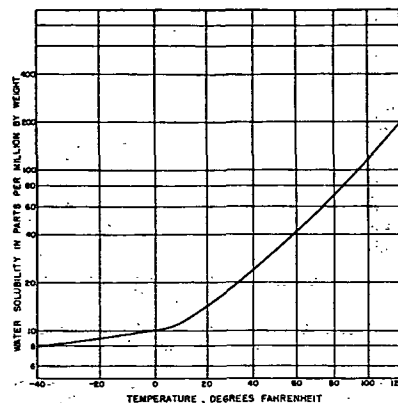




Normally refined transformer oil. Redrawn from Reference 37.

Fig. 41 Solubility of Water in Mineral Oil

white paraffin base oil and a medium refined naphthene base oil were heated for 30 days at 302 F in sealed tubes containing copper, steel and various refrigerants in addition to the oil. The refrigerants employed were Refrigerants 12, 13, 22 and 23. For a given oil, the order of decreasing plating was 12 > 23 > 22 > 13. However, some copper plating was observed in all tests, even in the absence of refrigerant. Also, more copper plating occurred with the medium refined naphthene oil than with the highly refined paraffinic oil, with the same refrigerant in both instances.

Other investigators have shown that mineral oils may differ in ability to withstand attack by refrigerants at the elevated

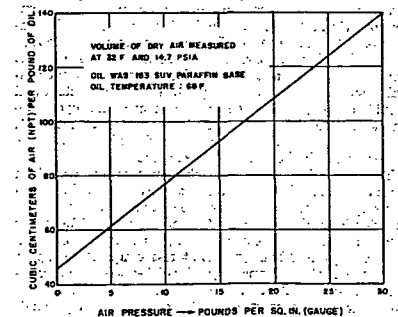


Fig. 42 Effect of Air Pressure on Solubility of Air in Mineral Oil

temperature (e.g., 347 F) of a refrigerant resistance test. Based on an extensive laboratory testing program, Walker, Rosen, and Levy⁴¹ have concluded that color darkening, corrosion, wall deposits and copper plating are generally less in paraffin base than in naphthene base oils. Type and severity of refining is also important.⁴²

Refrigerants also differ among themselves in ability to attack mineral oils. Carbon dioxide and the plain hydrocarbons (ethane, propane, isobutane, etc.) are said to have no significant chemical effect on petroleum oils.⁴³ Ammonia has no chemical effect on well refined, dry oils, but may form soaps and emulsions with poorly refined oils, especially if water happens to be present.⁴⁴ The halogenated refrigerants show considerable variation; some (e.g., Refrigerant 14) are practically inert and others (e.g., Refrigerant 11) react with oils quite readily in sealed tubes at 347 F.⁴⁵

When the test is made with a reactive refrigerant, so far as one can judge visually, the reaction seems to follow much the same pattern with all mineral oils. However, the reaction rate may be slow with one oil and comparatively fast with another. Hence refrigerant resistance is usually evaluated on a time basis. The reaction itself, assuming the oil is tested with one of the more reactive halogenated refrigerants, is almost invariably accompanied by a gradual destructive decomposition of the oil hydrocarbons so that, in time, only a black char remains (see References 42-45, 47, 49-51). The blackening and charring appears to be associated with the number and kind of atoms in the halogenated refrigerant molecule. It has been observed, in the case of a given mineral oil heated at 347 F with a number of different refrigerants and for time periods up to five years, that the charring reaction occurred only with those halogenated refrigerants which contain more than one chlorine atom in the molecule, e.g., Refrigerant 11, methylene chloride, Refrigerants 12, 21, 113, etc. Moreover, Refrigerant 11 (CCl₃F) with three chlorine atoms in the molecule reacted with the oil much more rapidly than Refrigerant 12 (CCl₂F₂) which contains only two chlorine atoms.⁴⁶ Increasing the number of fluorine atoms at the expense of the chlorine atoms seems to decrease the reactivity; thus an arrangement of common and potential refrigerants in order of increasing chemical stability in oil mixtures at 347 F is as follows:

Refrigerant 11 < methylene chloride < Refrigerant 21
Refrigerant 12 < methyl chloride < Refrigerant 22 < Refrigerant 13 < Refrigerant 115 < Refrigerant 14.

Owing to the widespread use of Refrigerants 12 and 22, the chemical stability of systems containing these refrigerants has been of greatest interest. So far as destructive attack on the oil is concerned, Refrigerant 22 appears less reactive than Refrigerant 12. This difference has been borne out in all comparative studies, some of which were based on the rate of darkening described in the previous paragraph⁴⁷ and others were actual quantitative measurements of the decomposition products of the reaction.^{48,49}

Recent evidence obtained by Spauschus and Doderer⁴⁸ shows that the oil-Refrigerant 12 reaction, catalyzed by iron at 347 F or 400 F, produces substantial quantities of Refrigerant 22 as a primary reaction product. Lagging behind this primary decomposition is a complex effect by which acidic decomposition products and carbonized sludges are formed.

Oil-refrigerant reactions are not yet well understood. The lack of understanding stems in large part from the fact that a mineral oil itself is a complex mixture of many different substances. Differences in base types, differences in viscosity grades, differences in refinement, and the catalytic effects of metals, additives, and possible contaminants all are influential in altering the reaction possibilities. Other system components (e.g., hermetic motor insulation, etc.) introduce

further complications (see Chapter 60), and the results of laboratory tests are not always indicative of actual behavior under service conditions. At the present time it is virtually impossible and certainly inadvisable to assess the chemical stability of different oil types, or even different oil brands, on general considerations. After screening by laboratory tests, the recommended practice for the ultimate selection of a new oil is to evaluate the stability on the basis of accelerated life tests in the system, or in a similar type of system, in which the oil is to be used.

REFERENCES

- Oils and Lubricants (Chapter 17, ASRE Data Book, 1949, 6th ed., p. 299).
- H. Steinle: *Kältemaschinenöle* (Springer-Verlag, Berlin, Germany, 1950, p. 81).
- R. R. Baldwin and S. G. Daniel (Journal of the Institute of Petroleum, Vol. 39, 1953, p. 105).
- A. Beerbower and D. F. Greene: The behavior of lubricating oils in inert gas atmospheres (ASLE Transactions, Vol. 4, No. 1, 1951, p. 87).
- Oils and Lubrication (Chapter 13, ASRE Data Book, 1942, 5th ed., p. 185).
- Private communication from E. S. Ross, Sun Oil Company.
- Unpublished data from Freon Products Division, E. I. duPont de Nemours and Co., Inc.
- H. M. Parmelee: Viscosity of refrigerant-oil mixtures at evaporator conditions (ASHRAE TRANSACTIONS, Vol. 70, 1964).
- H. J. Löffler: (a) Density of oil-refrigerant mixtures. (Kältezeitung, Vol. 11, No. 3, 1959, p. 70). (b) Viscosity of oil-refrigerant mixtures (ibid., Vol. 12, No. 3, 1960, p. 71).
- G. Bamback: The behavior of mineral oil-F12 mixtures in refrigerating machines (Abhandlungen des Deutschen Kältezeitung Vereines, No. 9, 1955. (Translated by Carl Demrick.) Also see abridgment in (Kältezeitung, Vol. 7, No. 7, 1955, p. 187).
- V. L. Shipp: Miscibility of Freon (Refrigerant F-12) with mineral lubricating oil (Socony-Vacuum Oil Co., General Laboratories Technical Memorandum, October 23, 1942).
- H. J. Löffler: Some properties of the binary system R12-R22 and the ternary system R12-R22-naphthene mineral oil (Kältezeitung, Vol. 12, No. 9, 1960, p. 256).
- L. F. Albright and A. S. Mandelbaum: Solubility and viscosity characteristics of mixtures of lubricating oils and "Freon 13" or "115" (REFRIGERATING ENGINEERING, October 1956, p. 37).
- L. F. Albright and J. D. Lawyer: Viscosity-solubility characteristics of mixtures of Refrigerant 13B1 and lubricating oils (ASHRAE JOURNAL, April 1959, p. 67).
- J. L. Little: Viscosity of lubricating oil-Freon-22 mixtures (REFRIGERATING ENGINEERING, November 1952, p. 1191).
- Private communication from A. B. Culbertson, Shell Oil Company.
- G. M. Bosworth: Predicting the behavior of oils in refrigeration systems (REFRIGERATING ENGINEERING, June 1952, p. 617).
- H. O. Spauschus: Thermodynamic properties of refrigerant-oil solutions (ASHRAE JOURNAL, April 1963, p. 47; October 1963, p. 63).
- W. O. Walker, A. A. Sakhanovsky, and S. Rosen: Behavior of refrigerant oils and Genetron-141 (REFRIGERATING ENGINEERING, March 1957, p. 38).
- H. J. Löffler: The effect of the physical properties of mineral oils on their miscibility with the refrigerant Frigen 22 (CHF₃Cl). Abhandlungen des Deutschen Kältezeitung Vereines, No. 12 (C. F. Müller Verlag, Karlsruhe, Germany, September 1956).
- H. J. Löffler: The miscibility of synthetic oils Fluistil S55K and Polynan M-15 with Frigen 22, Frigen 13 or mixtures of Frigen 22 and Frigen 13 (Kältezeitung, Vol. 9, No. 5, 1957, p. 135).
- Cloud and Pour Points. (Chapter 4, Physical Properties of Lubricants, The American Society of Lubrication Engineers, 1951, 2nd ed., p. 47).
- G. E. Beggs and V. A. Williams: Refrigeration Apparatus (U. S. Patent 3,092,981, June 11, 1963).
- W. O. Walker and W. R. Rinelli: The separation of wax from oil-refrigerant mixtures (REFRIGERATING ENGINEERING, June 1941, p. 395).
- H. J. Löffler: Separation of Frigen-insolubles (paraffin) from mineral oil-Frigen 22 mixtures (Kältezeitung, Vol. 9, No. 4, 1957, p. 103).
- Private communication from A. W. Jenkins, Humble Oil & Refining Co.
- A. F. Brewer: Good compressor performance demands the right lubricating oil (REFRIGERATING ENGINEERING, October 1951, p. 965).
- Private communication from B. Y. Carty, Texas Company.
- J. D. Bopp: Determination of moisture in refrigeration oils (REFRIGERATING ENGINEERING, September 1951, p. 891). See also: F. M. Roberts and H. Levin (Analytical Chemistry, Vol. 21, No. 12, 1949, p. 1553); R. H. Prince (The Analyst, Vol. 78, October 1953, p. 607); R. Weber (Kältezeitung, Vol. 8, No. 10, 1954, p. 267); H. Mandel (ibid., Vol. 6, No. 10, 1954, p. 269); Bulletin B-23 ("Kinetic" Chemicals Division, E. I. duPont de Nemours and Co. Inc., 1956); J. D. Morton and L. K. Fuchs, Determination of moisture in fluorocarbons (ASHRAE JOURNAL, May 1960, p. 62); H. G. Mosle and W. Wolf (Kältezeitung, Vol. 13, No. 9, 1961, p. 304).
- R. T. Divers: Better standards are needed for refrigeration lubricants (REFRIGERATING ENGINEERING, October 1958, p. 40).
- F. M. Clark: Water solution in high-voltage dielectric liquids (Electrical Engineering Transactions, Vol. 59, No. 8, 1940, p. 433).
- E. T. Neubauer: Compressor crankcase heaters reduce oil foaming (REFRIGERATING ENGINEERING, June 1958, p. 52).
- P. Berliner: (a) Heating of crankcase housing in Frigen compressors. (Kältezeitung, Vol. 11, No. 9, 1959, p. 289); (b) G. Skig: Reduction of the oil concentration in the circulating refrigerant (ibid., Vol. 13, No. 9, 1961, p. 302).
- A. Thelen: Lubrication of bearings by means of oil-refrigerant mixtures. (Kältezeitung, Vol. 11, No. 10, 1959, p. 341).
- R. W. Thorpe and R. G. Larsen (Industrial and Engineering Chemistry, Vol. 41, No. 5, 1949, p. 838).
- S. F. Murray, R. L. Johnson, and M. A. Swickert: Difluorodichloromethane as a boundary lubricant for steel and other metals (Mechanical Engineering, Vol. 78, No. 3, 1956, p. 233).
- G. R. Fox and R. C. Elwell: Radioactive determination of bearing wear in refrigerant compressors (Lubrication Engineering, Vol. 15, No. 4, 1959, p. 144).
- C. C. Gambill: Application of radioisotope wear study techniques (General Motors Engineering Journal, Vol. 5, No. 2, 1958, p. 21).
- E. W. McGovern: Copper plating in refrigerant compressors (REFRIGERATING ENGINEERING, July 1959, p. 31).
- C. J. Risatti, G. D. Staffin, and A. W. Jenkins: Effects of additives and oil refining on refrigerant-refrigerator oil stability (ASHRAE JOURNAL, July 1962, p. 31).
- U. S. Patents: F. L. Koethen, 2,186,028, Jan. 9, 1940; Downing and Markwood, 2,212,826, Aug. 27, 1940; Cook and Bishop, 2,523,863, Sept. 29, 1950; Bishop and Cook, 2,552,084, May 8, 1951; Davidson and Seitz, 2,824,061, Feb. 18, 1958.
- H. M. Eisey, L. C. Flowers, and J. B. Kelley: A method of evaluating refrigerant oils (REFRIGERATING ENGINEERING, July 1952, p. 737).
- A. H. Shaw and A. O'B. Brandon (Proceedings of the Institute of Refrigeration, Vol. 44, 1947-48, p. 93).
- H. Steinle: (a) Sulfur dioxide resistance and resin content of refrigerant oils (Kältezeitung, Vol. 1, No. 1, 1949, p. 14). (b) Chemical reactions between refrigerants and oils in refrigerators (ibid., Vol. 2, No. 7, 1950, p. 174). (c) The temperature resistance of nonmetallic materials in refrigerators (Werkstoffe und Korrosion, Vol. 3, No. 11, p. 419). (d) Determination of refrigerant resistance of refrigerant oils (Kältezeitung, Vol. 8, No. 12, 1954, p. 342). (e) Experiments on copper plating in refrigerators (ibid., Vol. 7, No. 4, 1955, p. 101). See also Reference 2, p. 46 and pp. 108-109.
- H. Seizels and W. Seemann: (1) Copper plating in refrigerating machines (Kältezeitung, Vol. 3, No. 8, 1951, p. 194). (b) Cause of copper plating in refrigerators (ibid., Vol. 5, No. 4, 1953, p. 90).
- H. O. Spauschus: Copper transfer in refrigerant-oil solutions (ASHRAE JOURNAL, June 1963, p. 89).
- W. O. Walker, S. Rosen, and S. L. Levy: (a) A study of the factors influencing the stability of the mixtures of Refrigerant 22 and refrigerating oils (ASHRAE TRANSACTIONS, Vol. 68, 1960, p. 445); (b) Stability of mixtures of refrigerants and refrigerating oils (ASHRAE JOURNAL, June 1962, p. 66).
- F. Musgrave (Refrigeration and Air Conditioning News, Vol. 5, No. 9, 1959, p. 19).
- H. Steinle: Testing refrigeration oils (REFRIGERATING ENGINEERING, October 1953, p. 1065).
- D. E. Kvalnes and H. M. Parmelee: Behavior of refrigerants 12 and 22 in sealed tubes (REFRIGERATING ENGINEERING, November 1957, p. 40).
- H. O. Spauschus and G. C. Doderer: Reaction of Refrigerant 12 with petroleum oils (ASHRAE JOURNAL, February 1961, p. 65).