogen, and to exhibit good chemical stability in general.

b. Ammonia. The principal chemical reactivity of ammonia involves its water solution. Water reacts with ammonia to form ammonium hydroxide. If the hydroxide is formed it can react with some of the components of oil to give ammonium soaps leading to oil deterioration and the formation of sludge. Ammonium hydroxide reacts rapidly with copper and copper alloys. Thus, ammonia can be used with these metals only in systems from which water is rigidly excluded. There is some evidence that the presence of air or oxygen accelerates the reactivity of ammonia in refrigeration systems, even in the absence of water.

c. Methyl Chloride. Methyl chloride was used successfully as a refrigerant for a number of years in spite of a rather high degree of chemical reactivity. It apparently does not react directly with oil but in contact with metals can be decomposed to form hydrochloric acid.[9] Hydrolysis (see Table 3) gives methyl alcohol and hydrochloric acid. It is flammable, indicating reactivity with oxygen when ignited. Methyl chloride can react directly with certain metals such as magnesium and aluminum. The product of the reaction with magnesium is used in chemical synthesis to introduce the methyl group into organic compounds. The reaction with aluminum forms spontaneously flammable products.

d. Other Refrigerants. Sulfur dioxide as a liquid is an active agent in the refining of oils and will react with many of the hydrocarbons and other of the compounds found therein. Thus highly refined lubricating oils must be used with sulfur dioxide just as is the case with many of the fluorocarbon refrigerants. Sulfur dioxide is also a good electrolytic solvent and is corrosive to metals when even limited amounts of water are present. In addition, sulfur dioxide is an excellent solvent for, or is reactive with, many of the materials which are presently used as motor insulation. The above problems as well as the irritating nature of the gas presently limits the usefulness of this thermally stable refrigerant.

The hydrocarbon refrigerants are flammable and react rapidly with oxygen when ignited. Although reactive under special conditions and used widely in chemical manufacture, the chemical reactivity of the hydrocarbons (other than flammability) is usually not a problem in refrigeration service.

Lubricants

The physical properties of the lubricant must be carefully considered, and the selection for equipment made on the basis of desired properties. These factors are covered in Chapter 50. In addition, lubricant selection is based on the type of refrigerant to be used, as well as system design, temperature and pressure. Consideration should also be given to its contact with the materials of construction, because its behavior is dependent to a great extent on other materials in the system. Specifications adapted from those for motor oils are not a guarantee for stability in operation and resistance to copper plating.[7]

In this section it will be the purpose to consider the lubricant

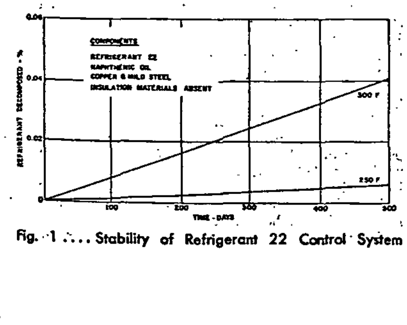

Fig. 1 .... Stability of Refrigerant 22 Control System

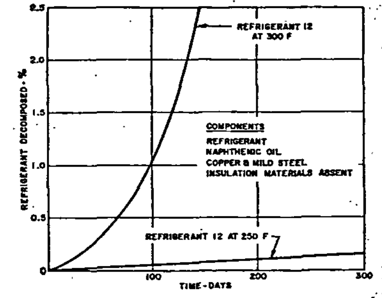

Fig. 2 .... Stability of Refrigerant 12 Control Systems at 250 F and 300 F

from the standpoint of its stability, or the tendency of its decomposition products to contribute to contamination of a system. The fundamental work of Steinle,[24,25] Elsey, Flowers and Kelley[8] and others has contributed greatly to the understanding of the primary characteristics required of a refrigeration grade oil. Usually the oil refrigerant breakdown is started by traces of air and moisture in the system as well as the catalytic action of steel, copper, and other materials of construction.

1. *Stability.* A wide variety of petroleum based lubricating oils have been used over the years with varying success in refrigerant systems. In general, during recent years, the usage has been primarily confined to low viscosity index naphthenic base oils due to their reduced tendency to separate wax from oil refrigerant mixtures at low operating temperatures. Naphthenic base oils have a low wax content and are usually further dewaxed. These oils are usually refined to a pale yellow color but ordinarily are not refined to the point where they are water-white, because this seems to reduce the general stability of the oil and in some cases reduces the lubricating qualities. Generally, pale oil has less stability to atmospheric oxygen in the system but when oleoresins and sulfur are kept sufficiently low the tendency of the oil to deposit copper and react chemically with the refrigerant is kept at a minimum.

The paraffin base oils have a high viscosity index (see Chapter 50). They have more wax and they are much more stable to high temperatures. Because of the wax content, they are not used for low temperature refrigeration applications.

Carbonaceous sludges due to the thermal decomposition of the organic materials of the system are frequently found in refrigerating units. Of particular interest, in this regard, are those formed by the interaction of the lubricating oil and the refrigerant. Philipp and Tiffany[23] developed a procedure whereby a solution of sulfur dioxide in oil is sealed in an air-free glass tube and stored at 500 F. The rate at which the oil darkens is taken as an indication of the stability of the oil towards the refrigerant. With slight modification of this procedure Steinle[24] and Elsey, Flowers and Kelley[8] studied the behavior of refrigerating oils with various refrigerants. Under equivalent conditions it was found that some oils are more stable towards refrigerants than others. On the other hand, it was also found that some refrigerants are more reactive with oils than others. In cases where significant reactivity occurred, acids were frequently formed in addition to sludges. Again, increased temperature accelerated the decomposition of the oil. These investigators found excellent correlation between unit performance and sealed tube tests. Elsey, Flowers, and Kelley found that sludging occurs when the oil loses hydrogen which combines with the chlorine in the halogenated hydrocarbon to form hydrogen chloride. Those halocarbons having the greatest number of chlorine atoms in the molecule were the most reactive. These oil sludges are related to the waxes which at times precipitate out of the refrigerant to clog the orifice of the refrigerant metering device. It has been noticed that the darker a used oil has become the higher its floc point may be.

With any refrigerant it is therefore necessary to choose the proper lubricant and to design for the lowest possible operating