1996

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Short, G. D.; Rajewski, T. E.; and Oberle, J. E., "Refrigeration Lubricants - Current Practice and Future Development" (1996). *International Refrigeration and Air Conditioning Conference.* Paper 335.
http://docs.lib.purdue.edu/iracc/335

REFRIGERATION LUBRICANTS - CURRENT PRACTICE AND FUTURE DEVELOPMENT

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Abstract

Manufacturers of refrigeration and air-conditioning compressors and systems have had to re-evaluate the requirements for lubricants. The HFC (hydrofluorocarbon) refrigerants that are replacing chlorofluorocarbon (CFC) refrigerants have a different influence on lubricants which effects both compressor durability and system performance. Other types of refrigerants such as ammonia and hydrocarbons are also alternatives to CFCs, and new lubricants are being evaluated to improve performance in these systems.

This paper provides an overview of several types of synthetic lubricants currently supported by equipment manufacturers. Practical examples are provided to improve the understanding of these new lubricants, how they are used, and suggested application guidelines. Also described are lubricants currently being developed.

1: Introduction

An increased awareness that chlorine containing refrigerants are depleting the ozone layer has resulted in the increased use of hydrofluorocarbon (HFC), ammonia, and hydrocarbon refrigerants. Synthetic lubricants improve performance with these refrigerants.

Polyalkylene glycol (PAG), polyol ester (POE), alkyl benzene (AB) and other new lubricants have been developed for commercial application with HFC and blends of HFC with other refrigerants. Mineral oils have generally been found to be unacceptable with these refrigerants due to poor miscibility. Major development considerations for the synthetic lubricants include: miscibility, solubility, stability, lubricity, and retrofitting requirements.

PAG and some new types of synthetic lubricants are soluble or miscible with ammonia. This allows the use of ammonia in refrigeration systems with direct expansion (DX) evaporators. Immiscible types of synthetic oils, such as polyalphaolefins (PAO), are used in traditional ammonia systems where their good low temperature properties allow operation at very low temperatures.

The efficient use of hydrocarbon refrigerants may require lubricants that are higher in viscosity or less soluble than available refrigeration grade mineral oils. Synthetic oils such as PAO and PAG are currently being used.

2: HFC refrigerants and suitable lubricant types

Table I provides an overview of synthetic lubricants which are used with many of the most common types of halocarbon refrigerants. Each type will be described.

In a 1985 publication, Kussi provided a good review of the chemistry of PAG lubricants [1]. The current PAGs being used for HFC applications are of three distinct groups: polypropylene glycol, polypropylene-polyethylene glycol and polypropylene-polyethylene ether. The glycols can be classified as mono-, di- or tri-functional. This is an indication of the number of terminal hydroxyl groups that are involved in the manufacture of the product.

Polyol esters (POE) include a wide variety of materials [2]. These lubricants are made by combining an organic neopentyl alcohol with an organic acid. Some of the alcohols used are: neopentyl glycol (NPG), trimethylol propane (TMP), pentaerythritol (PE) and di-pentaerythritol (Di-PE).

The major difference between the POEs currently being used for HFC refrigeration is the type of acids attached to the alcohols.. Acids may be classified as "linear" or "branched" or "mixed." For HFC applications, the acids used usually contain from four to ten carbons (C4 to C10), but can have up to twenty carbons if the initiating alcohol is neopentyl glycol.

Currently there are three other types of synthetic lubricants entering the market: carbonates, complex esters, and modified PAGs. Carbonates are esters or diesters of carbonic acid, usually made through transesterification of dimethyl carbonate [3]. Complex esters utilize malonate-acrylate chemistry [4]. Modified PAGs combine short chain acids with the standard type of PAG to form an ester [5].

Table 1. Common Types of Lubricants and Refrigerants

Lubricant	HFC-134a	HCFC-22	HCFC-123	HFC-23
PAG	2	2	3	2
PAG/Ester	2	2	3	2
Polyol Esters	1	2	3	1
Other Esters	3	2	3	3
Carbonates	E	E	E	E
Alkyl Benzene	3	1	2	3
Mineral Oil	3	1	1	3
Perfluoroether	3	3	3	3
Fluorosilicone	3	3	3	3

KEY 1.)Recommended 2.)Alt. Recom. 3.) Not Recom. E.) Experimental

3.1: Miscibility relationships with HFC refrigerants

Refrigeration system designers engineer piping and other components to best manage lubricant return to the compressor. The interactions between the lubricant/refrigerant pair can affect film characteristics on heat transfer surfaces and ultimately overall energy efficiency of the system. Generally, the first property considered is miscibility (lubricant with liquid refrigerant).

With PAG lubricants, higher functionality improves miscibility for a given viscosity grade. The incorporation of ethylene improves miscibility with HFCs but also increases water solubility. By replacing the hydroxyl group, making the product an ether, properties such as lower water solubility and reduced miscibility with HFCs are attained. The PAGs exhibit inverse solubility. Inverse solubility, becoming less soluble at increased temperatures, may improve compression efficiency in rotary compressors [6]. Figure 1 shows these general relationships with HFC-134a.

POE lubricants are manufactured from a multifunctional alcohol and an organic acid. Both portions of the POE can influence miscibility with the HFCs. POE lubricants based on lower molecular weight alcohols, such as neopentyl glycols, tend to be more miscible than those based on the higher molecular weight alcohols (Figure 2). POE lubricants utilizing linear acids become less miscible when manufactured in higher viscosity grades due to the use of higher molecular weight acids. Branched acids help improve miscibility with the HFCs.

Replacements for R-22 and R-502 have taken two courses of development. One is to use HFC blends (these sometimes contain R-22, for short term "retrofit" replacement refrigerants), another is to include a hydrocarbon such as butane in a blend with HFCs. Hydrocarbon gasses or R-22 in a refrigerant blend improves the miscibility with hydrocarbon oils. However, the improvement still may not allow the use of hydrocarbon lubricants. Figure 3 compares the miscibility relationships for various types of POE with HFC refrigerants.

The use of cost effective alkyl benzene lubricants where possible is desirable. AB oils are miscible with some less polar HFCs, HFC/HCFC blends and HFC/hydrocarbon blends. Even so, some OEMs have suggested that at least fifty percent POE be blended with alkyl benzenes for use with the HFC/HCFC blended refrigerants in lower temperature applications.

It is possible to use an oil with less miscibility provided there are equal amounts of lubricant entering and leaving the evaporator. A synthetic hydrocarbon, with a very low pour point (-90°C), has been successfully used in systems with HFC-23 and direct expansion evaporators. Low viscosity hydrocarbon lubricants have been recommended by at least one OEM for use in air-conditioning systems. Another has suggested that very low viscosity dialkylbenzes be used. With lower viscosity, miscibility is no longer a critical issue in oil return. This has proven suitable for applications with temperatures of -40°C and greater [7]. To exploit the cost advantages of mineral oils, some mineral oil manufacturers are testing additives to form oil-HFC mixtures or emulsions. A new type of hydrocarbon oil that exhibits miscibility with HFC-134a at low percentages has also been developed. These lubricants are not likely to be OEM approved for several years due to extensive testing requirements.

3.2: Solubility and viscosity with HFC refrigerants

OEMs examine viscosity-solubility information at various temperatures and pressures to determine the optimum viscosity to lubricate and seal compressors, and to provide adequate fluidity to return from evaporators. Figures 4 and 5 provide various examples.

The ideal solubility/viscosity relationship is to have a lubricant that exhibits minimum viscosity reduction, due to dilution in the compressor, and is miscible in the evaporator. Figure 6 shows the relative solubility of three 32 ISO POE lubricants with an HFC blend, R-404A, at saturation conditions. Excessive solubility may decrease compressor capacity due to expansion of the dissolved refrigerant and reduced sealing efficiency. The cooling effect of this expansion may also result in low compressor discharge temperatures. It is noteworthy that EXP-1105 has less solubility but was previously shown to have improved miscibility compared to the other POE lubricants.

3.3: Stability and system cleanliness with HFC refrigerants

Tests for lubricant stability predict the possible negative interactions of the lubricant and refrigerant at high temperatures. The sealed tube method most often uses steel, copper and aluminum metal strips. Metals act as a catalyst and also provide a measure of the effect of the lubricant/refrigerant pair on the metal. Visual results and chemical analysis indicate the possible breakdown of the refrigerant or the lubricant. This type of test is also useful in examining the effects of contaminants, such as moisture, and for screening additives.

POEs, PAGs, and carbonates all have a tendency to accumulate moisture during storage. Some POEs may break down rapidly in the presence of small amounts of water. Moisture levels for POE and PAG lubricants of greater than 100 ppm and 250 ppm, respectively, have been determined to be unacceptable in many applications. Specially designed additives such as antioxidants and hydrolysis stabilizers are effective in reducing problems with residual moisture and air.

Contaminant metals can cause deterioration of POEs in refrigerant systems. Metal catalysts, such as tin, must be avoided or completely removed during the lubricant manufacturing process. Some types of brazing flux can result in a rapid acid number increase [8]. The authors have found that certain plated components can cause similar results. These contaminants may result in copper transfer within the system. The presence of moisture or chlorine containing refrigerants increases the potential for these types of reactions.

POEs manufactured with a high percentage of branched acids are more stable, in the presence of water, than those with a high proportion of linear acids. Stability is also greatly influenced by the final manufacturing procedures during esterification. The removal of excess acids and catalysts should be closely monitored to be assured of a stable product. The carbon length of the acids used for manufacturing POEs should also be considered. One investigator found that the POE made from a linear pentanoic (C5) acid produced a Total Acid Number four times greater than that made with a branched octanoic (C8) acid in ambient air [8]. Acids produced may have a rapid effect on the system, such as corrosion or copper plating. The properly synthesized POE lubricant, EXP-1105, has about forty percent less acid forming tendency compared to three other commercial POE lubricants.

Carbonates were thought to be more stable, as they did not produce unwanted acids upon decomposition. It was later found that these lubricants were breaking down to form significant amounts of carbon dioxide. More recent efforts have been toward developing more stable carbonates.

3.5: Wear and compressor durability tests with HFC refrigerants

Compressor and Lubricant manufacturers are spending millions of dollars testing new lubricant/refrigerant combinations. These tests generally are a series of compressor bench tests beginning with short term (100 to 400 hours) followed by long term (4000 to 8000 hours). Each model type and refrigerant/lubricant pair are tested in the course of the program.

Some laboratory test methods are: Falex pin and vee block [9], ring and disk [10], Falex block and ring test, and a custom made High Pressure Tribometer [11]. More specific tests have also been conducted with roller bearings [12] with R-134a.

There are some common results of lubricity investigations with HFCs. All investigators note that refrigerants such as HFC-134a do not themselves have lubricating properties. CFC and HCFC refrigerants were shown to have relatively better lubrication properties, particularly boundary lubrication, most likely due to the anti-seizure properties of chlorine. Small amounts of oxygen (equivalent to 0.75% air) results in reduced friction and wear. Small amounts of moisture also decrease friction and wear but may effect the reactivity of refrigerants such as HFC-134a [10]. Lubricity additives, such as phosphorus, may require oxygen in the system to be effective. The HFC lubricants may exhibit erratic lubricating behaviors at high refrigerant dilution concentrations. This is in contrast to the CFCs and hydrocarbon lubricants, which demonstrate increased lubrication properties at high refrigerant concentrations.

Controlling lubricant solubility (less solubility) is more effective in reducing wear than the use of lubricity or EP additives [9]. EXP-1105 was formulated, with a balance of molecular components, to achieve desired lubrication properties, stability, solubility, and miscibility.

3.6: Retrofitting with HFC refrigerants

Retrofitting calls for draining as much of the mineral oil from the system as possible and replacing it with the new, POE lubricant. The POE is then used with the existing refrigerant for a period of time, drained and replaced with new POE. The second lubricant replacement is generally accompanied by replacement with the new refrigerant. The object is to remove as much of the mineral oil from the system as possible, using the old refrigerant to help make the mineral oil soluble. Additional "flushing" with new lubricant may be necessary until the mineral oil level drops below about three percent or lower. The cost of flushing systems is recovered quickly through evaporator efficiency improvements.

4: Lubricants for Ammonia as an alternative to CFC and HCFC refrigerants

Ammonia, which has no ozone depletion effect, has been a choice for efficient refrigeration for a hundred years. Limitations include a strong odor and limited range of flammability in air. Even with these limitations, ammonia is being considered for applications with limited exposure to dense populations. Applications include rooftop air-conditioning, water chillers, secondary and remote locations. Synthetic lubricants are now available that improve efficiency and expand application opportunities.

Mineral oils and synthetic hydrocarbon lubricants have low solubility and miscibility with ammonia. This is a benefit in flooded evaporator systems as these oils are heavier than ammonia and can be easily removed by draining from the bottom of evaporator vessels and returned to the compressor. Synthetic and semi-synthetic oils have been developed for optimum performance in these systems [13].

The solubility and miscibility of hydrocarbon oils limit applications in systems with direct exchange (DX) evaporators. PAO lubricants with improved low temperature fluidity offer some advantage over mineral oils and alkyl benzene oils. Other types of synthetics have been developed which are soluble with ammonia and provide more efficient heat transfer.

It has been known for over twenty years that PAG and PAG-ether lubricants are soluble with ammonia. Increasing the ethylene content in PAGs increases miscibility with both ammonia and water. Since ammonia systems often contain water, potential problems could arise. PAG copolymers of ethylene and propylene exhibit inverse solubility with water. Keeping compressor discharge temperatures at 70°C or higher can prevent water accumulation. The PAG-ether lubricants limit water solubility to a few percent. Restrictions, for the use of miscible PAG lubricants and ammonia, include low solubility with hydrocarbon oils. Upon retrofitting to a PAG lubricant, compressors and systems must be flushed to remove any residual mineral oil that may be present. Both PAG and PAG-ether lubricants are currently providing good field results.

A new type of synthetic has been developed that has a high degree of solubility with ammonia, good mixing properties with mineral oil and limited solubility with water. This new synthetic is currently being used in several water chiller applications equipped with rotary screw compressors and aluminum DX evaporators. Conversion from the mineral oil is not difficult, the mineral oil is drained and the new lubricant installed. This new product has a high degree of solubility, but limited miscibility. This property improves oil transport properties and heat transfer. Initial performance tests resulted in a twenty percent improvement in heat transfer efficiency when compared to mineral oil. Another, more miscible version of this lubricant was developed for low temperature applications.

5: Lubricants for hydrocarbon refrigerants

Propane, butane and other hydrocarbon refrigerants are being considered as substitutes for CFC and HCFC refrigerants due to their low ozone depletion potential. The major limitation for hydrocarbon refrigerants is extreme flammability. These refrigerants have historically been employed in refinery applications with PAG lubricants.[15, 16]. PAGs resist refrigerant dilution during compression, even at high pressures, and thus provide improved compression efficiency. Careful selection of the PAG lubricant will also result in adequate oil transport properties. PAO lubricants have also been utilized with hydrocarbon refrigerants. PAOs are miscible with hydrocarbon refrigerants and are available in high viscosity grades. High viscosity PAOs have been used to provide more efficient compression.

6: Conclusion

Several types of lubricants have been developed over the past several years. While many of these lubricant types are not new, many are modified to enhance their suitability for today's refrigerants. The performance of these lubricants has been tested in the laboratory and through collaboration with industry, compressor system and component manufacture experts throughout the world. Several lubricants for HFC applications are available for HFC-134a, HFC-23, as well as several blends. New lubricants for ammonia and hydrocarbon refrigerants that offer greatly improved efficiency. Research will continue to improve these lubricants and provide additional choices.

References

[1] Kussi S. "Polyethers as Base Fluids to Formulate High Performance Lubricants," Lubrication Engineering Magazine , L47, 11, 926-933,.STLE, 1991.

[2] Shubkin, R.L. editor. "Synthetic Lubricants and High-Performance Functional Fluids," Marcel Dekker, Inc., NY, USA, 1993.

[3] Takahata K. Et al., "New Lube Oil For Stationary Air Conditioner", International Refrigeration Conference at Purdue Proceedings, 1994.

[4] Lilje and Sabahi ,"A Novel Class of Synthetic Lubricants Designed for HFC Compressors", International CFC and Halon Alternatives Conference 1994, pp. 145-153.

[5] McGraw P. ASHRAE Symposium, Chicago, Jan. 1993.

[6] Sjoholm, L., and G.D. Short. "Twin Screw Compressor Performance and Suitable Lubricants with HFC-134a", International Refrigeration Conference at Purdue Proceedings, 1990.

[7] Sunami, M. Et al., "Optimization of POE Type Refrigeration Lubricants", International Refrigeration Conference at Purdue Proceedings, 1994.

[8] Takahashi, Y. , T. Komatsubara and T. Sunaga , " Development of Compressor Material Technology for HFC-134a Use," 1994 International Compressor Engineering Conference at Purdue, 1994.

[9] Komatsuzaki, S. Et al "Polyol Esters as HFC-134a Compressor Lubricants", Lubrication Engineering, Volume 50, 10, 801-807,1993.

[10] Mizuhara K. Et al, "The Friction and Wear Behavior In Controlled Alternative Refrigerant Atmosphere" Tribology Transactions, Volume 37(1994), 1, 120-128, 1992.

[11] Cusano, C. Et al , "Tribological Evaluation of Contacts Lubricated by Oil-Refrigerant Mixtures", ACRC Project 04, University of Illinois, ACRC TR-16, 1992.

[12] Wardle, F.P. Et al, "The Effects of Refrigerants on The Lubrication of Rolling Element Bearings Used in Screw Compressors", International Refrigeration Conference at Purdue Proceedings, 1992.

[13] Short, G. " Refrigeration Lubricants Update: Synthetic and Semi-Synthetic Oil are Solving Problems with Ammonia and Alternative Refrigerants", IIAR Annual Meeting, 1990.

Fig 1. Miscibility Limits of Difunctional Polyalkylene Glycols of Varying Molecular Weights with HFC-134a (AMU = average molecular weight)

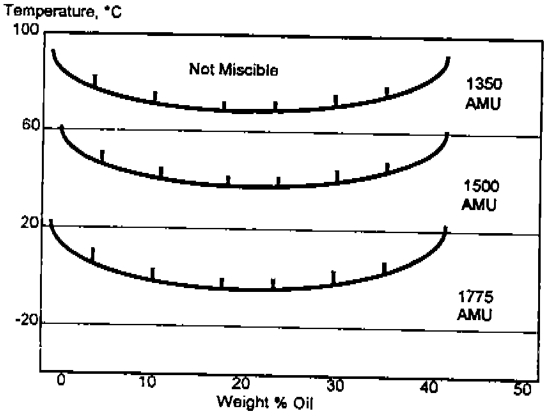

Fig 2. Miscibility Changes of Branched Chain Polyol Esters with HFC-134a, Based on Starting Alcohol

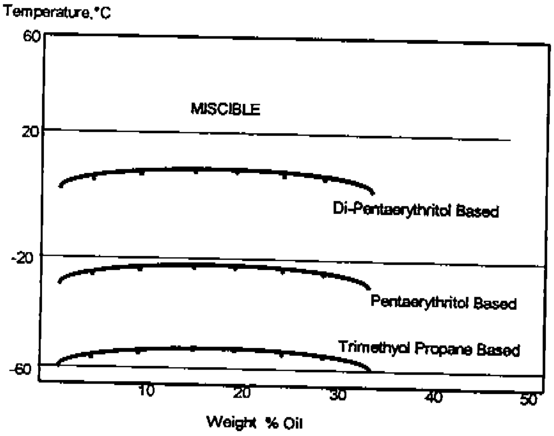

Fig 3. Miscibility of HFC Blends Compared to Non-Blended HFCs, 10% Lubricant Concentration

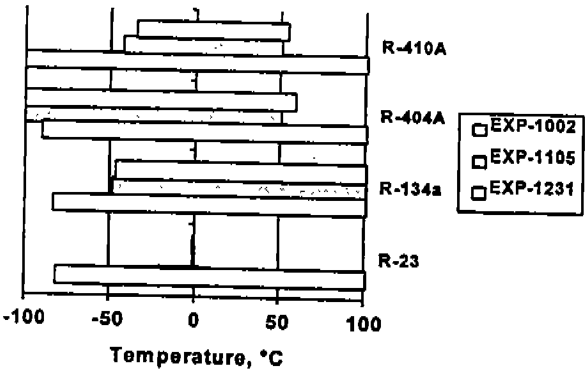

Fig 4. Daniel Plot of EXP-1105 and R-134a

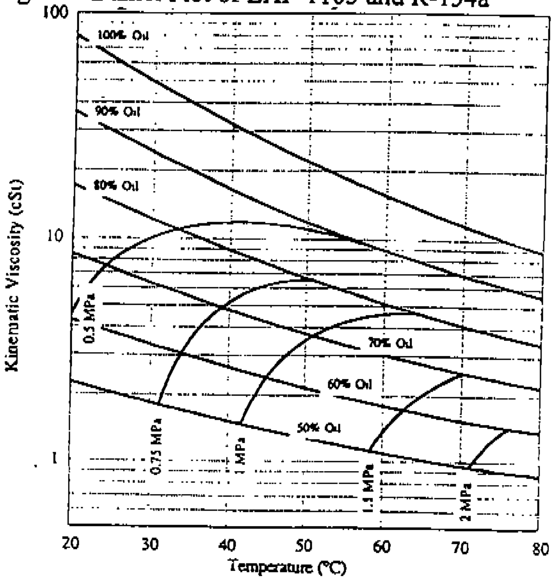

Fig 5. Daniel Plot of EXP-1231 and R-404A

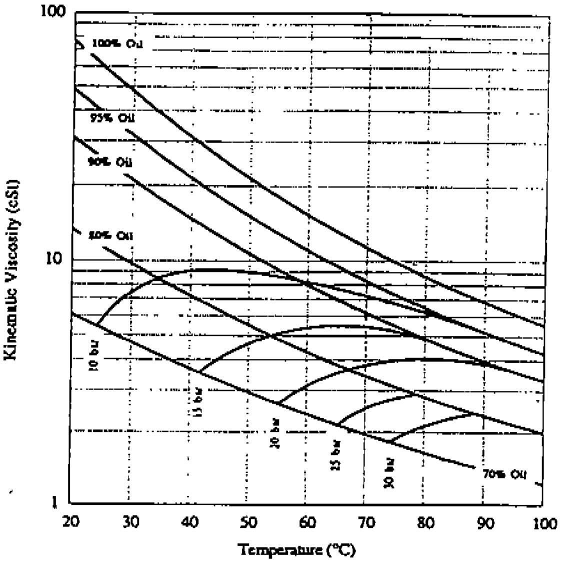

Fig 6. Relative dilution at saturation pressure with R-404A