CHAPTER 5

REFRIGERANT SYSTEM CHEMISTRY

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

REFRIGERANTS

Environmental Acceptability

Common chlorine-containing refrigerants contribute to depletion of the ozone layer. A material's **ozone depletion potential (ODP)** is a measure of its ability, compared to CFC-11, to destroy stratospheric ozone.

Halocarbon refrigerants also can contribute to global warming and are considered greenhouse gases. The **global warming potential (GWP)** of a greenhouse gas is an index describing its ability, compared to CO_2 (which has a very long atmospheric lifespan), to trap radiant energy. The GWP, therefore, is connected to a particular time scale (e.g., 100 or 500 years). For regulatory purposes, the convention is to use the **100-year integrated time horizon (ITH)**.

Appliances using a given refrigerant also consume energy, which indirectly produces CO_2 emissions that contribute to global warming; this indirect effect is frequently much larger than the refrigerant's direct effect. An appliance's **total equivalent warming impact (TEWI)** is based on the refrigerant's direct warming potential and indirect effect of the appliance's energy use The **life cycle climate performance (LCCP)**, which includes the TEWI as well as cradle-to-grave considerations such as the climate change effect of manufacturing the refrigerant, transportation-related energy, and end-of-life disposal, is becoming more prevalent.

Environmentally preferred refrigerants (1) have low or zero ODP, (2) provide good system efficiency, and (3) have low GWP or TEWI values. 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 boiling points, atmospheric lifetimes, ODPs, GWPs, and flammabilities of new refrigerants and the refrigerants being replaced. ODP values were 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 are essentially zero (Ravishankara et al. 1994).

GWP values were established as a reference point using Intergovernmental Panel on Climate Change (IPCC 1995) assessment values, as shown in Table 1, and are the official numbers used for reporting and compliance purposes to meet requirements of the United Nations Framework Convention on Climate Change (UNFCCC) and Kyoto Protocol. However, lifetimes and GWPs have since been reviewed (IPCC 2001) and are shown in Table 2, representing the most recent published values based on an updated assessment of the science. These values are subject to review and may change with future reassessments, but are currently not used for regulatory compliance purposes. Table 3 shows bubble points and calculated ODPs and GWPs for refrigerant blends, using the latest scientific assessment values.

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 significant 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, although many have already made considerable phaseout progress.

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 developed-country consumption of HCFCs beginning January 1, 1996, using a cap equal to 2.8% of the 1989 ODP weighted consumption of CFCs plus the 1989 ODP-weighted consumption of HCFCs. The CAP was reduced by 35% by January 1, 2004, and will be reduced by 65% on January 1, 2010; 90% by January 1, 2015; 99.5% by January 1, 2020; and total phaseout by January 1, 2030. From 2020 to 2030, HCFCs may only be used to service existing equipment. Developing countries must freeze HCFC ODP consumption at 2015 levels in 2016, and completely phase out by January 1, 2040.

In addition to the requirements of the Montreal Protocol, several countries have established their own regulations on HCFC phaseout of HCFCs. The United States has met the Montreal Protocol's requirements by banning consumption of R-141b (primarily used as a foam-blowing agent) on January 1, 2003, and phasing out HCFC-142b (primarily foams) and HCFC-22 for original equipment manufacturers (OEMs) beginning January 1, 2010. Production for service needs is allowed to continue. Production and consumption of all other HCFCs will be frozen on January 1, 2015. On January 1, 2020, production and consumption of R-22 and R-142b will be banned, 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 preparation of this chapter is assigned to TC 3.2, Refrigerant System Chemistry.

Table 1 Refrigerant Properties: Regulatory Compliance Values Used by Governments for UNFCCC Reporting and Kyoto Protocol Compliance

Refrigerant	Structure	Boiling Point,[a] °F	Atmospheric Lifetime,[b] Years	ODP[c]	GWP, ITH 100-Year	Flammable?
E125	$CHF_2OC\ F_3$	–43.6	165[a]		15,300[a]	No
E143	CHF_2OCH_2F	85.8[d]				Yes
E143a	CF_3OCH_3	–11.4	5.7[a]		5400[a]	Yes
11	$CC1_3F$	74.7	50	1	4600[a]	No
12	CCl_2F_2	–21.6	102	1	10,600[a]	No
22	$CHClF_2$	–41.4	12.1	0.055	1900[a]	No
23	CHF_3	–115.8	264		11,700	No
32	CH_2F_2	–61.1	5.6		650	Yes
113	CCl_2FCClF_2	117.7	85	0.8	6000[a]	No
114	$CClF_2CClF_2$	38.5	300	1	9800[a]	No
115	$CClF_2CF_3$	–38.0	1700	0.6	10,300[a]	No
116	CF_3CF_3	–108.8	10,000		11,400[a]	No
123	$CHCl_2CF_3$	82.0	1.4	0.02	120[a]	No
124	$CHClFCF_3$	10.4	6.1	0.022	620[a]	No
125	CHF_2CF_3	–54.6	32.6		2800	No
134a	CH_2FCF_3	–16.0	14.6		1300	No
142b	$CClF_2CH_3$	15.8	18.4	0.065	2300[a]	Yes
143	CH_2FCHF_2	41.0	3.8		300	Yes
143a	CF_3CH_3	–53.0	48.3		3800	Yes
152a	CHF_2CH_3	–11.2	1.5		140	Yes
218	$CF_3CF_2CF_3$	–33.9	2600[a]		8600[a]	No
227ea	CF_3CHFCF_3	3.9	36.5		2900	No
236ea	$CF_3CHFCHF_2$	43.7[d]	10[d]		9400[a]	No
236fa	$CF_3CH_2CF_3$	29.5	209		6300	No
245ca	$CHF_2CF_2CH_2F$	–13.2	6.6		560	Yes
245fa	$CF_3CH_2CHF_2$	59.2	8.8[a]		820[a]	No

[a] Data from Calm and Hourahan (1999).
[b] Data from IPCC (1995).
[c] Data from Montreal Protocol (2003).
[d] Data from Chapter 5 of the 2002 *ASHRAE Handbook—Refrigeration*.

Table 2 Refrigerant Properties: Current IPCC Scientific Assessment Values

Refrigerant	Structure	Boiling Point, °F	Atmospheric Lifetime, Years	ODP	GWP, ITH[a] 100-Year	Flammable?[b]
E125	CHF_2OCF_3	–43.6	165[c]		14,900	No
E143	CHF_2OCH_2F	85.1[b]			57	Yes
E143a	CF_3OCH_3	–11.4	5.7[c]		750	Yes
11	CHl_3F	74.7	50	1	4600	No
12	CCl_2F_2	–21.6	102	1	10,600	No
22	$CHClF_2$	–41.4	12.1	0.055	1700	No
23	CHF_3	–115.8	264		12,000	No
32	CH_2F_2	–61.1	5.6		550	Yes
113	CCl_2FCF_2Cl	117.7	85	0.8	6000	No
114	$CClF_2CClF_2$	38.5	300	1	9800	No
115	ClF_2CF_3	–38.0	1700	0.6	7200	No
116	CF_3CF_3	–108.8	10,000		11,900[c]	No
123	$CHCl_2CF_3$	82.0	1.4	0.02	120	No
124	$CHClFCF_3$	10.4	6.1	0.022	620	No
125	CHF_2CF_3	–54.6	32.6		3400	No
134a	CH_2FCF_3	–15.0	14.6		1300	No
142b	CH_3CClF_2	15.8	18.4	0.065	2400	Yes
143	CH_2FCHF_2	41.0	3.8		330	Yes
143a	CH_3CF_3	–53.0	48.3		4300	Yes
152a	CH_3CHF_2	–11.2	1.5		120	Yes
218	$CF_3CF_2CF_3$	–33.9	2600[c]		8600[c]	No
227ea	CF_3CHFCF_3	3.9	36.5		3500	No
236ea	$CF_3CHFCHF_2$	43.7[b]	10[b]		1200	No
236fa	$CF_3CH_2CF_3$	29.5	209		9400	No
245ca	$CHF_2CF_2CH_2F$	77.2	6.6		640	Yes
245fa	$CF_3CH_2CHF_2$	59.2	8.8[c]		950	No

[a] Data from IPCC (2001).
[b] Data from ASHRAE *Standard* 34.
[c] Data from Calm and Hourahan (1999).

Table 3 Properties of Refrigerant Blends[a]

Refrigerant	Composition	Bubble Point,[b] °F	ODP[c]	GWP,[d] 100-Year ITH
401A	(22/152a/124)/(53/13/34)	–27.9	0.027	1100
401B	(22/152a/124)/(61/11/28)	–30.8	0.028	1200
401C	(22/152a/124)/(33/15/52)	–19.1	0.025	900
402A	(125/C_3H_8/22)/(60/2/38)	–56.2	0.013	2700
402B	(125/C_3H_8/22)/(38/2/60)	–52.6	0.020	2300
403A	(C_2H_6/22/218)/(5/75/20)	–54.0	0.026	3000
403B	(C_2H_6/22/218)/(5/56/39)	–56.6	0.019	4300
404A	(125/143a/134a)/(44/52/4)	–51.2	0	3800
405A	(22/152a/142b/C318)/(45/7/5.5/42.5)	–27.2	0.018	5200
406A	(22/600a/142b)/(55/4/41)	–26.9	0.036	1900
407A	32/125/134a)/(20/40/40)	–49.5	0	2000
407B	(32/125/134a)/(10/70/20)	–52.2	0	2700
407C	(32/125/134a)/(23/25/52)	–46.5	0	1700
407D	(32/125/134a)/(15/15/70)	–39.1	0	1500
407E	(32/125/134a)/(25/15/60)	–45.2	0	1400
408A	(125/143a/22)/(7/46/47)	–48.3	0.016	3000
409A	(22/124/142b)/(60/25/15)	–30.5	0.039	1500
409B	(22/124/142b)/(65/25/10)	–32.1		
410A	(32/125)/(50/50)	–60.5	0	2000
411A	(R-1270/22/152a)/(1.5/87.5/11.0)	–39.1	0.030	1500
411B	(1270/22/152a)/(3/94/3)	–42.9	0.032	1600
412A	(22/218/142b)/(70/5/25)	–36.4	0.035	2200
413A	(218/134a/600a)/(9/88/3)	–23.1	0	1900
414A	(22/124/600a/142b)/(51/28.5/4/16.5)	–29.2	0.032	1400
414B	(22/124/600a/142b)/(50/39/1.5/9.5)	–27.2	0.031	1300
415A	(22/152a)/(82/18)	–35.5	0.028	1400
415B	(22/152a)/(25/75)	–17.9	0.009	500
416A	(134a/124/600)/(59/39.5/1.5)	–10.1	0.010	1000
417A	(125/134a/600)/(46.6/50/3.4)	–36.4	0.000	2200
418A	(290/22/152a)/(1.5/96/2.5)	–42.2	0.33	1600
500	(12/152a)/(73.8/26.2)	–28.5	0.605	7900
502	(22/115)/(48.8/51.2)	–49.4	0.221	4500
503	23/13/(40.1/59.9)	–127.8	0.599	13,000
507A	(125/143a)/(50/50)	–52.1	0	3900
508A	(23/116)/(39/61)	–125.3	0	12,000
508B	(23/116)/(46/54)	–124.6	0	12,000
509A	(22/218)/(44/56)	–57.6	0.015	5600

[a] Data from IPCC (2001).
[b] Data from ARI *Standard* 700.
[c] Data from Calm (2001).
[d] GWPs are weight fraction average for GWP values of individual components.

The European Union has already reduced the consumption cap on HCFCs and accelerated the phase-out schedule. E.U. consumption of HCFCs was reduced 15% on January 1, 2002, by 55% on January 1, 2003, and by 70% on January 1, 2004; future reductions are to be by 75% on January 1, 2008, and total phaseout on January 1, 2010. They also implemented several use restrictions on HCFCs in air-conditioning and refrigeration equipment.

U.S. and E.U. phaseout schedules allow continued, limited manufacture for developing-country needs or for export to other countries where HCFCs are still legally used.

Atmospheric studies (Calm et al. 1999; Wuebbles and Calm 1997) 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 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 used commercially in large chillers.

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 promoted as a replacement for R-22 and R-502. For very-low-temperature applications, R-23 (trifluoromethane, CHF_3) has been used as a replacement for R-13 and R-503 (Atwood and Zheng 1991).

Fluoroethanes. Refrigerant 134a (CF_3CH_2F) 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 (Sandvordenker 1992), but it is still being considered 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 R-245ca performance 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 used as a chlorine-free replacement for R-11 and R-141b in foams, and is being considered as a refrigerant and commercialized in organic Rankine-cycle and waste-heat-recovery systems. R-236fa has been commercialized as a replacement for R-114 in naval centrifugal chillers.

Fluoroethers. Booth (1937), Eiseman (1968), Kopko (1989), O'Neill (1992), O'Neill and Holdsworth (1990), and Wang et al. (1991) proposed these compounds as refrigerants. Fluoroethers are usually more physiologically and chemically reactive than fluorinated hydrocarbons. Fluorinated ethers have been used 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; Gross 1990; Simons et al. 1977). Misaki and Sekiya (1995, 1996) investigated 1-methoxyperfluoropropane (boiling point 93.6°F) and 2-methoxyperfluoropropane (boiling point 84.9°F) 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 widespread 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 used in air-conditioning and refrigeration equipment in Europe and China (Lohbeck 1996; Mianmiam 1996; Powell 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 ppm) that people automatically avoid exposure to it. Ammonia is considered toxic at 35 to 50 ppm. 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 1200°F.

Carbon Dioxide. Some governments are promoting use of CO_2 in refrigeration and air-conditioning cycles. Trial cascade systems are being used in Europe, and some countries in the European Union are promoting transcritical carbon dioxide systems to replace HFC-134a in automotive air-conditioning systems. Higher costs are expected because of the higher pressures and transcritical cycle.

Refrigerant Analysis

With the introduction of many new pure refrigerants and refrigerant mixtures, interest in refrigerant analysis has increased. Refrigerant analysis is addressed in ARI *Standards* 700 and 700c. Gas chromatographic methods are available to determine purity determination of R-134a and R-141b (Gehring et al. 1992a, 1992b). Gehring (1995) discusses measurement of water in refrigerants Bruno and Caciari (1994) and Bruno et al. (1995) have done extensive work developing chromatographic methods for analysis of refrigerants using a graphitized carbon black column with a coating of hexafluoropropene. Bruno et al. (1994) also published refractive indices for some alternative refrigerants. There is interest in developing methods for 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 determining 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 increased 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 200 psia) and fuel (R-22)-to-oxygen ratio. They found that R-22 was nonflammable under 75 psia. 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 at least 50% air are combustible. R-11 and R-12 did not ignite under similar conditions.

Lindley (1992) and Reed and Rizzo (1991), using different experimental arrangements, studied R-134a's combustibility at high temperature and pressure. Lindley notes that the results depend on the equipment used. Reed and Rizzo showed that R-134a is combustible above 15 psig at room temperature and air concentrations greater than 80% by volume. At 350°F, combustibility was observed at pressures above 5 psig and air concentrations above 60% by volume. Lindley found flammability limits of 8 to 22% by volume in air at 340°F and 100 psia. 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 combusted above 180°F at atmospheric pressure and above, with air concentrations above 80% by volume (Reed and Rizzo 1991).

Richard and Shankland (1991) followed ASTM *Standard* E681's method to study 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 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 flammability of R-152a/22 mixtures. Their measured lower flammability limit in air of R-152a is 11.4% by volume, though 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 flame length 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 Richard and Shankland's (1991) data, which showed a critical flammability ratio of 57.1% R-22 by mass. Comparison is difficult because results depend on the apparatus and methods used. Grob (1991), reporting on flammabilities of R-152a, R-141b, and R-142b, describes R-152a as having "the lowest flammable mixture percentage, highest explosive pressure and highest potential for ignition of the refrigerants studied." Womeldorf and Grosshandler (1995) used an opposed-flow burner to evaluate flammability limits of refrigerants.

CHEMICAL REACTIONS

Halocarbons

Thermal Stability in the Presence of Metals. All common halocarbon refrigerants have excellent thermal stability, as shown in Table 4. 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 392°F. This decomposition did not increase much with time. R-152a showed traces of HF at 356°F after five days in a steel container. Bier et al. suggested that vinyl fluoride forms during thermal decomposition of R-152a, and 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 agree-

Table 4 Inherent Thermal Stability of Halocarbon Refrigerants

Refrigerant	Formula	Decomposition Rated at 400°F in Steel, % per yr[a]	Temperature at Which Decomposition Readily Observed in Laboratory,[b] °F	Temperature at Which 1%/Year Decomposes in Absence of Active Materials, °F	Major Gaseous Decomposition Products[c]
22	$CHClF_2$	—	800	480	CF_2CF_2,[d] HCl
11	CCl_3F	2	1100	570[e]	R-12, Cl_2
114	$CClF_2CClF_2$	1	1100	710	R-12
115	$CClF_2CF_3$	—	1160	740	R-13
12	CCl_2F_2	Less than 1	1400	930	R-13, Cl_2
13	CClF3	—	1550	1000[f]	R-14, Cl_2, R-116

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

[a] Data from UL *Standard* 207.

[b] Decomposition rate is about 1% per min.

[c] Data from Borchardt (1975).

[d] Various side products are also produced, here and with the other refrigerants, some of which may be quite toxic.

[e] Conditions were not found where this reaction proceeds homogeneously.

[f] Rate behavior too complex to permit extrapolation to 1% per year.

Table 5 Rate of Hydrolysis in Water (Grams per Litre of Water per Year)

Refrig-erant	Formula	14.7 psi at 86°F Water Alone	14.7 psi at 86°F With Steel	Saturation Pressure at 122°F 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	$CClF_2$-$CClF$	<0.005	1	3
22	$CHClF_2$	<0.01	0.1	—

Source: DuPont (1959, 1969).

ment with Bier et al., they found that vinyl fluoride and acetaldehyde 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 HFCs to be more thermally stable than CFCs and HCFCs, and that, when molten aluminum is in contact with R-134a, a layer of unreactive aluminum fluoride forms and inhibits further reaction.

Hydrolysis. Halogenated refrigerants are susceptible to reaction with water (hydrolysis), but the rates of reaction are so slow that they are negligible (Table 5). Desiccants (see Chapter 6) are used to keep refrigeration systems dry. Cohen (1993) investigated compatibilities 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 is as follows:

$$NH_3 + RCOOH \Leftrightarrow RCOONH_4 \Leftrightarrow RCONH_2 + H_2O$$

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

At atmospheric pressure, ammonia starts to dissociate into nitrogen and hydrogen at about 570°F in the presence of active catalysts such as nickel and iron. However, because these high temperatures are unlikely to occur in open-type 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 and copper plating are excluded in ammonia systems. (See the section on Copper Plating for more information.)

Table 6 Influence of Type of Alcohol on Ester Viscosity

Type of Alcohol	Ester Viscosity at 104°F, centistokes
Neopentyl glycol (NPG)	13.3
Glycerin (GLY)	31.9
Trimethylolpropane (TMP)	51.7
Pentaerythritol (PER)	115

Note: Ester derived using the same carboxylic acid.

Table 7 R-134a Miscibility and Viscosity of Several Pentaerythritol-Based Esters

Acid Used	R-134a Miscibility at 20% Ester, °F	Ester Viscosity at 104°F, centistokes
5 carbon, linear	<–94	15.6
6 carbon, linear	–53	18.5
7 carbon, linear	34	21.2
8 carbon, linear	>149	26.7
9 carbon, linear	>149	31.0
5 carbon, branched	<–94	25.2
8 carbon, branched	5	44.4
9 carbon, branched	17	112.9

Source: Jolley (1997).

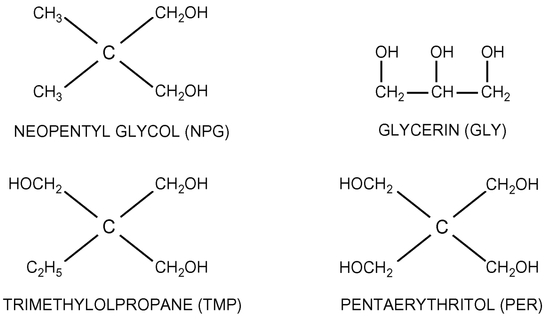

Fig. 1 Types of Alcohols Used for Ester Synthesis

Lubricants

Lubricants now in use and under consideration for 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; (1) neopentyl glycol (NPG), with two OH reaction sites; (2) glycerin (GLY), with three OH sites; (3) trimethylolpropane (TMP) with three OH sites; and (4) pentaerythritol (PER), with four OH sites. Formulas for the four alcohol types are shown in Figure 1. Viscosities of the esters formed by reaction of a given acid with each of the four alcohol types are given in Table 6.

Polyol esters are widely used as lubricants in HCFC refrigerant systems, mainly because of their physical properties. Because they are made from a wide variety of materials, polyol esters can be designed to optimize desired 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 7 gives R-134a miscibility and viscosity data for several esters based on pentaerythritol. Clearly, polyol ester lubricants rapidly lose refrigerant miscibility when linear carbon chain lengths exceed six carbons. Using branched chain acids to prepare these lubricants can greatly enhance refrigerant miscibility. Chain branching also enables preparation of higher-viscosity esters, which are needed in some industrial refrigeration applications.

The thermal stability of polyol esters is well known. 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 1), have outstanding thermal stability. Gunderson and Hart (1962) reviewed research measuring the thermal stability of various polyol esters and dibasic acid esters at 500°F by heating them in evacuated tubes for up to 250 h. These tests demonstrated the increased thermal stability expected from neo ester structures, with dibasic acid esters decomposing 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:

$$\underset{\text{Ester}}{\text{RCOOR}'} + \underset{\text{Water}}{\text{HOH}} \Leftrightarrow \underset{\text{Acid}}{\text{RCOOH}} + \underset{\text{Alcohol}}{\text{R}'\,\text{OH}}$$

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 [particularly total acid number (TAN), degree of esterification, nature of the catalyst used during production, and catalyst level remaining in the polyol ester after processing] and their structure. Dick et al. (1996) demonstrated that (1) using polyol esters prepared with acids known as α-branched acids significantly reduces ester hydrolysis and (2) using α-branched esters with certain additives can eliminate hydrolysis.

Hydrolysis is undesirable in refrigeration systems because free carboxylic acid can react with and corrode metal surfaces. Metal carboxylate soaps that may be produced by hydrolysis can also block capillary tubes. Davis et al. (1996) reported that polyol ester hydrolysis proceeds through autocatalytic reaction, and determined reaction rate constants for hydrolysis using sealed-tube tests. Jolley et al. (1996) and others 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 ppm) have gone 2000 h with no significant capillary tube blockage, indicating that under normal, much drier operating conditions, little or no detrimental ester hydrolysis occurs with use of polyol ester lubricants. Hansen and Snitkjær (1991) demonstrated ester hydrolysis 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 203°F and bubbling oxygen through it in the presence of steel and copper. Appropriate additives can suppress hydrolysis of esters. Although agreeing that esters can be 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, a common antiwear agent, on ester decomposition.

Field and Henderson (1998) studied the effect of elevated levels of organic acids and moisture on 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 392°F, 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 high-temperature (600°F) 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 365°F. Cottington and Ravner (1969) reported that the presence of TCP inhibits the POE/iron reaction, which Lilje (2000) concluded 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 (PAGs). Polyalkylene glycols are of the general formula $\text{RO—[CH}_2\text{—CHR}'\text{—O]—R}'$. 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 Finkenstadt (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 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. Clark et al. (1985) and Lockwood and Klaus (1981) found that iron and copper catalyze the oxidative degradation of esters. These reaction products are detrimental to the refrigeration system and can cause failure. Komatsuzaki et al. (1991) have suggested that the oxidative breakdown products of PAG lubricants and perhaps of esters are volatile, whereas those of mineral oils are more likely to include sludges.

Sanvordenker (1991) studied thermal stability of PAG and ester lubricants and found that, above 400°F, 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 metallic bearing surfaces, which can experience 400°F 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 lubricant performance in refrigeration systems, and have become more important as use of HFC refrigerants has increased. Chlorine in CFC refrigerants acted as an antiwear agent, so 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, etc., are not normally used because the conditions they treat are absent from most refrigeration systems. Many HFC/polyol ester refrigeration systems function well without lubricant additives. However, some systems that have aluminum 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) showed 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 used 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 in both wear and capillary 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 400°F. He proposed using a metal passivator 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 using 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 78, 93, and 100 kcal/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. In this reaction, characteristic of chlorine-containing refrigerants, 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 (CF_3—CH_2—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 2000 psi) usually cause the sealed glass tubes to explode.

Breakdown of CFCs and HCFCs can usually be tracked by observing the concentration of 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 (Spauschus 1991; Thomas and Pham 1989; Thomas et al. 1993); according to this test, 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 is 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 2 and 3 show sealed-tube test data for reaction rates of R-22 and R-12 with oil in the presence of copper and mild steel. Formation of chloride ion was taken as a measure of decomposition. These figures show the extent to which temperature accelerates reactions, and 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.

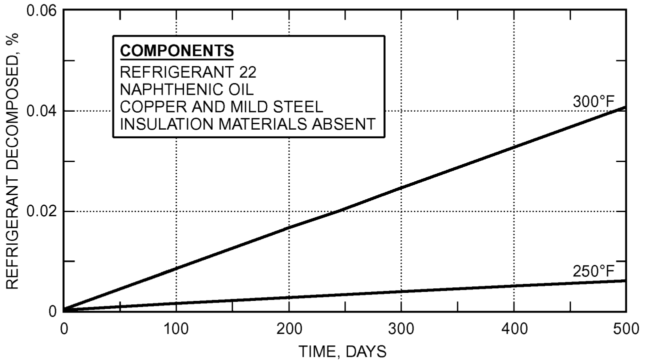

Fig. 2 Stability of Refrigerant 22 Control System
(Kvalnes and Parmelee 1957)

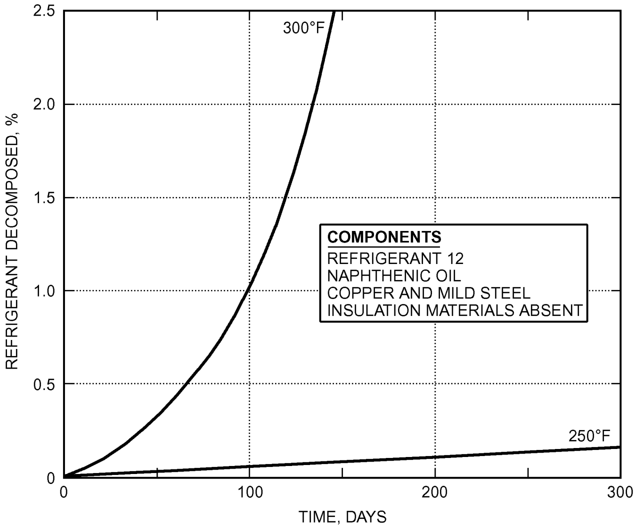

Fig. 3 Stability of Refrigerant 12 Control System
(Kvalnes and Parmelee 1957)

The chemistry 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 chlorinated 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 blush 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.

Although the exact mechanism of copper plating is not completely understood, early work by Spauschus (1963), Steinle and Bosch (1955), and Steinle and Seeman (1951, 1953) demonstrated that three distinct steps must occur: (1) copper oxidation, (2) solubilization and transport of copper ions, and (3) deposition of copper onto iron or steel.

In step 1, copper oxidizes from the metallic (0 valent) state to either the +1 or +2 oxidation state. Under normal operating conditions, this chemical process does not occur with a lubricant, and is unlikely to occur with carboxylic acids. The most likely source of oxidizing agents is system contaminants, such as air (oxygen), chlorine-containing species (CFC refrigerants or cleaning solvents, solder fluxes), or strong acids.

Step 2 is 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 and/or complexes via coordination with the oxygen atoms. Once soluble, the copper can move throughout the refrigeration system.

Step 3 is deposition of the copper onto iron surfaces, an electrochemical process in which electrons transfer 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 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, and that water did not significantly affect the amount of copper produced. In the R-134a/PAG system, 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 refrigerant decomposition had little effect on copper solubility, but facilitated plating. 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 300°F. Prolonged exposure to these thermal excursions can damage motor insulation, depending on the insulation materials' thermal stability and 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, but 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 lubricant cracking by 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, compressor temperature and deterioration rate 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 refrigeration system, where they clog oil passages; interfere with operation of expansion, suction, and discharge valves; or plug capillary tubes.

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

COMPATIBILITY OF MATERIALS

Electrical Insulation

Insulation on electric motors is affected by the refrigerant and/or the lubricant in two main ways: 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 (e.g., capillary tubes) to clog.

Refrigerant absorption can change the material's dielectric strength or physical integrity through softening or swelling. Rapid desorption (off-gassing) of refrigerant caused by internal heating can be more serious, because it results in high internal pressures that cause blistering or voids within the insulation, decreasing its 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 insulation damage after desorption of R-32, R-134, and R-152a in a 300°F oven, but not as much as with 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, and R-123. Most motor materials were unaffected, except for increased brittleness in polyethylene terephthalate (PET) caused by moisture and blistering between layers of sheet insulation from the adhesive. Many of the same materials were completely destroyed when exposed to ammonia; 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 ppm moisture level in 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 breakdown products of a simulated motor burnout in HFC refrigerant atmospheres.

Magnet Wire Insulation. Magnet wire is coated with heat-cured enamels. 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 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.

Magnet wire insulation is the primary source of electrical insulation and the most critical in 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, degree of cure, and 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 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 4. 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 8 shows values of t_{max} for several hermetic enamels. Continued heating above t_{max} causes aging, shown by the irreversible alteration of dielectric properties and increased 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 aging rates 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 some wire enamels. Beacham and Divers (1955) demonstrated that polyvinyl formal's resistance drops drastically when it 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 R-22's low volume resistivity and other electrical properties of the two refrigerants, explains the phenomenon.

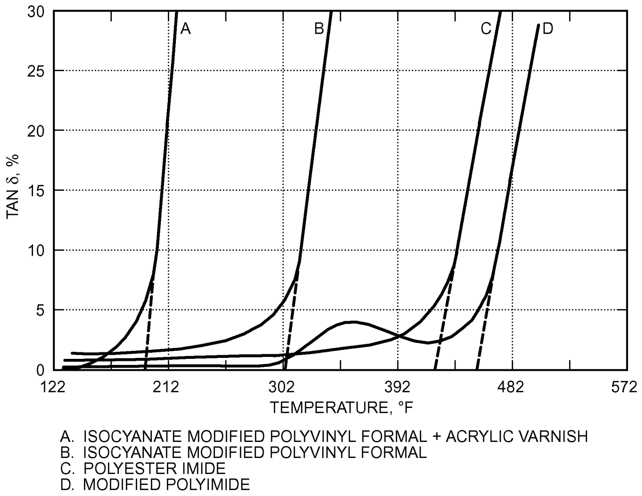

Fig. 4 Loss Curves of Various Insulating Materials
(Spauschus and Sellers 1969)

Table 8 Maximum Temperature t_{max} for Hermetic Wire Enamels in R-22 at 65 psia

Enamel Type	t_{max}, °F
Acrylic	226
Polyvinyl formal	277
Isocyanate-modified polyvinyl formal	304
Polyamide imide	361
Polyester imide	419
Polyimide	450

With certain combinations of coatings and refrigerants, wire coatings can soften, which can cause the insulation to fail. Table 9 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 abrasion resistance more slowly, approaching, over three months, 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. Modern 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 275 to 350°F 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 abrades and wears 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 heat and cold; thermal stability; good dielectric properties; and chemical compatibility with wire enamel, sheet insulation, and refrigerant/lubricant mixture.

Table 9 Effect of Liquid R-22 on Abrasion Resistance

		After Time in Liquid R-22		
Magnet Wire Insulation	As Received	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).

Varnish compatibility is determined by exposing the cured varnish (in the form of a section of a thin disk and varnished magnet wire in single strands, helical coils, and twisted pairs) to a refrigerant at elevated temperatures. The varnish's properties are then compared to samples not exposed to refrigerant and to other exposed samples placed in a hot oven to rapidly remove absorbed refrigerant. 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 it 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 compatibility testing of motor materials with alternative refrigerants, researchers observed that varnish can absorb considerable amounts of refrigerant, especially R-123. Doerr (1992) studied the effects of time and temperature on absorption and desorption rates of R-123 and R-11 by epoxy motor varnishes. Absorption was faster at higher temperatures. Desorption was slow at temperatures as high as 250°F. 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, used singly or laminated together. PET or aramid films have 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 temperature-dependent solubility in mineral lubricants and tend to precipitate as noncohesive granules at temperatures lower than those of the motor. Another limitation is that, like most polyesters, this film is susceptible to degradation by hydrolysis; however, the amount 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 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 swelling or shrinkage (e.g., 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 seven 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 elastomer's specific formulation as well as by its general type.

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, whereas 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 use. 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 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, described in ASHRAE *Standard* 97, is widely used to assess stability of refrigerant system materials and 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, and 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. Contents can be analyzed for changes by gas, ion, or liquid chromatography; infrared spectroscopy; specific ion electrode; or wet methods, such as total acid number analysis.

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

Despite its proven utility, the sealed-tube test 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, as 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 aging, autoclave tests can include external stresses (e.g., mechanical vibration, on/off electrical voltages, liquid refrigerant floodback) that may accelerate phenomena likely to occur in an operating system.

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 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.

Refrigerant and lubricant are chemically analyzed before, during, and after the test.

In most cases, tests are conducted under severe operating conditions to obtain results quickly. Analyzing lubricant and refrigerant samples during the test and inspecting the components after teardown can yield information on the (1) nature and rate of chemical reactions taking place in the system, (2) 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.

REFRIGERANT DATABASE AND ARTI/MCLR RESEARCH PROJECTS

The U.S. Department of Energy (DOE) funded research through the Air-Conditioning and Refrigeration Technology Institute to accelerate phaseout of CFCs and conversion to alternative refrigerants and lubricants. The funds supported about 40 materials compatibility and lubricants research (MCLR) projects and a refrigerants database (Calm 2001).

The 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.

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