CHAPTER 7

LUBRICANTS IN REFRIGERANT SYSTEMS

THE primary function of a lubricant is to reduce friction and minimize wear. A lubricant achieves this by interposing a film between moving surfaces that reduces direct solid-to-solid contact or lowers the coefficient of friction.

Understanding the role of a lubricant requires an analysis of the surfaces to be lubricated. Although bearing surfaces and other machined parts may appear and feel smooth, close examination reveals microscopic peaks (asperities) and valleys. With a sufficient quantity of lubricant, a layer is provided that has a thickness greater than the maximum height of the mating asperities, so that moving parts ride on a lubricant cushion.

These dual conditions are not always easily attained. For example, when the shaft of a horizontal journal bearing is at rest, the static loads squeeze out the lubricant, producing a discontinuous film with metal-to-metal contact at the bottom of the shaft. When the shaft begins to turn, there is no layer of liquid lubricant separating the surfaces. As the shaft picks up speed, the lubricating fluid is drawn into the converging clearance between the bearing and the shaft, generating a hydrodynamic pressure that eventually can support the load on an uninterrupted fluid film (Fuller 1984).

Various regimes or conditions of lubrication can exist when surfaces are in motion with respect to one another. Regimes of lubrication are defined as follows:

- *Full fluid film or hydrodynamic*. Mating surfaces are completely separated by the lubricant film.
- *Boundary*. Gross surface-to-surface contact occurs because the bulk lubricant film is too thin to separate the mating surfaces.
- *Mixed fluid film or quasi-hydrodynamic*. Occasional or random surface contact occurs.

Many materials can be used to separate and lubricate contacting surfaces. Separation can be maintained by a boundary layer on a metal surface, a fluid film, or a combination of both.

The function of a lubricant extends beyond preventing surface contact. It also removes heat, provides a seal to keep out contaminants or to retain pressures, inhibits corrosion, and carries away debris created by wear. Lubricating oils are best suited to meet these various requirements.

Viscosity is the most important property to consider in choosing a lubricant under full fluid film conditions. Under boundary conditions, the asperities are the contact points and support much, if not all, of the load; and the contact pressures are usually sufficient to cause welding and surface deformation. However, even under these conditions, wear can be controlled effectively with nonfluid, multimolecular films formed on the surface. These films must be strong enough to resist rupturing, yet have acceptable frictional and shear characteristics to reduce surface fatigue, adhesion, abrasion, and corrosion, which are the four major sources (either singularly or together) of rapid wear under boundary conditions. The slightly active constituents left in commercially refined mineral oils give them their natural film-forming properties.

Additives have also been developed to improve lubrication under boundary conditions. These materials are characterized by terms such as oiliness agents, lubricity improvers, and antiwear additives. They form a film on the metal surface through polar attraction or chemical action. These films or coatings have lower coefficients of friction under the loads imposed during boundary conditions. In chemical action, the temperature increase brought about by friction-generated heat brings about a reaction between the additive and the metal surface. Films such as iron sulfide and iron phosphate can be formed depending on the additives and the energy available for the reaction. In some instances, organic phosphates and phosphites are used in refrigeration oils to improve boundary lubrication. The nature and condition of the metal surfaces are important. Refrigeration compressor designers often treat ferrous pistons, shafts, and wrist pins with phosphating processes that impart a crystalline, discontinuous film of metal phosphate to the surface. This film aids boundary lubrication during the break-in period.

TESTS FOR BOUNDARY LUBRICATION

Film strength or load-carrying ability are terms often used to describe lubricant lubricity characteristics under boundary conditions. Laboratory tests that measure the degree of scoring, welding, or wear have been developed to evaluate lubricants. However, bench-type tests cannot be expected to accurately simulate actual field performance in a given compressor and are, therefore, merely screening devices. Some of these tests have been standardized by ASTM and other organizations.

In the **four-ball extreme-pressure method** (ASTM D2783), the antiwear property is determined from the average scar diameter on the stationary balls and is stated in terms of a load-wear index. The smaller the scar, the better the load-wear index. The maximum load-carrying capability is defined in terms of a weld point (i.e., the load at which welding by frictional heat occurs).

The **Falex** method (ASTM D2670) allows measurement of wear during the test itself, and the scar width on the V-blocks and/or the mass loss of the pin can be used as a measure of the antiwear properties. The load-carrying capability is determined from a failure, which can be caused by excess wear or extreme frictional resistance. The **Timken** method (ASTM D2782) determines the load at which rupture of the lubricant film occurs, and the **Alpha** LFW-1 machine (ASTM D2714) measures frictional force and wear.

The FZG gear test facility can provide useful information on how a lubricant performs in a gear box. Specific applications include

---

The preparation of this chapter is assigned to TC 3.4, Lubrication.

gear-driven centrifugal compressors in which the dilution of the lubricant by a refrigerant is expected to be quite low.

However, because all these machines operate in air, available data may not apply to a refrigerant environment. Divers (1958) questioned the validity of tests in air because several of the oils that performed poorly in Falex testing have been used successfully in refrigerant systems. Murray et al. (1956) suggest that halocarbon refrigerants can aid in boundary lubrication. Refrigerant 12, for example, when run hot in the absence of oil, reacted with steel surfaces to form a lubricating film. These studies emphasize the need for laboratory testing in a simulated refrigerant environment.

In Huttenlocher's (1969) method of simulation, refrigerant vapor is bubbled through the lubricant reservoir before the test to displace the dissolved air. The refrigerant is bubbled continually during the test to maintain a blanket of refrigerant on the lubricant surface. Using the Falex tester, Huttenlocher showed the beneficial effect of R-22 on the load carrying capability of the same lubricant compared with air or nitrogen. Sanvordenker and Gram (1974) describe a further modification of the Falex test using a sealed sample system.

Both R-12 (a CFC) and R-22 (an HCFC) atmospheres had beneficial effects on a lubricant's boundary lubrication characteristics when compared with tests in air. HFC refrigerants, which are chlorine-free, provide beneficial effects to boundary lubrication when compared to tests conducted in air. However, they contribute to increased wear as compared to a chlorinated refrigerant with the same lubricant.

Komatsuzaki and Homma (1991) used a modified four-ball tester to determine the antiseizure and antiwear properties of R-12 and R-22 in mineral oil and R-134a in a propylene glycol.

Test parameters must simulate as closely as possible the system conditions (the base material from which the test specimens are made, their surface condition, the processing methods, and the operating temperature). There are several bearings or rubbing surfaces in a refrigerant compressor, each of which may use different materials and may operate under different conditions. A different test may be required for each bearing. Moreover, bearings in hermetic compressors have very small clearances. Permissible bearing wear is minimal because wear debris remains in the system and can cause other problems even if the clearances stay within working limits. Compressor system mechanics must be understood to perform and interpret simulated tests.

Some aspects of compressor lubrication are not suitable for laboratory simulation. One aspect, the return of liquid refrigerant to the compressor, can cause the lubricant to dilute or wash away from the bearings, creating conditions of boundary lubrication. Tests using operating refrigerant compressors have also been considered, and one such wear test has been proposed as a German *Standard* (DIN 8978). The test is functional for a given compressor system and may permit comparison of lubricants within that class of compressors. However, it is not designed to be a generalized test for the boundary lubricating capability of a lubricant. Other tests using radioactive tracers in refrigerant systems have given useful results (Rembold and Lo 1966).

REFRIGERATION LUBRICANT REQUIREMENTS

Regardless of size or system application, refrigerant compressors are classified as either positive-displacement or dynamic (*ASH-RAE Handbook—Fundamentals*). The function of both types is to increase the pressure of the refrigerant vapor. Positive-displacement compressors increase the refrigerant pressure by reducing the volume of a compression chamber through work applied to the mechanism. Positive-displacement compressor mechanisms include scroll, reciprocating, rotary, and screw. In contrast, dynamic compressors increase the refrigerant pressure by a continuous transfer of angular momentum from the rotating member. As the gas is decelerated, the imparted momentum is converted into a pressure rise. Centrifugal compressors function based on these principles.

Refrigerant compressors require the lubricant to do more than simply lubricate bearings and mechanism elements. Oil delivered to the mechanism serves as a barrier that separates the gas on the discharge side from the gas on the suction sides. Oil also acts as a coolant, transferring heat from the bearings and mechanism elements to the crankcase sump, which, in turn, transfers heat to the surroundings. Moreover, oil helps reduce noise generated by moving parts inside the compressor. Generally, the higher the viscosity of the lubricant, the better the sealing and noise reduction capabilities.

A hermetic system, in which the motor is exposed to the lubricant, requires a lubricant with electrical insulating properties. The refrigerant gas normally carries some lubricant with it as it flows through the condenser, flow-control device, and evaporator. This lubricant must return to the compressor in a reasonable time and must have adequate fluidity at low temperatures. The lubricant must also be free of suspended matter or components such as wax that might clog the flow control device or deposit in the evaporator and adversely affect heat transfer. In a hermetic system, the lubricant is charged only once, so it must function for the lifetime of the compressor. The chemical stability required of the lubricant in the presence of refrigerants, metals, motor insulation, and extraneous contaminants is perhaps the most important characteristic distinguishing refrigeration lubricants from those used for all other applications (see Chapter 5).

Although the compression components of centrifugal compressors require no internal lubrication, rotating shaft bearings, seals, and couplings must be adequately lubricated. Turbine or other types of lubricants can be used when the lubricant is not in contact or circulated with the refrigerant.

As expected, an ideal lubricant does not exist; a compromise must be made to balance the requirements. A high-viscosity lubricant seals the gas pressure best, but may offer more frictional resistance. Slight foaming can reduce noise, but excessive foaming can carry too much lubricant into the cylinder and cause structural damage. Lubricants that are most stable chemically are not necessarily good lubricants. The lubricant should not be considered alone, because it functions as a lubricant-refrigerant mixture.

The precise relationship between composition and performance is not well defined. Standard ASTM bench tests can provide such information as (1) viscosity, (2) viscosity index, (3) color, (4) specific gravity, (5) refractive index, (6) pour point, (7) aniline point, (8) oxidation resistance, (9) dielectric breakdown voltage, (10) foaming tendency in air, (11) moisture content, (12) wax separation, and (13) volatility. Other properties, particularly those involving interactions with a refrigerant, must be determined by special tests described in the refrigeration literature. Among these nonstandard properties are (1) mutual solubility with various refrigerants, (2) chemical stability in the presence of refrigerants and metals, (3) chemical effects of contaminants or additives that may be in the oils, (4) boundary film-forming ability, (5) solubility of air, and (6) viscosity, vapor pressure, and density of oil-refrigerant mixtures.

MINERAL OIL COMPOSITION

For typical applications, the numerous compounds in refrigeration oils of mineral origin can be grouped into the following structures: (1) paraffins, (2) naphthenes (cycloparaffins), (3) aromatics, and (4) nonhydrocarbons. **Paraffins** consist of all straight chain and branched carbon chain saturated hydrocarbons. N-Pentane and isopentane are examples of paraffinic hydrocarbons. **Naphthenes** are also completely saturated but consist of cyclic or ring structures; cyclopentane is a typical example. **Aromatics** are unsaturated cyclic hydrocarbons containing one or more rings characterized by alternate double bonds; benzene is a typical example. The **nonhydrocarbons** are molecules containing atoms such as sulfur, nitrogen, or oxygen in addition to carbon and hydrogen.

The preceding structural components do not necessarily exist in pure states. In fact, a paraffinic chain frequently is attached to a naphthenic or aromatic structure. Similarly, a naphthenic ring to which a paraffinic chain is attached may in turn be attached to an aromatic molecule. Because of such complications, mineral oil composition is usually described by carbon type and molecular analysis.

In carbon type analysis, the number of carbon atoms on the paraffinic chains, naphthenic structures, and aromatic rings is determined and represented as a percentage of the total. Thus, % C_P, the percentage of carbon atoms having a paraffinic configuration, includes not only the free paraffins but also those paraffinic chains attached to naphthenic or to aromatic rings.

Similarly, % C_N includes the carbon atoms on the free naphthenes as well as those on the naphthenic rings attached to the aromatic rings, and % C_A represents the carbon atoms on the aromatic rings. Carbon analysis describes a lubricant in its fundamental structure and correlates and predicts many physical properties of the lubricant. However, direct methods of determining carbon composition are laborious. Therefore, common practice uses a correlative method, such as the one based on the refractive index-density-relative molecular mass (n-d-m) (Van Nes and Weston 1951) or one standardized by ASTM D2140 or ASTM D3288. Other methods are ASTM D2008, which uses ultraviolet absorbency and a rapid method using infrared spectrophotometry and calibration from known oils.

Molecular analysis is based on methods of separating the structural molecules. For refrigeration oils, important structural molecules are (1) saturates or nonaromatics, (2) aromatics, and (3) nonhydrocarbons. All the free paraffins and naphthenes (cycloparaffins), as well as mixed molecules of paraffins and naphthenes are included in the saturates. However, any paraffinic and naphthenic molecules attached to an aromatic ring are classified as aromatics. This representation of lubricant composition is less fundamental than carbon analysis. However, many properties of the lubricant relevant to refrigeration can be explained with this analysis, and the chromatographic methods of analysis are fairly simple (ASTM D2549; ASTM D2007; Mosle and Wolf 1963; Sanvordenker 1968).

The traditional classification of oils as paraffinic or naphthenic refers to the amount of paraffinic or naphthenic molecules in the refined lubricant. Paraffinic crudes contain a higher proportion of paraffin wax, and thus have a higher viscosity index and pour point than to naphthenic crudes.

COMPONENT CHARACTERISTICS

Saturates have excellent chemical stability, but poor solubility with polar refrigerants, such as R-22; they are also poor boundary lubricants. Aromatics are somewhat more reactive but have very good solubility with refrigerants and good boundary lubricating properties. Nonhydrocarbons are the most reactive but are beneficial for boundary lubrication, although the amounts needed for that purpose are small. The reactivity, solubility, and boundary lubricating properties of a refrigeration lubricant are affected by the relative amounts of these components in the lubricant.

The saturate and aromatic fractions separated from a lubricant do not have the same viscosity as the parent lubricant. The saturate fraction is much less viscous, and the aromatic fraction is much more viscous than the parent lubricant. Both fractions have the same boiling range. Thus, for this range, the aromatics are more viscous than the saturates. For the same viscosity, the aromatics have a higher volatility than the saturates. Also, the saturate fraction has a lower density and a lower refractive index, but a higher viscosity index and molecular mass than the aromatic fraction of the same lubricant.

Among the saturates, the straight chain paraffins are undesirable for refrigeration applications because they precipitate as wax crystals when the lubricant is cooled to its pour point and tend to form flocs in certain refrigerant solutions (see the section on Wax Separation). The branched chain paraffins and naphthenes are less viscous at low temperatures and have extremely low pour points.

Nonhydrocarbons are mostly removed during the refining of refrigeration oils. Those that remain are expected to have little effect on the physical properties of the lubricant, except, perhaps, on its color, stability, and lubricity. Because not all the nonhydrocarbons (e.g., sulfur compounds) are dark, even a colorless lubricant does not necessarily guarantee the absence of nonhydrocarbons. Kartzmark et al. (1967) and Mills and Melchoire (1967) found indications that nitrogen-bearing compounds cause or act as catalysts toward the deterioration of oils. The sulfur and oxygen compounds are thought to be less reactive, with some types considered to be natural inhibitors and lubricity enhancers.

Solvent refining, hydrofinishing, or acid treatment followed by a separation of the acid tar formed are often used to remove more thermally unstable aromatic and unsaturated compounds from the base stock. These methods also produce refrigeration oils that are free from carcinogenic materials sometimes found in crude oil stocks.

The properties of the components naturally are reflected in the parent oil. An oil with a very high saturate content, as is frequently the case with paraffinic oils, also has a high viscosity index, low specific gravity, high relative molecular mass, low refractive index, and low volatility. In addition, it would have a high aniline point and would be less miscible with polar refrigerants. The reverse is true of naphthenic oils. Table 1 lists typical properties of several mineral-based refrigeration oils.

SYNTHETIC LUBRICANTS

The limited solubility of mineral oils with R-22 and R-502 originally led to the investigation of synthetic lubricants for refrigeration use. In more recent times, the lack of solubility of mineral oils in nonchlorinated fluorocarbon refrigerants, such as R-134a and R-32, has led to the commercial use of some synthetic lubricants. Gunderson and Hart (1962) describe a number of commercially available synthetic lubricants such as synthetic paraffins, polyglycols, dibasic acid esters, neopentyl esters, silicones, silicate esters, and fluorinated compounds. Many have properties suited to refrigeration purposes. Sanvordenker and Larime (1972) describe the properties of these synthetic lubricants, alkylbenzenes, and phosphate esters in regard to refrigeration applications using chlorinated fluorocarbon refrigerants. The phosphate esters are unsuitable for refrigeration use because of their poor thermal stability. Although very stable and compatible with refrigerants, the fluorocarbon lubricants are expensive. Among others, only the synthetic paraffins have poor miscibility relations with R-22. Dibasic acid esters, neopentyl esters, silicate esters, and polyglycols all have excellent viscosity temperature relations and remain miscible with R-22 and R-502 to very low temperatures. At this time, the three synthetic lubricants seeing the greatest use are alkylbenzene, for R-22 and R-502 service, and polyglycols and polyol esters, for use with R-134a and refrigerant blends using R-32.

There are two basic types of alkylbenzenes: branched and linear. The products are synthesized by reacting an olefin or chlorinated paraffin with benzene in the presence of a catalyst. Catalysts commonly used for this reaction are aluminum chloride and hydrofluoric acid. After the catalyst is removed, the product is distilled into fractions. The relative size of these fractions can be changed by adjusting the relative molecular mass of the side chain (olefin or chlorinated paraffin) and by changing other variables. The quality of alkylbenzene refrigeration lubricant varies, depending on the type (branched or linear) and manufacturing scheme. In addition to good solubility with refrigerants, such as R-22 and R-502, these lubricants have better high-temperature and oxidation stability than mineral oil-based refrigeration oils. Typical properties for a branched alkylbenzene are shown in Table 1.

Table 1 Typical Properties of Refrigerant Lubricants

		Mineral Lubricants				Synthetic Lubricants				
Property	**ASTM**	**Naphthenic**			**Paraffinic**	**Alkyl-benzene**	**Ester**		**Glycol**	
Viscosity, cSt (SSU) at 100°F	D 445	33.1 (155)	61.9 (287)	68.6 (318)	34.2 (160)	31.7 (149)	30 (142)	100 (463)	29.9 (141)	90 (417)
Viscosity index	D 2270	0	0	46	95	27	111	98	210	235
Specific gravity	D 1298	0.913	0.917	0.9	0.862	0.872	0.995	0.972	0.99	1.007
Color	D 1500	0.5	1	1	0.5					
Refractive index	D 1747	1.5015	1.5057	1.4918	1.4752					
Molecular weight	D 2503	300	321	345	378	320	570	840	750	1200
Pour point, °F	D 97	–45	–40	–35	0	–50	–54	–22	–51	–40
Floc point, °F	ASHRAE 86	–68	–60	–60	–31	–100				
Flash point, °F	D 92	340	360	400	395	350	453	496	399	334
Fire point, °F	D 92	390	400	450	450	365				
Composition							Branched acid pentaerythritol	Branched acid pentaerythritol	PP monol monofunctional polypropylene glycol	PP diol difunctional polypropylene glycol
Carbon-type										
%C_A	Van Nes and Weston (1951)	14	16	7	3	24				
%C_N		43	42	46	32	None				
%C_P		43	42	47	65	76				
Molecular composition	D 2549									
% Saturates		62	59	78	87	None				
% Aromatics		38	41	22	13	100				
Aniline point, °F	D 611	160	165	197	220	125				
Critical solution temp. with R-22, °F	—	25	35	74	81	–100				

Polyalkylene glycols (PAGs) derive from ethylene oxide or propylene oxide. The polymerization is usually initiated either with an alcohol, such as butyl alcohol, or by water. Initiation by an alcohol results in a monol; initiation by water results in a diol. PAGs are commonly used as lubricants in automotive air-conditioning systems using R-134a. PAGs have excellent lubricity, low pour points, good low-temperature fluidity, and good compatibility with most elastomers. Major concerns are that these oils are somewhat hygroscopic, are immiscible with mineral oils, and require additives for good chemical and thermal stability (Short 1990).

Polyalphaolefins (PAOs) are normally manufactured from linear α-olefins. The first step in manufacture is the synthesis of a mixture of oligomers in the presence of a $BF_3 \cdot ROH$ catalyst. Several parameters can be varied to control the distribution of the oligomers so formed. The second step involves a hydrogenation processing of the unsaturated oligomers in the presence of a metal catalyst (Shubkin 1993). PAOs have good miscibility with R-12 and R-114. Some R-22 applications have been tried but are limited by the low miscibility of the fluid in R-22. PAOs are immiscible in R-134a (Short 1990). PAOs are mainly used as an immiscible oil in ammonia systems.

Neopentyl esters (polyol esters) are derived from a reaction between an alcohol and a normal or branched carboxylic acid. The most common alcohols used are pentaerythritol, trimethylolpropane, and neopentyl glycol. For higher viscosities, a dipentaerythritol is often used. The acids are usually selected to give the correct viscosity and fluidity at low temperatures matched to the miscibility requirements of the refrigerant. Complex neopentyl esters are derived by a sequential reaction of the polyol with a dibasic acid followed by a reaction with mixed monoacids (Short 1990). This results in a lubricant with a higher relative molecular mass, high viscosity indices, and higher ISO viscosity grades. Polyol ester lubricants are used commercially with HFC refrigerants in all types of compressors.

LUBRICANT ADDITIVES

Additives are used to enhance certain lubricant properties or impart new characteristics. They generally fall into three groups, namely polar compounds, polymers, and compounds containing active elements such as sulfur or phosphorous. Additive types include (1) pour point depressants for mineral oil, (2) floc point depressants for mineral oil, (3) viscosity index improvers for mineral oil, (4) thermal stability improvers, (5) extreme pressure and antiwear additives, (6) rust inhibitors, (7) antifoam agents, (8) metal deactivators, (9) dispersants, and (10) oxidation inhibitors.

Some additives offer performance advantages in one area but are detrimental in another. For example, antiwear additives can reduce the wear on compressor components, but because of the chemical reactivity of these materials, the additives can reduce the overall stability of the lubricant. Some additives work best when combined with other additives. They must be compatible with materials in the system (including the refrigerant) and be present in the optimum concentration; too little may be ineffective, whereas too much can be detrimental or offer no incremental improvement.

In general, additive lubricants are not required to lubricate a refrigerant compressor. However, lubricants that contain additives give highly satisfactory service and some additives, such as antiwear additives, offer some performance advantages over straight mineral oils. Their use is justified as long as the user knows of their presence and provided the additives are not significantly degraded with use. Additives can often be used with synthetic lubricants to reduce wear because, unlike mineral oil, they do not contain sulfur.

An additive lubricant is only used after thorough testing to determine whether the additive material (1) is removed by system dryers, (2) is inert to system components, (3) is soluble in refrigerants at low temperatures so as not to cause deposits in capillary tubes or expansion valves, and (4) is stable at high temperatures to avoid adverse chemical reactions such as harmful deposits. This can best be done by sealed tube and compressor testing using the actual additive/base lubricant combination intended for field use.

LUBRICANT PROPERTIES

Viscosity and Viscosity Grades

Viscosity defines a fluid's resistance to flow. It can be expressed as absolute or dynamic viscosity (centipoises, cP), kinematic viscosity (centistokes, cSt), or Saybolt Seconds Universal viscosity (abbreviated SSU or SUS). ASTM *Standard* D2161 contains tables to convert SSU to kinematic viscosity. The density must be known to convert kinematic viscosity to absolute viscosity; that is, absolute or dynamic viscosity (cP) equals density (g/cm^3) times kinematic viscosity (cSt). Refrigeration oils are sold in viscosity grades, and ASTM has proposed a system of standardized viscosity grades (D2422).

In selecting the proper viscosity grade, the environment to which the lubricant will be exposed should be considered. The viscosity of the lubricating fluid decreases if temperatures rise or if the refrigerant dissolves appreciably in the lubricant. Synthetic oils, with the exception of alkyl benzenes, are less affected by temperature change than mineral oils.

A large reduction in the viscosity of the lubricating fluid may affect the lubricity and, more likely, the sealing function of the lubricant, depending on the nature of the machinery. The design of some types of hermetically sealed units, such as the single-vane, rotary units, requires the lubricating fluid to act as an efficient sealing agent. In reciprocating compressors, the lubricant film is spread over the entire area of contact between the piston and the cylinder wall, providing a very large area to resist leakage from the high- to the low-pressure side. In a single-vane rotary type, however, the critical sealing area is a line contact between the vane and a roller. In this case, viscosity reduction is serious.

The lubricant with the lowest viscosity that gives the necessary sealing properties with the refrigerant used for the entire range of temperatures and pressures encountered should be chosen to minimize power consumption. A practical method for determining the minimum safe viscosity is to calculate the total volumetric efficiency of a given compressor using several lubricants of widely varying viscosities. The lubricant of lowest viscosity that gives satisfactory volumetric efficiency should be selected. Tests should be run at several ambient temperatures, for example, 70, 90, and 110°F. As a guideline, Table 2 lists the viscosity ranges recommended for various refrigeration systems.

The International Organization for Standardization (ISO) has established a series of viscosity levels as a standard for specifying or selecting lubricant for industrial applications. This system, covered in the United States by ASTM D2422, is designed to eliminate intermediate or unnecessary viscosity grades while providing enough viscosity grades for operating equipment. The system reference point is kinematic viscosity at 40°C, and each viscosity grade with suitable tolerances is identified by the kinematic viscosity at this temperature. Therefore an ISO VG 32 grade lubricant would identify a lubricant with a viscosity of 32 cSt at 40°C. Table 3 lists various standardized viscosity grades of lubricants.

Viscosity Index

Lubricant viscosity decreases as temperature increases and increases as temperature decreases. The relationship between temperature and kinematic viscosity is represented by the following equation (ASTM D341):

$$\log \log(\nu + 0.7) = A + B \log T \qquad (1)$$

where

ν = kinematic viscosity, cSt, $2 \le \nu \le 2 \times 10^7$
T = thermodynamic temperature, K or °R
A, B = constants for each lubricant

Table 2 Recommended Viscosity Ranges

Small and Commercial Systems

Refrigerant	Type of Compressor	Lubricant Viscosities at 100°F SSU	Lubricant Viscosities at 100°F cSt
Ammonia	Screw	280-300	60-65
	Reciprocating	150-300	32-65
Carbon dioxide	Reciprocating	280-300[a]	60-65[a]
R- 11	Centrifugal	280-300	60-65
R- 12	Centrifugal	280-300	60-65
	Reciprocating	150-300	32-65
	Rotary	280-300	60-65
R- 123	Centrifugal	280-300	60-65
R- 22	Centrifugal	280-400	60-86
	Reciprocating	150-300	32-65
	Scroll	280-300	60-65
	Screw	280-800	60-173
R-134a	Scroll	100-300	22-68
	Screw	150-500	32-100
	Centrifugal	280-300	60-65
R-407C	Scroll	100-300	22-68
	Reciprocating	150-300	32-68
R-410A	Scroll	100-300	22-68
Halogenated refrigerants	Screw	150-4000	32-800

Industrial Refrigeration[b]

Type of Compressor	Lubricant Viscosities at 100°F SSU	Lubricant Viscosities at 100°F cSt
Where lubricant may enter refrigeration system or compressor cylinders	150-300	32-65
Where lubricant is prevented from entering system or cylinders:		
In force-feed or gravity systems	500-600	108-129
In splash systems	150-160	32-34
Steam-driven compressor cylinders when condensate is reclaimed for ice-making	High-viscosity lubricant [30-35 cSt (140-165 SSU) viscosity at 210°F]	

[a] Some applications may require lighter lubricants of 75-85 SSU (14-17 cSt); others, heavier lubricants of 500-600 SSU (108-129 cSt).

[b] Ammonia and carbon dioxide compressors with splash, force-feed, or gravity circulating systems.

This relationship is the basis for the viscosity-temperature charts published by ASTM and permits a straight line plot of viscosity over a wide temperature range. Figure 1 shows a plot for two different lubricants, such as a naphthenic mineral oil (LVI) and a synthetic lubricant (HVI). This plot is applicable over the temperature range in which the oils are homogenous liquids.

The slope of the viscosity-temperature lines is different for different lubricants. The viscosity-temperature relationship of a lubricant is described by an empirical number called the viscosity index (VI) (ASTM D2270). A lubricant with a high viscosity index (HVI) shows less change in viscosity over a given temperature range than a lubricant with a low viscosity index (LVI). In the example shown in Figure 1, both oils possess equal viscosities (32 cSt or 151 SSU) at 104°F. However, the viscosity of the LVI lubricant (a naphthenic mineral oil), as shown by the steeper slope of the line, increases to 520 cSt (2400 SSU) at 32°F, whereas the HVI lubricant (a synthetic lubricant) viscosity increases only to 280 cSt (1280 SSU).

The viscosity index is related to the composition of the mineral oil. Generally, an increase in cyclic structure, aromatic and naphthenic, decreases the viscosity index. Paraffinic oils usually have a high viscosity index and low aromatic content. Naphthenic oils, on the other hand, have a lower viscosity index and are usually higher

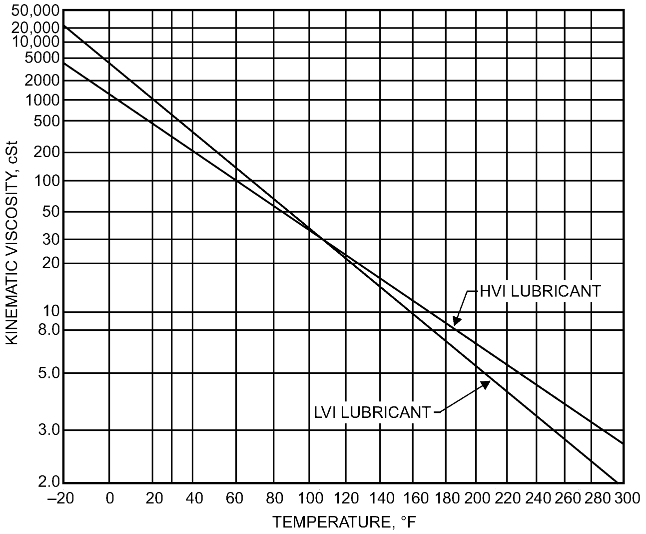


Fig. 1 Viscosity-Temperature Chart for 108 cSt (500 SSU) HVI and LVI Lubricants

Table 3 Viscosity System for Industrial Fluid Lubricants (ASTM D2422)

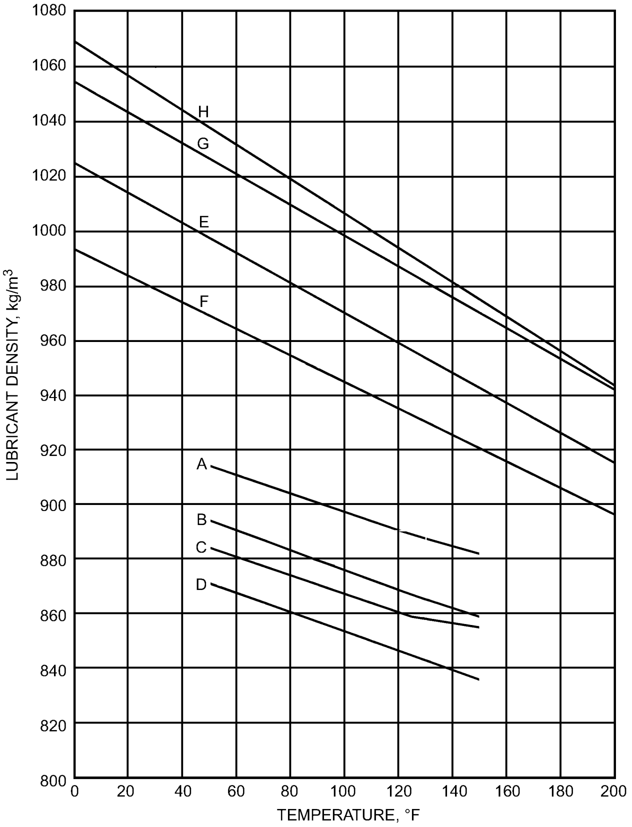
Viscosity System Grade Identification	Midpoint Viscosity cSt at 40°C	Kinematic Viscosity Limits cSt at 40°C Minimum	Kinematic Viscosity Limits cSt at 40°C Maximum	Approximate Equivalents, SSU Units
ISO VG 2	2.2	1.98	2.42	32
ISO VG 3	3.2	2.88	3.52	*
ISO VG 5	4.6	4.14	5.06	40
ISO VG 7	6.8	6.12	7.48	*
ISO VG 10	10	9.00	11.00	60
ISO VG 15	15	13.50	16.50	75
ISO VG 22	22	19.80	24.20	105
ISO VG 32	32	28.80	35.20	150
ISO VG 46	46	41.40	50.60	215
ISO VG 68	68	61.20	74.80	315
ISO VG 100	100	90	110	465
ISO VG 150	150	135	165	700
ISO VG 220	220	198	242	1000
ISO VG 320	320	288	352	1500
ISO VG 460	460	414	506	2150
ISO VG 680	680	612	748	3150
ISO VG 1000	1000	900	1100	4650
ISO VG 1500	1500	1350	1650	7000

*The 36 and 50 SSU grades are not standard grades in the United States.

in aromatics. For the same base lubricant, the viscosity index decreases with increasing aromatic content. Generally, among common synthetic lubricants, polyalphaolefins, polyalkylene glycols, and polyol esters will have high viscosity indices. As shown in Table 1, alkylbenzenes have lower viscosity indices.

Density

Figure 2 shows published values for pure lubricant densities over a range of temperatures. These density-temperature curves all have approximately the same slope and appear merely to be displaced from one another. If the density of a particular lubricant is known at one temperature but not over a range of temperatures, a reasonable estimate at other temperatures can be obtained by drawing a line paralleling those in Figure 2.



Lubricants		Viscosity at 100°F cSt	Viscosity at 100°F SSU	Ref.
A	Naphthene	64.7	300	1
B	Naphthene	15.7	80	1
C	Paraffin	64.7	300	1
D	Paraffin	32.0	150	1
E	Branched acid POE	32		2
F	Branched acid POE	100		2
G	Polypropylene glycol mono butyl ether	32		2
H	Polyoxypropylene diol	80		2

References: 1. Albright and Lawyer (1959) 2. Cavestri (1993)

Fig. 2 Variation of Refrigeration Lubricant Density with Temperature

Density indicates the composition of a lubricant for a given viscosity. As shown in Figure 2, naphthenic oils are usually more dense than paraffinic oils and synthetic lubricants are generally more dense than mineral oils. Also, the higher the aromatic content, the higher the density. For equivalent compositions, higher viscosity oils have higher densities, but the change in density with aromatic content is greater than it is with viscosity.

Relative Molecular Mass

In refrigeration applications, the relative molecular mass of a lubricant is often needed. Albright and Lawyer (1959) showed that, on a molar basis, Refrigerants 22, 115, 13, and 13B1 have about the same viscosity-reducing effects on a paraffinic lubricant.

For most mineral oils, a reasonable estimate of the average molecular mass can be obtained by a standard test (ASTM D2502), based on kinematic viscosities at 100°F and 210°F; or from viscosity-gravity correlations of Mills et al. (1946). Direct methods (ASTM D2503) can also be used when greater precision is needed or when the correlative methods are not applicable.

Pour Point

Any lubricant intended for low-temperature service should be able to flow at the lowest temperature that it will encounter. This requirement is usually met by specifying a suitably low pour point. The pour point of a lubricant is defined as the lowest temperature at which it will pour or flow, when tested according to the standard method prescribed in ASTM D97.

The loss of fluidity at the pour point may manifest itself in two ways. Naphthenic oils and synthetic lubricants usually approach the pour point by a steady increase in viscosity. Paraffinic oils, unless heavily dewaxed, tend to separate out a rigid network of wax crystals, which may prevent the flow while still retaining unfrozen liquid in the interstices. Pour points can be lowered by adding chemicals known as pour point depressants. These chemicals are believed to modify the wax structure, possibly by depositing a film on the surface of each wax crystal, so that the crystals no longer adhere to form a matrix, and do not interfere with the lubricant's ability to flow. Pour point depressants are not suitable for use with halogenated refrigerants.

Standard pour test values are significant in the selection of oils for ammonia and carbon dioxide systems, and any other system in which refrigerant and lubricant are almost totally immiscible. In such a system, any lubricant that gets into the low side is essentially refrigerant free; therefore, the pour point of the lubricant itself determines whether loss of fluidity, congealment, or wax deposition will occur at low-side temperatures.

Because oil in the low-pressure side of halogenated refrigerant systems contains significant amounts of dissolved refrigerant, the pour point test, which is conducted on pure oils and in air, is of little significance. The viscosity of the lubricant-refrigerant solutions at the low-side conditions and the wax separation (or floc test) are important considerations.

The pour point for a lubricant should not be confused with the freezing point. Pour point is determined by exposing the lubricant to a low temperature for a short time. Refrigeration lubricants will solidify after long-term exposure to a low temperature, even if the temperature is higher than the pour point.

Some refrigerant lubricants stored at a low temperature become unstable. Typically, components of the lubricant separate and form crystals or deposits on the container.

Volatility—Flash and Fire Points

Because the boiling ranges and vapor pressure data on lubricants are not readily available, an indication of the volatility of a lubricant is obtained from the flash and fire points (ASTM D92). These properties are normally not significant in refrigeration equipment. However, some refrigerants, such as sulfur dioxide, ammonia, and methyl chloride, have a high ratio of specific heats (c_p/c_v) and consequently have a high adiabatic compression temperature. These refrigerants frequently carbonize oils with low flash and fire points when operating in high ambient temperatures. Carbonization of the lubricant can also occur in some applications that use halogenated refrigerants and require high compression ratios (such as domestic refrigerator-freezers operating in high ambient temperatures). Because such carbonization or coking of the valves is not necessarily accompanied by the general lubricant deterioration, the tendency of a lubricant to carbonize is referred to as **thermal instability** as opposed to chemical instability. Some manufacturers circumvent such problems by using paraffinic oils, which in comparison to naphthenic oils have higher flash and fire points. Others prevent them through appropriate design.

Vapor Pressure

Vapor pressure is the pressure at which the vapor phase of a substance is in equilibrium with the liquid phase at a specified temperature. The composition of the vapor and liquid phases (when not pure) influences the equilibrium pressure. With refrigeration lubricants, the type, boiling range, and viscosity are also factors influencing vapor pressure; naphthenic oils of a specific viscosity grade generally show higher vapor pressures than paraffinic oils.

Table 4 Increase in Vapor Pressure and Temperature

Temperature, °F	Vapor Pressure 32 cSt (150 SSU) Oil	
	Alkylbenzene, mm Hg	Naphthene Base, mm Hg
300	0.72	0.93
325	1.58	1.92
350	3.36	3.78
375	6.70	7.15
400	13.0	13.1
425	24.3	23.0
450	43.8	39.4

The vapor pressure of a lubricant increases with increasing temperature, as shown in Table 4. In practice, the vapor pressure of a refrigeration lubricant at an elevated temperature is negligible compared with that of the refrigerant at that temperature. The vapor pressure of narrow boiling petroleum fractions can be plotted as straight line functions. If the lubricant's boiling range and type are known, standard tables may be used to determine the lubricant's vapor pressure up to 760 mm Hg at any given temperature (API 1970).

Aniline Point

Aniline, an aromatic compound, is more soluble in oils containing a greater quantity of similar compounds. The temperature at which a lubricant and aniline are mutually soluble is the lubricant's aniline point (ASTM D611). Therefore, the relative aromaticity of a mineral oil can be determined by its solubility in aniline. In comparing mineral oils, lower aniline points correspond to the presence of more naphthenic and/or aromatic molecules.

Aniline point can also predict a mineral oil's effect on elastomer seal materials. Generally, a highly naphthenic lubricant swells a specific elastomer material more than a paraffinic lubricant. This is caused by the greater solvency of aromatic and naphthenic compounds present in a naphthenic lubricant. However, aniline point gives only a general indication of lubricant-elastomer compatibility. Within a given class of elastomer material, lubricant resistance varies widely because of differences in compounding practiced by the elastomer manufacturer. Finally, in some retrofit applications, a high aniline point mineral oil may cause elastomer shrinkage and possible seal leakage.

Elastomers in synthetic lubricants, such as alkylbenzenes, polyalkylene glycols, and polyol esters, behave differently than they do in mineral oils. For example, an alkylbenzene has an aniline point lower than that of a mineral oil of the same viscosity grade. However, the amount of swell in a chloroneoprene O ring is generally less than that found with the mineral oil. For these reasons, lubricant-elastomer compatibility needs to be tested under conditions anticipated in actual service.

Solubility of Refrigerants in Oils

All gases are soluble to some extent in lubricants, and many refrigerant gases are highly soluble. The amount dissolved depends on the pressure of the gas and the temperature of the lubricant, on the nature of the gas, and on the nature of the lubricant. Because refrigerants are much less viscous than lubricants, any appreciable amount in solution causes a marked reduction in viscosity.

Two refrigerants usually regarded as poorly soluble in mineral oil are ammonia and carbon dioxide. Data showing the slight absorption of these gases by mineral oil are given in Table 5. The amount absorbed increases with increasing pressure and decreases with increasing temperature. In ammonia systems, where pressures are moderate, the 1% or less refrigerant that dissolves in the

Table 5 Absorption of Low Solubility Refrigerant Gases in Oil

Absolute Pressure, psi	Ammonia[a] (Percent by Mass) Temperature, °F 32	68	149	212	302
14.2	0.246	0.180	0.105	0.072	0.054
28.4	0.500	0.360	0.198	0.144	0.108
42.7	0.800	0.540	0.304	0.228	0.166
57.0	—	0.720	0.398	0.300	0.222
142.0	—	—	1.050	0.720	0.545

Absolute Pressure, psi	Carbon Dioxide[b] (Percent by Mass) Temperature, °F 32	68	149	212
14.7	0.26	0.19	0.13	0.072

[a] Type of oil: Not given (Steinle 1950)
[b] Type of oil: HVI oil, 34.8 cSt (163 SSU) at 100°F (Baldwin and Daniel 1953)

lubricant should have little, if any, effect on lubricant viscosity. However, operating pressures in CO_2 systems tend to be much higher (not shown in Table 5), and in that case, the quantity of gas dissolved in the lubricant may be enough to substantially reduce viscosity. At 390 psig, for example, Beerbower and Greene (1961) observed a 69% reduction when a 32 cSt (150 SSU) lubricant (HVI) was tested under CO_2 pressure at 80°F.

LUBRICANT-REFRIGERANT SOLUTIONS

Many chlorinated refrigerants are highly soluble in oils at any temperature likely to be encountered. The only limit to the amount of these refrigerants that the lubricant can dissolve is established by the refrigerant pressure at a given temperature. Chlorinated refrigerants such as R-22 and R-114 may show limited solubilities with some lubricants at evaporator temperatures (exhibited in the form of phase separation) and unlimited solubilities in the higher temperature regions of a refrigerant system. In some systems using HFC refrigerants, a second, distinct two-phase region may occur at high temperatures. For such refrigerants, solubility studies must therefore be carried out over an extended temperature range.

Because halogenated refrigerants have such high solubilities, the lubricating fluid can no longer be treated as a pure lubricant, but rather as a lubricant-refrigerant solution whose properties are markedly different from those of pure lubricant. The amount of refrigerant dissolved in a lubricant depends on the pressure and temperature. Therefore, the composition of the lubricating fluid is different in different sections of a refrigeration system operating at steady state and changes from the time of start-up until the system attains the steady state. The most pronounced effect is on viscosity.

The crankcase of a compressor can be used as an example. For this case, the refrigerant and lubricant are assumed to be in equilibrium and the viscosity is as shown in Figure 37. If the lubricant in the crankcase at start-up is 75°F, the viscosity of pure 32 ISO VG branched acid polyol ester is about 60 cSt. Under operating conditions, the lubricant in the crankcase is typically about 125°F. At this temperature the viscosity of the pure lubricant is about 20 cSt. If R-134a is the refrigerant and the pressure in the crankcase is 51 psia, the viscosity of the lubricant-refrigerant mixture at start-up is about 10 cSt and decreases to 9 cSt at 125°F.

Hence, if only lubricant properties are considered, an erroneous picture of the system is obtained. As another example, when the lubricant returns from the evaporator to the compressor, the highest viscosity does not occur at the lowest temperature, because the lubricant contains a large amount of dissolved refrigerant. As the temperature increases, the lubricant loses some of the refrigerant and the viscosity reaches a maximum at a point away from the coldest spot in the system.

Similar to the lubricating fluid, the properties of the working fluid (a high refrigerant concentration solution) are also affected. The vapor pressure of a lubricant-refrigerant solution is markedly lower than that of the pure refrigerant. Consequently, the evaporator temperature is higher than if the refrigerant is pure. Another result is what is sometimes called the flooded start-up. When the crankcase and the evaporator are at about the same temperature, the fluid in the evaporator (which is mostly refrigerant) has a higher vapor pressure than the fluid in the crankcase (which is mostly lubricant). This difference in vapor pressures drives the refrigerant to the crankcase and it is absorbed in the lubricant until the pressures are equalized. At times, the moving parts in the crankcase may be completely immersed in this lubricant-refrigerant solution. At start-up, the change in pressure and turbulence can cause excessive amounts of liquid to enter the cylinders, causing damage to the valves and starving the crankcase of lubricant. The use of crankcase heaters to prevent such problems caused by highly soluble refrigerants is discussed in Chapter 2 and by Neubauer (1958). The problems associated with rapid outgassing from the lubricant are more pronounced with synthetic oils than with mineral oils. Synthetic oils release absorbed refrigerant more quickly and have a lower surface tension, which results in a lack of stable foam found with mineral oils (Swallow et al. 1995).

Density

When estimating the density of a lubricant-refrigerant solution, the solution is assumed ideal so that the specific volumes of the components are additive. The formula for calculating the ideal density (ρ_{id}) is

$$\rho_{id} = \frac{\rho_o}{1 + W(\rho_o/\rho_R - 1)} \tag{2}$$

where

ρ_o = density of pure lubricant at the solution temperature
ρ_R = density of refrigerant liquid at the solution temperature
W = mass fraction of refrigerant in solution

Depending on the refrigerant, the actual density of a lubricant-refrigerant solution may deviate from the ideal by as much as 8%. The solutions are usually more dense than calculated, but sometimes they are less. For example, R-11 forms ideal solutions with oils, whereas R-12 and R-22 show significant deviations. Density correction factors for R-12 and R-22 solutions are depicted in Figure 3. The corrected densities can be obtained from the relation

$$\text{Mixture Density} = \rho_m = \frac{\rho_{id}}{A} \tag{3}$$

where A is the density correction factor read from Figure 3 at the desired temperature and refrigerant concentration.

Van Gaalen et al. (1990, 1991a, 1991b) provide values of density for four refrigerant/lubricant pairs: R-22/mineral oil, R-22/ alkylbenzene, R-502/mineral oil, and R-502/alkylbenzene. Figures 4, 5, 6, and 7 provide data on the variation of density with temperature for R-134a in combination with a 32 ISO VG polyol ester, a 100 ISO VG polyol ester, a 32 ISO VG polyalkylene glycol, and an 80 ISO VG polyalkylene glycol, respectively (Cavestri 1993).

Cavestri (1993) provides density data as a function of temperature and pressure for R-134A/polyol ester oils as shown in Figures 4 through 7. Additionally, Cavestri and Schafer (2000) provide density data as a function of temperature and pressure R-410A/ polyol ester oils as shown in Figures 8 through 11.

Thermodynamics and Transport Phenomena

Dissolving lubricant in liquid refrigerant affects the thermodynamic properties of the working fluid. The vapor pressures of refrigerant-lubricant solutions at a given temperature are always

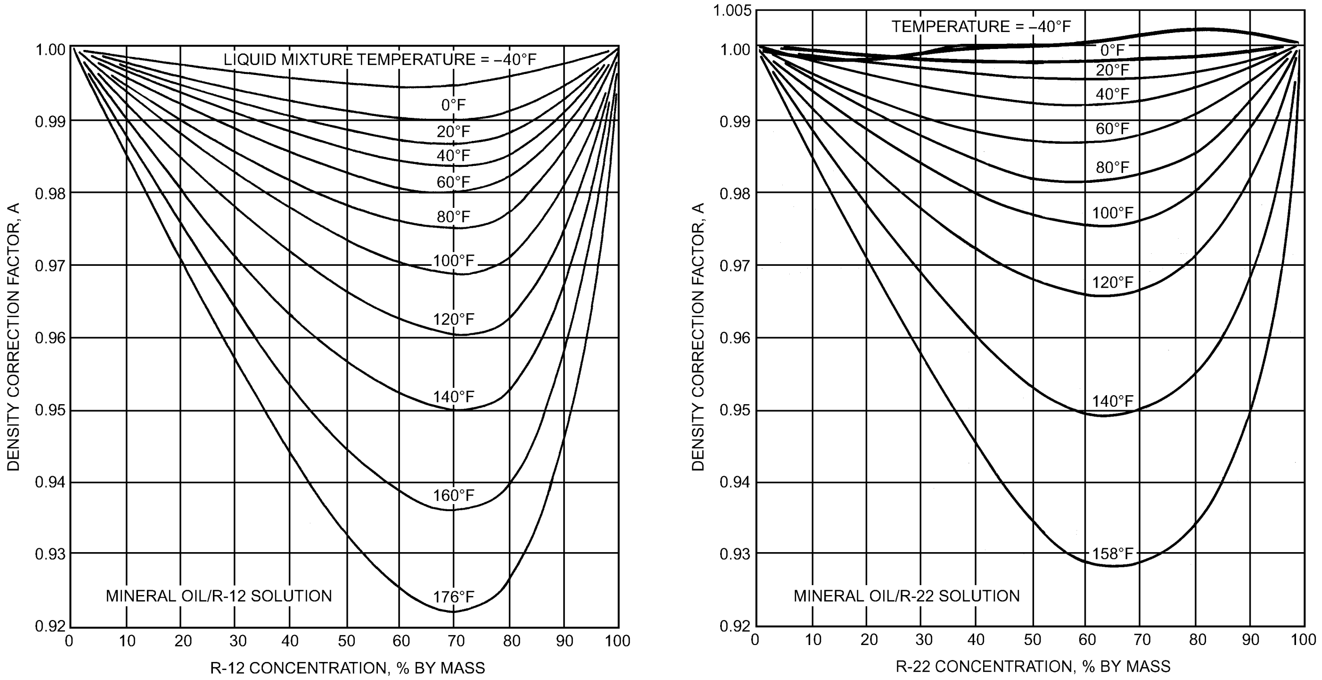


Fig. 3 Density Correction Factors
(Loffler 1959)

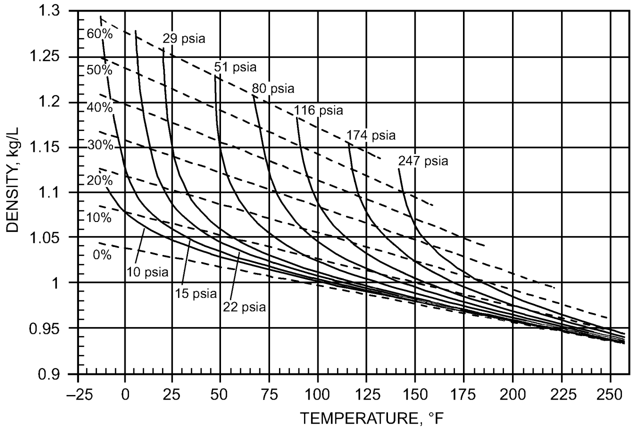


Fig. 4 Density as Function of Temperature and Pressure for Mixture of R-134a and 32 ISO VG Branched Acid Polyol Ester Lubricant

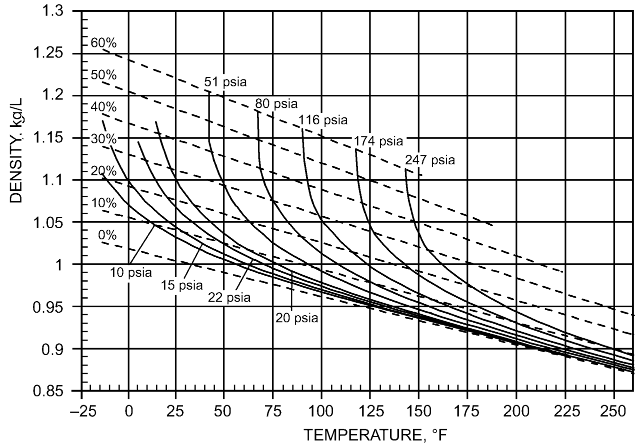


Fig. 5 Density as Function of Temperature and Pressure for Mixture of R-134a and 100 ISO VG Branched Acid Polyol Ester Lubricant

less than the vapor pressure of pure refrigerant at that temperature. Therefore, dissolved lubricant in an evaporator leads to lower suction pressures and higher evaporator temperatures than those expected from pure refrigerant tables. Bambach (1955) gives an enthalpy diagram for R-12/lubricant solutions over the range of compositions from 0 to 100% lubricant and temperatures from –40 to 240°F. Spauschus (1963) developed general equations for calculating thermodynamic functions of refrigerant-lubricant solutions and applied them to the special case of R-12/mineral oil solutions.

Pressure-Temperature-Solubility Relations

When a refrigerant is in equilibrium with a lubricant, a fixed amount of refrigerant is present in the lubricant at a given temperature and pressure. This is evident if the Gibbs phase rule is applied to basically a two-phase, two-component mixture. The lubricant, although a mixture of several compounds, may be considered one component, and the refrigerant the other. The two phases are the liquid phase and the vapor phase. The phase rule defines this mixture as having two degrees of freedom. Normally, the variables involved are pressure, temperature, and the compositions of the liquid and of the vapor. Since the vapor pressure of the lubricant is negligible compared with that of the refrigerant, the vapor phase is essentially pure refrigerant, and only the composition of the liquid phase needs to be considered. If the pressure and temperature are defined, the system is invariant (i.e., the liquid phase can have only one composition). This is a different but more precise way of stating that a lubricant-refrigerant mixture having a known composition exerts a certain vapor pressure at a certain temperature. If the temperature is changed, the vapor pressure also changes.

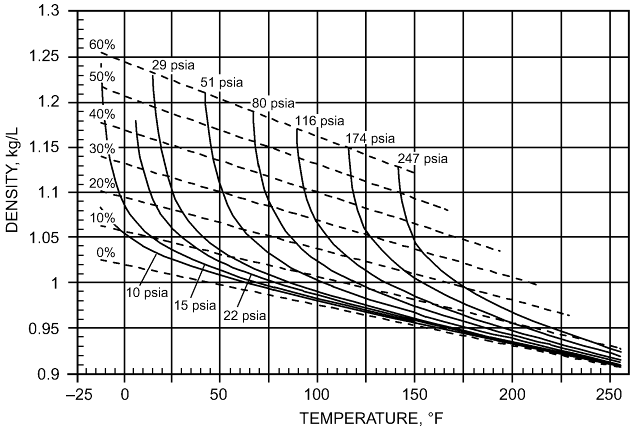


Fig. 6 Density as Function of Temperature and Pressure for Mixture of R-134a and 32 ISO VG Polypropylene Glycol Butyl Ether Lubricant

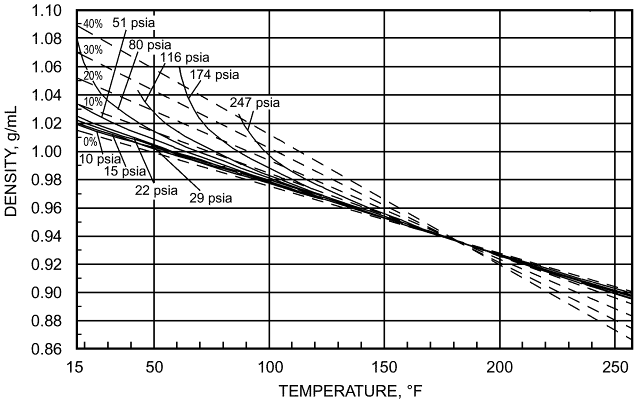


Fig. 9 Density as Function of Temperature and Pressure for Mixture of R-410A and 68 ISO VG Branched Acid Polyol Ester Lubricant

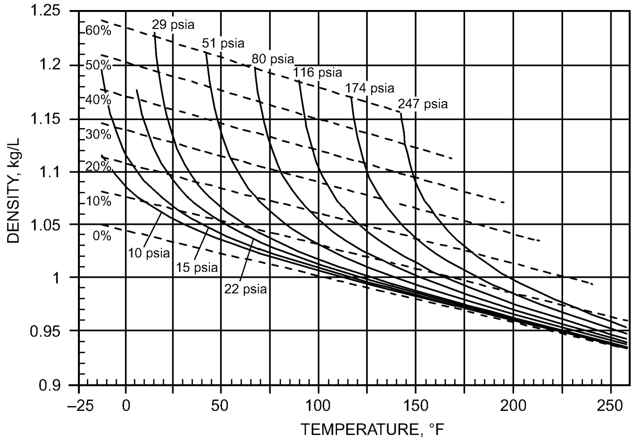


Fig. 7 Density as Function of Temperature and Pressure for Mixture of R-134a and 80 ISO VG Polyoxypropylene Glycol Diol Lubricant

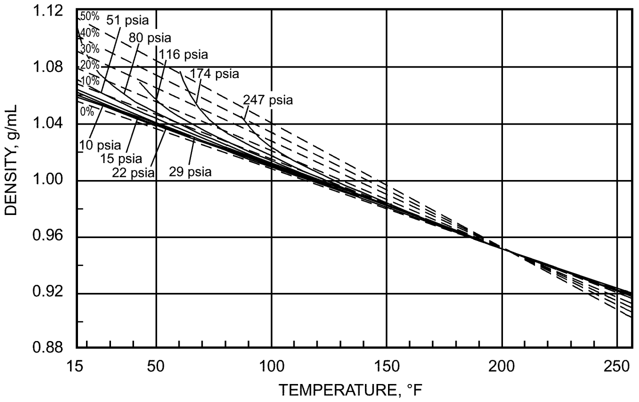


Fig. 10 Density as Function of Temperature and Pressure for Mixture of R-410A and 32 ISO VG Mixed Acid Polyol Ester Lubricant

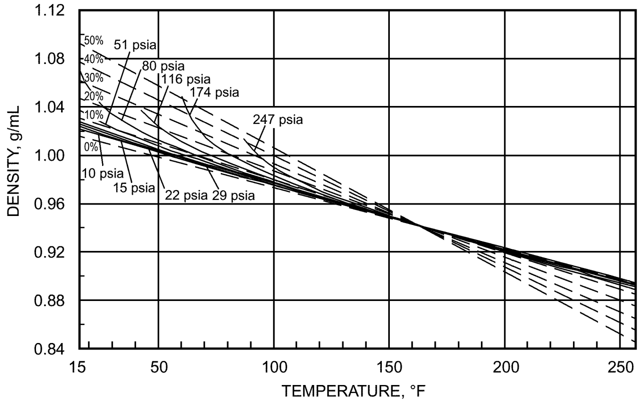


Fig. 8 Density as Function of Temperature and Pressure for Mixture of R-410A and 32 ISO VG Branched Acid Polyol Ester Lubricant

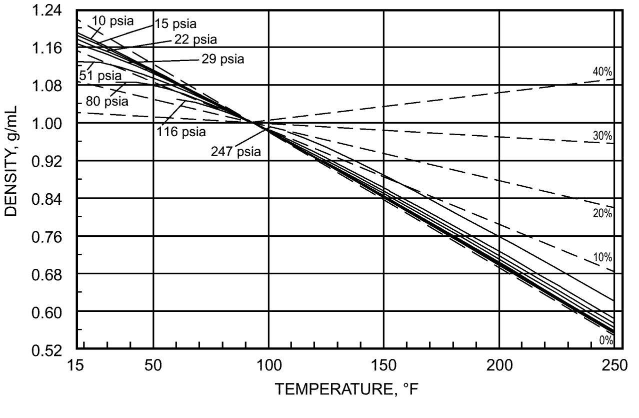


Fig. 11 Density as Function of Temperature and Pressure for Mixture of R-410A and 68 ISO VG Mixed Acid Polyol Ester Lubricant

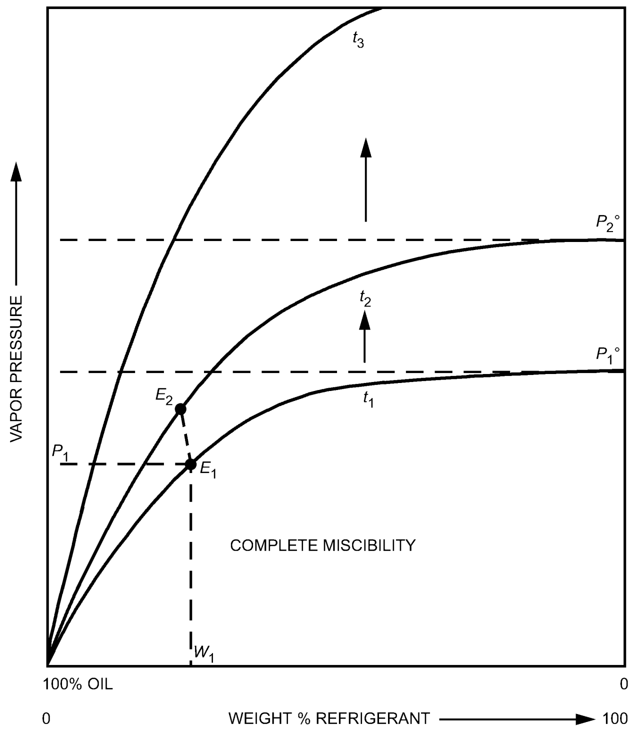


Fig. 12 P-T-S Diagram for Completely Miscible Refrigerant-Lubricant Solutions

Table 6 Mutual Solubility of Refrigerants and Mineral Oil

	Partially Miscible			
Completely Miscible	**High Miscibility**	**Intermediate Miscibility**	**Low Miscibility**	**Immiscible**
R-11	R-123	R-22	R-13	Ammonia
R-12		R-114	R-14	CO_2
R-113			R-115	R-134a
			R-152a	R-407C
			R-C318	R-410A
			R-502	

Pressure-temperature-solubility relations are usually presented in the form shown in Figure 12. On this graph, $P_1°$ and $P_2°$ represent the saturation pressures of the pure refrigerant at temperatures t_1 and t_2, respectively. Point E_1 represents an equilibrium condition, where one and only one composition of the liquid, represented by W_1, is possible at the pressure P_1. If the temperature of this system is increased to t_2, some of the liquid refrigerant evaporates, and the equilibrium point shifts to E_2, corresponding to a new pressure P_2. In either case, the lubricant-refrigerant solution exerts a vapor pressure less than that of the pure refrigerant at the same temperature.

Mutual Solubility

In a compressor, the lubricating fluid is a solution of refrigerant dissolved in lubricant. In other parts of the refrigerant system, the solution is a lubricant in liquid refrigerant. In both instances, either the lubricant or the refrigerant could exist alone as a liquid if the other were not present; therefore, any distinction between the dissolving and dissolved component merely reflects a point of view. Either of the liquids can be considered as dissolving the other. This relationship is termed mutual solubility.

Refrigerants are classified as completely miscible, partially miscible, or immiscible, according to their mutual solubility relations with mineral oils. Because several commercially important refrigerants are partially miscible, further designation as having high, intermediate, or low miscibility is shown in Table 6.

Completely miscible refrigerants and lubricants are mutually soluble in all proportions at any temperature encountered in a refrigeration or air-conditioning system. This type of mixture always forms a single liquid phase under equilibrium conditions, no matter how much refrigerant or lubricant is present.

Partially miscible refrigerant-lubricant solutions are mutually soluble to a limited extent. Above the critical solution temperature (CST) or consolute temperature, many refrigerant/lubricant mixtures in this class are completely miscible, and their behavior is identical to that just described. As mentioned previously, R-134a and some synthetic lubricants exhibit a region of immiscibility at higher temperatures.

Below the critical solution temperature, however, the liquid may separate into two phases. Such phase separation does not mean that the lubricant and the refrigerant are insoluble in each other. Each liquid phase is a solution; one is lubricant-rich and the other refrigerant-rich, depending on the predominant component. Each phase may contain substantial amounts of the leaner component, and these two solutions are themselves immiscible with each other.

The importance of this concept is best illustrated by R-502, which is considered a low miscibility refrigerant exhibiting a high CST as well as a broad immiscibility range. However, even at –4°F, the lubricant-rich phase contains about 20 mass % of dissolved refrigerant (see Figure 15). Examples of partially miscible systems, in addition to R-502, are R-22, R-114, and R-13 with mineral oils.

The basic properties of the immiscible region can be recognized by applying the phase rule. With three phases (two liquid and one vapor) and two components, there can be only one degree of freedom. Therefore, either the temperature or the pressure automatically determines the composition of both liquid phases. If the system pressure is changed, the temperature of the system changes and the two liquid phases assume somewhat different compositions determined by the new equilibrium conditions.

Figure 13 illustrates the behavior of partially miscible mixtures. Point C on the graph represents the critical solution temperature t_3. There are three separate regions below this temperature on the diagram. Reading from left to right, a family of the smooth solid curves represents a region of completely miscible lubricant-rich solutions. These curves are followed by a wide break representing a region of partial miscibility in which there are two immiscible liquid phases. On the right side, the partially miscible region disappears into a second completely miscible region of refrigerant-rich solutions. A dome-shaped envelope (broken line curve OCR) encloses the partially miscible region; everywhere outside this dome the refrigerant and lubricant are completely miscible. In a sense, Figure 13 is a variant of Figure 12 in which the partial miscibility dome (OCR) blots out a substantial portion of the continuous solubility curves. Under the dome (i.e., in the immiscible region), the two points E_1 and E_2 on the temperature line t_1 represent the two phases coexisting in equilibrium.

These two phases differ considerably in composition (W_1 and W_2) but have the same refrigerant pressure P_1. The solution pressure P_1 lies not far below the saturation pressure of pure refrigerant $P_1°$. Commonly, refrigerant-lubricant solutions near the partial miscibility limit show less reduction in refrigerant pressure than is observed at the same lubricant concentration with completely miscible refrigerants.

Totally immiscible lubricant-refrigerant solutions are defined in this chapter as only very slightly miscible. In such mixtures, the immiscible range is so broad that mutual solubility effects can be ignored. Critical solution temperatures are seldom

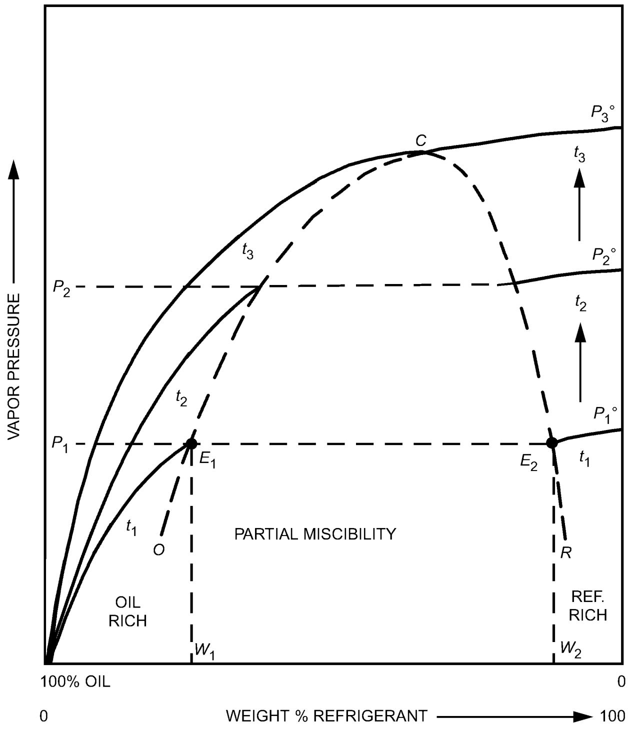


Fig. 13 P-T-S Diagram for Partially Miscible Refrigerant-Oil Solutions

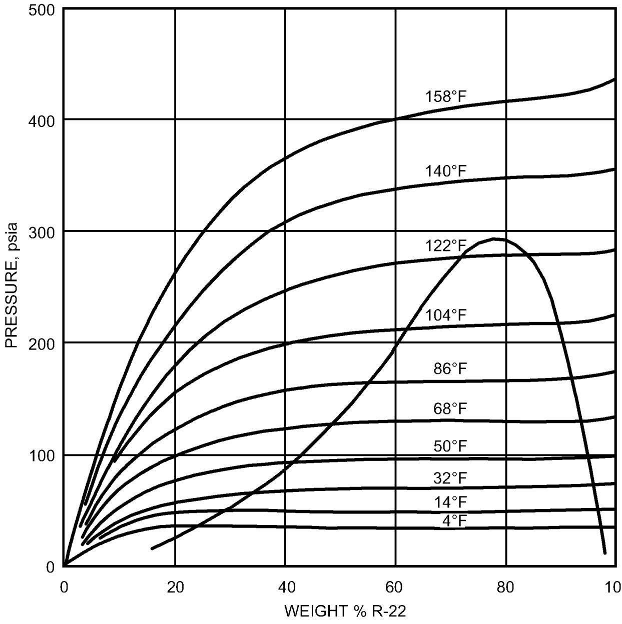


Fig. 14 P-T-S Relations of R-22 with 43 cSt (200 SSU) White Oil (0% C_A, 55% C_N, 45% C_P)
(Spauschus 1964)

found in mixtures of the totally immiscible type. Examples are ammonia and lubricant, and carbon dioxide and mineral oil.

Effects of Partial Miscibility in Refrigerant Systems

Evaporator. The evaporator is the coldest part of the system and the most likely part in which immiscibility or phase separation will occur. If the evaporator temperature is below the critical solution temperature, phase separation is likely to occur in some part of the evaporator. The fluid entering the evaporator is mostly liquid refrigerant containing a small fraction of lubricant, whereas the liquid leaving the evaporator is mostly lubricant, since the refrigerant is in vapor form. No matter how little lubricant the entering refrigerant carries, the liquid phase, as it progresses through the evaporator, passes through the critical composition which usually lies in 15% to 20% lubricant in the total liquid phase.

Phase separation in the evaporator can sometimes cause problems. In a dry-type evaporator, there is usually enough turbulence to cause the phases to emulsify. In this case, the heat transfer characteristics of the evaporator may not be significantly affected. In flooded-type evaporators, however, the working fluid may separate into layers, and the lubricant-rich phase may float on top of the boiling liquid. In addition to the heat transfer, partial miscibility may also affect the lubricant's return from the evaporator to the crankcase. Usually the lubricant is moved by high-velocity suction gas transferring momentum to the droplets of lubricant on the return line walls.

If a lubricant-rich layer separates at the evaporator temperatures, this viscous, nonvolatile liquid can migrate and collect in pockets or blind passages not easily reached by the high-velocity suction gas. The lubricant return problem may be magnified and, in some cases, an oil logging can occur. The design of the system should take into account all these possibilities, and evaporators should be designed to promote entrainment (see Chapter 2). Oil separators are frequently required in the discharge line to minimize lubricant circulation when refrigerants of poor solvent power are used or in systems involving very low evaporator temperatures (Soling 1971).

Crankcase. With certain refrigerant and lubricant pairs, such as R-502 and mineral oil, or even with R-22 in applications such as heat pumps, phase separation sometimes occurs in the crankcase when the system is shut down. When this happens, the refrigerant-rich layer settles to the bottom, often completely immersing the pistons, bearings, and other moving parts. At start-up, the fluid that lubricates these moving parts is mostly refrigerant with little lubricity, and severe bearing damage may result. The turbulence at start-up may cause the liquid refrigerant to enter the cylinders, carrying large amounts of lubricant with it. Precautions in design will prevent such problems in partially miscible systems.

Condenser. Partial miscibility is not a problem in the condenser, since the liquid flow lies in the turbulent region and the temperatures are relatively high. Even if phase separation occurs, there is little danger of separation of layers, the main obstacle to efficient heat transfer.

Solubility Curves and Miscibility Diagrams

Figure 14 shows mutual solubility relations of partially miscible refrigerant-lubricant mixtures. More than one curve of this type can be plotted on a miscibility diagram. Each single dome then represents the immiscible ranges for one lubricant and one refrigerant. Miscibility curves for R-13, R-13B1, R-502 (Parmelee 1964), R-22, and mixtures of R-12 and R-22 (Walker et al. 1957) are shown in Figure 15. Miscibility curves for R-13, R-22, R-502, and R-503 in an alkylbenzene refrigeration lubricant are shown in Figure 16. A comparison with Figure 15 illustrates the greater solubility of refrigerants in this type of lubricant.

Effect of Lubricant Type on Solubility and Miscibility

When compared on a mass basis, low-viscosity oils absorb more refrigerant than high-viscosity oils do. Also, naphthenic oils absorb more than paraffinic oils. However, when compared on a mol basis, some confusion arises. Paraffinic oils absorb more refrigerant than naphthenic oils (i.e., reversal of the mass basis),

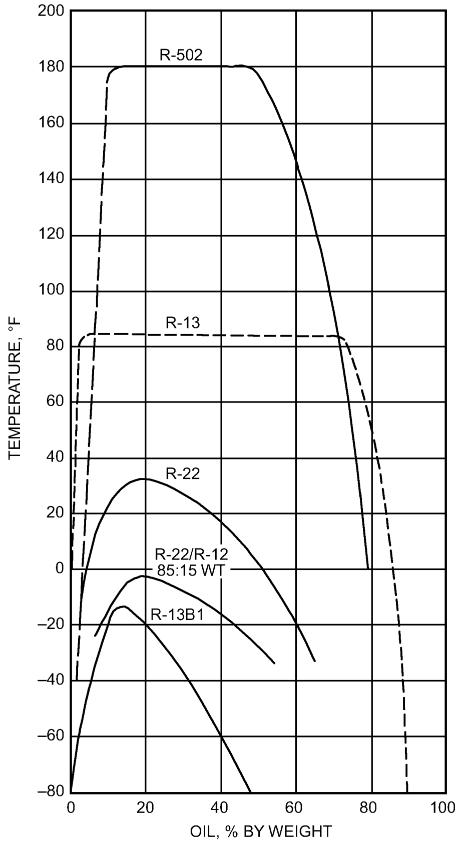


Fig. 15 Critical Solubilities of Refrigerants with 32 cSt (150 SSU) Naphthenic Lubricant (C_A 12%, C_N 44%, C_P 44%)

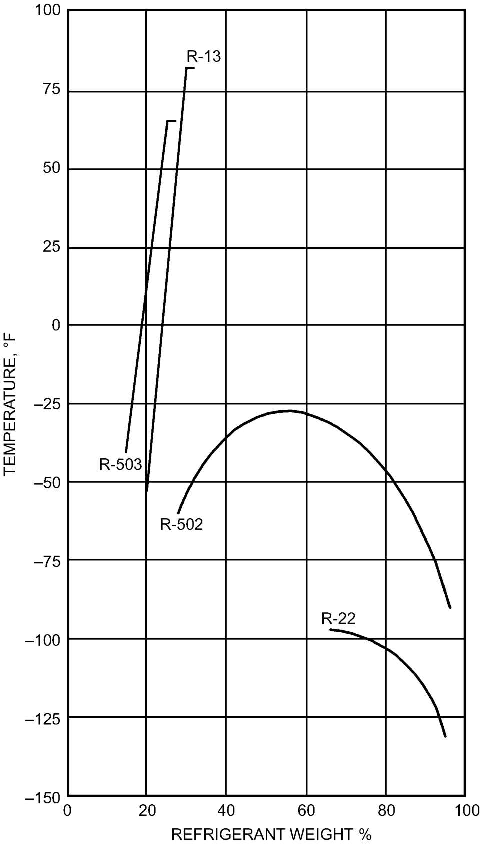


Fig. 16 Critical Solubilities of Refrigerants with 32 cSt (150 SSU) Alkylbenzene Lubricant

and there is little difference between a 15.7 cSt (80 SSU) and a 64.7 cSt (300 SSU) naphthenic lubricant (Albright and Lawyer 1959; Albright and Mandelbaum 1956). The differences on either basis are small (i.e., within 20% of each other). Comparisons of oils by their carbon type analyses are not available, but in view of the data on naphthenic and paraffinic types, differences between oils with different carbon type analyses, except perhaps for extreme compositions, are unlikely.

The effect of lubricant type and composition on miscibility is better defined than solubility. When the critical solution temperature (CST) is used as the criterion of miscibility, oils with higher aromatic contents show a lower CST. Higher-viscosity-grade oils show a higher CST than lower-viscosity-grade oils, and paraffinic oils show a higher CST than naphthenic oils (see Figures 17 and 29). When the entire dome of immiscibility is considered, a similar result is noticeable. Oils that exhibit a lower CST usually show a narrowing of the immiscibility range (i.e., the mutual solubility is greater at any given temperature).

Miscibility of R-22 with Lubricants

Parmelee (1964) showed that polybutyl silicate improves miscibility with R-22 (and also R-13) at low temperatures. Alkylbenzenes, by themselves or mixed with mineral oils, also have better miscibility with R-22 than do mineral oils alone (Seeman and Shellard 1963). Polyol esters, which are HFC miscible, are completely miscible with R-22 irrespective of viscosity grade.

For mineral oils, Walker et al. (1962) provide detailed miscibility diagrams of 12 brand-name oils commonly used for refrigeration systems. Walker's data show that in every case, higher-viscosity lubricant of the same base and type has a higher critical solution temperature.

Loffler (1957) provides complete miscibility diagrams of R-22 and 18 oils. A portion of the properties of the oils used and the critical solution temperatures are summarized in Table 7. Although precise correlations are not evident in the table, certain trends are clear. For the same viscosity grade and base, the effect of aromatic carbon content is seen in oils 2, 3, 7, and 8 and between oils 4 and 6. Similarly, for the same viscosity grades, the effect of paraffinic structure (with essentially the same % C_A) is noticeable between oils 6 and 17 and between oils 8 and 18.

According to Loffler, the most pronounced effect on the critical solution temperature is exerted by the aromatic content of the lubricant; the table indicates that the paraffinic structure reduces the miscibility compared with naphthenic structures. Sanvordenker (1968) reported the miscibility relations of the saturated fractions and the aromatic fractions of mineral oils as a function of their physical properties. The critical solution temperatures with R-22 increase with increasing viscosities for the saturates, as well as for the aromatics. For equivalent viscosities, aromatic fractions with naphthenic linkages show lower critical solution temperatures than aromatics with only paraffinic linkages.

Pate et al. (1993) developed miscibility data for 10 refrigerants and 14 lubricants. Table 8 lists lower and upper critical solution temperatures for several of the refrigerant-lubricant pairs studied.

Solubilities and Viscosities of Lubricant-Refrigerant Solutions

Although the differences are small on a mass basis, naphthenic oils are better solvents than paraffinic oils. When considering the viscosity of lubricant-refrigerant mixtures, naphthenic oils show greater viscosity reduction than paraffinic oils for the same mass

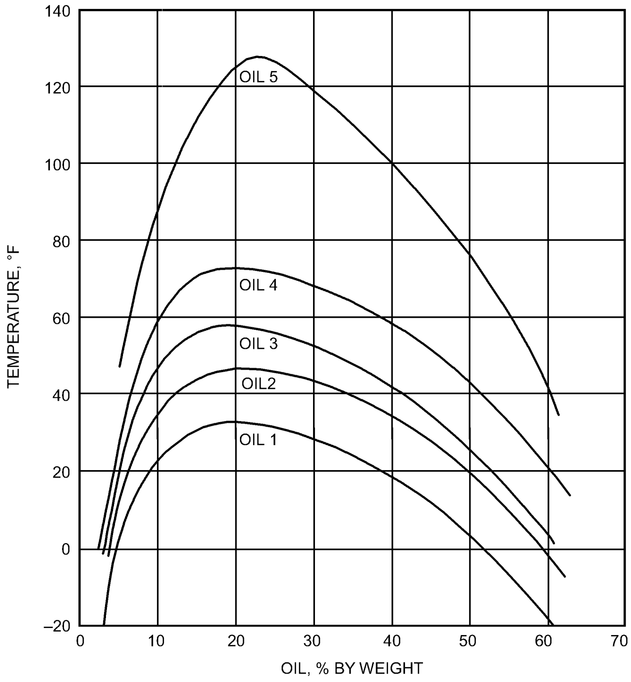
Table 7 Critical Miscibility Values of R-22 with Different Oils

Oil No.	Oil Base Type[a]	Approximate Viscosity Grade		Viscosity at 122°F Converted		Carbon-Type Composition			Critical Solution Temperature, °F
		SSU	cSt	to SSU	to cSt	$\%C_A$	$\%C_N$	$\%C_P$	
2	N	75	15	63	11.2	23	34	43	–35
3	N	75	15	60	10.2	2.5	48.5	49	21
1	N	150	32	92	18.5	13	43	44	37
8	N	200	46	118	24.6	0.6	45	55	75
7	N	200	46	127	26.7	2.8	44	54	68
5	N	200+	46+	132	27.9	22	30	47	3
4	N	250	46	135	28.6	26	28	46	–4
6	N	250	46	140	29.7	4	45	51	63
13	N	500	100	253	54.5	1.9	41	56	None[b]
12	N	500	100	282	60.7	4	41	55	None[b]
11	N	700	150	320	69.1	7	40	53	None[b]
10	N	1000	220	434	93.2	21	27	52	61
9	N	1200	220	502	109.0	27	24	50	48
18	P	200+	46+	138	29.3	0.5	33	67	None[b]
17	P	250	46	148	31.6	3.5	34	63	None[b]
16	P	300	68	164	35.2	6.4	30	63	None[b]
15	P	350	68	210	45.2	14.3	25	61	None[b]
14	P	400	100	232	50.0	18.1	22	60	111[c]

[a] P = Paraffinic, N = Naphthenic

[b] Never completely miscible at any temperature

[c] A second (inverted) miscibility dome was observed above 136°F. Above this temperature, the oil/R-22 mixture again separated into two immiscible solutions.



Oil No.	Viscosity at 100°F		Compositions, %			Ref.
	cSt	SSU	C_A	C_N	C_P	
1	34.0	159	12	44	44[a]	1
2	33.5	157	7	46	47[a]	1
3	63.0	292	12	44	44[a]	1
4	67.7	314	7	46	47[a]	1
5	41.3	192	0	55	45	2

References: 1. Walker et al. (1957) 2. Spauschus (1964)

[a] Estimated composition, not in original reference.

Fig. 17 Effect of Oil Properties on Miscibility with R-22

Table 8 Critical Solution Temperatures for Selected Refrigerant-Lubricant Pairs

Refrigerant	Lubricant	Critical Solution Temperature, °F	
		Lower	Upper
R-22	ISO 32 Naphthenic mineral oil	23	>140
	ISO 32 Modified polyglycol	10	>140
	ISO 68 Naphthenic mineral oil	59	>140
R-123	ISO 68 Naphthenic mineral oil	−38	>140
	ISO 58 Polypropylene glycol butyl monoether	−58	57
R-134a	ISO 58 Polypropylene glycol butyl monoether	−58	133
	ISO 32 Modified polyglycol	50	>194
	ISO 22 Pentaerythritol, mixed-acid ester	−44	>194
	ISO 58 Polypropylene glycol butyl monoether	−51	43
	ISO 100 Polypropylene glycol diol	−50	52
	ISO 100 Pentaerythritol, mixed-acid ester	−31	>90
	ISO 100 Pentaerythritol, branched-acid ester	−51	54

percent of dissolved refrigerant. When the two effects are compounded, under the same conditions of temperature and pressure, a naphthenic lubricant in equilibrium with a given refrigerant shows a significantly lower viscosity than a paraffinic lubricant.

Refrigerants also differ in their viscosity-reducing effects when the solution concentration is measured in mass percent. However, when the solubility is plotted in terms of mol percent, the reduction in viscosity is approximately the same, at least for Refrigerants 13, 13B1, 22, and 115 (Figure 18).

Spauschus (1964) reports numerical vapor pressure data on a R-22/white oil system; solubility-viscosity graphs on naphthenic and paraffinic oils have been published by Loffler (1960), Little (1952), and Albright and Mandelbaum (1956). Some discrepancies, particularly at high R-22 contents, have been shown in data on viscosities that apparently could not be attributed to the properties of the lubricant and remain unexplained. However, general plots reported by the aforementioned authors are satisfactory for engineering and design purposes.

Spauschus and Speaker (1987) have compiled references of solubility and viscosity data. Selected solubility-viscosity data are summarized in Figure 14 and Figures 19 through 31.

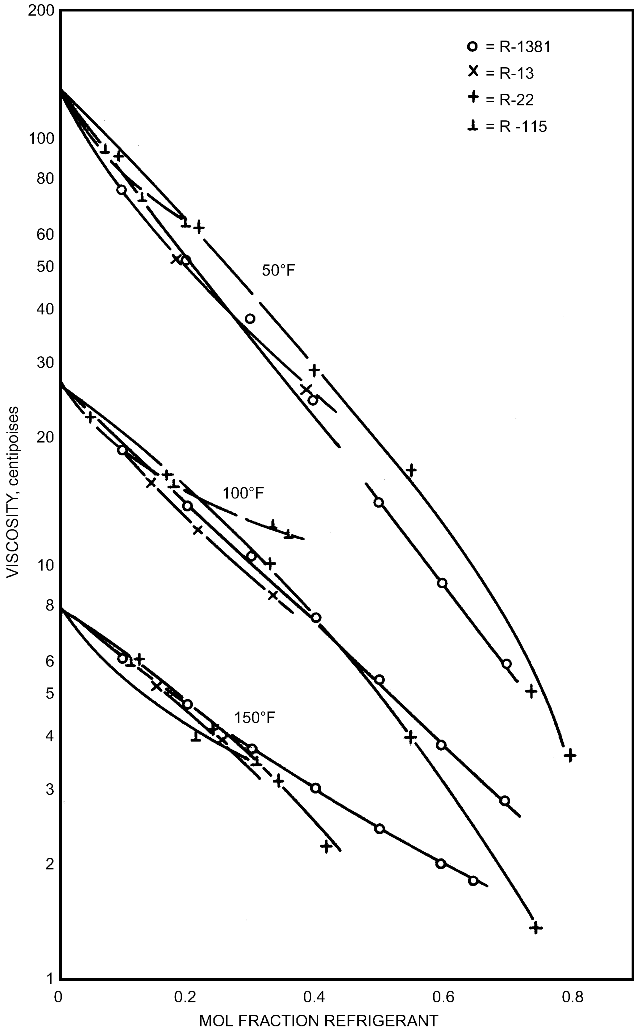


Fig. 18 Viscosity of Mixtures of Various Refrigerants and 32 cSt (150 SSU) Paraffinic Oil
(Albright and Lawyer 1959)

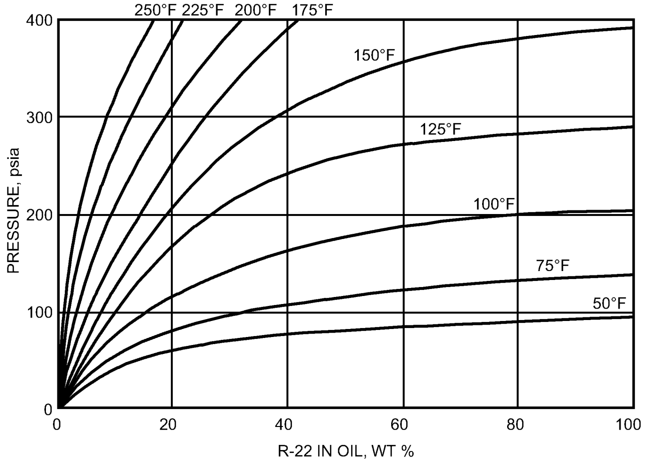


Fig. 19 Solubility of R-22 in 32 cSt (150 SSU) Naphthenic Oil

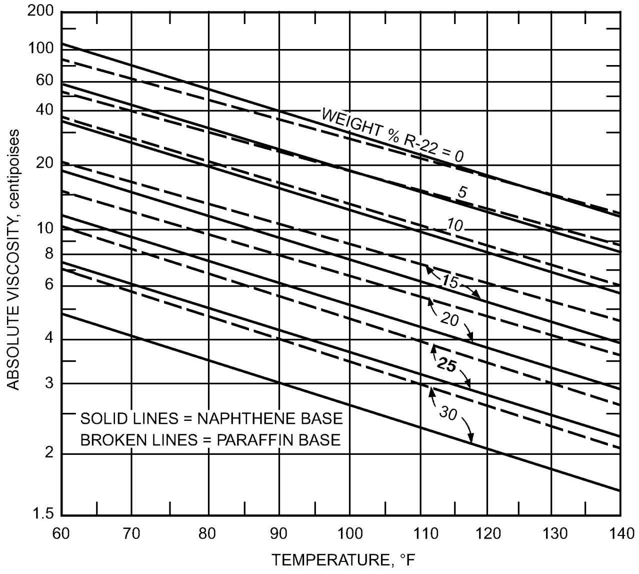


Fig. 20 Viscosity-Temperature Chart for Solutions of R-22 in 32 cSt (150 SSU) Naphthene and Paraffin Base Oils

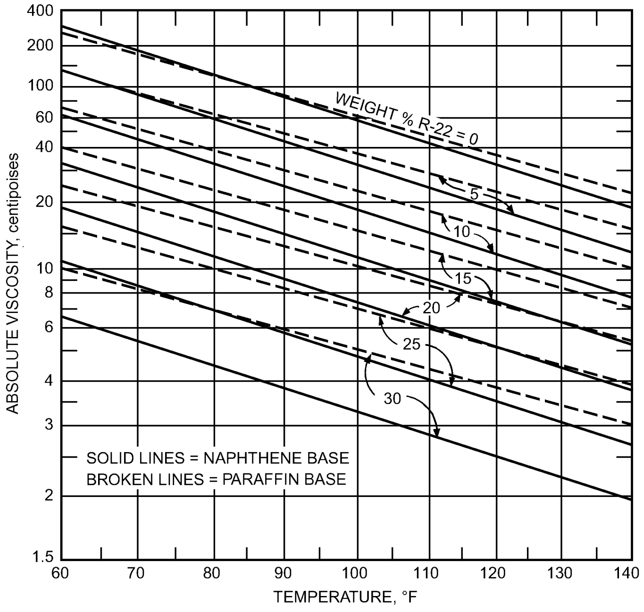


Fig. 21 Viscosity-Temperature Chart for Solutions of R-22 in 65 cSt (300 SSU) Naphthene and Paraffin Base Oils

Where possible, solubilities have been converted to mass percent to provide consistency among the various charts. Figure 14 and Figures 19 through 23 contain data on R-22 and oils, Figure 24 on R-502, Figures 25 and 26 on R-11, Figures 27 and 28 on R-12, and Figures 29 and 30 on R-114. Figure 31 contains data on the solubility of various refrigerants in alkylbenzene lubricant. Viscosity-solubility characteristics of mixtures of R-13B1 and lubricating oils have been investigated by Albright and Lawyer (1959). Similar studies on R-13 and R-115 are covered by Albright and Mandelbaum (1956).

The solubility of refrigerants in oils, in particular of HFC refrigerants in ester oils, is usually determined experimentally. Wahlstrom and Vamling (2000) have developed a predictive scheme

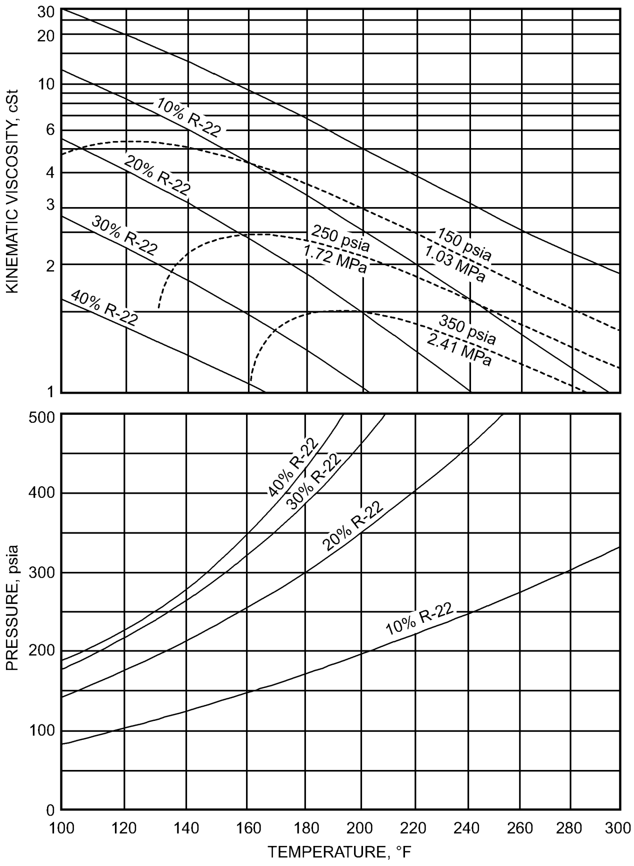


Fig. 22 Viscosity-Temperature Chart for Solutions of R-22 in 32 cSt (150 SSU) Naphthenic Oil
(Van Gaalen et al. 1990, 1991a)

based on group contributions that is predictive for the solubilities of pentaerythritol esters and five HFCs (HFC-125, HFC-134a, HFC-143a, HFC-152a and HFC-32). The scheme uses a modified Flory-Huggins model and a Unifac model. With these schemes, knowing only the structure of the pentaerythritol and the HFC refrigerant, the solubility can be predicted.

LUBRICANT RETURN FROM EVAPORATORS

Regardless of the miscibility relations of a lubricant with refrigerants, for a refrigeration system to function properly, the lubricant must return adequately from the evaporator to the crankcase. Parmelee (1964) showed that the viscosity of the lubricant, saturated with refrigerant under low-pressure and low-temperature conditions, is important in providing good lubricant return. The viscosity of the lubricant-rich liquid that accompanies the suction gas changes as it sees rising temperatures on its way back to the compressor. Two opposing factors then come into play. First, the increasing temperature tends to decrease the viscosity of the fluid. Second, since the pressure remains unchanged, the increasing temperature also tends to drive off some of the dissolved refrigerant from the solution, thereby increasing its viscosity (Loffler 1960).

Figures 32 through 34 show the variation in viscosity with temperature and pressure for three lubricant-refrigerant solutions ranging from –40 to 70°F. In all cases, the viscosities of the solutions passed through maximum values as the temperature was changed at constant pressure, a finding that was also consistent with previous data obtained by Bambach (1955) and Loffler (1960). According to Parmelee, the existence of a viscosity maximum is significant, because the lubricant-rich solution becomes most viscous not in the coldest regions in the evaporator, but at some intermediate point where much of the refrigerant has escaped from the lubricant. This condition is possibly in the suction line. The velocity of the return vapor, which may be high enough to move the lubricant-refrigerant solution in the colder part of the evaporator, may be too low to achieve the same result at the point of maximum viscosity. The designer must consider this factor to minimize any lubricant return problems. Chapters 2 and 3 have further information on velocities in return lines.

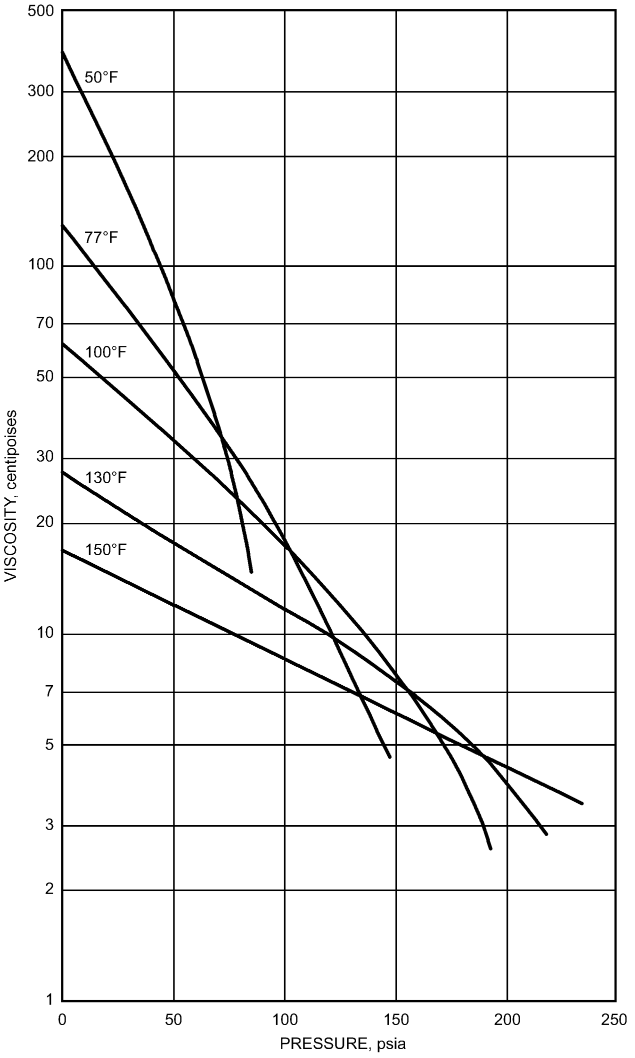


Fig. 23 Viscosity of Mixtures of 65 cSt (300 SSU) Paraffin Base Oil and R-22
(Albright and Mandelbaum 1956)

Another aspect of viscosity data at the evaporator conditions is shown in Figure 35, which compares a synthetic alkylbenzene lubricant with a naphthenic mineral oil. The two oils are the same viscosity grade, but the highly aromatic alkylbenzene lubricant has a much lower viscosity index in the pure state and shows a higher viscosity at low temperatures. However, at 19.7 psia or approximately –40°F evaporator temperature, the viscosity of the lubricant/R-502 mixture is considerably lower for alkylbenzene than for naphthenic lubricant. In spite of the lower viscosity index, alkylbenzene returns more easily than naphthenic lubricant.

Estimated viscosity-temperature-pressure relationships for a naphthenic lubricant with R-502 are shown in Figure 36. Figures 37 and 38 show viscosity-temperature-pressure plots of alkylbenzene

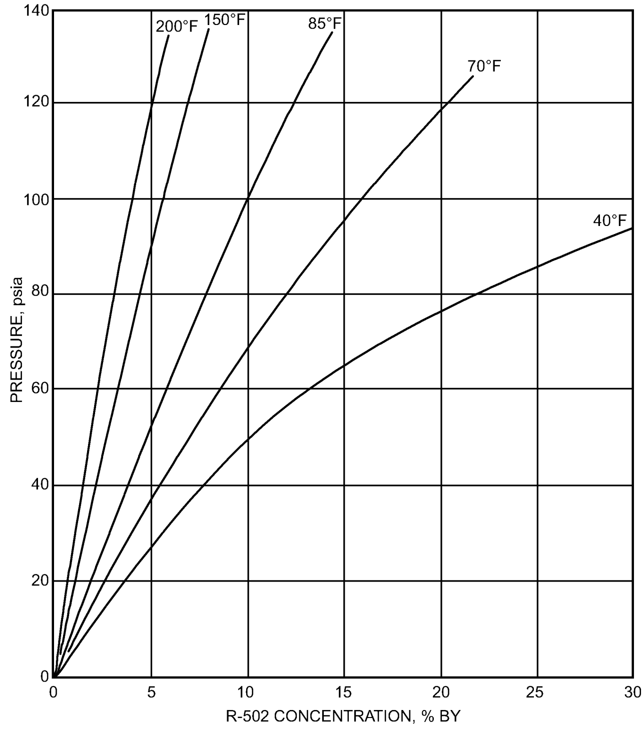


Fig. 24 Solubility of R-502 in 32 cSt (150 SSU) Naphthenic Oil (C_A 12%, C_N 44%, C_P 44%)

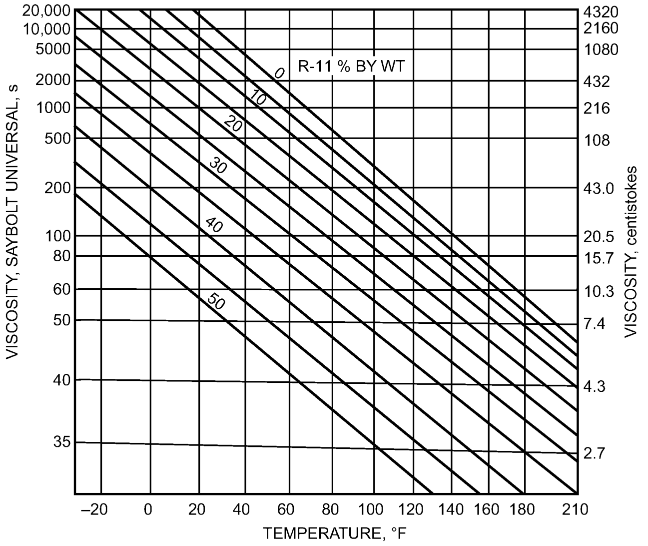


Fig. 25 Viscosity-Temperature Curves for Solutions of R-11 in 65 cSt (300 SSU) Naphthene Base Oil

and R-22 and R-502, respectively. These data are based on experimental data from Van Gaalen et al. (1991a, 1991b). Figures 39 and 40 show viscosity-temperature-pressure data for mixtures of R-134a and a 32 ISO VG polyalkylene glycol and an 80 ISO VG polyalkylene glycol, respectively. Figures 41 and 42 show similar data for R-134a and a 32 ISO VG polyol ester and a 100 ISO VG polyol ester, respectively (Cavestri 1993). Cavestri and Schafer (2000) provide viscosity data as a function of temperature and pressure for R-410A/polyol ester oils as shown in Figures 43

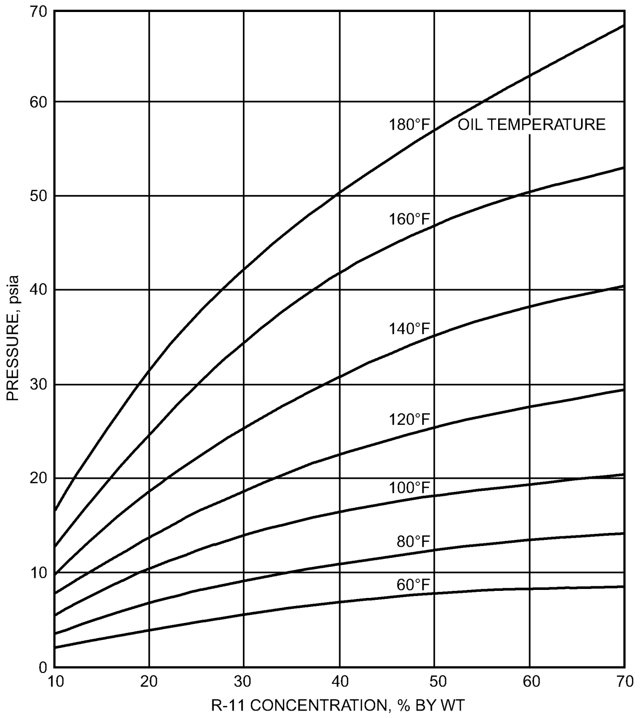
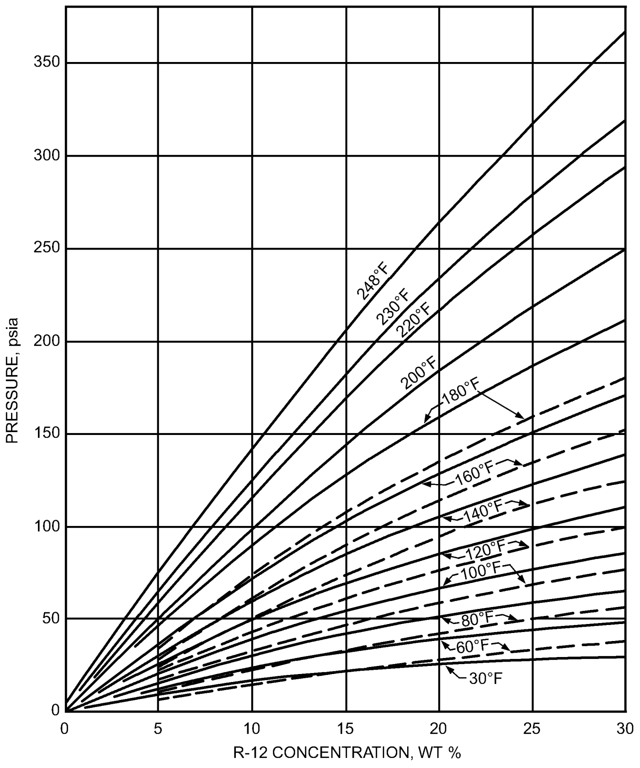


Fig. 26 Solubility of R-11 in 65 cSt (300 SSU) Oil



Solid lines: 32 cSt (150 SSU) naphthene base oil.
Also 52 cSt (240 SSU) German base oil (Bambach 1955).
Broken lines: 32 cSt (150 SSU) and 70 cSt (325 SSU) mixed base oils.

Fig. 27 Solubility of R-12 in Refrigerant Oils

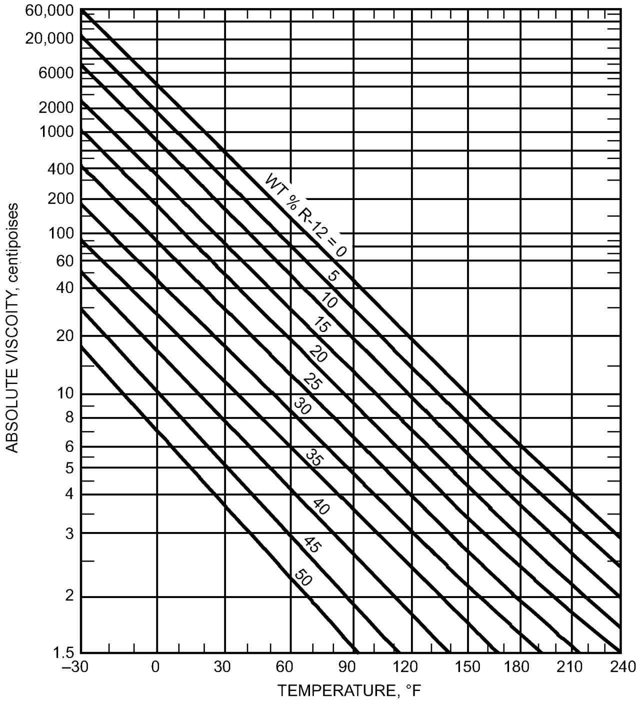


Fig. 28 Viscosity-Temperature Chart for Solutions of R-12 in 32 cSt (150 SSU) Naphthene Base Oil

through 46. Viscosity and pressure data at constant concentrations are given in Figures 47 through 50.

Sundaresan and Radermacher (1996) observed oil return in a small air-to-air heat pump. Three refrigerant lubricant pairs (R-22/mineral oil, R-407C/mineral oil, and R-407C/polyol ester) were studied under four conditions—steady-state cooling, steady-state heating, cyclic operation, and a simulated lubricant pumpout situation. The lubricant returned rapidly to the compressor in the R-22/mineral oil and R-407C/polyol ester tests, but oil return was unreliable in the R-407C/mineral oil test.

Kesim et al. (2000) developed general relationships for calculating the required refrigerant speed for carrying lubricant oil up vertical sections of refrigerant lines. For these relationships they assumed the thickness of the oil film to be 2% of the inner pipe diameter. They converted these minimum speeds to the corresponding refrigeration load or capacities for R-134a and copper suction and discharge risers.

WAX SEPARATION (FLOC TESTS)

Wax separation properties are of little importance with synthetic lubricants because they do not contain wax or wax-like molecules. However, petroleum-derived lubricating oils are mixtures of large numbers of chemically distinct hydrocarbon molecules. At low temperatures in the low-pressure side of refrigeration units, some of the larger molecules separate from the bulk of the lubricant, forming wax-like deposits. This wax can clog capillary tubes and cause expansion valves to stick, which is undesirable in refrigeration systems. Bosworth (1952) describes other wax separation problems.

In selecting a lubricant to use with completely miscible refrigerants, the wax-forming tendency of the lubricant can be determined by the floc test. The floc point is the highest temperature at which wax-like materials or other solid substances precipitate when a mixture of 10% lubricant and 90% R-12 is cooled under specific conditions. Because different refrigerant and lubricant

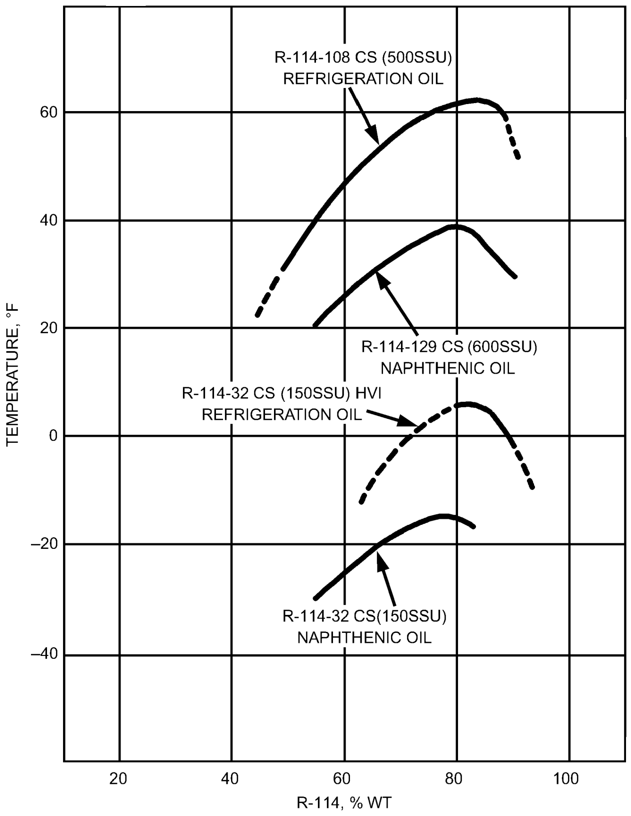


Fig. 29 Critical Solution Temperatures of R-114/Oil Mixtures

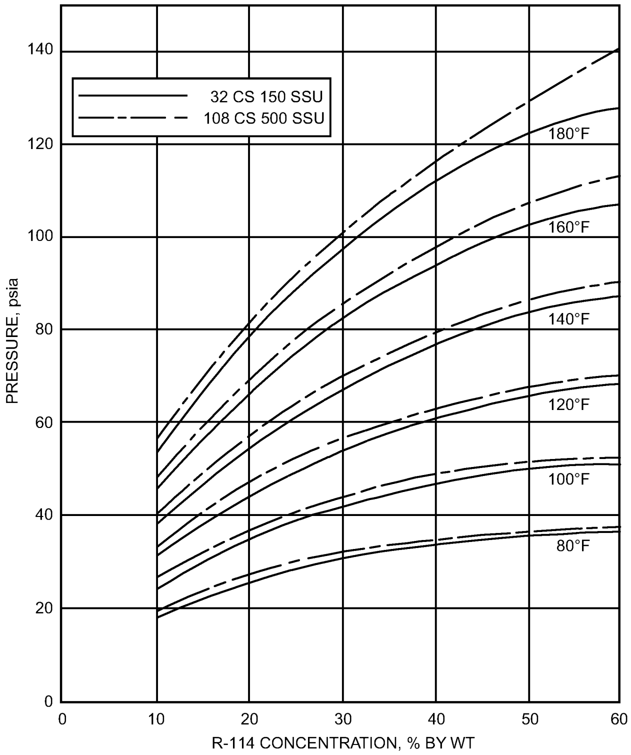


Fig. 30 Solubility of R-114 in HVI Oils

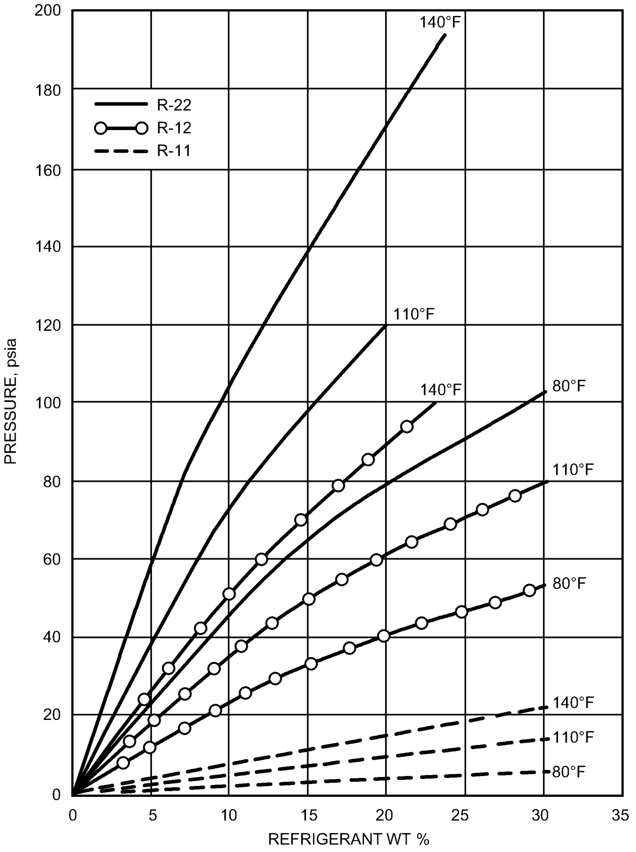


Fig. 31 Solubility of Refrigerants in 32 cSt (150 SSU) Alkylbenzene Oil

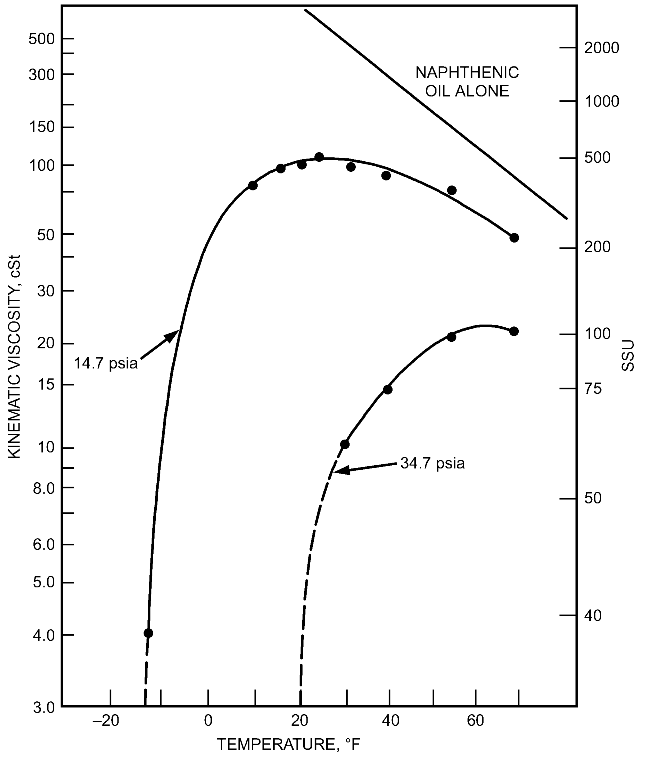


Fig. 32 Viscosity of R-12/Oil Solutions at Low-Side Conditions
(Parmelee 1964)

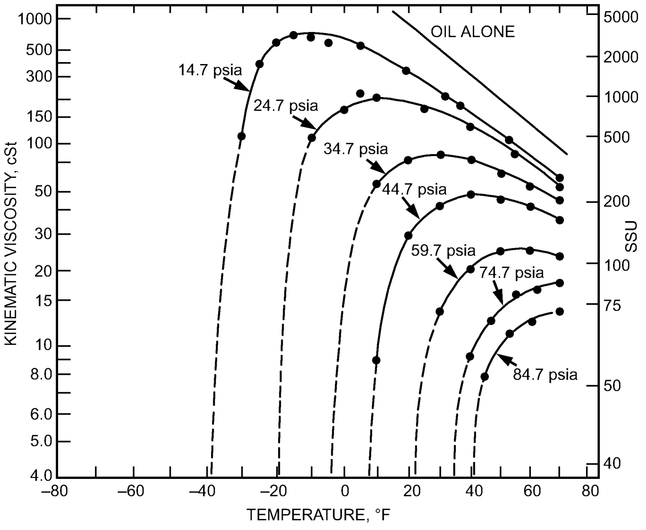


Fig. 33 Viscosity of R-22/Naphthenic Oil Solutions at Low-Side Conditions
(Parmelee 1964)

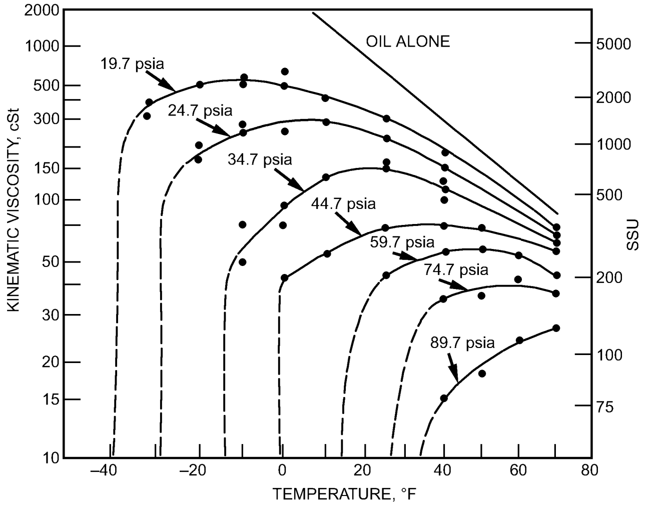


Fig. 34 Viscosity of R-502/Naphthenic Oil Solutions at Low-Side Conditions

concentrations are encountered in actual equipment, test results cannot be used directly to predict performance. The lubricant concentration in the expansion devices of most refrigeration and air-conditioning systems is considerably less than 10%, resulting in significantly lower temperatures at which wax separates from lubricant-refrigerant mixture. ASHRAE *Standard* 86 describes a standard method of determining the floc characteristics of refrigeration oils in the presence of R-12.

Attempts to develop a test for the floc point of partially miscible refrigerants for use with R-22 have not been successful. The solutions being cooled often separate into two liquid phases. Once phase separation occurs, the components of the lubricant distribute themselves into the lubricant-rich phase and the refrigerant-rich phase in such a way that the highly soluble aromatics concentrate into the refrigerant phase, while the less soluble saturates concentrate into the lubricant phase. The waxy materials stay dissolved in the refrigerant-rich phase only to the extent of their solubility limit. On further cooling, any wax that separates from the refrigerant-rich phase migrates into the lubricant-rich phase. Therefore, a

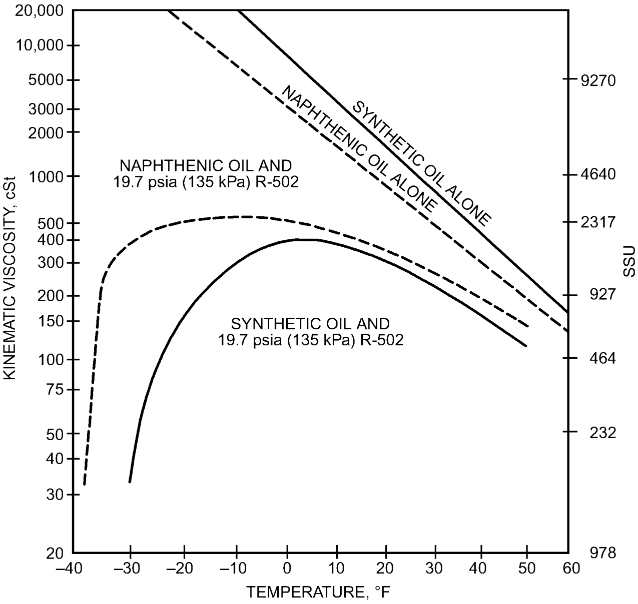


Fig. 35 Viscosities of Solutions of R-502 with 32 cSt (150 SSU) Naphthenic Oil (C_A 12%, C_N 44%, C_P 44%) and 32 cSt (150 SSU) Synthetic Alkylbenzene Oil

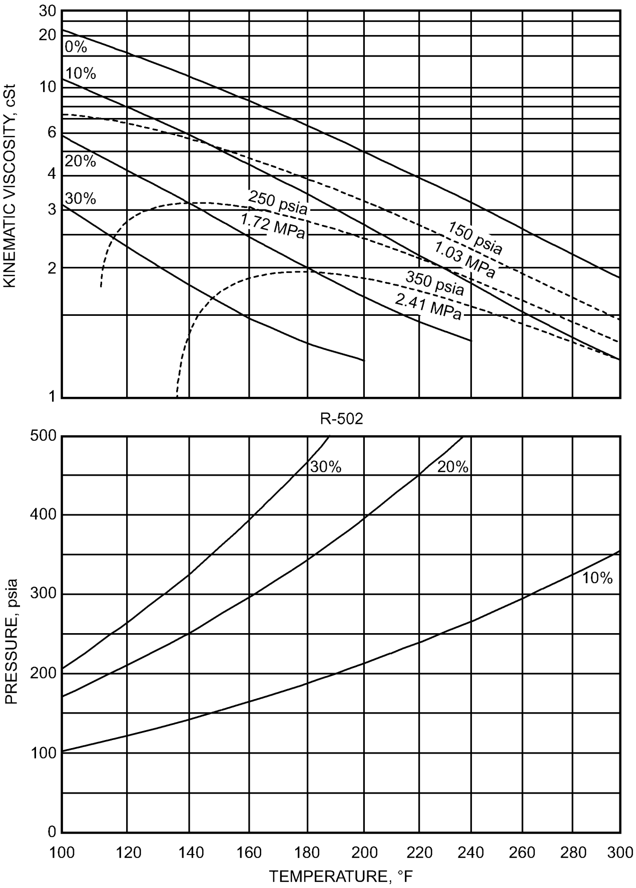


Fig. 36 Viscosity-Temperature-Pressure Chart for Solutions of R-502 in 32 Naphthenic Oil

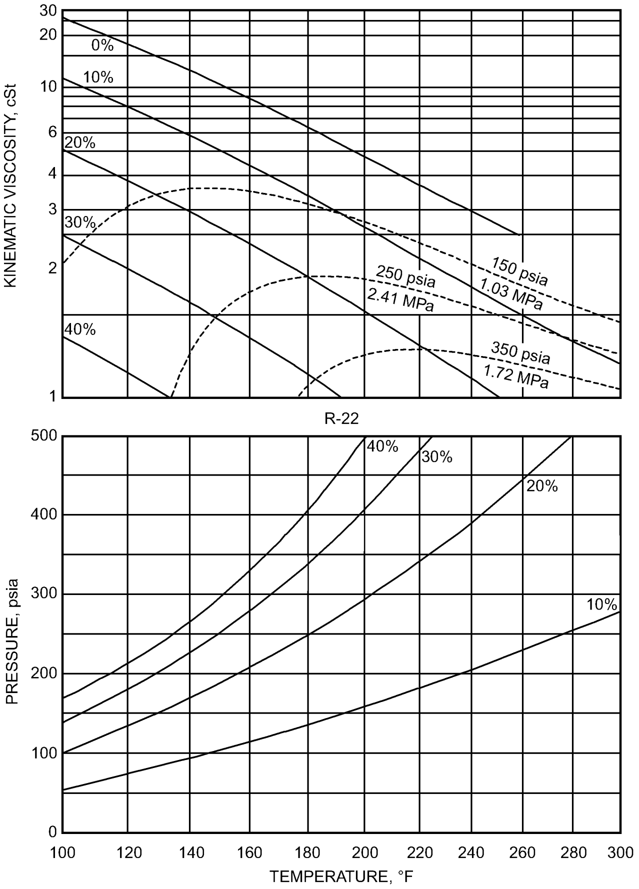


Fig. 37 Viscosity-Temperature-Pressure Chart for Solutions of R-22 in 32 cSt (150 SSU) Alkylbenzene Oil

significant floc point cannot be obtained with partially miscible refrigerants once phase separation has occurred. However, lack of flocculation does not mean lack of wax separation. Wax may separate in the lubricant-rich phase, causing it to congeal. Parmelee (1964) reported such phenomena with a paraffinic lubricant and R-22.

Floc point might not be reliable when applied to used oils. A part of the original wax may already have been deposited, and the used lubricant may contain extraneous material from the operating equipment.

Good design practice suggests selecting oils that do not deposit wax on the low-pressure side of a refrigeration system, regardless of single-phase or two-phase refrigerant-lubricant solutions. Mechanical design affects how susceptible equipment is to wax deposition. Wax deposits at sharp bends and the suspended wax particles build up on the tubing walls by impingement. Careful design avoids bends and materially reduces the tendency to deposit wax.

SOLUBILITY OF HYDROCARBON GASES

Hydrocarbon gases such as propane (R-290) and ethylene (R-1150) are miscible with the compressor lubricating oil and are absorbed by the lubricant. The lower the boiling point or critical temperature, the less soluble the gas, all other values being equal. Gas solubility increases with decreasing temperature and increasing pressure (Figures 51 and 52). As with other lubricant miscible refrigerants, absorption of the hydrocarbon gas reduces lubricant viscosity.

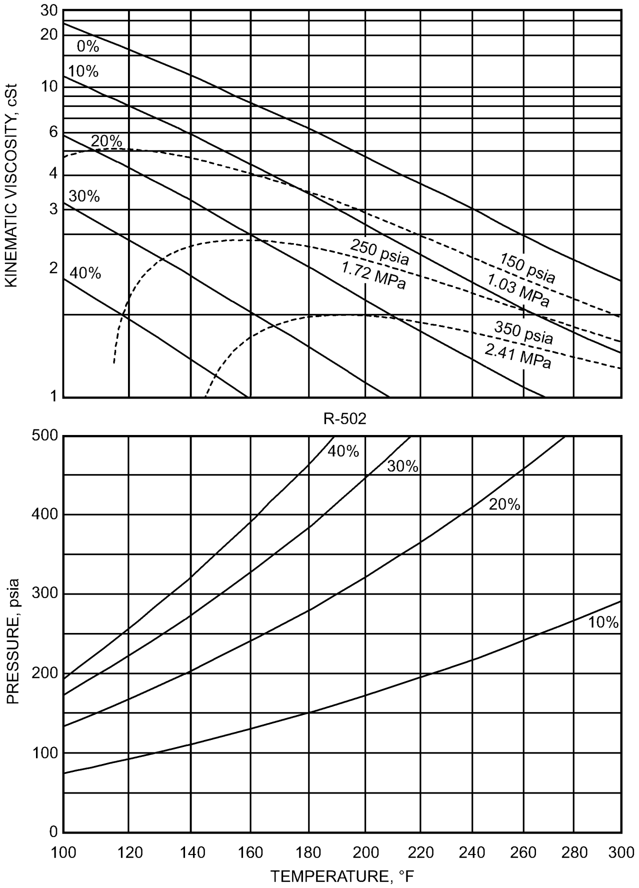


Fig. 38 Viscosity-Temperature-Pressure Chart for Solutions of R-502 in 32 cSt (150 SSU) Alkylbenzene Oil

SOLUBILITY OF WATER IN LUBRICANTS

Refrigerant systems must be dry internally because high moisture content can cause ice to form in the expansion valve or capillary tube, corrosion of bearings, reactions that affect the lubricant/refrigerant stability, or other operational problems.

As with other components, the refrigeration lubricant must be as dry as practical. Normal manufacturing and refinery handling practices result in a moisture content of about 30 ppm for almost all hydrocarbon-based lubricants. Polyalkylene glycols generally contain several hundred ppm of water. Polyol esters usually contain 50 to 100 ppm moisture. However, this amount may increase between the time of shipment from the refinery and the time of actual use, unless proper preventive measures are taken. Small containers are usually sealed. Tank cars are not normally pressure sealed or nitrogen blanketed except for shipment of synthetic polyol ester and polyalkylene lubricants, which are quite hygroscopic.

During transit, changes in ambient temperatures cause the lubricant to expand and contract and draw in humid air from outside. Depending on the extent of such cycling, the moisture content of the lubricant may be significantly higher than at the time of shipment. Users of large quantities of refrigeration oils frequently dry the lubricant before use. Chapter 43 discusses the methods of drying lubricants. Normally, removing any moisture present will also deaerate the lubricant.

Because POE and PAG lubricants are quite hygroscopic, when they are in a refrigeration system they should circulate through a filter/dryer designed for liquids. A filter/dryer can be installed in the line carrying liquid refrigerant or in a line returning lubricant to the compressor. The material in the filter/dryer must be compatible with the lubricant. Also, desiccants can remove some additives in the lubricant.

Spot checks show that water solubility data for transformer oils obtained by Clark (1940) also apply to refrigeration oils (Figure 53).

A simple method, previously used in industry to detect free water in refrigeration oils, is the dielectric breakdown voltage (ASTM D877), which is designed to control moisture and other contaminants in electrical insulating oils. The method does not work with polyester and polyalkylene glycol oils, however. According to Clark (1940), the dielectric breakdown voltage decreases with increasing moisture content at the same test temperature and increases with temperature for the same moisture content. At 80°F, when the solubility of water in a 32 cSt (150 SSU) naphthenic lubricant is between 50 to 70 ppm, a dielectric breakdown voltage of about 25 kV indicates that no free water is present in the lubricant. However, the lubricant may contain dissolved water up to the solubility limit. Therefore, a dielectric breakdown voltage of 35 kV is commonly specified to indicate that the moisture content is well below saturation.

The ASTM D877 test is not sensitive below about 60% saturation. Current practice is to measure directly the total moisture content by procedures such as the Karl Fischer (ASTM D1533) method.

SOLUBILITY OF AIR IN LUBRICANTS

Refrigerant systems should not contain excessive amounts of air or other noncondensable gases. Oxygen in air can react with the lubricant to form oxidation products. More importantly, nitrogen in the air (which does not react with lubricant) is a noncondensable gas that can interfere with performance. In some systems, the tolerable volume of noncondensables is very low. Therefore, if the lubricant is added after the system is evacuated, it must not contain an excessive amount of dissolved air or other noncondensable gas. Dissolved air is removed when a vacuum is used to dry the lubricant. However, if the deaerated lubricant is stored under pressure in dry air, it will reabsorb air in proportion to the pressure (Baldwin and Daniel 1953). Dry nitrogen blankets are preferred over using dry air for keeping lubricants dry because introducing air into a system can cause problems with unintended oxidation.

FOAMING AND ANTIFOAM AGENTS

Excessive foaming of the lubricant is undesirable in refrigeration systems. Brewer (1951) suggests that abnormal refrigerant foaming reduces the lubricant's effectiveness in cooling the motor windings and removing heat from the compressor. Too much foaming also can cause too much lubricant to pass through the pump and enter the low-pressure side. Foaming in a pressure oiling system can result in starved lubrication under some conditions.

However, moderate foaming is beneficial in refrigeration systems, particularly for noise suppression. A foamy layer on top of the lubricant level dampens the noise created by the moving parts of the compressor. Moderate foam also lubricates effectively, yet it is pumpable, which minimizes the risk of vapor lock of the oil pump at start-up. There is no general agreement on what constitutes excessive foaming or how it should be prevented. Some manufacturers add small amounts of an antifoam agent, such as silicone fluid, to refrigerator oils. Others believe that foaming difficulties are more easily corrected by equipment design.

Goswami et al. (1997) observed the foaming characteristics of R-32, R-125, R-134a, R-143a, R-404A, R-407C, and R-410A with two ISO 68 polyol ester lubricants. They compared them to R-12 and R-22 paired with both an ISO 32 and ISO 68 mineral oil and found that the foamability and foam stability of the HFC/POE pairs were much lower than those of the R-12 and R-22/mineral oil pairs.

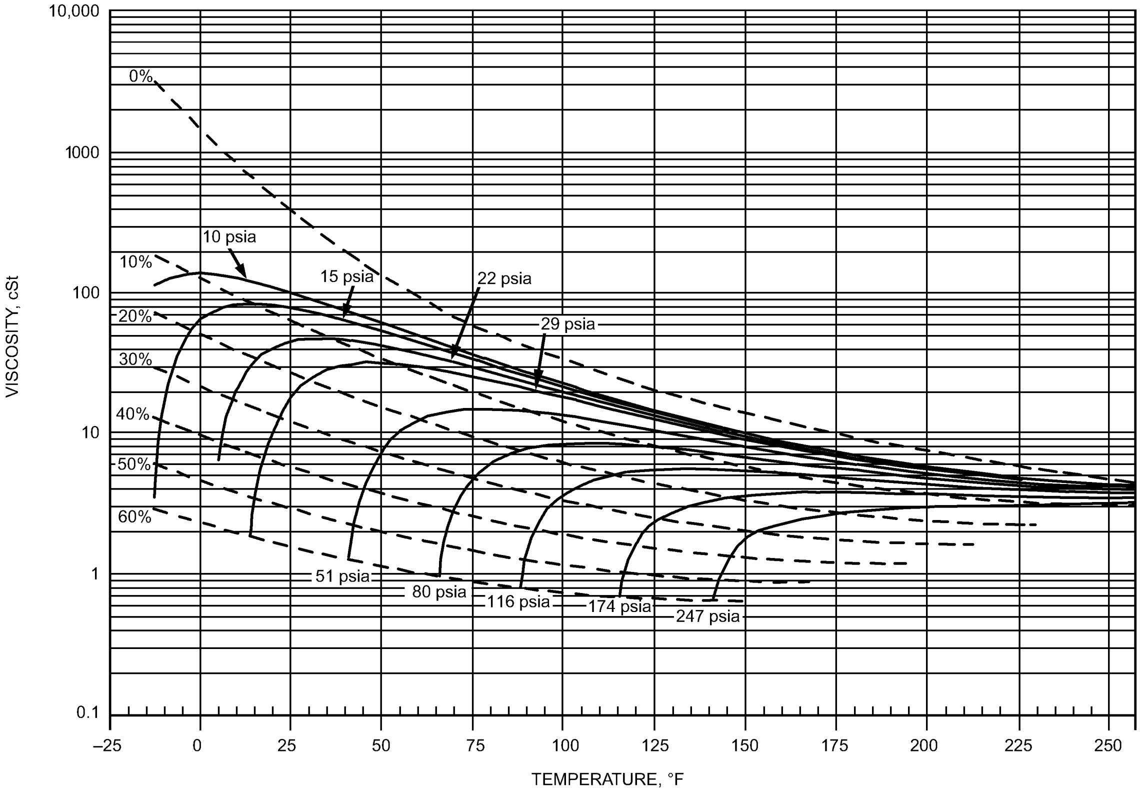


Fig. 39 Viscosity-Temperature-Pressure Plot for 32 ISO VG Polypropylene Glycol Butyl Mono Ether with R-134a

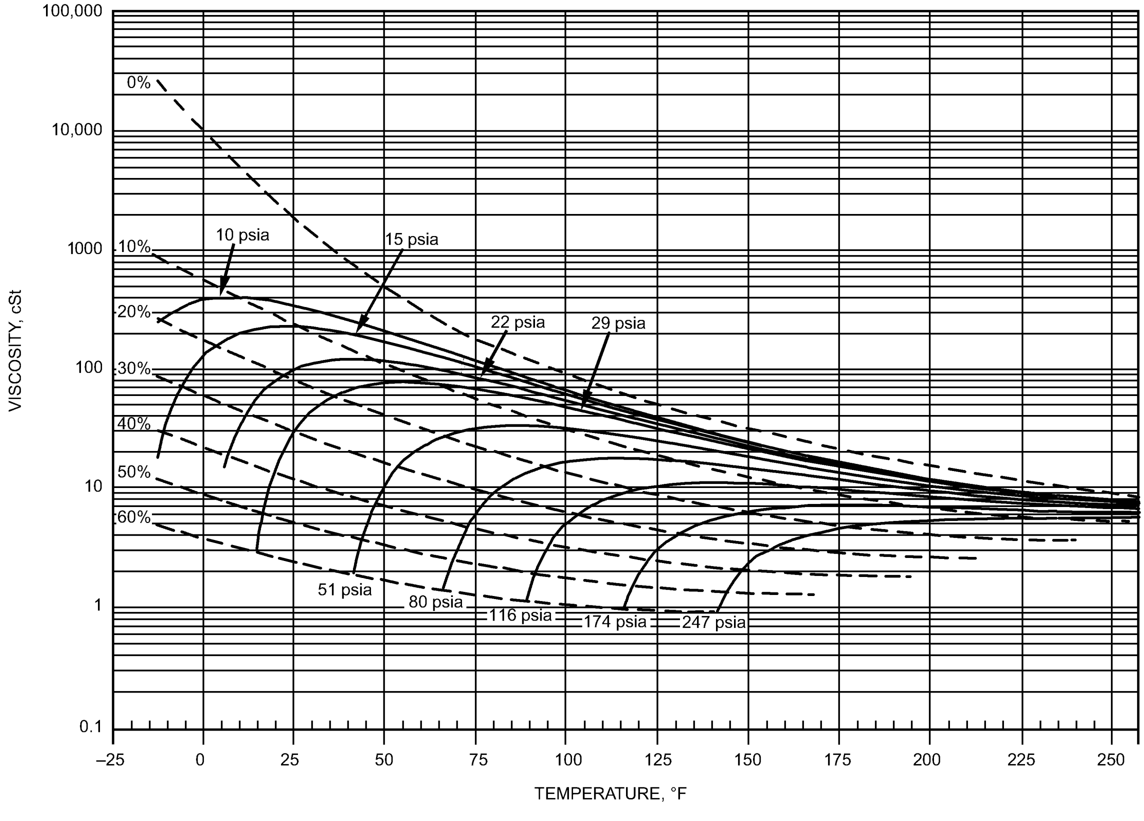


Fig. 40 Viscosity-Temperature-Pressure Plot for 80 ISO VG Polyoxypropylene Diol with R-134a

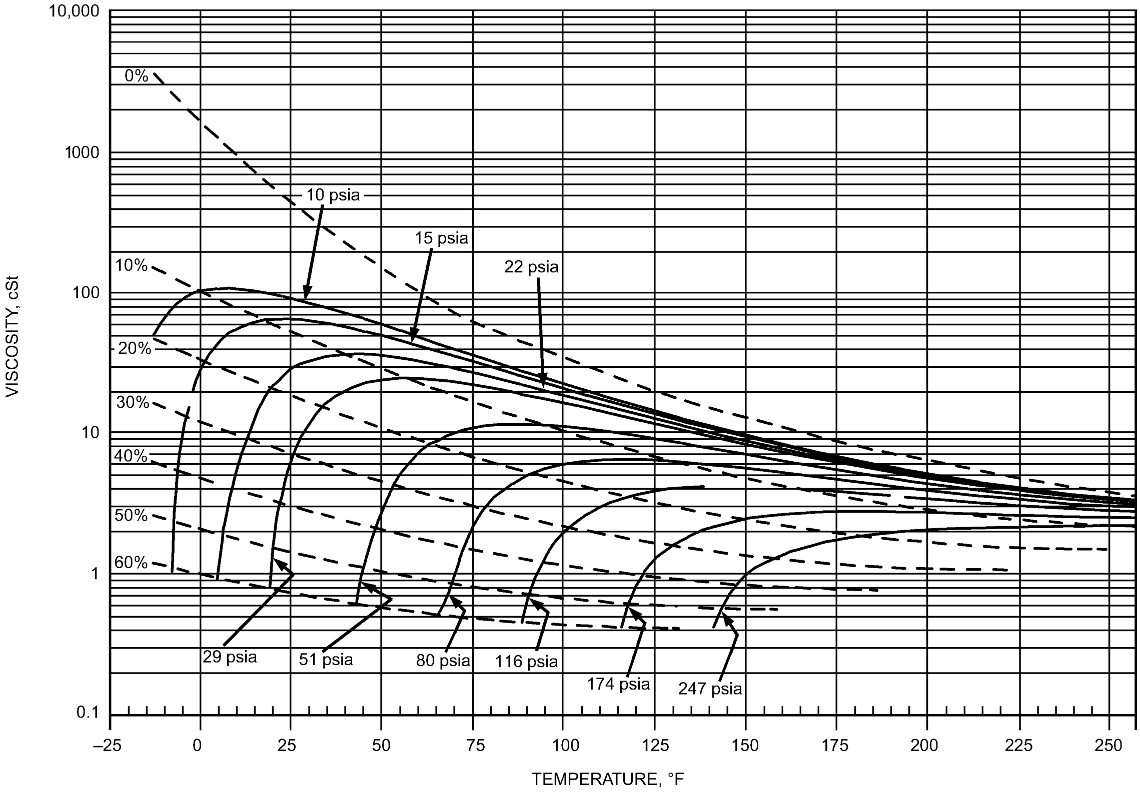


Fig. 41 Viscosity-Temperature-Pressure Plot for 32 ISO VG Branched Acid Polyol Ester with R-134a

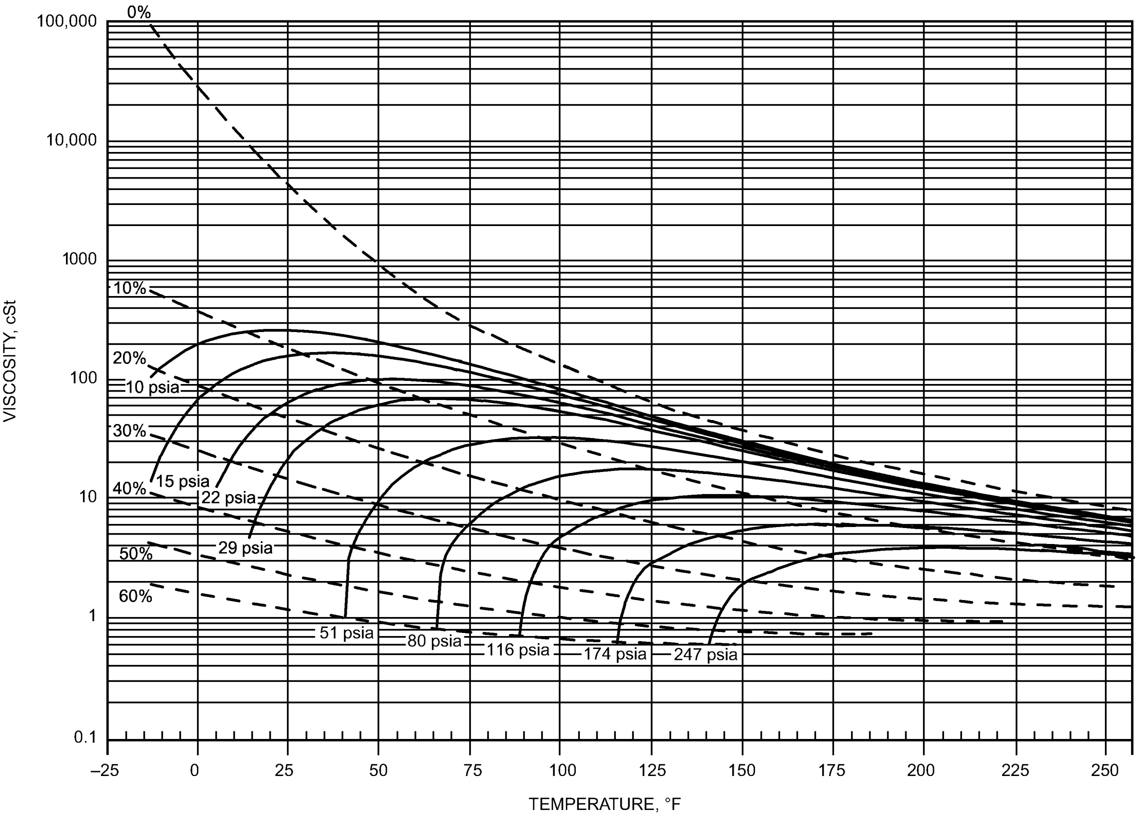


Fig. 42 Viscosity-Temperature-Pressure Plot for 100 ISO VG Branched Acid Polyol Ester with R-134a

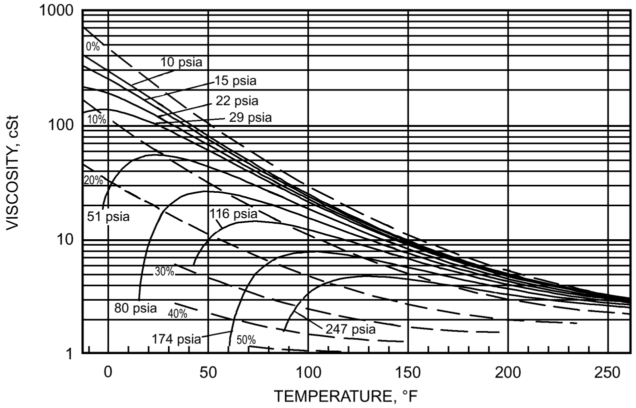


Fig. 43 Viscosity-Temperature-Pressure Plot for a Mixture of R-410A and 32 ISO VG Mixed Acid Polyol Ester Lubricant

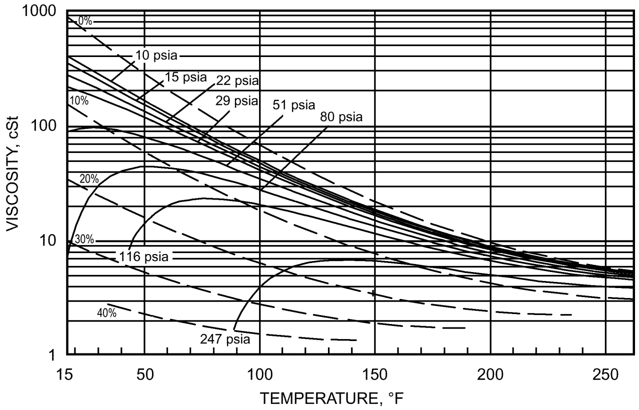


Fig. 44 Viscosity-Temperature-Pressure Plot for a Mixture of R-410A and 68 ISO VG Mixed Acid Polyol Ester Lubricant

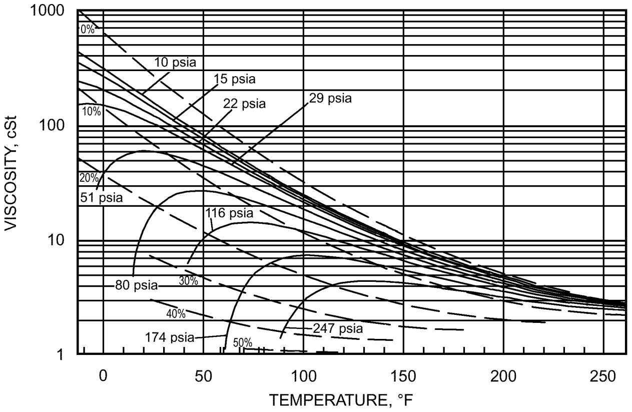


Fig. 45 Viscosity-Temperature-Pressure Plot for a Mixture of R-410A and 32 ISO VG Branched Acid Polyol Ester Lubricant

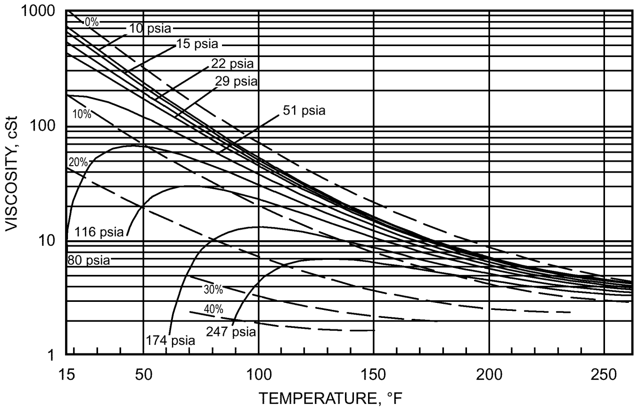


Fig. 46 Viscosity-Temperature-Pressure Plot for a Mixture of R-410A and 68 ISO VG Branched Acid Polyol Ester Lubricant

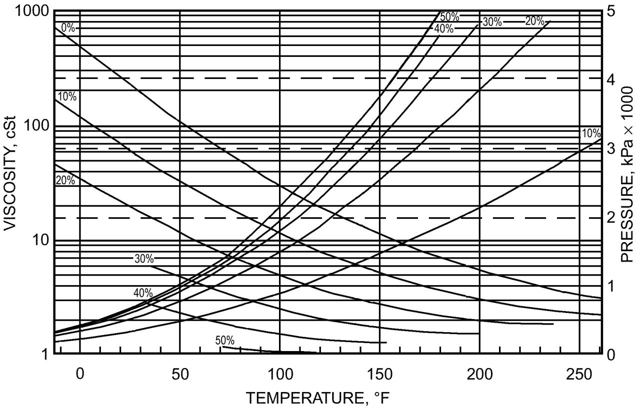


Fig. 47 Viscosity as a Function of Temperature and Pressure at Constant Concentrations for a Mixture of R-410A and 32 ISO VG Mixed Acid Polyol Ester Lubricant

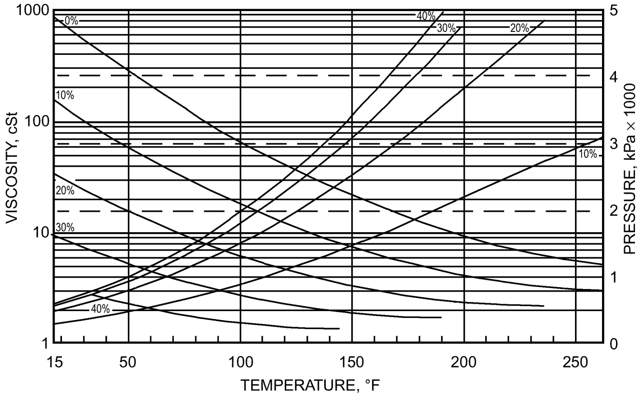


Fig. 48 Viscosity as a Function of Temperature and Pressure at Constant Concentrations for a Mixture of R-410A and 68 ISO VG Mixed Acid Polyol Ester Lubricant

OXIDATION RESISTANCE

Refrigeration oils are seldom exposed to oxidizing conditions in hermetic systems. Once a system is sealed against air and moisture, the oxidation resistance of a lubricant is not significant unless it reflects the chemical stability. Handling and manufacturing practices include elaborate care to protect lubricants against air, moisture, or any other contaminant. Oxidation resistance by itself is rarely included in refrigeration lubricant specifications.

Nevertheless, oxidation tests are justified, because oxidation reactions are chemically similar to the reactions between oils and refrigerants. An oxygen test, using power factor as the measure, correlates with established sealed-tube tests. However, such oxidation resistance tests are not used as primary criteria of chemical

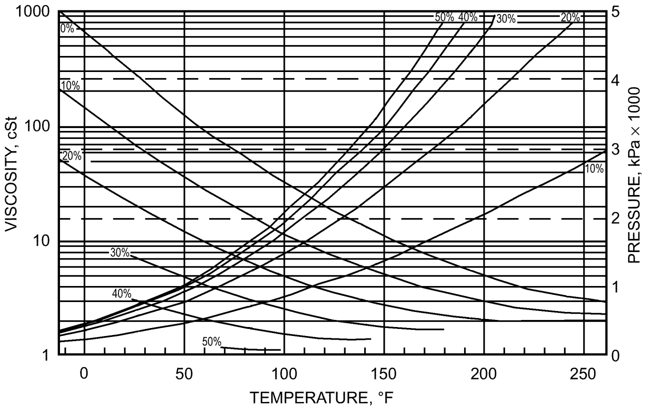


Fig. 49 Viscosity as a Function of Temperature and Pressure at Constant Concentrations for a Mixture of R-410A and 32 ISO VG Branched Acid Polyol Ester Lubricant

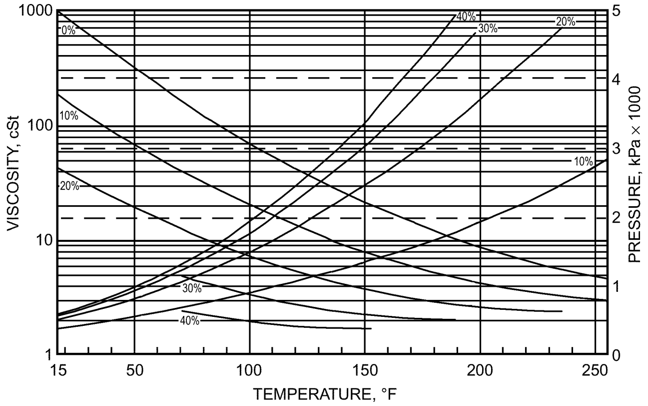


Fig. 50 Viscosity as a Function of Temperature and Pressure at Constant Concentrations for a Mixture of R-410A and 68 ISO VG Branched Acid Polyol Ester Lubricant

reactivity, but rather to support the claims of chemical stability determined by sealed-tube and other tests.

Oxidation resistance may become a prime requirement during manufacture. The small amount of lubricant used during compressor assembly and testing is not always completely removed before the system is dehydrated. If the subsequent dehydration process is carried out in a stream of hot, dry air, as is frequently the case, the hot oxidizing conditions can cause the residual lubricant to become gummy, leading to stuck bearings, overheated motors, and other operating difficulties. For these purposes, the lubricant should have high oxidation resistance. However, the lubricant used under such extreme conditions should be classed as a specialty process lubricant rather than a refrigeration lubricant.

CHEMICAL STABILITY

Refrigeration lubricants must have excellent chemical stability. Within the enclosed refrigeration environment, the lubricant must resist chemical attack by the refrigerant in the presence of all the materials encountered, including the various metals, motor insulation, and any unavoidable contaminants trapped in the system. The presence of air and water is the most common cause of problems with the chemical stability of lubricants in refrigeration and air-conditioning systems. This is true for all lubricants, especially for polyol esters and to some extent for polyalkylene glycols. Lubricant might react with a chlorine-containing refrigerant at elevated temperatures, and the reaction can be catalyzed by metals. Methods for evaluating the chemical stability of lubricant-refrigerant mixtures are covered in Chapter 5.

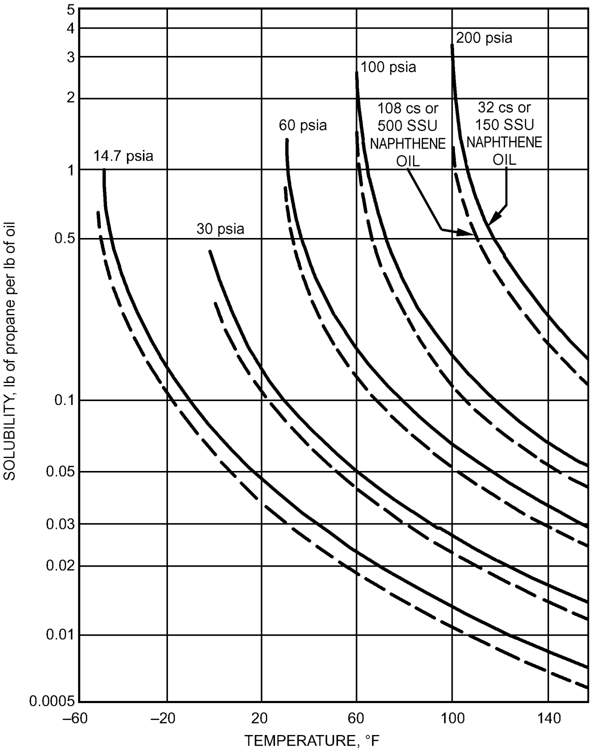


Fig. 51 Solubility of Propane in Oil
(Witco)

Various phenomena in an operating system, such as sludge formation, carbon deposits on valves, gumming, and copper plating of bearing surfaces, have been attributed to lubricant decomposition in the presence of the refrigerant. In addition to the direct reactions of the lubricant and refrigerant, the lubricant may also act as a medium for reactions between the refrigerant and the motor insulation, particularly when the refrigerant extracts the lighter components of the insulation. Factors affecting the stability of various components such as wire insulation materials in hermetic systems are also covered in Chapter 5.

Effect of Lubricant Type

Mineral oils differ in their ability to withstand chemical attack by a given refrigerant. In an extensive laboratory sealed-tube test program, Walker et al. (1960, 1962) showed that color darkening, corrosion of metals, deposits, and copper plating occur less in paraffinic oils than in naphthenic oils. Using gas analysis, Spauschus and Doderer (1961) and Doderer and Spauschus (1965) show that a white oil containing only saturates and no aromatics is considerably more stable in the presence of R-12 and R-22 than a medium-refined lubricant is. Steinle (1950) reported the effect of oleoresin (nonhydrocarbons) and sulfur content on the reactivity of the lubricant, using the Philipp test. A decrease in the oleoresin content, accompanied by a decrease in sulfur and aromatic content, showed an improvement in the chemical stability with R-12, while the oil's lubricating properties became poorer. Schwing's (1968) study on a synthetic polyisobutyl benzene lubricant reports that it is not only chemically stable but also has good lubricating properties.

HFC refrigerants are chemically very stable and show very little tendency to degrade under conditions found in refrigeration and air-conditioning systems. HFC refrigerants are therefore not a factor in the degradation of lubricants that might be used with them. Hygroscopic synthetic POE and PAG lubricants are less chemically stable

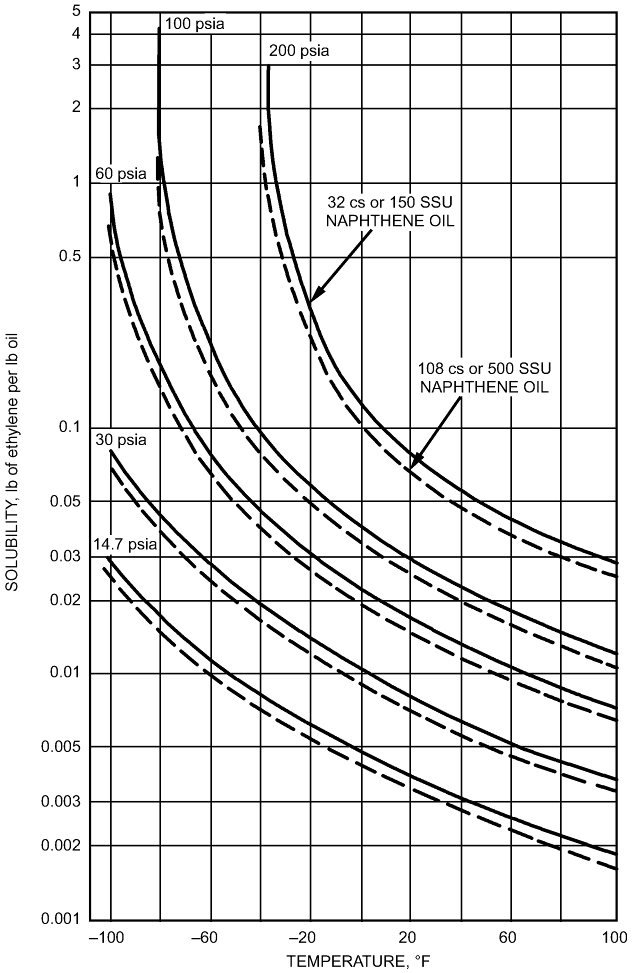


Fig. 52 Solubility of Ethylene in Oil
(Witco)

with chlorinated refrigerants than mineral oil due to the interaction of moisture with the refrigerant at high temperatures.

CONVERSION FROM CFC REFRIGERANTS TO OTHER REFRIGERANTS

The most common conversion from a CFC refrigerant to another refrigerant is retrofitting to use HCFC or HFC refrigerants. A conversion may require draining each component to completely remove an incompatible lubricant. Often, flushing in some manner is the only way to remove old lubricant. The flushing medium may be liquid refrigerant, an intermediate fluid, or the lubricant that will be charged with the alternate refrigerant. Liquid CFC refrigerants circulated through the entire system are preferable for flushing, although other refrigerants are used. The refrigerant is recovered with equipment modified for this use.

The refrigeration equipment must be operated if intermediate fluids and lubricants are used for flushing. The system is charged with the flushing material and CFC refrigerant and operated for at least eight hours. After operation, the lubricant charge is drained from the compressor. This process is repeated until the lubricant in the drained material is reduced to a specified level. Chemical test kits or portable refractometers are available to determine the amount of old lubricant that is mixed with the flushed material.

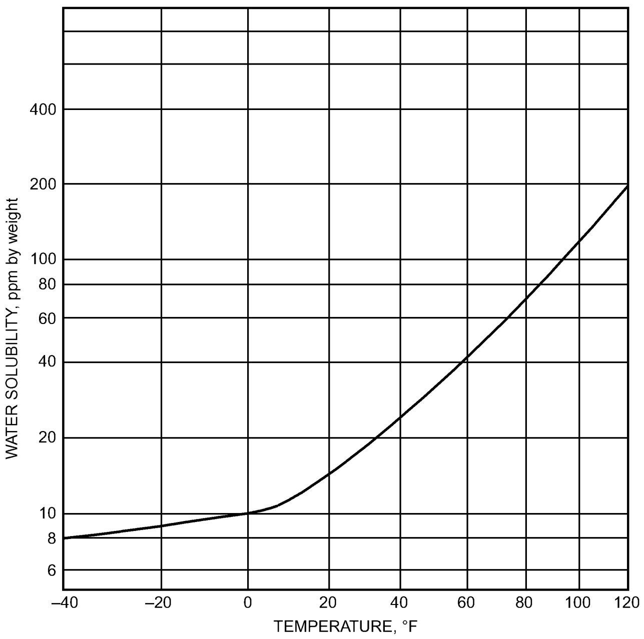


Fig. 53 Solubility of Water in Mineral Oil

REFERENCES

Albright, L.F. and J.D. Lawyer. 1959. Viscosity-solubility characteristics of mixtures of Refrigerant 13B1 and lubricating oils. *ASHRAE Journal* (April):67.

Albright, L.F. and A.S. Mandelbaum. 1956. Solubility and viscosity characteristics of mixtures of lubricating oils and “Freon-13 or -115.” *Refrigerating Engineering* (October):37.

API. 1970. *Technical data book—Petroleum refining*, 2nd ed. American Petroleum Institute, Washington, D.C.

ASHRAE. 1994. Methods of testing the floc point of refrigeration grade oils. *Standard* 86.

Baldwin, R.R. and S.G. Daniel. 1953. *Journal of the Institute of Petroleum* 39:105.

Bambach, G. 1955. The behavior of mineral oil-F12 mixtures in refrigerating machines. *Abhandlungen des Deutschen Kältetechnischen Vereins*, No. 9. (Translated by Carl Demrick.) Also see abridgement in *Kältetechnik* 7(7):187.

Beerbower, A. and D.F. Greene. 1961. The behavior of lubricating oils in inert gas atmospheres. *ASLE Transactions* 4(1):87.

Bosworth, C.M. 1952. Predicting the behavior of oils in refrigeration systems. *Refrigerating Engineering* (June):617.

Brewer, A.F. 1951. Good compressor performance demands the right lubricating oil. *Refrigerating Engineering* (October):965.

Cavestri, R.C. 1993. Measurement of the solubility, viscosity and density of synthetic lubricants with HFC-134a. Final Report for ASHRAE 716-RP.

Cavestri, R.C. and W.R. Schafer. 2000, Measurement of solubility, viscosity, and density of R-410A refrigerant/lubricant mixtures, *ASHRAE Transactions* 106(1):277.

Clark, F.M. 1940. Water solution in high-voltage dielectric liquids. *Electrical Engineering Transactions* 59(8):433.

Divers, R.T. 1958. Better standards are needed for refrigeration lubricants. *Refrigeration Engineering* (October):40.

Doderer, G.C. and H.O. Spauschus. 1965. Chemical reactions of R-22. *ASHRAE Transactions* 71(I):162.

Fuller, D.D. 1984. *Theory and practice of lubrication for engineers*. John Wiley and Sons, New York.

Goswami, D.Y., D.O. Shah, C.K. Jotshi, S. Bhagwat, M. Leung, and A.S. Gregory. 1997. Foaming characteristics of HFC refrigerants. *ASHRAE Journal* 39(6):39-44.

Gunderson, R.C. and A.W. Hart. 1962. *Synthetic lubricants*. Reinhold, New York.

Huttenlocher, D.F. 1969. A bench scale test procedure for hermetic compressor lubricants. *ASHRAE Journal* (June):85.

Kartzmark, R., J.B. Gilbert, and L.W. Sproule. 1967. Hydrogen processing of lube stocks. *Journal of the Institute of Petroleum* 53:317.

Kesim, S.C., K. Albayrak, and A. Ileri. 2000. Oil entrainment in vertical refrigerant piping. *International Journal of Refrigeration* 23(2000):626-631.

Komatsuzaki, S. and Y. Homma. 1991. Antiseizure and antiwear properties of lubricating oils under refrigerant gas environments. *Lubrication Engineering* 47(3):193.

Little, J.L. 1952. Viscosity of lubricating oil-Freon-22 mixtures. *Refrigerating Engineering* (Nov.):1191.

Loffler, H.J. 1957. The effect of physical properties of mineral oils on their miscibility with R-22. *Kältetechnik* 9(9):282.

Loffler, H.J. 1959. Density of oil-refrigerant mixtures. *Kältetechnik*. 11(3):70.

Loffler, H.J. 1960. Viscosity of oil-refrigerant mixtures. *Kältetechnik*. 12(3):71.

Mills, I.W., et al. 1946. Molecular weight-physical property correlations for petroleum fractions. *Industrial and Engineering Chemistry* 38:442.

Mills, I.W. and J.J. Melchoire. 1967. Effect of aromatics and selected additives on oxidation stability of transformer oils. *Industrial and Engineering Chemistry* (Product Research and Development) 6:40.

Mosle, H. and W. Wolf. 1963. *Kältetechnik* 15:11.

Murray, S.F., R.L. Johnson, and M.A. Swikert. 1956. Difluoro-dichloromethane as a boundary lubricant for steel and other metals. *Mechanical Engineering* 78(3):233.

Neubauer, E.T. 1958. Compressor crankcase heaters reduce oil foaming. *Refrigerating Engineering* (June):52.

Parmelee, H.M. 1964. Viscosity of refrigerant-oil mixtures at evaporator conditions. *ASHRAE Transactions* 70:173.

Pate, M.B., S.C. Zoz, and L.J. Berkenbosch. 1993. Miscibility of lubricants with refrigerants. Report No. DOE/CE/23810-18. U.S. Department of Energy.

Rembold, U. and R.K. Lo. 1966. Determination of wear of rotary compressors using the isotope tracer technique. *ASHRAE Transactions* 72:VI.1.1.

Sanvordenker, K.S. 1968. Separation of refrigeration oil into structural components and their miscibility with R-22. *ASHRAE Transactions* 74(I):III.2.1.

Sanvordenker, K.S. and W.J. Gram. 1974. Laboratory testing under controlled environment using a falex machine. Compressor Technology Conference, Purdue University.

Sanvordenker, K.S. and M.W. Larime. 1972. A review of synthetic oils for refrigeration use. ASHRAE Symposium, Lubricants, Refrigerants and Systems—Some Interactions.

Schwing, R.C. 1968. Polyisobutyl benzenes and refrigeration lubricants. *ASHRAE Transactions* 74(1):III.1.1.

Seeman, W.P. and Shellard, A.D. 1963. Lubrication of Refrigerant 22 machines. IX International Congress of Refrigeration, Paper III-7, Munich, Germany.

Short, G.D. 1990. Synthetic lubricants and their refrigeration applications. *Lubrication Engineering* 46(4):239.

Shubkin, R.L. 1993. Polyalphaolefins, in *Synthetic lubricants and high performance functional fluids*. Marcel Dekker, New York.

Soling, S.P. 1971. Oil recovery from low temperature pump recirculating halocarbon systems. ASHRAE Symposium PH-71-2.

Spauschus, H.O. 1963. Thermodynamic properties of refrigerant-oil solutions. ASHRAE *Journal* (April):47; (October):63.

Spauschus, H.O. 1964. Vapor pressures, volumes and miscibility limits of R-22-oil solutions. *ASHRAE Transactions* 70:306.

Spauschus, H.O. and G.C. Doderer. 1961. Reaction of Refrigerant 12 with petroleum oils. *ASHRAE Journal* (February):65.

Spauschus, H.O. and L.M. Speaker. 1987. A review of viscosity data for oil-refrigerant solutions. *ASHRAE Transactions* 93(2):667.

Steinle, H. 1950. *Kaltemaschinenole*. Springer-Verlag, Berlin, Germany, 81.

Sundaresan, S.G. and R. Radermacher. 1996. Oil return characteristics of refrigerant oils in split heat pump system. *ASHRAE Journal* 38(8):57.

Swallow, A., A. Smith, and B. Greig. 1995. Control of refrigerant vapor release from polyol ester/halocarbon working fluids. *ASHRAE Transactions* 101(2):929.

Van Gaalen, N.A., M.B. Pate, and S.C. Zoz. 1990. The measurement of solubility and viscosity of oil/refrigerant mixtures at high pressures and temperatures: Test facility and initial results for R-22/naphthenic oil mixtures. *ASHRAE Transactions* 96(2):183.

Van Gaalen, N.A., S.C. Zoz, and M.B. Pate. 1991a. The solubility and viscosity of solutions of HCFC-22 in naphthenic oil and in alkylbenzene at high pressures and temperatures. *ASHRAE Transactions* 97(1):100.

Van Gaalen, N.A., S.C. Zoz, and M.B. Pate. 1991b. The solubility and viscosity of solutions of R-502 in naphthenic oil and in an alkylbenzene at high pressures and temperatures. *ASHRAE Transactions* 97(2):285.

Van Nes, K. and H.A. Weston. 1951. *Aspects of the constitution of mineral oils*. Elsevier, New York.

Walker, W.O., A.A. Sakhanovsky, and S. Rosen. 1957. Behavior of refrigerant oils and Genetron-141. *Refrigerating Engineering* (March):38.

Walker, W.O., S. Rosen, and S.L. Levy. 1960. A study of the factors influencing the stability of the mixtures of Refrigerant 22 and refrigerating oils. *ASHRAE Transactions* 66:445.

Walker, W.O., S. Rosen, and S.L. Levy. 1962. Stability of mixtures of refrigerants and refrigerating oils. *ASHRAE Transactions* 68:360.

Wahlstrom, A. and L. Vamling. 2000. Development of models for prediction of solubility for HFC working fluids in pentaerythritol ester compressor oils. *International Journal of Refrigeration* 23(2000):597-608.

Witco. Sonneborn Division, *Bulletin* 8846.