

REFRIGERANT SYSTEM CHEMISTRY

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GOOD understanding of the chemical interactions of the refrigerant, lubricant, and materials in a refrigeration system is necessary for designing systems that are reliable and have a long service life. This chapter covers the chemical aspects of both old refrigerants and new, environmentally acceptable refrigerants. Physical aspects such as measurement and contaminant control (including moisture) are discussed in [Chapter 6](#). Physical properties of lubricants are discussed in [Chapter 7](#).

CHEMICAL EVALUATION TECHNIQUES

Chemical problems can often be attributed to inadequate testing of a new material, improper application of a previously tested material, or inadvertent introduction of contaminants into the system. Three techniques are used to chemically evaluate materials: (1) sealed tube material tests, (2) component tests, and (3) system tests.

Sealed Tube Material Tests

The glass sealed tube test, as described by ASHRAE *Standard 97*, is widely used to assess the stability of refrigerant system materials. It is also used to identify chemical reactions that are likely to occur in operating units.

Generally, glass tubes are charged with refrigerant, oil, metal strips, and other materials to be tested. The tubes are then sealed and aged at elevated temperatures for a specified time. The tubes are inspected for color and appearance and compared to control tubes that are processed identically to the specimen tubes, but might contain a reference material rather than the test material. The contents of the tubes can be analyzed for changes in the test materials by methods such as gas chromatography, ion chromatography, liquid chromatography, infrared spectroscopy, and specific ion electrode. Wet methods, such as total acid number analysis, are also used.

The sealed tube test was originally designed to compare lubricants, but it is effective in testing other materials as well. For example, Huttenlocher (1972) evaluated zinc die castings, Guy et al. (1992) reported on the compatibilities of motor insulation materials and elastomers, and Mays (1962) studied the decomposition of R-22 in the presence of 4A-type molecular sieve desiccants.

Although the sealed tube is very useful, it has some disadvantages. Because chemical reactions likely to occur in a refrigeration system are greatly magnified, results can be misinterpreted. Also, reactions in which mechanical energy plays a role (e.g., in a failing bearing) are not easily studied in a static sealed tube.

The sealed tube test, in spite of its proven utility, is only a screening tool and not a full simulation of a refrigeration system. Sealed tube tests alone should not be used to predict field behavior. Material selection for refrigerant systems requires follow-up with component or system tests or both.

Component Tests

Component tests carry material evaluations a step beyond sealed tube tests; materials are tested not only in the proper environment, but also under dynamic conditions. Motorette (enameled wire, ground insulation, and other motor materials assembled into a simulated motor) tests, used to evaluate hermetic motor insulation, and described in Underwriters Laboratories (UL) *Standard 984*, are a good example of this type of test. Component tests are conducted in large pressure vessels or autoclaves in the presence of a lubricant and a refrigerant. Unlike sealed tube tests, in which temperature and pressure are the only means of accelerating the aging process, autoclave tests can include external stresses that may accelerate the phenomena likely to occur in an operating system. These stresses can include mechanical vibration, on-off electrical voltages, and refrigerant liquid floodback.

System Tests

System tests can be divided into two major categories:

- Testing a sufficient number of systems under a broad spectrum of operating conditions to obtain a good statistical reference base. Failure rates of units containing the new materials can be compared to those of units containing proven materials.
- Testing under well-controlled conditions. Temperatures, pressures, and other operating conditions are continuously monitored. Chemical analysis of the refrigerant and lubricant is done before, during, and after the test.

In most cases, the tests are conducted under severe operating conditions to obtain results quickly. Analyzing the lubricant and refrigerant samples during the test and inspecting the components after teardown can yield information on (1) the nature and rate of chemical reactions taking place in the system, (2) the products formed by these reactions, and (3) possible effects on system life and performance. Accurate interpretation of these data determines system operating limits that keep chemical reactions at an acceptable level.

REFRIGERANTS

Environmental Acceptability

The common chlorine-containing refrigerants contribute to the depletion of the ozone layer. The ozone depletion potential (ODP) of a material is a measure of its ability to destroy stratospheric ozone.

Halocarbon refrigerants also contribute to global warming and are considered greenhouse gases. The global warming potential (GWP) of a greenhouse gas is an index describing its relative ability to trap radiant energy. This index is based on carbon dioxide, which has a very long atmospheric lifetime. The GWP, therefore, is connected to a particular time scale, for example 100 or 500 years. Appliances using a given refrigerant also produce indirect (energy-related) emissions that contribute to global warming; this indirect

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effect may be much larger than the direct effect of the refrigerants. The total equivalent warming impact (TEWI) of an appliance is based on the direct warming potential of the refrigerant and the indirect effect of the energy used by the appliance.

Environmentally preferred refrigerants (1) have low or zero ODP, (2) provide good system efficiency, and (3) have low GWP. Hydrogen-containing compounds such as the hydrochlorofluorocarbon HCFC-22 or the hydrofluorocarbon HFC-134a have shorter atmospheric lifetimes than chlorofluorocarbons (CFCs) because they are largely destroyed in the lower atmosphere by reactions with OH radicals, resulting in lower ODP and GWP values.

Tables 1 and 2 show the boiling points, atmospheric lifetimes, ODPs, GWPs, and flammability of new refrigerants and the refrigerants being replaced. The ODP values have been established through the Montreal Protocol and are unlikely to change. ODP values calculated using the latest scientific information are sometimes lower but are not used for regulatory purposes. Because HFCs do not contain chlorine atoms, their ODP values would be essentially zero (Ravishankara et al. 1994). The lifetimes and GWPs were last reviewed by the International Panel on Climate Change (IPCC) in 1995 and are subject to review in the future.

Compositional Groups

Chlorofluorocarbons. CFC refrigerants such as R-12, R-11, R-114, and R-115 have been used extensively in the air-conditioning and refrigeration industries. Because of their chlorine content, these materials have nonzero ODP values. The Montreal Protocol, which governs the elimination of ozone-depleting substances, was strengthened at the London meeting in 1990 and confirmed at the Copenhagen meeting in 1992. In accordance with this international

agreement, production of CFCs in industrialized countries was totally phased out as of January 1, 1996. Production in developing countries will be phased out in 2010.

Hydrochlorofluorocarbons. HCFC refrigerants such as R-22 and R-123 have shorter atmospheric lifetimes (and lower ODP values) than CFCs. Nevertheless, the Montreal Protocol limited production of HCFCs beginning January 1, 1996, by placing a cap on consumption equal to 2.8% of the 1989 ODP-weighted consumption of CFCs plus the 1989 ODP-weighted consumption of HCFCs. It will be followed by a 35% reduction by January 1, 2004, a 65% reduction by January 1, 2010, a 90% reduction by January 1, 2015, a 99.5% reduction by January 1, 2020, and finally a total phaseout by January 1, 2030. From 2020 to 2030, HCFCs may only be used to service existing equipment.

In addition to the requirements of the Montreal Protocol, several countries have established their own regulations on the phaseout of HCFCs. The United States will meet the requirements of the Montreal Protocol by banning production and consumption of R-141b (primarily used as a foam blowing agent) beginning January 1, 2003, and placing a freeze on production and consumption of R-22 and R-142b beginning January 1, 2010. At that time, virgin R-22 will not be allowed for use in new equipment. Production and consumption of all other HCFCs will be frozen on January 1, 2015. On January 1, 2020, there will be a ban on production and consumption of R-22 and R-142b, followed by a ban on production and consumption of all other HCFCs on January 1, 2030. As required by the Montreal Protocol, from 2020 to 2030, virgin HCFCs may only be used to service existing equipment.

The European Union has already reduced the consumption cap on HCFCs and accelerated the phaseout schedule. In the EU, con-

Table 1 Refrigerant Properties

Refrigerant	Structure	Boiling Point, °C	Atmospheric Lifetime, Years	Ozone Depletion Potential (ODP)	Greenhouse Warming Potential (GWP)	Flammable*
					100 Year Integrated Time Horizon	
E125	CHF ₂ OCF ₃	-34.6	150	0	14 900	No
E143	CHF ₂ OCH ₂ F	29.9	—	0	—	Yes
E143a	CF ₃ OCH ₃	-24.1	4.4	0	750	Yes
11	CCl ₃ F	23.6	45	1.0	4600	No
12	CCl ₂ F ₂	-29.8	100	0.820	10 600	No
22	CHClF ₂	-40.8	11.9	0.034	1700	No
23	CHF ₃	-82.1	260	0	12 000	No
32	CH ₂ F ₂	-52.5	5.0	0	550	Yes
113	CCl ₂ FCClF ₂	47.6	85	0.090	6000	No
114	CClF ₂ CClF ₂	3.8	300	0.850	9800	No
115	CClF ₂ CF ₃	-39.1	1700	0.400	7200	No
116	CF ₃ CF ₃	-78.1	10 000	0	11 900	No
123	CHCl ₂ CF ₃	27.9	1.4	0.012	120	No
124	CHClF ₂ CF ₃	-12.1	6.1	0.026	620	No
125	CHF ₂ CF ₃	-47.8	29	0	3400	No
134a	CH ₂ FCF ₃	-26.5	13.8	0	1300	No
142b	CClF ₂ CH ₃	-9.8	19	0.043	2400	Yes
143	CH ₂ FCHF ₂	3.8	3.4	0	330	Yes
143a	CF ₃ CH ₃	-47.8	52	0	4300	Yes
152a	CHF ₂ CH ₃	-25.0	1.4	0	120	Yes
218	CF ₃ CF ₂ CF ₃	-31.5	2600	0	8600	No
227ea	CF ₃ CHF ₂ CF ₃	-18.3	33	0	3500	No
236ea	CF ₃ CHF ₂ CHF ₂	6.5	10	0	1200	No
236fa	CF ₃ CH ₂ CF ₃	-0.7	220	0	9400	No
245ca	CHF ₂ CF ₂ CH ₂ F	25.0	5.9	0	640	Yes
245fa	CF ₃ CH ₂ CHF ₂	15.3	7.2	0	950	No

*ASHRAE Standard 34.

Sources: Calm and Hourahan (2001), Calm (2001), IPCC (2001), Ozone Secretariat UNEP (1996).

sumption of HCFCs will be reduced 15% on January 1, 2002, followed by a 55% reduction on January 1, 2003, a 70% reduction on January 1, 2004, a 75% reduction on January 1, 2008, and a total phaseout on January 1, 2010. They have already implemented several use restrictions on HCFCs in air-conditioning and refrigeration equipment.

Recent studies (Wuebbles and Calm 1997; Calm et al. 1999) suggest that phaseout of HCFC refrigerants with low atmospheric lives, low ozone depletion potentials, low global warming potentials, low emissions, and high thermodynamic efficiencies will result in an increase in global warming, but will have a negligible effect on ozone depletion.

HCFC-22 is the most widely used hydrochlorofluorocarbon. R-410A is now the leading alternative for HCFC-22 for new equipment. R-407C is another HCFC-22 replacement and can be used in retrofits as well as in new equipment. HCFC-123 is now used commercially as a replacement for CFC-11.

Hydrofluorocarbons. These refrigerants contain no chlorine atoms, so their ODP is zero. HFC methanes, ethanes, and propanes have been extensively considered for use in air conditioning and refrigeration.

Fluoromethanes. Mixtures that include R-32 (difluoromethane, CH_2F_2) are being considered as a replacement for R-22 and R-502. For very-low-temperature applications, R-23 (trifluoromethane, CHF_3) is being considered as a replacement for R-13 and R-503 (Atwood and Zheng 1991).

Fluoroethanes. Refrigerant 134a ($\text{CF}_3\text{CH}_2\text{F}$) of the fluoroethane series is used extensively as a direct replacement for R-12 and as a replacement for R-22 in higher-temperature applications. R-125 and R-143a are used in azeotropes or zeotropic blends with R-32 and/or R-134a as replacements for R-22 or R-502. R-152a is flammable and less efficient than R-134a in applications using suction line heat exchangers (Sanvordenker 1992), but it is still being considered as a candidate for R-12 replacement. R-152a is also being considered as a component, with R-22 and R-124, in zeotropic blends (Bateman et al. 1990; Bivens et al. 1989) that can be R-12 and R-500 alternatives.

Fluoropropanes. Desmarteau et al. (1991) identified a number of fluoropropanes as potential refrigerants. R-245ca is being considered as a chlorine-free replacement for R-11. Evaluation by Doerr et al. (1992) showed that R-245ca is stable and compatible with key components of the hermetic system. However, Smith et al. (1993) demonstrated that R-245ca is slightly flammable in humid air at room temperature. Keuper et al. (1996) investigated the performance of R-245ca in a centrifugal chiller; they found that the refrigerant might be useful in new equipment but posed some problems when used as a retrofit for R-11 and R-123 machines. R-245fa is being developed as a foam-blowing agent and may also be considered as a refrigerant. R-236fa is currently under investigation as a replacement for R-114 in naval centrifugal chillers.

Fluoroethers. Booth (1937), Eiseman (1968), Kopko (1989), O'Neill and Holdsworth (1990), O'Neill (1992), and Wang et al. (1991) proposed these compounds as refrigerants. The fluoroethers are usually more reactive than the fluorinated hydrocarbons, both physiologically and chemically. Fluorinated ethers have found use as anesthetics and convulsants (Krantz and Rudo 1966; Terrell et al. 1971a, 1971b). Reactivity with glass is characteristic of some fluoroethers (Doerr et al. 1993; Simons et al. 1977; Gross 1990). Misaki and Sekiya (1995, 1996) investigated 1-methoxyperfluoropropane (boiling point 34.2°C) and 2-methoxyperfluoropropane (boiling point 29.4°C) as potential low-pressure refrigerants. Bivens and Minor (1997) reviewed the status of fluoroethers currently under consideration and concluded that none appear to have a balance of refrigerant fluid requirements to challenge the HFCs.

Hydrocarbons. Hydrocarbons such as propane, *n*-butane (R-600), isobutane (R-600a), and blends of these are being used as refrigerants. Hydrocarbons have zero ODP and low GWP. However, they are very flammable, which is a serious obstacle to their wide-

Table 2 Properties of Refrigerant Blends

Refrigerant	Composition	Bubble Point, $^\circ\text{C}$	ODP	GWP,* 100 year
401A	22/152a/124 (53/13/34)	-33.1	0.027	1100
401B	22/152a/124 (61/11/28)	-34.7	0.028	1200
401C	22/152a/124 (33/15/52)	-28.4	0.025	900
402A	125/290/22 (60/2/38)	-49.2	0.013	2700
402B	125/290/22 (38/2/60)	-47.4	0.020	2300
403A	C_2H_6 /22/218 (5/75/20)	-50.0	0.026	3000
403B	C_2H_6 /22/218 (5/56/39)	-46.5	0.019	4300
404A	125/143a/134a (44/52/4)	-49.5	0	3800
405A	22/152a/142b/C318 (45/7/5.5/42.5)	-27.3	0.018	5200
406A	22/600a/142b (55/4/41)	-32.3	0.036	1900
407A	32/125/134a (20/40/40)	-45.5	0	2000
407B	32/125/134a (10/70/20)	-47.3	0	2700
407C	32/125/134a (23/25/52)	-43.7	0	1700
407D	32/125/134a (15/15/70)	-39.5	0	1500
408A	125/143a/22 (7/46/47)	-43.5	0.016	3000
409A	22/124/142b (60/25/15)	-34.2	0.039	1500
410A	32/125 (50/50)	-52.7	0	2000
411A	1270/22/152a (1.5/87.5/11.0)	-38.6	0.030	1500
411B	1270/22/152a (3/94/3)	-41.6	0.032	1600
412A	22/218/142b (70/5/25)	-38.5	0.035	2200
500	12/152a (73.8/26.2)	-34	0.605	7900
501	22/12 (75/25)	-41.0	0.231	3900
502	22/115 (48.8/51.2)	-45.4	0.221	4500
503	23/13 (40.1/59.9)	-88.7	0.599	13000
504	32/115 (48.2/51.8)	-57.2	0.207	4000
507A	125/143a (50/50)	-46.7	0	3900
508A	23/116 (39/61)	-122.3	0	12000
508B	23/116 (46/54)	-124.4	0	12000
509A	22/218 (44/56)	-47.1	0.015	5600

*GWPs are the weight fraction average for the GWP values for individual components. Sources: Calm and Hourahan (2001), Calm (2001), IPCC (2001).

spread use as refrigerants. Hydrocarbons are commonly used in small proportions in mixtures with nonflammable halogenated refrigerants and in small equipment requiring low refrigerant charges. Hydrocarbons are currently being used in air-conditioning and refrigeration equipment in Europe and China (Powell 1996; Lohbeck 1996; Mianmian 1996).

Ammonia. Used extensively in large, open-type compressors for industrial and commercial applications, ammonia (R-717) has high refrigerating capacity per unit displacement, low pressure losses in connecting piping, and low reactivity with refrigeration lubricants (mineral oils). See [Chapter 3](#) for detailed information.

The toxicity and flammability of ammonia offset its advantages. Ammonia is such a strong irritant to the human nose (detectable below 5 mg/kg) that people automatically avoid exposure to it. Ammonia is considered toxic at 35 to 50 mg/kg. Ammonia-air mixtures are flammable, but only within a narrow range of 15.2 to 27.4% by volume. These mixtures can explode but are difficult to ignite because they require an ignition source of at least 650°C .

Refrigerant Analysis

With the introduction of many new pure refrigerants and refrigerant mixtures, interest in the analysis of refrigerants has increased. Refrigerant analysis is addressed in ARI *Standard 700* and its Analytical Procedures Appendix. Gas chromatographic methods have been published for the purity determination of R-134a and R-141b (Gehring et al. 1992a, 1992b). Gehring (1995) deals with the measurement of water in refrigerants. Bruno and Caciari (1994) and

Bruno et al. (1995) have done extensive work developing chromatographic methods for the analysis of refrigerants using a graphitized carbon black column with a coating of hexafluoropropene. Bruno et al. (1994) have also published the refractive indices of some of the alternative refrigerants. There is interest in developing methods for the field analysis of refrigerant systems. Systems for field analysis of both oils and refrigerants are commercially available. Rohatgi et al. (2001) compared ion chromatography to other analytical methods for the determination of chloride, fluoride, and acids in refrigerants. They also investigated sample vessel surfaces and liners for absorption of hydrochloric and oleic acids.

Flammability and Combustibility

Refrigerant flammability testing is defined in UL *Standard* 2182, Section 7. For many refrigerants, flammability is enhanced by increase in temperature and humidity. These factors must be controlled accurately to obtain reproducible, reliable data.

Fedorko et al. (1987) studied the flammability envelope of R-22/air as a function of pressure (up to 1.4 MPa) and fuel (R-22)-to-oxygen ratio. They found that R-22 was nonflammable under 500 kPa. In addition, the flammable compositions between 30 and 45% generated maximum heats of reaction. Their results were in general agreement with those of Sand and Andrjeski (1982), who found that pressurized mixtures of R-22 and air containing at least 50% air are combustible. R-11 and R-12 did not ignite under similar conditions.

Reed and Rizzo (1991) and Lindley (1992), using different experimental arrangements, studied the combustibility of R-134a at high temperature and pressure. Lindley notes that the results depend on the nature of the equipment used in the tests. Reed and Rizzo showed that R-134a is combustible at pressures above 100 kPa (gage) at room temperature and air concentrations greater than 80% by volume. At 177°C, combustibility was observed at pressures above 36 kPa (gage) and air concentrations above 60% by volume. Lindley found flammability limits of 8 to 22% by volume in air at 170°C and 700 kPa. Both researchers found R-134a to be nonflammable at ambient conditions and under the likely operating conditions of air-conditioning and refrigeration equipment. Blends of R-22/152a/114 showed combustion at temperatures above 82°C at atmospheric pressure and above, with air concentrations above 80% by volume (Reed and Rizzo 1991).

Richard and Shankland (1991) followed the ASTM *Standard* E 681 method to study the flammability of R-32, R-141b, R-142b, R-152a, R-152, R-143, R-161, methylene chloride, 1,1,1-trichloroethane, propane, pentane, dimethyl ether, and ammonia. They used several ignition methods, including the electrically activated match ignition source as specified in ASHRAE *Standard* 34. They also reported on the critical flammability ratio of mixtures such as R-32/125, R-143a/134a, R-152a/125, propane/R-125, R-152a/22, R-152a/124, and R-152a/134a. The **critical flammability ratio** is the maximum amount of flammable component that a mixture can contain and still be nonflammable, regardless of the amount of air. These data are important because mixtures containing flammable components are being considered as refrigerants.

Zhigang et al. (1992) published data on the flammability of R-152a/22 mixtures. Their measured lower flammability limit in air of R-152a is 11.4% by volume. They state that values reported in the literature range from 4.7 to 16.8% by volume. Richard and Shankland (1991) reported an average flammable range of 4.1 to 20.2% by mass for R-152a. Zhigang et al. (1992) also provide data on the length of the flame as a function of R-22 concentration. They found that the flame no longer existed somewhere between 17 and 40% R-22 by mass in the mixture. This is in apparent disagreement with the data of Richard and Shankland (1991), who found a critical flammability ratio of 57.1% R-22 by mass. Comparison of results is difficult because results depend on the apparatus and methods used. Grob (1991) reported on the flammabilities of R-152a, R-141b, and R-142b. He describes R-152a as having "the lowest flammable mix-

ture percentage, highest explosive pressure and highest potential for ignition of the refrigerants studied." Womeldorf and Grosshandler (1995) used an opposed-flow burner to evaluate the flammability limits of refrigerants.

COMPATIBILITY OF MATERIALS

Electrical Insulation

The insulation on electric motors is affected by the refrigerant and/or the lubricant through two primary modes: extraction of insulation polymer into the refrigerant or absorption of refrigerant by the polymer.

Extraction of insulation material causes embrittlement, delamination, and general degradation of the material. In addition, extracted material can separate from solution, deposit out, and cause components to stick or passages such as capillary tubes to clog.

Absorption of refrigerant can change the dielectric strength or physical integrity of the material through softening or swelling. Rapid desorption (off-gassing) of the refrigerant by internal heating can have a more serious effect than refrigerant absorption. Rapid desorption results in high internal pressures that cause blistering or voids within the insulation, causing a decrease in dielectric or physical strength.

In compatibility studies of 10 refrigerants and 7 lubricants with 24 motor materials in various combinations, Doerr and Kujak (1993) showed that R-123 was absorbed to the greatest extent, but R-22 caused more damage because of more rapid desorption and higher internal pressures. They also observed damage to insulation after desorption of R-32, R-134, and R-152a in a 150°C oven, but not to the extent exhibited by R-22.

Compatibility studies of motor materials were also conducted under retrofit conditions in which materials were exposed to the original refrigerant/mineral oil followed by exposure to the alternative refrigerant/polyolester lubricant (Doerr and Waite 1995, 1996a). Alternative refrigerants included R-134a, R-407C, R-404A, R-123, and R-245ca. Most of the motor materials were unaffected except for increased brittleness in polyethylene terephthalate (PET) due to moisture and blistering between layers of sheet insulation from the adhesive. Exposure of many of the same materials to ammonia resulted in complete destruction. The magnet wire enamel was degraded, and the PET sheet insulation completely disappeared, having been converted to a terephthalic acid diamide precipitate (Doerr and Waite 1996b).

Ratanaphruks et al. (1996) determined the compatibility of metals, desiccants, motor materials, plastics, and elastomers with the HFCs R-245ca, R-245fa, R-236ea, and R-236fa, and HFE-125. Most metals and desiccants were compatible. Plastics and elastomers were compatible except for excessive absorption of refrigerant or lubricant (resulting in unacceptable swelling) observed with fluoropolymers, hydrogenated nitrile butyl rubber, and natural rubber. Corr et al. (1994) tested compatibility with R-22 and R-502 replacements. Kujak and Waite (1994) studied the effect on motor materials of HFC refrigerants with polyol ester lubricants containing elevated levels of moisture and organic acids. They concluded that a 500 mg/kg moisture level in the polyol ester lubricant had a greater effect on the motor materials than an organic acid level of 2 mg KOH/g. Exposure to R-134a/polyol ester with a high moisture level had less effect than exposure to R-22/mineral oil with a low moisture level.

Ellis et al. (1996) developed an accelerated test to determine the life of motor materials in alternative refrigerants using a simulated stator unit. Hawley-Fedder (1996) studied the breakdown products of a simulated motor burnout in HFC refrigerant atmospheres.

Magnet Wire Insulation. The magnet wire is coated with enamels, which are cured by heating. The most common insulation is a polyester base coat followed by a polyamide-imide top coat. A polyester-imide base coat is also used. Acrylic and polyvinyl formal

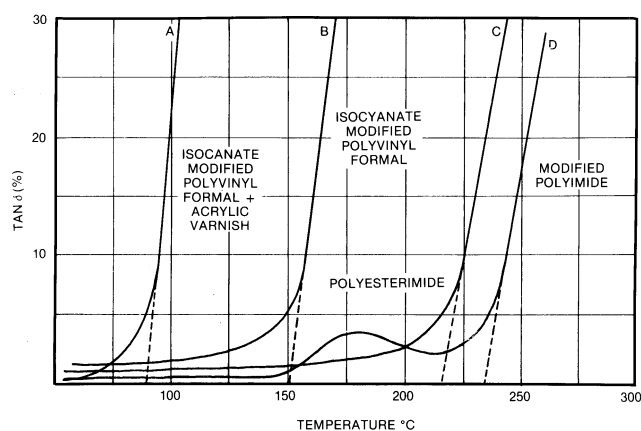


Fig. 1 Loss Curves of Various Insulating Materials
(Spauschus and Sellers 1969)

enamels are found on older motors. An enameled wire with an outer layer of polyester-glass is used in larger hermetic motors for greater wire separation and thermal stability.

The magnet wire insulation is the primary source of electrical insulation and the most critical in regard to compatibility with refrigerants. Most electrical tests (NEMA *Standard* MW 1000) are conducted in air and may not be valid for hermetic motors. For example, wire enamels absorb R-22 up to 15 to 30% by mass (Hurtgen 1971) and at different rates depending on their chemical structure and degree of cure and the conditions of exposure to the refrigerant. Refrigerant permeation is shown by changes in electrical, mechanical, and physical properties of the wire enamels. Fellows et al. (1991) measured the dielectric strength, Paschen curve minimum, dielectric constant, conductivity, and resistivity for 19 HFCs in order to predict electrical properties in the presence of these refrigerants.

Wire enamels in refrigerant vapor typically exhibit **dielectric loss** with increasing temperature, as shown in Figure 1. Depending on the atmosphere and degree of cure, each wire enamel or enamel/varnish combination exhibits a characteristic temperature t_{max} above which dielectric losses increase sharply. Table 3 shows values of t_{max} for several hermetic enamels. Continued heating above t_{max} causes aging, evidenced by the irreversible alteration of dielectric properties and an increase in the conductance of the insulating material.

Spauschus and Sellers (1969) showed that the change rate in conductance is a quantitative measure of aging in a refrigerant environment. They proposed an aging rate for varnished and unvarnished enamels at two levels of R-22 pressure typical of high- and low-side hermetic motor operation.

Apart from the effects on long-term aging, R-22 can also affect the **short-term insulating properties** of certain wire enamels. Beacham and Divers (1955) demonstrated that the resistance of polyvinyl formal drops drastically when the material is submerged in liquid R-22. A parallel experiment using R-12 showed a much smaller drop, followed by quick recovery to the original resistance. The relatively rapid permeation of R-22 into polyvinyl formal, coupled with the low volume resistivity of liquid R-22 and other

Table 3 Maximum Temperature t_{max} for Hermetic Wire Enamels in R-22 at 450 kPa

Enamel Type	t_{max} , °C
Acrylic	108
Polyvinyl formal	136
Isocyanate-modified polyvinyl formal	151
Polyamide-imide	183
Polyester-imide	215
Polyimide	232

electrical properties of the two refrigerants, explains the phenomenon.

Softening of the wire coating, which can cause the insulation to fail, occurs with certain combinations of coatings and refrigerants. Table 4 shows data on softening measured in terms of abrasion resistance for a number of wire enamels exposed to R-22. At the end of the shortest soaking period, the urethane-modified polyvinyl formal had lost all its abrasion resistance. All the other insulations, except polyimide, lost their abrasion resistance at a slower rate, which over a 3-month period approached the rate of the urethane-polyvinyl formal. The polyimide showed only a minimal effect, although its abrasion resistance was originally among the lowest.

Because of the time dependency of softening, which is related to the rate of R-22 permeation into the enamel, Sanvordenker and Larime (1971) proposed that comparative tests on magnet wire be made only after the enamel is completely saturated with refrigerant, so that the effect on enamel properties of long-term exposure to R-22 can be evaluated.

The second consequence of R-22 permeation is **blistering**, caused by the rapid change in pressure and temperature after a wire enamel is exposed to R-22. Heating greatly increases the internal pressure as the dissolved R-22 expands; because the polymer film has already been softened, portions of the enamel lift up in the form of blisters. Although blistered wire has a poor appearance, field experience indicates that mild blistering is not cause for concern, as long as the blisters do not break and the enamel film remains flexible. Currently used wire enamels have the characteristics mentioned previously and maintain dielectric strength even after blistering. However, hermetic wire enamel with strong resistance is preferred.

Varnishes. After the stator of an electric motor is wound, it is usually treated with a varnish by a vacuum-and-pressure impregnation process for form-wound, high-voltage motors or a dip-and-bake process for low-voltage, random wound motors. The varnished motor is cured in a 135 to 177°C oven. The varnish holds the windings together in the magnetic field and acts as a secondary source of electrical insulation. The windings have a tendency to move, and independent movement of the wires causes abrasion and wear of the insulation. High-voltage motors contain form-wound coils wrapped with a porous fiberglass, which is saturated with varnish and cured as an additional layer.

Many different chemicals are used as motor varnishes. The most common are epoxies, polyesters, phenolics, and modified polyimides. Characteristics important to a varnish are good adhesion and bond strength to the wire enamel; flexibility and strength under both hot and cold conditions; thermal stability; good dielectric properties; and chemical compatibility with the wire enamel, sheet insulation, and refrigerant/lubricant mixture.

The compatibility of a varnish is determined by exposing the cured varnish (in the form of a section of a thin disk and varnished

Table 4 Effect of Liquid R-22 on Abrasion Resistance

Magnet Wire Insulation	Average Cycles to Failure			
	As Received	After Time in Liquid R-22		
		7 to 10 Days	One Month	Three Months
Urethane-polyvinyl formal batch 1	40	3	2	2
Urethane-polyvinyl formal batch 2	42	2	2	7
Polyester-imide batch 1	44	15	18	6
Polyester-imide batch 2	24	10	5	6
Dual coat amide-imide top coat, polyester base	79	35	23	11
Dual coat, polyester	35	5	5	9
Polyimide	26	25	23	21

Source: Sanvordenker and Larime (1971).

magnet wire in single strands, helical coils, and twisted pairs) to a refrigerant at elevated temperatures. The properties of the varnish are then compared to samples not exposed to refrigerant and to other exposed samples placed in a hot oven to rapidly remove absorbed refrigerant. The disk sections are evaluated for absorption, extraction, degradation, and changes in flexibility. The single strands are wound around a mandrel, and the varnish is examined for flexibility and effect on the wire enamel. In many cases, the varnish does not flex as well as the enamel; if bound tightly to the enamel, the varnish removes the enamel from the copper wire. The helical coils are evaluated for bond strength (ASTM *Standard* D2519) before and after exposure to a refrigerant/lubricant mixture. The twisted pair is tested for dielectric breakdown voltage, or burnout time, while subjected to resistance heating (ASTM *Standard* D1676).

During the compatibility testing of motor materials with alternative refrigerants, researchers observed that the varnish could absorb considerable amounts of refrigerant, especially R-123. Doerr (1992) studied the effects of time and temperature on the rate of absorption and desorption of R-123 and R-11 by epoxy motor varnishes. Absorption of refrigerant was faster at higher temperatures. Desorption of refrigerant at temperatures as high as 120°C was slow. The equilibrium absorption value for R-123 was linearly dependent on temperature, with higher absorption at lower temperatures. Absorption of R-11 remained the same at all test temperatures.

Ground Insulation. Sheet insulation material is used in slot liners, phase insulation, and wedges in hermetic motors. The sheet material is usually a PET film or an aramid (aromatic polyamide) mat. These can be used singly or laminated together. PET or aramid films possess excellent dielectric properties and good chemical resistance to refrigerants and oils.

The PET film selected must contain little of the low relative molecular mass polymers that exhibit a temperature-dependent solubility in mineral lubricants and tend to precipitate as noncohesive granules at temperatures lower than those of the motor. Another limitation of this film is that, like most polyesters, it is susceptible to degradation by hydrolysis; however, the quantity of water required is more than that generally found in refrigerant systems. Sundaresan and Finkenstadt (1991) discuss the effect of synthetic lubricants on PET films. Dick and Malone (1996) reported that low-viscosity polyol esters (POEs) tend to extract more low-oligomeric PET components than higher-viscosity esters.

Elastomers

Refrigerants, oils, or mixtures of both can, at times, extract enough filler or plasticizer from an elastomer to change its physical or chemical properties. This extracted material can harm the refrigeration system by increasing its chemical reactivity or by clogging screens and expansion devices. Many elastomers are unsuitable for use with refrigerants because of excessive swell or shrinkage. Some neoprenes tend to shrink in HFC refrigerants, and nitriles swell in R-123. Hamed and Seiple (1993a, 1993b) determined swell data on 95 elastomers in 10 refrigerants and 7 lubricants. Compatibility data on general classifications of elastomers such as neoprenes or nitriles should be used with caution because results depend on the particular formulation. Users should be aware that elastomeric behavior is strongly affected by the specific formulation of an elastomer as well as by the general type of elastomer.

Plastics

The effect of refrigerants on plastics usually decreases as the amount of fluorine in the molecule increases. For example, R-12 has less effect than R-11, while R-13 is almost entirely inert. Cavestri (1993) studied the compatibility of 23 engineering plastics with alternative refrigerants and lubricants.

Each type of plastic material should be tested for compatibility with the refrigerant before it is used. Two samples of the same type

of plastic might be affected differently by the refrigerant because of differences in polymer structure, relative molecular mass, and plasticizer.

CHEMICAL REACTIONS

Halocarbons

Thermal Stability in the Presence of Metals. All common halocarbon refrigerants have excellent thermal stability, as shown in [Table 5](#). Bier et al. (1990) studied R-12, R-134a, and R-152a. For R-134a in contact with metals, traces of hydrogen fluoride (HF) were detected after 10 days at 200°C. This decomposition did not increase much with time. R-152a showed traces of HF at 180°C after five days in a steel container. Bier et al. suggested that vinyl fluoride is formed during the thermal decomposition of R-152a. Vinyl fluoride can then react with water to form acetaldehyde. Hansen and Finsen (1992) conducted lifetime tests on small hermetic compressors with a ternary mixture of R-22/152a/124 and an alkyl benzene lubricant. In agreement with Bier et al., they found that vinyl fluoride and acetaldehyde were formed in the compressor. Aluminum, copper, and brass and solder joints lower the temperature at which decomposition begins. Decomposition also increases with time.

Under extreme conditions, such as above red heat or with molten metal temperatures, refrigerants react exothermically to produce metal halides and carbon. Extreme temperatures may occur in devices such as centrifugal compressors if the impeller rubs against the housing when the system malfunctions. Using R-12 as the test refrigerant, Eiseman (1963) found that aluminum was most reactive, followed by iron and stainless steel. Copper is relatively unreactive. Using aluminum as the reactive metal, Eiseman reported that R-14 causes the most vigorous reaction, followed by R-22, R-12, R-114, R-11, and R-113. Dekleva et al. (1993) studied the reaction of various CFCs, HCFCs, and HFCs in vapor tubes at very high temperatures in the presence of various catalysts and measured the onset temperature of decomposition. These data also showed the HFCs to be more thermally stable than the CFCs and HCFCs. The researchers found that when molten aluminum is in contact with R-134a, a layer of unreactive aluminum fluoride forms and inhibits further reaction.

Hydrolysis. The halogenated refrigerants are susceptible to reaction with water (hydrolysis), but the rates of reaction are so slow that they are negligible ([Table 6](#)). Desiccants, which are discussed in [Chapter 6](#), are used to keep refrigeration systems dry. Cohen (1993) investigated the compatibility of desiccants with R-134a and refrigerant blends.

Ammonia

Reactions involving ammonia, oxygen, oil degradation acids, and moisture are common factors in the formation of ammonia compressor deposits. Sedgwick (1966) suggested that ammonia or ammonium hydroxide reacts with organic acids produced by oxidation of the compressor oil to form ammonium salts (soaps), which can decompose further to form amides (sludge) and water. The reaction may be described as follows:



Water may be consumed or released during the reaction, depending on system temperature, metallic catalysts, and chemical state (acidic or basic condition). Compressor deposits can be minimized by keeping the system clean and dry, preventing entry of air, and maintaining proper compressor temperatures. Care should be taken to ensure that ester lubricants and ammonia are not used together, as large quantities of soaps and sludges would be produced.

Table 5 Inherent Thermal Stability of Halocarbon Refrigerants

Refrigerant	Formula	Decomposition Rated at 200°C in Steel, % per yr ^a	Temperature at Which Decomposition is Readily Observed in Laboratory, ^b °C	Temperature at Which 1%/Year Decomposes in Absence of Active Materials, °C	Major Gaseous Decomposition Products ^c
22	CHClF ₂	—	430	250	CF ₂ CF ₂ , ^d HCl
11	CCl ₃ F	2	590	300 ^e	R-12, Cl ₂
114	CClF ₂ CClF ₂	1	590	380	R-12
115	CClF ₂ CF ₃	—	630	390	R-13
12	CCl ₂ F ₂	Less than 1	760	500	R-13, Cl ₂
13	CClF ₃	—	840	540 ^f	R-14, Cl ₂ , R-116

Sources: Norton (1957), DuPont (1959, 1969), and Borchardt (1975).

^aData from UL Standard 207.

^bDecomposition rate is about 1% per min.

^cData from Borchardt (1975).

^dA variety of side products are also produced, here and with the other refrigerants, some of which may be quite toxic.

^eConditions were not found where this reaction proceeds homogeneously.

^fRate behavior too complex to permit extrapolation to 1% per year.

Table 6 Rate of Hydrolysis in Water
(Grams per Litre of Water per Year)

Refrigerant	Formula	101.3 kPa at 30°C		Saturation Pressure at 50°C with Steel
		Water Alone	With Steel	
113	CCl ₂ FCClF ₂	< 0.005	50	40
11	CCl ₃ F	< 0.005	10	28
12	CCl ₂ F ₂	< 0.005	1	10
21	CHCl ₂ F	< 0.01	5	9
114	CClF ₂ -CClF ₂	< 0.005	1	3
22	CHClF ₂	< 0.01	0.1	—

Source: DuPont (1959, 1969).

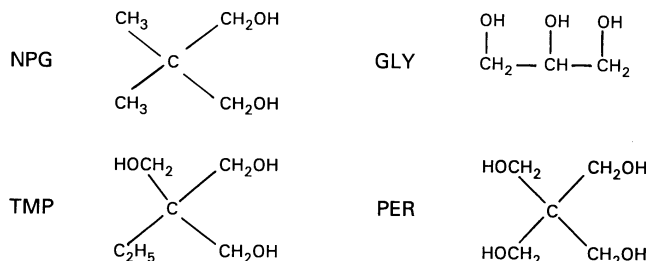


Fig. 2 Types of Alcohols Used for Ester Synthesis

At atmospheric pressure, ammonia starts to dissociate into nitrogen and hydrogen at about 300°C in the presence of active catalysts such as nickel and iron. However, because these high temperatures are unlikely to occur in open compression systems, thermal stability is not a problem. Ammonia attacks copper in the presence of even small amounts of moisture; therefore, except for some specialty bronzes, copper-bearing materials are excluded in ammonia systems. A corollary to this design practice is that copper plating (see the section on Copper Plating) is nonexistent in ammonia systems.

Lubricants

Lubricants now in use and under consideration for the new refrigerants are mineral oils, alkyl benzenes, polyol esters, polyalkylene glycols, modified polyalkylene glycols, and polyvinyl ethers. Gunderson and Hart (1962) give an excellent introduction to synthetic lubricants, including polyglycols and esters.

Polyol Esters. Commercial esters (Jolley 1991) are manufactured from four types of alcohols. They are neopentyl glycol (NPG) with two OH reaction sites, glycerin (GLY) with three OH sites, trimethylolpropane (TMP) with three OH sites, and pentaerythritol (PER) with four OH sites. The formulas for the four alcohol types

Table 7 Influence of Type of Alcohol on Ester Viscosity

Type of Alcohol	Ester Viscosity at 40°C, mm ² /s
NPG	13.3
GLY	31.9
TMP	51.7
PER	115

Note: Ester derived using the same carboxylic acid.

Table 8 R-134a Miscibility and Viscosity of Several
Pentaerythritol-Based Esters

Acid Used	R-134a Miscibility at 20% Ester, °C	Ester Viscosity at 40°C, mm ² /s
5 carbon, linear	< -70	15.6
6 carbon, linear	-47	18.5
7 carbon, linear	1	21.2
8 carbon, linear	> 65	26.7
9 carbon, linear	> 65	31.0
5 carbon, branched	< -70	25.2
8 carbon, branched	-15	44.4
9 carbon, branched	-27	112.9

Source: Jolley (1997).

are shown in Figure 2. The viscosities of the esters formed by the reaction of a given acid with each of the four alcohol types are given in Table 7.

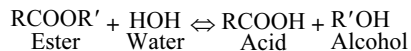
Polyol esters are widely used as lubricants in HCFC refrigerant systems, due mainly to their physical properties. Because they are made from a wide variety of materials, polyol esters can be designed to optimize desirable physical characteristics. The system chemistry of the lubricant can be significantly influenced by the type and chain length of the carboxylic acid used to prepare the ester.

Table 8 gives R-134a miscibility and viscosity data for several esters based on pentaerythritol. From these data it can be seen that polyol ester lubricants rapidly lose refrigerant miscibility when linear carbon chain lengths exceed six carbons. The data also show that the use of branched chain acids in the preparation of these lubricants can greatly enhance refrigerant miscibility. Chain branching also enables the preparation of higher-viscosity esters, which are needed in some industrial refrigeration applications.

The thermal stability of polyol esters is well known. Those esters made from polyols that possess a central “neo” structure, which consists of a carbon atom attached to four other carbon atoms (i.e., structures corresponding to NPG, TMP, and PER in Figure 2), have demonstrated outstanding thermal stability. Gunderson and Hart (1962) have reviewed research measuring the thermal stability of various polyol esters and dibasic acid esters at 260°C by heating them in evacuated tubes for up to 250 hours.

Such tests demonstrated the increased thermal stability expected from neo ester structure, with the dibasic acid esters decomposing at a rate three times faster than the polyol esters.

Hydrolysis of Esters. An alcohol and an organic acid react to produce an organic ester and water; this reaction is called esterification, and it is reversible. The reverse reaction of an ester and water to produce an alcohol and an organic acid is called **hydrolysis**:



Hydrolysis may be the most important chemical stability issue associated with esters. The degree to which esters are subject to hydrolysis is related to their processing parameters and their structure. Important processing parameters are total acid number (TAN), degree of esterification, the nature of the catalyst used during production, and the catalyst level remaining in the polyol ester after processing. Dick et al. (1996) have demonstrated that (1) the use of polyol esters prepared with acids known as α -branched acids significantly reduces ester hydrolysis and (2) the use of α -branched esters with certain additives can eliminate hydrolysis.

Hydrolysis is undesirable in refrigeration systems because free carboxylic acid can react with metal surfaces to cause corrosion. The metal carboxylate soaps that may be produced by hydrolysis can also cause capillary tube blockage. Davis et al. (1996) have reported that polyol ester hydrolysis proceeds via autocatalytic reaction. They were able to determine reaction rate constants for hydrolysis through sealed tube tests. Jolley et al. (1996) and others have used compressor testing, along with variations of the ASHRAE *Standard* 97 sealed tube test, to examine the potential for lubricant hydrolysis in operating systems. Compressor tests run with lubricant saturated with water (2000 mg/kg) have gone 2000 hours with no significant capillary tube blockage, indicating that under normal, much drier operating conditions, little or no detrimental ester hydrolysis will occur with the use of polyolester lubricants. Hansen and Snitkjær (1991) demonstrated the hydrolysis of esters in compressor life tests run without desiccants and in sealed tubes. They detected hydrolysis by measuring the total acid number and showed that desiccants can reduce the extent of hydrolysis in a compressor. They concluded that with filter driers, refrigeration systems using esters and R-134a can be very reliable.

Greig (1992) ran the thermal and oxidation stability test (TOST) by heating an oil/water emulsion to 95°C and bubbling oxygen through the emulsion in the presence of steel and copper. Greig shows that the hydrolysis of esters can be suppressed by appropriate additives. While agreeing that esters can be successfully used in refrigeration, Jolley et al. (1996) point out that some additives are themselves subject to hydrolysis. Cottington and Ravner (1969) and Jones et al. (1969) studied the effect of tricresyl phosphate (TCP), a common antiwear agent, on the decomposition of esters.

Field and Henderson (1998) studied the effect of elevated levels of organic acids and moisture on the corrosion of metals in the presence of R-134a and POE lubricant. Copper, brass, and aluminum showed little corrosion, but cast iron and steel were severely corroded. At 200°C, iron caused the POE lubricant to break down, even in the absence of additional acid and moisture. Similar chemistry was reported by Klauss et al. (1970), who found that the high-temperature (315°C) decomposition of POE was catalyzed by iron. Naidu et al. (1988) showed that this POE/iron reaction did not occur at a measurable rate at 185°C. Cottington and Ravner (1969) reported that the presence of TCP inhibits this POE/iron reaction. Lilje (2000) concluded that the POE/iron reaction is a high-energy process and does not occur in properly operating refrigeration systems. Field lubricant analysis data after 5 years of operation support this conclusion: no lubricant degradation was observed (Riemer and Hansen 1996).

Polyalkylene Glycols. Polyalkylene glycols (PAGs) are of the general formula $\text{RO}-[\text{CH}_2-\text{CHR}'-\text{O}]-\text{R}'$. They are used as lubricants in automotive applications that use R-134a. Linear PAGs can have one or two terminal hydroxyl groups. Modified PAG molecules have both ends capped by various groups. Sundaresan and Finkenshtadt (1990) discuss the use of PAGs and modified PAGs in refrigeration compressors. Short and Cavestri (1992) present data on PAGs.

These lubricants and their additive packages may (1) oxidize, (2) degrade thermally, (3) react with system contaminants such as water, and/or (4) react with the refrigerant or system materials such as polyester films.

Oxidation is usually not a problem in hermetic systems using hydrocarbon oils because no oxygen is available to react with the lubricant. However, if a system is not adequately evacuated or if air is allowed to leak into the system, organic acids and sludges can be formed. Lockwood and Klaus (1981) and Clark et al. (1985) found that iron and copper catalyze the oxidative degradation of esters. These reaction products are detrimental to the refrigeration system and can cause failure. Some have suggested that the oxidative breakdown products of PAG lubricants (Komatsuzaki et al. 1991) and perhaps of esters are volatile, whereas those of mineral oils are more likely to include sludges.

Sanvordenker (1991) studied the thermal stability of PAG and ester lubricants and found that above 204°C, water is one of the decomposition products of esters (in the presence of steel) and of PAG lubricants. He recommends that polyol esters be used with metal passivators to enhance their stability when in contact with the metallic bearing surfaces, which can experience 204°C temperatures. Sanvordenker presents data on the kinetics of the thermal decomposition of polyol esters and PAGs. These reactions are catalyzed by metal surfaces in the following order: low carbon steel > aluminum > copper (Naidu et al. 1988).

Lubricant Additives

Additives are often used to improve the performance of lubricants in refrigeration systems. Additives have become more important with the increased use of HFC refrigerants. The chlorine found in CFC refrigerants acted as an antiwear agent, so the mineral oil lubricants needed minimal or no additives to provide wear protection. HFC refrigerants such as R-134a do not contain chlorine and thus do not provide this antiwear benefit. Additives such as antioxidants, detergents, dispersants, rust inhibitors, and so forth, are not normally used because the conditions they treat are absent in most refrigeration systems. Many HFC/polyol ester refrigeration systems function well without lubricant additives. However, some systems that have aluminium wear surfaces require an additive to supplement wear protection. Antiwear protection is likely to be necessary in future systems with lower-viscosity lubricants to improve energy efficiency, especially if branched acid polyol esters are used. Randles et al. (1996) discuss the advantages and disadvantages of using additives in polyol ester lubricants for refrigeration systems.

The active ingredient in antiwear additives is typically phosphorous, sulfur, or both. Organic phosphates, phosphites, and phosphonates are typical phosphorous-containing antiwear agents. Tricresylphosphate (TCP) is the best known of these. Sulfurized olefins and disulfides are typical of sulfur-containing additives for wear protection. Zinc dithiophosphates are the best examples of mixed additives. Vinci and Dick (1995) have shown that additives containing phosphorous can perform well as antiwear agents and that sulfur-containing additives are not thermally stable as determined by the ASHRAE *Standard* 97 sealed tube stability test.

Other additives finding some use in HFC/polyol ester combinations are foam-producing agents (compressor start-up noise reduction) and hydrolysis inhibitors. Vinci and Dick (1995) show that a combination of antiwear additive and hydrolysis inhibitor can produce exceptional performance with respect to both wear and capil-

lary tube blockage in bench testing and long-term compressor endurance tests. Sanvordenker (1991) has shown that iron surfaces can catalyze the decomposition of esters at 200°C. He proposed using a metal passivator as an additive to minimize this effect in systems where high temperatures are possible. Schmitz (1996) describes the use of a siloxane ester foaming agent for noise reduction. Swallow et al. (1995, 1996) suggested the use of additives to control the release of refrigerant vapor from polyol ester lubricants.

System Reactions

Average strengths of carbon-chlorine, carbon-hydrogen, and carbon-fluorine bonds are 326, 389, and 418 kJ/mole, respectively (Pauling 1960). The relative stabilities of refrigerants that contain chlorine, hydrogen, and fluorine bonded to carbon can be understood by considering these bond strengths. The CFCs have characteristic reactions that depend largely on the presence of the C-Cl bond. Spauschus and Doderer (1961) concluded that R-12 can react with a hydrocarbon oil by exchanging a chlorine for a hydrogen. This reaction is characteristic of chlorine-containing refrigerants. In the reaction, R-12 forms the reduction product R-22, R-22 forms R-32 (Spauschus and Doderer 1964), and R-115 forms R-125 (Parmelee 1965). For R-123, Carrier (1989) demonstrated that the reduction product R-133a is formed at high temperatures.

Factor and Miranda (1991) studied the reaction between R-12, steel, and oil sludge. They concluded that it can proceed by a predominantly Friedel-Crafts mechanism in which Fe^{3+} compounds are key catalysts. They also concluded that oil sludge can be formed by a pathway that does not generate R-22. They suggest that, except for the initial formation of Fe^{3+} salts, the free-radical mechanism plays only a minor role. Further work is needed to clarify this mechanism.

Huttenlocher (1992) tested 23 refrigerant-lubricant combinations for stability in sealed glass tubes. HFC refrigerants were shown to be very stable even at temperatures much higher than normal operating temperatures. HCFC-124 and HCFC-142b were slightly more reactive than the HFCs, but less reactive than CFC-12. HCFC-123 was less reactive than CFC-11 by a factor of approximately 10.

Fluoroethers were studied as alternative refrigerants. Sealed glass tube and Parr bomb stability tests with E-245 ($\text{CF}_3\text{-CH}_2\text{-O-CHF}_2$) showed evidence of an autocatalytic reaction with glass that proceeds until either the glass or the fluoroether is consumed (Doerr et al. 1993). High pressures (about 14 MPa) usually cause the sealed glass tubes to explode.

The breakdown of CFCs and HCFCs can usually be tracked by observing the concentration of the reaction products formed. Alternatively, the amount of fluoride and chloride formed in the system can be observed. For HFCs, no chloride will be formed, and reaction products are highly unlikely because the C-F bond is strong. Decomposition of HFCs is usually tracked by measuring the fluoride ion concentration in the system (Thomas and Pham 1989; Spauschus 1991; Thomas et al. 1993). This test showed that R-125, R-32, R-143a, R-152a, and R-134a are quite stable.

The possibility that hydrogen fluoride released by the breakdown of the refrigerants being studied will react with glass of the sealed tube has been a concern. Sanvordenker (1985) confirmed this possibility with R-12. Spauschus et al. (1992) found no evidence of fluoride on the glass surface of sealed tubes with R-134a.

Figures 3 and 4 show sealed tube test data for reaction rates of R-22 and R-12 with oil in the presence of copper and mild steel. The formation of chloride ion was taken as a measure of decomposition. These figures show the extent to which temperature accelerates reactions; it also shows that R-22 is much less reactive than R-12. The data only illustrate the chemical reactivities involved and do not represent actual rates in refrigeration systems.

The chemistry that occurs in CFC systems retrofitted to use HFC refrigerants and their lubricants is an area of growing interest. Corr et al. (1992) point out that a major problem is the effect of chlori-

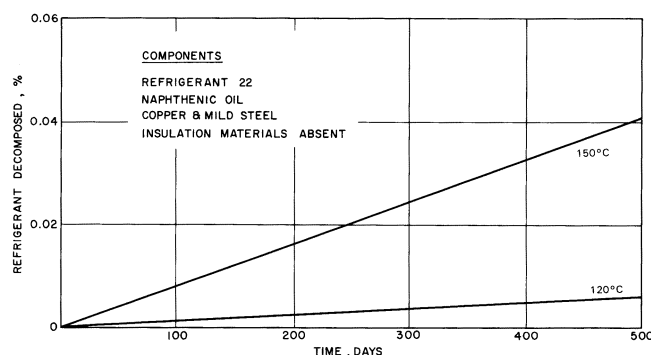


Fig. 3 Stability of Refrigerant 22 Control System
(Kvalnes and Parmelee 1957)

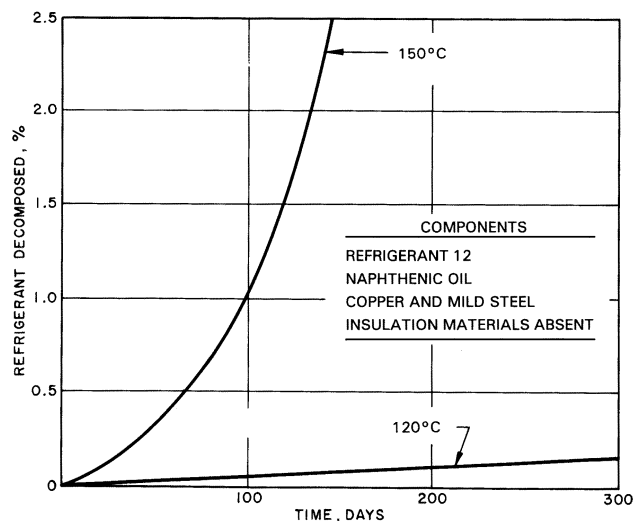


Fig. 4 Stability of Refrigerant 12 Control Systems
(Kvalnes and Parmelee 1957)

nated residues in the new system. Komatsuzaki et al. (1991) showed that R-12 and R-113 degrade PAG lubricants. Powers and Rosen (1992) performed sealed tube tests and concluded that the threshold of reactivity for R-12 in R-134a and PAG lubricant is between 1 and 3%.

Copper Plating

Copper plating is the formation of a copper film on steel surfaces in refrigeration and air-conditioning compressors. A bluish of copper is often discernible on compressor bearing and valve surfaces when machines are cut apart. After several hours of exposure to air, this thin film becomes invisible, probably because metallic copper is converted to copper oxide. In severe cases, the copper deposit can build up to substantial thickness and interfere with compressor operation. Extreme copper plating can cause compressor failure.

Steinle and Seemann (1951, 1953), Steinle and Bosch (1955), and Spauschus (1963) demonstrated a number of factors required for copper plating to occur. Although the exact mechanism of copper plating is not completely understood, three distinct steps must occur: (1) oxidation of the copper, (2) solubilization and transport of the copper ions, and (3) deposition of the copper onto iron or steel.

Step 1, the oxidation of the copper from the metallic (0 valent) state to either the +1 or +2 oxidation state, does not occur under normal operating conditions with a lubricant. It is also unlikely to occur with carboxylic acids. The most likely source of oxidizing agents is

system contaminants, including air (oxygen), chlorine-containing species (CFC refrigerants or cleaning solvents, solder fluxes), or strong acids.

The second step in copper plating is the dissolution of the copper ions. Spauschus postulated that an organic complex of the copper and olefins is the soluble species in mineral oils. Oxygen-containing lubricants are much more likely to solubilize metal ions or complexes by coordination with the oxygen atoms. Once soluble, the copper can move throughout the refrigeration system.

Step 3, the deposition of the copper onto iron surfaces, is an electrochemical process that involves the transfer of electrons from iron to copper, resulting in copper metal (0 valent) plating on the surface of the iron and the concomitant generation of iron ions. This process is more likely to occur on hot, clean iron surfaces and is often seen on bearing surfaces.

Thomas and Pham (1989) compared copper plating in R-12/mineral oil and R-134a/PAG systems. They showed that R-134a/PAG systems produced much less total copper (in solution and as precipitate) than R-12/mineral oil systems. They also showed that water did not significantly affect the amount of copper produced. They found that in the R-134a/PAG system, the copper was largely precipitated. In the R-12/mineral oil system, the copper was found in solution when dry and precipitated when wet. Walker et al. (1960) found that water below the saturation level had no significant effect on copper plating for R-12/mineral oil systems. Spauschus (1963) observed that copper plating in sealed glass tubes was more prevalent with medium-refined naphthenic pale oil than with a highly refined white oil. He concluded that the refrigerant-lubricant reaction was an essential precursor for gross copper plating. The excess acid produced by the decomposition of the refrigerant had little effect on copper solubility but facilitated the plating process. Herbe and Lundqvist (1996, 1997) examined a large number of systems retrofitted from R-12 to R-134a for contaminants and copper plating. They reported that copper plating did not occur in retrofitted systems where the level of contaminants was low.

Contaminant Generation by High Temperature

Hermetic motors can overheat well beyond design levels under adverse conditions such as line voltage fluctuations, brownouts, or inadequate airflow over the condenser coils. Under these conditions, motor winding temperatures can exceed 150°C. Prolonged exposure to these thermal excursions can damage the motor insulation, depending on the thermal stability of the insulation materials, their reactivity with the refrigerant and lubricant, and the temperature levels encountered.

Another potential for high temperatures is in the bearings. Oil film temperatures in hydrodynamically lubricated journal bearings are usually not much higher than the bulk oil temperature; however, in elastohydrodynamic films in bearings with a high slide/roll ratio, the temperature can be several hundred degrees above the bulk oil temperature (Keping and Shizhu 1991). Local hot spots in boundary lubrication can reach very high temperatures. Fortunately, the amount of material exposed to these temperatures is usually very small. The appearance of methane or other small hydrocarbon molecules in the refrigerant indicates cracking of the lubricant due to high bearing temperatures.

Thermal decomposition of organic insulation materials and some types of lubricants produces noncondensable gases such as carbon dioxide and carbon monoxide. These gases circulate with the refrigerant, increasing the discharge pressure and lowering unit efficiency. At the same time, the compressor temperature and the rate of deterioration of the insulation or lubricant increase. Liquid decomposition products circulate with the lubricating oil either in solution or as colloidal suspensions. Dissolved and suspended decomposition products circulate throughout the refriger-

ation system, where they clog oil passages; interfere with the operation of expansion, suction, and discharge valves; or plug capillary tubes.

Appropriate control mechanisms in the refrigeration system minimize exposure to such high temperatures. Identifying potential reactions, performing adequate laboratory tests to qualify the materials before using them in the field, and finding means to remove the contaminants generated by high-temperature excursions are equally important (see [Chapter 6](#)).

REFRIGERANT DATABASE AND ARTI/MCLR RESEARCH PROJECTS

The U.S. Department of Energy (DOE) funded research to accelerate the phaseout of CFCs and the conversion to alternative refrigerants and lubricants. The funds supported about 40 materials compatibility and lubricants research (MCLR) projects and a refrigerants database. This database is maintained by the Air-Conditioning and Refrigeration Technology Institute (Calm 1995). The computer-searchable database covers over 5000 references with abstracts or summaries of presentations and technical papers. Performance, physical property, toxicity, compatibility, and flammability data for refrigerants are also included.

REFERENCES

- ARI. 1995. Specifications for fluorocarbons and other refrigerants. *ARI Standard 700-95*. Air-Conditioning and Refrigeration Institute, Arlington, VA.
- ARI. 1995. Analytical procedures for *ARI Standard 700-95*. Air-Conditioning and Refrigeration Institute, Arlington, VA.
- ASHRAE. 1983. Sealed glass tube method to test the chemical stability of material for use within refrigerant systems. *ANSI/ASHRAE Standard 97-1983* (RA 89).
- ASHRAE. 1992. Number designation and safety classification of refrigerants. *ANSI/ASHRAE Standard 34-1992*.
- ASTM. 1994. Test method for concentration limits of flammability of chemicals. *ASTM Standard E681-94*. American Society for Testing and Materials, West Conshohocken, PA.
- ASTM. 1995. Test methods for film-insulated magnet wire. *ANSI/ASTM Standard D1676-95*. American Society for Testing and Materials, West Conshohocken, PA.
- ASTM. 1996. Test method for bond strength of electrical insulating varnishes by the helical coil test. *ASTM Standard D2519-96*. American Society for Testing and Materials, West Conshohocken, PA.
- Atwood, T. and J. Zheng. 1991. Cascade refrigeration systems: The HFC-23 solution. *International CFC and Halon Alternatives Conference*, Baltimore, MD, sponsored by The Alliance for Responsible CFC Policy, Arlington, VA. pp. 442-450.
- Bateman, D.J., D.B. Bivens, R.A. Gorski, W.D. Wells, R.A. Lindstrom, R.A. Morse, and R.L. Shimon. 1990. Refrigerant blends for the automotive air conditioning aftermarket. *SAE Technical Paper Series 900216*. Society of Automotive Engineers, Warrendale, PA.
- Beacham, E.A. and R.T. Divers. 1955. Some practical aspects of the dielectric properties of refrigerants. *Refrigerating Engineering* (July):33.
- Bier, K., M. Crone, M. Tuerk, W. Leuckel, M. Christill, and B. Leisenheimer. 1990. Studies of the thermal stability and ignition behavior and combustion properties of the refrigerants R-152a and R-134a. *DKV-bTagungsbericht* 17:169-191.
- Bivens, D.B. and B.H. Minor. 1997. Fluoroethers and other next-generation fluids. *Refrigerants for the 21st Century Proceedings*. Gaithersburg, MD, October 6-7.
- Bivens, D.B., R.A. Gorski, W.D. Wells, A. Yokozeki, R.A. Lindstrom, and R.L. Shimon. 1989. Evaluation of fluorocarbon blends as automotive air conditioning refrigerants. *SAE Technical Paper Series 890306*. Society of Automotive Engineers, Warrendale, PA.
- Booth, H.S. 1937. Halogenated methyl ethers. U.S. Patent 2,066,905.
- Borchardt, H.J. 1975. *DuPont Innovation G(2)*.
- Bruno, T.J. and M. Caciari. 1994. Retention of halocarbons on a hexafluoropropylene epoxide modified graphitized carbon black. Part 1: Methane based fluids. *Journal of Chromatography A* 672:149-158.

- Bruno, T.J., M. Wood, and B.N. Hansen. 1994. Refractive indices of alternative refrigerants. *Journal of Research of the National Institute of Standards and Technology* 99(3):263-266.
- Bruno, T.J., M. Caciari, and K.H. Wertz. 1995. Retention of halocarbons on a hexafluoropropylene epoxide modified graphitized carbon black, Part 4: Propane based fluids. *Journal of Chromatography A* 708:293-302.
- Calm, J.M. 1995. Refrigerants and lubricants—Data for screening and application. Proceedings of the International CFC and Halon Alternatives Conference, Washington, D.C., pp. 169-178.
- Calm, J.M. 2001. ARTI Refrigerant Database, Air-Conditioning and Refrigeration Technology Institute (ARTI), Arlington, VA.
- Calm, J.M. and G.C. Hourahan. 2001. Engineered Systems, November, pp. 74-88.
- Calm, J.M., D.J. Wuebbles, and A.K. Jain. 1999. Impacts of global ozone and climate from use and emissions of 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123). *Journal of Climatic Change* 42:439-474.
- Carrier. 1989. Decomposition rates of R-11 and R-123. Carrier Corporation, Syracuse, NY. Available from ARTI Refrigerant Database. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Cavestri, R.C. 1993. Compatibility of refrigerants and lubricants with plastics. *Final Report No. DOE/CE 23810-15*. ARTI Refrigerant Database (December). Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Clark, D.B., E.E. Klaus, and S.M. Hsu. 1985. The role of iron and copper in the degradation of lubricating oils. *Journal of ASLE* (May):80-87. Society of Tribologists and Lubrication Engineers, Park Ridge, IL.
- Cohen, A.P. 1993. Test methods for the compatibility of desiccants with alternative refrigerants. *ASHRAE Transactions* 99(1):408-412.
- Corr, S., R.D. Gregson, G. Tompsett, A.L. Savage, and J.A. Schukraft. 1992. Retrofitting large refrigeration systems with R-134a. *Proceedings of the International Refrigeration Conference—Energy Efficiency and New Refrigerants* 1:221-230. Purdue University, West Lafayette, IN.
- Corr, S., P. Dowdle, G. Tompsett, R. Yost, T. Dekleva, J. Allison, and R. Brutsch. 1994. Compatibility of non-metallic motor components with R-22 and R-502 replacements. ASHRAE Winter Meeting, New Orleans, LA. ARTI Refrigerant Database 4216. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Cottingham, R.L. and H. Ravner. 1969. Interactions in neopentyl polyol ester-tricresyl phosphate-iron systems at 500°F. *ASLE Transactions* 12:280-286. Society of Tribologists and Lubrication Engineers, Park Ridge, IL.
- Davis, K.E., S.T. Jolley, and J.R. Shanklin. 1996. Hydrolytic stability of polyolester refrigeration lubricants. ARTI Refrigerant Database. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Desmarteau, D., A. Beyerlein, S. Hwang, Y. Shen, S. Li, R. Mendonca, K. Naik, N.D. Smith, and P. Joyner. 1991. Selection and synthesis of fluorinated propanes and butanes as CFC and HCFC alternatives. *International CFC and Halon Alternatives Conference*.
- Dekleva, T.D., A.A. Lindley, and P. Powell. 1993. Flammability and reactivity of select HFCs and mixtures. *ASHRAE Journal* (12):40-47.
- Dick, D.L. and G.R. Malone. 1996. Compatibility of polymetric materials with low-viscosity refrigeration lubricants. *Proceedings of the 1996 International Refrigeration Conference at Purdue*, pp. 391-396.
- Dick, D.L., J.N. Vinci, K.E. Davis, G.R. Malone, and S.T. Jolley. 1996. ARTI Refrigerant Database. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Doerr, R.G. 1992. Absorption of HCFC-123 and CFC-11 by epoxy motor varnish. *ASHRAE Transactions* 98(2):227-234.
- Doerr, R.G. and S.A. Kujak. 1993. Compatibility of refrigerants and lubricants with motor materials. *ASHRAE Journal* 35(8):42-47.
- Doerr, R.G., D. Lambert, R. Schafer, and D. Steinke. 1992. Stability and compatibility studies of R-245ca, CHF₂-CF₂-CH₂F, a potential low-pressure refrigerant. *International CFC and Halon Alternatives Conference*, Washington, D.C. pp. 147-152.
- Doerr, R.G., D. Lambert, R. Schafer, and D. Steinke. 1993. Stability studies of E-245 fluoroether, CF₃-CH₂-O-CHF₂. *ASHRAE Transactions* 99(2):1137-1140.
- Doerr, R.G. and T.D. Waite. 1995. Compatibility of refrigerants and lubricants with motor materials under retrofit conditions. *Proceedings of the International CFC and Halon Alternatives Conference*, Washington, D.C., pp. 159-168.
- Doerr, R.G. and T.D. Waite. 1996a. Compatibility of refrigerants and lubricants with motor materials under retrofit conditions. *Final Report No. DOE/CE 23810-63*. ARTI Refrigerant Database. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Doerr, R.G. and T.D. Waite. 1996b. Compatibility of ammonia with motor materials. ASHRAE Annual Meeting, February, Atlanta, GA. ARTI Refrigerant Database. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- DuPont. 1959. Properties and application of the "Freon" fluorinated hydrocarbons. *Technical Bulletin B-2*. Freon Products Division, E.I. DuPont de Nemours and Co.
- DuPont. 1969. Stability of several "Freon" compounds at high temperatures. *Technical Bulletin XIA*. Freon Products Division, E.I. DuPont de Nemours and Co.
- Eiseman, B.J. 1968. Chemical processes. U.S. Patent 3,362,180.
- Eiseman, B.J. 1963. Reactions of chlorofluoro-hydrocarbons with metals. *ASHRAE Journal* 5(5):63.
- Ellis, P.F., A.F. Ferguson, and K.T. Fuentes. 1996. Accelerated test methods for predicting the life of motor materials exposed to refrigerant-lubricant mixtures. *Report No. DOE/CE 23810-69*. ARTI Refrigerant Database. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Factor, A. and P.M. Miranda. 1991. An investigation of the mechanism of the R-12-oil-steel reaction. *Wear* 150:41-58.
- Fedorko, G., G. Fredrick, and J.G. Hansel. 1987. Flammability characteristics of chlorodifluoromethane (R-22)-oxygen-nitrogen mixtures. *ASHRAE Transactions* 93(2):716-724.
- Fellows, B.R., R.C. Richard, and I.R. Shankland. 1991. Electrical characterization of alternative refrigerants. *XVIIIth International Congress of Refrigeration*, Montreal, 45:398.
- Field, J.E. and D.R. Henderson. 1998. Corrosion of metals in contact with new refrigerants/lubricants at various moisture and organic acid levels. *ASHRAE Transactions* 104(1).
- Gehring, D.G. 1995. How to determine concentration of water in system refrigerants. *ASHRAE Journal* 37(9):52-55.
- Gehring, D.G., D.J. Barsotti, and H.E. Gibbon. 1992a. Chlorofluorocarbons alternatives analysis, Part I: The determination of HFC-134a purity by gas chromatography. *Journal of Chromatographic Science* 30:280.
- Gehring, D.G., D.J. Barsotti, and H.E. Gibbon. 1992b. Chlorofluorocarbons alternatives analysis, Part II: The determination of HCFC-141b purity by gas chromatography. *Journal of Chromatographic Science* 30:301.
- Greig, B.D. 1992. Formulated polyol ester lubricants for use with HFC-134a. The role of additives and conversion of existing CFC-12 plant to HFC-134a. *International CFC and Halon Alternatives Conference*. Washington, D.C. pp. 135-145.
- Grob, D.P. 1991. Summary of flammability characteristics of R-152a, R-141b, R-142b and analysis of effects in potential applications. Household Refrigerators. *42nd Annual International Appliance Technical Conference*, Batavia, IL.
- Gross, T.P. 1990. Sealed tube tests—Grace ether (E-134). ARTI Refrigerant Database RDB0904. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Gunderson, R.C. and A.W. Hart. 1962. *Synthetic lubricants*. Reinhold, New York.
- Guy, P.D., G. Tompsett, and T.W. Dekleva. 1992. Compatibilities of non-metallic materials with R-134a and alternative lubricants in refrigeration systems. *ASHRAE Transactions* 98(1):804-816.
- Hamed, G.R. and R.H. Seiple. 1993a. Compatibility of elastomers with refrigerant/lubricant mixtures. *ASHRAE Journal* 35(8):173-176.
- Hamed, G.R. and R.H. Seiple. 1993b. Compatibility of refrigerants and lubricants with elastomers. *Final Report No. DOE/CE 23810-14*. ARTI Refrigerant Database. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Hansen, P.E. and L. Finsen. 1992. Lifetime and reliability of small hermetic compressors using a ternary blend HCFC-22/HFC-152a/HCFC-124. *International Refrigeration Conference—Energy Efficiency and New Refrigerants*. D. Tree, ed. Purdue University, West Lafayette, IN.
- Hansen, P.E. and L. Snitkjaer. 1991. Development of small hermetic compressors for R-134a. *XVIIIth International Congress of Refrigeration*, Montreal, 223:1146.
- Hawley-Fedder, R. 1996. Products of motor burnout. *Report No. DOE/CE 23810-74*. ARTI Refrigerant Database. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Herbe, L. and P. Lundqvist. 1996. Refrigerant retrofit in Sweden—Field and laboratory studies. *Proceedings of the International Refrigeration Conference at Purdue University*, West Lafayette, IN, pp. 71-76.

- Herbe, L. and P. Lundqvist. 1997. CFC and HCFC refrigerants retrofit—Experiences and results. *International Journal of Refrigeration* 20(1): 49-54.
- Hurtgen, J.R. 1971. R-22 blister testing of magnet wire. *Proceedings of the 10th Electrical Insulation Conference, Chicago*, pp. 183-185.
- Huttenlocher, D.F. 1972. Accelerated sealed-tube test procedure for Refrigerant 22 reactions. *Proceedings of the 1972 Purdue Compressor Technology Conference*. Purdue University, West Lafayette, IN.
- Huttenlocher, D.F. 1992. Chemical and thermal stability of refrigerant-lubricant mixtures with metals. *Final Report No. DOE/CE 23810-5*. ARTI Refrigerant Database. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- IPCC. 2001. *Climate Change 2001: The scientific basis*. Contribution of Working Group I to the IPCC Third Assessment Report of the International Panel on Climate Change of the WMO and UNEP, Cambridge University Press, Cambridge, UK.
- Jolley, S.T. 1991. The performance of synthetic ester lubricants in mobile air conditioning systems. *U.S. DOE Grant No. DE-F-G02-91 CE 23810*. Unpublished paper at 1991 International CFC and Halon Alternatives Conference, Baltimore, MD, sponsored by The Alliance for Responsible CFC Policy, Arlington, VA. ARTI Refrigerant Database Abstract RDB2C07. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Jolley, S.T. 1997. Polyolester lubricants for use in environmentally friendly refrigeration applications. American Chemical Society National Meeting, San Francisco, CA. *Preprints of Papers, Division of Petroleum Chemistry* 42(1):238-241.
- Jolley, S.T., K.E. Davis, and G.R. Malone. 1996. The effect of desiccants in HFC refrigeration systems using ester lubricants. ARTI Refrigerant Database. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Jones, R.L., H.L. Ravner, and R.L. Cottingham. 1969. Inhibition of iron-catalyzed neopentyl polyol ester thermal degradation through passivation of the active metal surface by tricresyl phosphate. Paper presented at ASLE/ASME Lubrication Conference, Houston, TX.
- Keping, H. and W. Shizhu. 1991. Analysis of maximum temperature for thermo elastohydrodynamic lubrication in point contacts. *Wear* 150:1-10.
- Keuper, E.F., F.B. Hamm, and P.R. Glamm. 1996. Evaluation of R-245ca for commercial use in low pressure chiller. *Final Report DOE/CE23810-67*. ARTI Refrigerant Database (March). Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Klaus, E.E., E.J. Tewksbury, and S.S. Fietelson. 1970. Thermal characteristics of some organic esters. *ASLE Transactions*, 13(1):11-20.
- Komatsuzaki, S., Y. Homma, K. Kawashima, and Y. Itoh. 1991. Polyalkylene glycol as lubricant for HCFC-134a compressors. *Lubrication Engineering* (Dec.):1018-1025.
- Kopko, W.L. 1989. Extending the search for new refrigerants. *Proceedings of CFC Technology Conference*, Gaithersburg, MD.
- Krantz, J.C. and F.G. Rudo. 1966. The fluorinated anesthetics. In *Handbook of Experimental Pharmacology* XX(1):501-564. Eichler, O., H. Herken, and A.D. Welch, eds. Springer Verlag, Berlin.
- Kujak, S.A., and T.D. Waite. 1994. Compatibility of motor materials with polyolester lubricants: Effect of moisture and weak acids. *Proceedings of the International Refrigeration Conference at Purdue University*, pp. 425-429. West Lafayette, IN.
- Kvalnes, D.E. and H.M. Parmelee. 1957. Behavior of Freon-12 and Freon-22 in sealed-tube tests. *Refrigerating Engineering* (November):40.
- Lilje, K. 2000. The impact of chemistry on the use of polyol ester lubricants in refrigeration. *ASHRAE Transactions* 106(2):661-667.
- Lindley, A.A. 1992. KLEA 134a flammability characteristics at high-temperatures and pressures. ARTI Refrigerant Database. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Lockwood, F. and E.E. Klaus. 1981. Ester oxidation—The effect of an iron surface. *ASLE Transactions* 25(2):236-244. Society of Tribologists and Lubrication Engineers, Park Ridge, IL.
- Lohbeck, W. 1996. *Proceedings of International Conference on Ozone Protection Technologies*, pp. 247-251. Washington, D.C.
- Mays, R.L. 1962. Molecular sieve and gel-type desiccants for refrigerants. *ASHRAE Transactions* 68:330.
- Mianmiam, Y. 1996. *Proceedings of International Conference on Ozone Protection Technologies*, pp. 260-262. Washington, D.C.
- Misaki, S. and A. Sekiya. 1995. Development of a new refrigerant. *Proceedings of International CFC and Halon Alternatives Conference*, pp. 278-285. Washington, D.C.
- Misaki, S. and A. Sekiya. 1996. Update on fluorinated ethers as alternatives to CFC refrigerants. *Proceedings of International Conference on Ozone Protection Technologies*, pp. 65-70. Washington, D.C.
- Naidu, S.K., B.E. Klaus, and J.L. Duda. 1988. Thermal stability of esters under simulated boundary lubrication conditions. *Wear* 121:211-222.
- NEMA. 1987. Magnet wire. *Standard MW 1000-87*. National Electrical Manufacturer's Association, Washington, D.C.
- Norton, F.J. 1957. Rates of thermal decomposition of CHClF_2 and Cl_2F_2 . *Refrigerating Engineering* (September):33.
- O'Neill, G.J. 1992. Synthesis of fluorinated dimethyl ethers. U.K. Patent Application 2,248,617.
- O'Neill, G.J. and R.S. Holdsworth. 1990. Bis(difluoromethyl) ether refrigerant. U.S. Patent 4,961,321.
- Ozone Secretariat UNEP. 1996. *Handbook for the international treaties for the protection of the ozone layer*, 4th ed.
- Parmelee, H.M. 1965. Sealed-tube stability tests on refrigerant materials. *ASHRAE Transactions* 71(1):154.
- Pauling, L. 1960. The nature of the chemical bond and the structure of molecules and crystals. In *An introduction to modern structural chemistry*. Cornell University, Ithaca, NY.
- Powell, L. 1996. Field experience of HC's in commercial applications. *Proceedings of International Conference on Ozone Protection Technologies*, pp. 237-246. Washington, D.C.
- Powers, S. and S. Rosen. 1992. Compatibility testing of various percentages of R-12 in R-134a and PAG lubricant. *International CFC and Halon Alternatives Conference*, Washington, D.C.
- Randles, S.J., P.J. Tayler, S.H. Colmery, R.W. Yost, A.J. Whittaker, and S. Corr. 1996. The advantages and disadvantages of additives in polyol esters: An overview. ARTI Refrigerant Database. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Ratanaphraks, K., M.W. Tufts, A.S. Ng, and N.D. Smith. 1996. Material compatibility evaluations of HFC-245ca, HFC-245fa, HFE-125, HFC-236ea, and HFC-236fa. *Proceedings of the International Conference on Ozone Protection Technologies*, Washington, D.C., pp. 113-122.
- Ravishankara, A.R., A.A. Turnipseed, N.R. Jensen, and R.F. Warren. 1994. Do hydrofluorocarbons destroy stratospheric ozone? *Science* 248: 1217-1219.
- Reed, P.R. and J.J. Rizzo. 1991. Combustibility and stability studies of CFC substitutes with simulated motor failure in hermetic refrigeration equipment. *Proceedings of the XVIIIth International Congress of Refrigeration*, Montreal, 2:888-891.
- Richard, R.G. and I.R. Shankland. 1991. Flammability of alternative refrigerants. *Proceedings of the XVIIIth Congress of Refrigeration*, Montreal, p. 384.
- Riemer, A., and P.E. Hansen. 1996. Analysis of R-134a Cabinets from the First Series Production in 1990. *Proceedings of the 1996 International Refrigeration Conference at Purdue*, pp. 501-505.
- Rohatgi, N.D.T., T.T. Whitmire, and R.W. Clark. 2001. Chloride, fluoride and acidity measurements in refrigerants. *ASHRAE Transactions* 107(1):141-146.
- Sand, J.R. and D.L. Andrjeski. 1982. Combustibility of chlorodifluoromethane. *ASHRAE Journal* 24(5):38-40.
- Sanvordenker, K.S. 1985. Mechanism of oil-R12 reactions—The role of iron catalyst in glass sealed tubes. *ASHRAE Transactions* 91(1A):356-363.
- Sanvordenker, K.S. 1991. Durability of HFC-134a compressors—The role of the lubricant. *Proceedings of the 42nd Annual International Appliance Technical Conference, University of Wisconsin, Madison*.
- Sanvordenker, K.S. 1992. R-152a versus R-134a in a domestic refrigerator-freezer, energy advantage or energy penalty. *Proceedings of the International Refrigeration Conference—Energy Efficiency and New Refrigerants, Purdue University, West Lafayette, IN*.
- Sanvordenker, K.S. and M.W. Larime. 1971. Screening tests for hermetic magnet wire insulation. *Proceedings of the 10th Electrical Insulation Conference*, pp. 122-136. Institute of Electrical and Electronics Engineers, Piscataway, NJ.
- Schmitz, R. 1996. Method of making foam in an energy efficient compressor. U.S. Patent 549908.
- Sedgwick, N.V. 1966. *The organic chemistry of nitrogen*, 3rd ed. Clarendon press, Oxford, UK.
- Short, G.D. and R.C. Cavestri. 1992. High viscosity ester lubricants for alternative refrigerants. *ASHRAE Transactions* 98(1):789-795.
- Simons, G.W., G.J. O'Neill, and J.A. Gribens. 1977. New aerosol propellants for personal products. U.S. Patent 4,041,148.

- Smith, N.D., K. Ratanaphruks, M.W. Tufts, and A.S. Ng. 1993. R-245ca: A potential far-term alternative for R-11. *ASHRAE Journal* 35(2):19-23.
- Spauschus, H.O. 1963. Copper transfer in refrigeration oil solutions. *ASHRAE Journal* 5:89.
- Spauschus, H.O. 1991. Stability requirements of lubricants for alternative refrigerants. *Paper No. 148. XVIIIth International Congress of Refrigeration*, Montreal.
- Spauschus, H.O. and G.C. Doderer. 1961. Reaction of Refrigerant 12 with petroleum oils. *ASHRAE Journal* 3(2):65.
- Spauschus, H.O. and G.C. Doderer. 1964. Chemical reactions of Refrigerant 22. *ASHRAE Journal* 6(10).
- Spauschus, H.O. and R.A. Sellers. 1969. Aging of hermetic motor insulation. *IEEE Transactions* E1-4(4):90.
- Spauschus, H.O., G. Freeman, and T.L. Starr. 1992. Surface analysis of glass from sealed tubes after aging with HFC-134a. ARTI *Refrigerant Database* RDB2729. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Steinle, H. and W. Seemann. 1951. Über die Kupferplattierung in Kältemaschinen. *Kältetechnik*. 3(8):194-197.
- Steinle, H. and W. Seemann. 1953. Ursache der Kupferplattierung in Kältemaschinen. *Kältetechnik*. 5(4):90-94.
- Steinle, H. and R. Bosch. 1955. Versuche über Kupferplattierung an Kältemaschinen. *Kältetechnik*. 7(4):101-104.
- Sundaresan, S.G. and W.R. Finkenstadt. 1990. Status report on polyalkylene glycol lubricants for use with HFC-134a in refrigeration compressors. *Proceedings of the 1990 USNC/IIR-Purdue Conference*, ASHRAE-Purdue Conference, 138-144.
- Sundaresan, S.G. and W.R. Finkenstadt. 1991. Degradation of polyethylene terephthalate films in the presence of lubricants for HFC-134a: A critical issue for hermetic motor insulation systems. *International Journal of Refrigeration* 14:317.
- Swallow, A., A. Smith, and B. Greig. 1995. Control of refrigerant vapor release from polyol ester/halocarbon working fluids. *ASHRAE Transactions* 101(2):929-934.
- Swallow, A.P., A.M. Smith, and D.G.V. Jones. 1996. Control of refrigerant vapor release from polyolester/halocarbon working fluids. *Proceedings of the International Conference on Ozone Protection Technologies*, Washington, D.C., pp. 123-132.
- Terrell, R.C., L. Spears, A.J. Szur, J. Treadwell, and T.R. Ucciardi. 1971a. General anesthetics. 1. Halogenated methyl ethers as anesthetics agents. *Journal of Medical Chemistry* 14:517.
- Terrell, R.C., L. Spears, T. Szur, T. Ucciardi, and J.F. Vitche. 1971b. General anesthetics. 3. Fluorinated methyl ethyl ethers as anesthetic agents. *Journal of Medical Chemistry* 14:604.
- Thomas, R.H. and H.T. Pham. 1989. Evaluation of environmentally acceptable refrigerant/lubricant mixtures for refrigeration and air conditioning. SAE Passenger Car Meeting and Exposition. Society of Automotive Engineers, Warrendale, PA.
- Thomas, R.H., W.T. Wu, and R.H. Chen. 1993. The stability of R-32/125 and R-125/143a. *ASHRAE Transactions* 99(2).
- UL. 1993. Refrigerant-containing components and accessories, nonelectrical, 6th ed. ANSI/UL *Standard* 207-93. Underwriters Laboratories, Northbrook, IL.
- UL. 1994. Refrigerants. *Standard* 2182-94. Underwriters Laboratories, Northbrook, IL.
- UL. 1996. Hermetic refrigerant motor-compressors, 7th ed. *Standard* 984-96. Underwriters Laboratories, Northbrook, IL.
- Vinci, J.N. and D.L. Dick. 1995. Polyol ester lubricants for HFC refrigerants: A systematic protocol for additive selection. *International CFC and Halon Alternatives Conference*. Washington, D.C.
- Walker, W.O., S. Rosen, and S.L. Levy. 1960. A study of the factors influencing the stability of mixtures of Refrigerant 22 and refrigerating oils. *ASHRAE Transactions* 66:445.
- Wang, B., J.L. Adcock, S.B. Mathur, and W.A. Van Hook. 1991. Vapor pressures, liquid molar volumes, vapor non-idealities and critical properties of some fluorinated ethers: CF₃-O-CF₂-O-CF₃, CF₃-O-CF₂-CF₂H, c-CF₂-CF₂-CF₂-O-, CF₃-O-CF₂H, and CF₃-O-CH₃ and of CCl₃F and CF₂ClH. *Journal of Chemical Thermodynamics* 23:699-710.
- Wuebbles, D.J. and J.M. Calm. 1997. An environmental rationale for retention of endangered chemicals, *Science* 278:1090-1091.
- Womeldorf, C. and W. Grosshandler. 1995. Lean flammability limits as a fundamental refrigerant property. *Final Report* No. DOE/CE 23810-68. ARTI *Refrigerant Database*. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.
- Zhigang, L., L. Xianding, Y. Jianmin, T. Xhufang, J. Pingkun, C. Zhehua, L. Dairu, R. Mingzhi, Z. Fan, and W. Hong. 1992. Application of HFC-152a/HCFC-22 blends in domestic refrigerators. ARTI *Refrigerant Database* RDB2514. Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.

BIBLIOGRAPHY

- ASTM. 1995. Test method for acid number of petroleum products by potentiometric titration. ANSI/ASTM *Standard* D664-95. American Society for Testing and Materials, West Conshohocken, PA.
- DeMore, W.B., S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, and M.J. Molina. 1997. Chemical kinetics and photochemical data for use in stratospheric modeling. *Evaluation Number 12*, January 15, 1997. NASA and JPL, California Institute of Technology.
- Gierczak, T., R.K. Talukdar, J.B. Burkholder, R.W. Portman, J.S. Daniel, S. Solomon, and A.R. Ravishankara. 1996. Atmospheric fate and greenhouse warming potentials of HFC 236fa and HFC 236ea. *Journal of Geophysical Research* 101(D8).
- Houghton, J.T., L.G. Filho, B.A. Callander, N. Harris, A. Kattenberg, and K. Maskell. 1995. *Climate change 1994: The science of climate change*. Contribution of WGI to the First Assessment Report of the International Panel on Climate Change, Cambridge University, Cambridge, UK.
- Houghton, J.T., L.G. Filho, B.A. Callander, N. Harris, A. Kattenberg, and K. Maskell. 1996. *Climate change 1995: The science of climate change*. Contribution of WGI to the Second Assessment Report of the International Panel on Climate Change, Cambridge University, Cambridge, UK.
- Keuper, E.F. 1996. Performance characteristics of R-11, R-123 and R-245ca in direct drive low pressure chillers. *Proceedings of the International Compressor Conference at Purdue*.
- Ko, M., R.L. Shia, and N.D. Sze. 1997. *Report on calculations of global warming potentials*. Prepared for AFEAS, Contract P97-134, July.
- Reed, P.R. and H.O. Spauschus. 1991. HCFC-124: Applications, properties and comparison with CFC-114. *ASHRAE Journal* 40(2).