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ABSTRACT

The lubricant is a critical component of an automotive A/C system. Besides providing good lubricity, it must exhibit sufficient solubility in the refrigerant to ensure lubricant return to the compressor. Stability in the presence of the refrigerant, metals, and common contaminants such as air, water, and mineral oil is critical. The lubricant must also be compatible with the hoses and other elastomeric parts.

This paper will focus on the development of polyalkylene glycol (PAG) lubricants for use in automotive A/C systems. It will review the properties of PAG lubricants that has led to their use with R-134a, including their good solubility, stability, and lubricity. The tradeoffs between competing properties such as lubricity and high temperature solubility will also be discussed.

INTRODUCTION

In 1987 the Montreal Protocol set in motion a program to eliminate the use of chlorofluorocarbons because of their adverse affect on the earth's ozone layer. The automotive industry chose refrigerant R-134a, a hydrofluorocarbon, as a replacement for CFC-12. R-134a was chosen because of its thermodynamic similarities to R-12 and because it is nonflammable and exhibits low toxicity.

A major problem with R-134a was its poor solubility in mineral oil lubricants. In automotive air conditioners, the lubricant travels through the system with the refrigerant. In order to ensure that sufficient amounts of lubricant return to the compressor, the lubricant must exhibit good solubility in the refrigerant, especially in the cold evaporator. Because of their good solubility, stability, and lubricity in R-134a, PAG lubricants were chosen by the automotive industry for use in the new, ozone-friendly A/C systems.

LUBRICANT REQUIREMENTS FOR AUTOMOTIVE A/C SYSTEMS

The primary function of a refrigeration lubricant is to provide good compressor lubrication. There are three lubrication regimes that exist within a compressor: hydrodynamic; elastohydrodynamic (EHL); and boundary or extreme pressure (EP). Automotive A/C compressors are designed to run under hydrodynamic or EHL lubrication regimes where the moving metal surfaces are always separated by a lubricant film. However, metal-metal contact can occur during break-in or excessive loading, requiring boundary or EP lubrication. Particulate contamination of the A/C system can also cause metal-metal contact, as can lubricant starvation. For these reasons, the A/C lubricant must be able to provide all three types of lubrication inside the compressor.

A/C system lubricants must meet a number of requirements in addition to providing good lubricity. It is critical that the lubricant be sufficiently soluble in the refrigerant to ensure adequate return to the compressor. Low pour points are needed to enable lubricant flow through the cold evaporator, and to allow trouble-free operation during the winter. Refrigeration lubricants must be stable in the refrigerant and in the presence of common contaminants such as air, water, residual petroleum oil, and refrigerant R-12. Lubricant compatibility with the elastomers, plastics, and molecular sieves used in the A/C system is also necessary.

POLYALKYLENE GLYCOL LUBRICANTS

Polyalkylene glycols are synthetic lubricants which were invented in the early 1940's during a joint development project between Union Carbide Corporation and the Mellon Research Institute [1]. Since then they have found use as compressor, gear, and food grade lubricants, metalworking and hydraulic fluids, fiber lubricants, heat transfer fluids, and aqueous quenchants [2, 3].

Polyalkylene glycols are made from the polymerization of the monomers ethylene oxide (EO) and propylene oxide (PO). PAGs are synthesized by adding the oxide monomers to an alcohol starter in the presence of a catalyst (Figure 1). The molecular weight, and thus the viscosity of the PAG is controlled by the oxide to starter ratio. The reaction proceeds until all of the oxide monomers are consumed [2]. Higher molecular weight monomers such as butylene oxide can be used to make polyalkylene glycols, but virtually all commercially available PAGs are made from either PO or mixtures of EO and PO [4].

Polyalkylene glycols are unique among synthetic lubricants in that their solubility characteristics can be tailored to meet the needs of a specific application. This can be done by changing the starter, the EO to PO ratio in the monomer feed, and the end groups (Figure 2).

DEVELOPING A POLYALKYLENE GLYCOL REFRIGERATION LUBRICANT

The automotive industry chose PAG refrigeration lubricants for use with refrigerant R-134a for a number of reasons. This section will examine some of the factors and tradeoffs that need to be considered when developing a PAG refrigeration lubricant.

R-134a Solubility

Polyalkylene glycols exhibit excellent low temperature solubility in refrigerant R-134a which helps the lubricant maintain good flow properties in the cold evaporator and compressor suction lines. Good low temperature flow properties are necessary to ensure sufficient lubricant return to the compressor.

As the temperature of a solution of polyalkylene glycol in R-134a increases, the solubility of the PAG decreases. Eventually a temperature will be reached where the solution splits into a two phase mixture. The high temperature solubility of PAGs increases with decreasing lubricant viscosity. The solubility curves can also be affected by the PAG's starter, end group, and the EO to PO ratio used during manufacture. Figure 3 shows the solubility curves of a family of PAGs that vary only in viscosity.

It is important to note that in the high temperature insolubility region, the two layers that form do not consist of pure PAG and pure R-134a. Instead they form a lubricant-rich phase and a refrigerant-rich phase. As can be seen in Figure 4, the composition of the two phases can be obtained from the intersection of the horizontal temperature tie line with the solubility curve of the polyalkylene glycol [4].

Early concerns about the high temperature insolubility of PAGs leading to heat transfer and lubricant flow problems in the hot condenser have not been realized. However, this high temperature insolubility does pose a problem in TXV A/C systems where a sight glass is used to determine if sufficient refrigerant is present [5]. If the PAG lubricant has a low separation temperature, it will cause the sight glass to appear cloudy regardless of the amount of refrigerant present. This could cause an unwary technician to overfill an A/C system.

Much work has been done over the last decade to improve the high temperature solubility of PAGs in R-134a so that they can be used in TXV A/C systems that employ sight glasses. It is generally believed that the 3 percent solubility of the PAG must be greater than 60^{o}C if a sight glass is to be used. In hotter climates, however, a higher separation temperature is probably needed.

The large influence of PAG viscosity on high temperature solubility is evident in Figure 3. Changes in starter, monomer composition, and end groups have yielded small improvements, but no major breakthroughs. As a result, low viscosity PAGs in the neighborhood of 50 cSt at 40°C have been used successfully in TXV A/C systems that employ sight glasses to determine refrigerant charge. However, it has not been possible to use compressors that require a higher viscosity PAG lubricant (75-50 cSt at 40°C) in A/C systems that use sight glasses.

Lubricity

One reason for the good lubricity of polyalkylene glycols is their polarity. Because every third atom on the polymer's backbone is an oxygen, PAGs have a high affinity for metal surfaces. This natural attraction to metal surfaces results in the formation of a protective layer which generally results in better wear and scuffing characteristics when compared to nonpolar, hydrocarbon-based lubricants [6].

The high viscosity indexes (VIs) of PAGs also helps to account for their good performance in R-134a A/C systems. The higher a lubricant's VI, the smaller the change in viscosity from a given change in temperature. PAGs have the highest VIs of any R-134a soluble lubricant, typically ranging from 180 to 230. In contrast, the mineral oils used with R-12 have VIs of less than 100. The effect of VI on a lubricant's high and low temperature viscosities are shown in Figure 5. The high VI's of PAGs means that they will be more fluid at low temperatures, and still be viscous enough to lubricant the hot compressor.

The high temperature insolubility of PAGs in R-134a is actually beneficial in the hot compressor. The advantages of using a lubricant that is insoluble in the gas being compressed are well known among the users of hydrocarbon gas compressors [7]. These benefits include better viscosity retention, reduced cylinder wear, and reduced lubricant loss with the discharged gas.

While PAG base fluids perform better than mineral oils in many common lubricity tests, they cannot by themselves make up for the loss of boundary or EP lubricity that was provided by the chlorine in the R-12 [8, 9, 10]. For this reason, all widely used PAG refrigeration lubricants incorporate additional additives to enhance their lubricity [8, 11]. However, it is important to remember that lubricity enhancers, as well as all other additives in the lubricant, must be soluble in the refrigerant and compatible with all A/C system components [10].

The lubricity of PAG lubricant candidates is often evaluated using common bench tests such as the 4-Ball and Pin & V-Block tests. However, more specialized tests will often be run to attempt to more closely simulate a particular wear mechanism that occurs in a given type of compressor. When testing a lubricant for use in a swash plate compressor, a test employing sliding steel and aluminum contacts such as the one described by Komatsuzaki might be used [8]. If the lubricant is being developed for use in a wobble plate compressor, an oscillating ring-on-block test could be employed to simulate the wear mechanism that occurs in the swaged socket plate [12].

Pour Point

The pour point of a refrigeration lubricant should be below -30°C, preferably below -40°C. The pour point of PAGs starts to increase when the polymerized EO content exceeds 50 weight percent. Isoviscous EO/PO copolymers containing 50 percent polymerized EO or less all have roughly equivalent pour points. The pour points for these PAGs range from -50°C to -40°C for ISO viscosity ranges of 50 to 150 respectively. Since all commercially available PAG refrigeration lubricants contain 0 to 50 percent polymerized EO (50 to 100 percent polymerized PO), achieving an acceptably low pour point has not been a problem.

Stability

The excellent stability of dry PAG monols and ether capped PAGs in R-134a are well documented [4, 8, 9, 11, 13, 14]. Neither the PAG's molecular weight or the EO/PO ratio of the monomer feed had any significant effect on the stability of these lubricants in the presence of R-134a. Literature references regarding the stability of dry, ester capped PAGs are mixed [8, 11].

PAGs are hygroscopic by nature and will absorb water from the air. While this tendency can be reduced by decreasing the amount of polymerized EO in the polymer and by capping the hydroxyl end groups, all PAGs are hygroscopic relative to mineral oils [4]. For this reason, much work has been done on the stability of PAGs in the presence of R-134a and various amounts of water. Komatsuzaki found that the water did not significantly effect the stability of a polypropylene glycol monoether, an ester capped polypropylene glycol monoether, and an ether capped polypropylene glycol in the presence of R-134a [8]. Kaneko also found that polyalkylene glycol monols and ether capped PAGs were very stable in the presence of R-134a and water regardless of molecular weight or the ratio of polymerized EO to PO. In contrast to Komatsuzaki, Kaneko found that the presence of water led to the hydrolysis of an acetoxy capped polypropylene glycol monomethyl ether [11].

Air is also a common contaminant in automotive A/C systems. PAGs oxidize when held at elevated temperatures in the presence of air [8, 11, 13]. There does not appear to be much effect of PAG structure on oxidative stability [11]. However, the addition of antioxidants greatly improves the oxidative stability of all polyalkylene glycol lubricants [8, 11]. For this reason antioxidants may be formulated into PAG refrigeration lubricants.

Mineral oils are also commonly found in automotive A/C systems. PAGs are chemically compatible with mineral oils in that they do not undergo any adverse chemical or physical reactions upon mixing [4]. The solubility of mineral oils in PAG lubricants varies significantly with the composition of the mineral oil and the structure of the polyalkylene glycol. Napthenic oils are more soluble in PAGs than paraffinic oils. PAGs exhibit better oil solubility as the percentage of polymerized PO increases. Alkyl capping also improves the oil solubility of a PAG. However, the oil solubility of PAGs does not appear to effect their performance as refrigeration lubricants. PAGs with very limited oil solubility have been widely used in both new R-134a A/C systems and retrofit vehicles where relatively large amounts of mineral oil have been left behind.

In retrofit applications, refrigerant R-12 is always present. PAGs are not very stable in the presence of high concentrations of R-12 [4, 14]. However, when the concentration of R-12 is below 2 percent, as recommended in SAE Standard J1661, PAGs have proven to be quite stable [4]. The R-12 stability of PAGs can also be greatly enhanced through the use of stabilizers. These additives are often incorporated in PAG lubricants for protection in the event of gross R-12 contamination [4].

Elastomer and Desiccant Compatibility

A refrigeration lubricant must be compatible with the elastomers that are used in the A/C system. In general, PAGs are compatible with most common elastomers [2, 4, 5]. However, it is important to consider the effect of R-134a in combination with the lubricant before selecting an elastomer. A number of studies show that H-NBR, NBR, EPDM and chloroprene rubber all show good compatibility in the PAG/R-134a combination [5, 9, 15]. Neoprene has also been shown to perform well, but its use at high temperatures is limited [4, 15]. The structure of the PAG lubricant does not appear to have a significant effect on elastomer compatibility [5, 9].

Desiccant compatibility with the refrigerant/lubricant pair is also important. Stability tests showed that fresh or new XH-5 desiccant (used in R-12 A/C systems) is not compatible with R-134a. Further tests did show good compatibility between the PAG/R-134a pair and desiccants XH-6, XH-7, and XH-9 [5, 14]. XH-7 molecular sieves are used in most new R-134a dryers because of their good physical characteristics and relative low cost. Subsequent testing has shown that aged XH-5 molecular sieves can be used with R-134a in retrofit applications.

SYSTEM TESTING OF A NEW PAG REFRIGERATION LUBRICANT

Once a lubricant candidate has met all of the chemical and physical requirements, it is ready for system testing. Typically a lubricant will first undergo evaluation in a series of compressor stand tests designed to simulate a variety of driving conditions. If the lubricant performs well in these tests, it will then be charged into vehicles for fleet trials. Upon successful completion of the fleet tests, the lubricant is ready for commercial use.

CONCLUSIONS

Polyalkylene glycols are the automotive industry's lubricant of choice for use with refrigerant R-134a. PAGs are unique among synthetic lubricants in the degree to which their chemical and physical properties can be modified by changes in molecular weight, starter, end groups, and monomer selection. The properties of PAGs such as R-134a solubility, hygroscopicity, and pour point are very dependent on the lubricant's structure. Other properties, such as stability and elastomer and desiccant compatibility are relatively unaffected by the chemical makeup of the polyalkylene glycol, although the poor hydrolytic stability of ester capped PAGs has prevented them from gaining any widespread commercial acceptance.

The good response of PAGs to additives has led to significant improvements in their performance. The use of antioxidants and stabilizers has greatly enhanced the stability of PAG lubricants in the presence of air and residual R-12. Lubricity additives have helped the R-134a/PAG pair to overcome the loss of extreme pressure lubricity that had formerly been provided by the chlorine in refrigerant R-12.

To conclude, polyalkylene glycols can be synthesized that provide good inherent lubricity, solubility, and stability in R-134a. These properties, in combination with their good additive response, has allowed the formulation of PAG based lubricants that provide excellent lubricity and system compatibility in automotive air conditioners that use refrigerant R-134a.

REFERENCES

1. Matlock, P. L. and Clinton, N. A. (1993). Polyalkylene Glycols, **Synthetic Lubricants and High-Performance Functional Fluids** (Shubkin, R. L.- editor), Marcel Deker, Inc., New York, NY
2. Brown, W. L. (1994). Polyalkylene Glycols, **Handbook of Lubrication and Tribology, Vol III** (Boozer, E. R.- editor), CRC Press Inc., Boca Raton, FL
3. UCON® Fluids and Lubricants, (1992). Union Carbide Corporation, Danbury, CT, Tech Literature
4. Brown, W. L. (1993). **SAE Technical Paper Series 932904**, Warrendale, PA
5. Refrigerant changes for A/C systems (1991). **Automotive Engineering**, Vol 99, Number 2, pp 25-29
6. Konishi, T., Klaus, E. E., and Duda, J. L. (1996). **Tribology Trans.**, Vol. 39, 4, 811-818)
7. Short, G. D. and Miller, J. W. (1993). Compressors and Pumps, **Synthetic Lubricants and High-Performance Functional Fluids** (Shubkin, R. L.- editor), Marcel Deker, Inc., New York, NY
8. Komatsuzaki, S., Homma, Y., Kawashima, K., and Itoh, Y. (1991). **Lub. Eng.**, Vol 47, 12, 1018-1025
9. Yamada, A., Sonoda, Y., Arakawa, Y. (1992). **SAE Technical Paper Series 920216**, Warrendale, PA
10. Komatsuzaki, S., Homma, Y. (1991). **Lubrication Engineering**, March, 193-198
11. Kaneko, M., Konishi, T., Kawaguchi, Y., Takagi, M. (1995). **SAE Technical Paper Series 951052**, Warrendale, PA
12. Tseregounis, S. I. (1995). **STLE Preprint**, No. 95-AM-1C-1
13. Sundaresan, S. G., Findenstadt, W. R. (1992). **ASHRAE Transactions 1992**, Vol 98, Pt. 1

14. SUVA® Trans A/C for Mobile Air Conditioning, DUPONT, Wilmington, DE, ARDT-31

15. UCON® Stationary Refrigeration Lubricant 68, (1995). Union Carbide Corporation, Danbury, CT, Tech Literature UC-348A

FIGURES

Figure 1
Polyalkylene Glycols

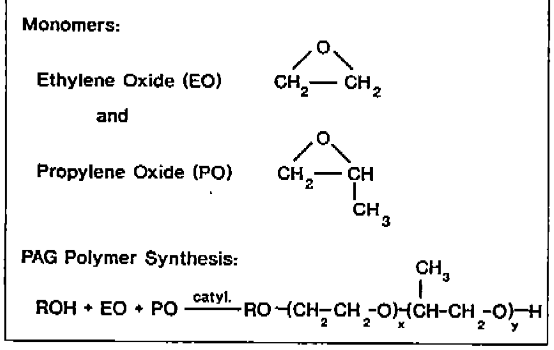

Figure 2
PAG End Groups

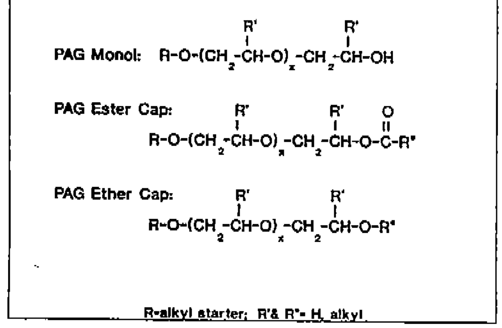

Figure 3
Solubility of PAGs in R-134a

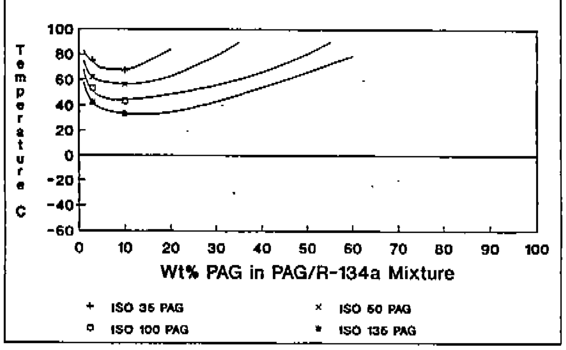

Figure 4
PAG Phase Concentrations

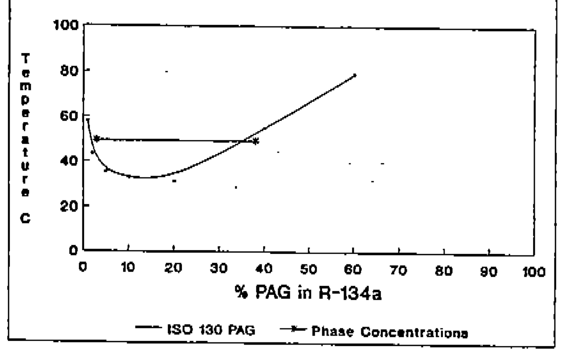

Figure 5
Viscosity Index