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Tribological Analysis of Metal Interface Reactions in Lubricant Oils/CFC12 and HFC 134a System

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NEW AND UNIQUE LUBRICANTS FOR USE IN COMPRESSORS UTILIZING R-134a REFRIGERANT

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Abstract

Environmental concerns (ozone layer depletion, global warming) have forced those using CFC-12 (R-12) refrigerant to find a substitute for this highly useful gas. HFC-134a (R-134a) has been identified as a potential replacement for R-12. The use of R-134a will also require the use of a new fluid to lubricate the compressor of a cooling system. The search for this R-134a-compatible lubricant has led primarily to the evaluation of various synthetic fluids such as fluorinated hydrocarbons, silicones, ethers and polyalkylene glycols to solve this problem. This paper reports on the evaluation of several alternative synthetic lubricant types. Physical data such as solubility, thermal stability, viscosity, elastomer compatibility, and water adsorption characteristics are reported. Data detailing both laboratory wear testing and automotive air conditioner compressor evaluations are also given.

Introduction

In 1974, Rowland and Molina[1] first announced their famous hypothesis that chlorofluorocarbons (CFCs) were the cause of substantial ozone depletion in the earth's atmosphere. The use of CFCs as propellants in aerosols was banned in the US as a result. In the mid-1980's further alarming evidence of the connection between CFCs and ozone depletion led to the Montreal Protocols' being signed by most industrial nations in September of 1987. Although this protocol provides for a 50% reduction in the production of CFCs by 1998, most industrial nations have agreed to accelerate the time until they will no longer produce CFCs. A complete phaseout of CFCs is expected to occur in the year 2000.

In the meantime, the search for CFC alternates has identified a non-ozone-depleting candidate that will replace CFC-12 for use in refrigeration. HFC-134a (R-134a), since it contains no chlorine in the molecule, will not undergo the same ozone destroying mechanism in the atmosphere. This refrigerant is currently undergoing extensive testing in the stationary and mobile refrigeration and air conditioning industries. In 1988, Spauschus[2] pointed out that many technological barriers needed to be overcome for the successful use of R-134a. This paper shall address one of the most important of these barriers - the need to find a new lubricant for use with this refrigerant.

Lubricant Considerations

Most refrigeration engineers agree that for optimum efficiency, the refrigerant and compressor lubricant should be soluble in one another over the entire range of temperatures, pressures, and concentrations present in the system. Complete solubility allows two important functions to take place. First, with proper solubility, an adequate return of lubricant to the compressor is insured, thus providing for proper lubrication of the compressor's moving parts. Second, this facile movement of the lubricant through the system allows maximum heat transfer to occur. Insoluble lubricant has the potential to "pool out" or coat the walls of system tubing, leading to reduced heat transfer and lower efficiencies. One of the disadvantages to the use of R-134a is the insolubility of mineral oils in this refrigerant. In order to achieve refrigerant/lubricant compatibility, a synthetic lubricant must be used. The use of a synthetic lubricant automatically introduces a number of potential problems. These are above and beyond the initial question of whether the use of this lubricant allows for the desired durability of the compressor. This lubricant must also be compatible with the system components such as elastomers, insulation, metallurgy, and the refrigerant itself. Other important considerations are the thermal stability of the lubricant, its viscosity characteristics and its hygroscopicity. A number of R-134a-soluble synthetic lubricants have been identified. Polyalkyleneglycols (PAGs) have received the greatest amount of industry evaluation to date. PAGs have excellent thermal stability and show good lubricity. Questions concerning PAG lubricants still need to be answered, especially in the areas of inverse solubility, water adsorption, insulation compatibility, mineral oil miscibility and insufficient compressor durability.

In order to address the overall requirements of a refrigeration system as fully as possible, a number of other synthetic lubricant types have been investigated. This paper describes the physical testing performed to date on these new lubricants. Some initial lubricity performance is also reported.

Solubility

In order for a lubricant to show the proper solubility in R-134a, the temperature range of approx. -40°C to +90°C (-40°F to 195°F) should be considered. Table 1 shows the solubility of 10 experimental lubricants, evaluated at 10% weight concentration in R-134a. These initial solubility tests were run in a thick walled glass vessel equipped with a removable pressure gauge. 0.5g of lubricant was charged to the vessel. The contents were then cooled to -60°C (-75°F) in a dry ice/i-propyl alcohol bath. Four and a half grams of R-134a were then condensed into the vessel. The pressure valve was then attached and the contents heated until the lubricant sample had dissolved. The vessel was then cooled slowly. The temperature at which any haziness or insolubility was noted. It is important to note that most of these fluids are fully soluble from an upper temperature greater than 90°C (195°F) down to a minimum temperature, characteristic of each individual lubricant. The "inverse" solubility phenomenon shown by the PAG in Table 1 is not observed in the other fluids evaluated. Several lubricant candidates (Items 4, 8) do show solubility points significantly higher than -40°C. These fluids, if used as compressor lubricants, might result in the loss of proper heat transfer in the system.

Thermal Stability

Refrigerant discharge temperatures can, under some conditions, exceed 175°C (~350°F). These temperatures require the lubricant used to have a high degree of thermal stability. The thermal stability of a lubricant can be further complicated by chemical reactions that can occur in the system. These reactions can be catalyzed by the metal surfaces (iron, aluminum, copper) found in the refrigeration systems or promoted by the presence of the refrigerant. The thermal stability of a lubricant must be such that it does not break down when subjected to the combination of high temperatures, potentially catalytic metal surfaces, and the presence of the refrigerant. In order to determine the thermal stability of a lubricant, a sealed tube test is performed. These tests are done by charging a known amount of lubricant and refrigerant (condensed at a temperature below its boiling point) into a thick-walled glass vessel. Iron, aluminum, and copper coupons are also placed in the tube in order to evaluate any high temperature reactions that may occur between the lubricant and system metallurgy. These tubes are then sealed and heated to the desired temperature. After a designated time period at this temperature, the tubes are cooled, opened, and the color of the oil, condition of the coupons, and amount of refrigerant decomposition are evaluated. Table 2 shows the results of thermal stability tests run on 11 different lubricants. These tests were run at 175°C (350°F) for 14 days. The lubricant was present at 20% by weight of the total lubricant/refrigerant charge. The results are given as a numerical rating from 0 (excellent) to 4 (poor). A rating was given to each metal coupon and also to the oil itself, indicating the amount of color change that the oil had undergone. A fluoride ion analysis of the oil was also performed after the 14-

day test. The lubricant was mixed with 20 ml of water and extracted for 24 hours. The water was then separated from the oil and diluted to 100 ml. A selective fluoride ion probe was then used to measure the F^- ion concentration present quantitatively. The results are based upon the assumption that the presence of one F^- ion represents the decomposition of one HFC-134a molecule. The thermal stability of the mineral oil sample indicates that a rating can be as high as 2 and still be acceptable. Fluids 3, 4, and 5 show poor thermal stability and would very likely not be suitable lubricants for compressor use. All lubricant candidates shown have very little interaction with the R-134a refrigerant.

Viscosity

In order for a fluid to function properly as a compressor lubricant it must possess the proper viscosity. Normal operating temperatures from <-25°C (-10°F) to >175°C (350°F) dictate that the lubricant would have enough viscosity to provide proper boundary lubrication in the compressor but not be so viscous at very cold temperatures that this fluid would become too thick to flow freely through the cold areas of the system. Fluid viscosity requirements differ when comparing stationary refrigeration systems to mobile air-conditioning. The mobile air-conditioning industry prefers higher viscosity fluids, on the order of $\simeq$ 110 cSt (500 SUS) at 40°C (104°F). Stationary refrigeration systems and especially hermetic reciprocating type compressors prefer lower viscosity fluids, in the range of 20-30 cSt (100-150 SUS) at 40°C (104°F). This lower viscosity requirement is due primarily because of the tendency of higher viscosity mineral oils to "wax out" and plug the capillary tube expansion devices used in these systems. Synthetic fluids are, for the most part, not prone to "waxing". They remain liquids at very low temperatures. This phenomenon could prove useful in allowing the use of higher viscosity fluids in stationary systems, which would provide better boundary lubrication of the compressor. Table 3 gives the viscosities and pour points of 10 synthetic lubes. Ester, amide, and cyclic lubricant #1 are all high viscosity fluids intended for automotive applications. The remaining fluids display the range of viscosities seen in use with stationary refrigeration systems. Most of these fluids exhibit pour points well below any minimum temperature that would be encountered in a refrigeration system. Amides as a group seem to exhibit low VI character, while other lubricant types show VIs similar or slightly below that of mineral oil.

Water Adsorption

Considerable concern has been expressed by the industry over the amount of water that may be introduced into the refrigeration system through the use of a new synthetic lubricant. Mineral oil is very easy to dry and keep dry. Many synthetic lubricants, especially if they are highly polar, will be much more compatible with water and, as a result, have the potential to introduce small quantities of water into the system. In the past, when an R-12/mineral oil system was contaminated with high levels of water, this water would more than likely be found as free water and two distinctive phases would be present. Ice crystals could then be formed in the cold areas of the system and have the potential to cause system blockage. Water found in synthetic lubricants is seldom seen as free water and thus would not be able to freeze into problem-forming ice crystals. Other potential problems such as copper transfer, in-system corrosion, and materials degradation (Lubricant/refrigerant reactions, elastomer attack) are or could be accelerated by high levels of water. Figure 1 illustrates the ability of several synthetic lubricants to adsorb water over a period of time. Each lubricant was dried initially by sparging the sample for 2 hours at 125°C (257°F) with a 0.5 SCFH N_2 flow. After taking an initial sample, the fluids were transferred to open 250 ml beakers. Small samples were then periodically removed for water analysis via Karl Fischer reagent. Figure 1 shows that a wide difference in water adsorption ability exists among these fluids. As expected, mineral oil picks up practically no water compared with the other fluids evaluated. Cyclic Nitrogen B is exceptionally succeptible to water adsorption from the air. Actual water levels reached as high as 5% with this sample. Esters A & B showed excellent resistance to moisture adsorption. PAGs and amides show fairly high levels of water adsorption after several days. It is difficult to say what effect moderate or high levels of water associated with synthetic fluids will have on a refrigeration system. Testing by compressor manufacturers will probably need to be done to address this question.

Elastomer Effects

In a typical refrigeration system a lubricant comes into contact with various polymeric materials. Seals, hoses, and insulation are typically made of elastomers. These materials must maintain their properties after long exposure to the lubricant. Synthetic lubricants, as a family, would be expected to have a greater effect on elastomers than that of mineral oil. This is again due to the higher polarity that a synthetic lubricant exhibits compared with mineral oil. Preliminary data obtained on the effects of several synthetic fluids on elastomeric seal materials indicate that some fluids have large effects on some elastomers and little effect on others. Evaluation of elastomers in several potential fluids is presently underway.

Lubricant Compatibility

It is possible that in the future several different types of synthetic lubricant may be used by the refrigeration industry at the same time. If this should be the case, then these different lubricants must be compatible one with another. A short time frame may also exist when compatibility with mineral oil might be necessary. These requirements are important because a high possibility for lubricant cross-contamination exists when R-134a systems are serviced or assembled. This problem may also occur if any type of retrofitting is used in the industry. The compatibility of all synthetic lubricants listed in Table 1 were evaluated one in another at 10%, 50%, and 90% by weight levels. In all cases, the synthetic lubricants were compatible with one another at these three concentrations. The PAG, Cyclic N A and Cyclic N B lubricants were not compatible with mineral oil at 50 and 90% weight concentrations of mineral oil. All other synthetic fluids were fully compatible with the mineral oil.

Lubricity

The primary function of a compressor lubricant is to ensure the durability of the device. If a lubricant does not do its required job, any excellent physical properties it may possess will have little meaning. Table 4 lists a number of lubricants that were evaluated in a short screen test designed to look at the lubricity of various fluids. This set of evaluations was run on a Falex 6 type apparatus using a steel ring and steel pin. A failure in this test was determined by a noticeable increase in torque when the applied load had reached the point where the individual fluid began to lose boundry lubrication. No additives were used with these fluids and the presence of R-134a refrigerant was not included in this set of evaluations. The data in Table 4 are intended only as a gauge for evaluating base fluid lubricity compared to the mineral oil base line. If the data in Table 4 were taken at face value, mineral oil would not be the best choice as a lubricant. It is known, however, that the presence of the refrigerant (both R-12 or R-134a) has a definite influence on the lubricity of the fluid. In fact, were it not for the additive-like effect that mineral oil derives from the R-12 refrigerant in present systems, it is probable that mineral oil would in fact, by itself, be a poor choice as a lubricant. Additives can have a wide range of effects when evaluated in different fluids. Synergistic effects are often seen when a particular additive/base fluid combination is used. For this reason a fluid with low lubricity by itself (such as mineral oil in the data presented in Table 4) can become an outstanding lubricant with the proper use of additives. Table 4 shows that those fluids that contain sulfur, phosphorus, and certain types of nitrogen exhibit excellent lubricity. These fluids are also the least thermally stable fluids on this list. It has been established that additives containing sulfur, phosphorus, or other effective antiwear agents do indeed decompose on metal surfaces under extreme pressure situations. This decomposition is the basis for their effectiveness and may also explain why the lubricant base fluids listed in this paper that contain these elements show the highest failure loads. As a general rule, low viscosity fluids have given values between 150 - 300 lbs in this test while higher viscosity fluids have given load values anywhere from 200 to 650 lbs. Exceptions are those fluids that contain sulfur, phosphorus, or other elements that improve expreme pressure performance.

Conclusions

When the initial data presented on the 10 synthetic lubricants listed in this paper are examined, it becomes apparent that several fluids possess many of the physical characteristics necessary to qualify them as potential compressor lubricants. When the three most critical criteria (R-134a solubility, viscosity, and thermal stability) are considered, three classes of lubricant appear to be acceptable. Polyalkylene glycols, esters, and amides each possess the range of R-134a solubility, viscosity, and thermal stability necessary to merit their further evaluation as compressor lubricants. When further physical parameters are evaluated on these three types, each class reveals further strengths and weaknesses. Based on the comparisons seen in Table 5, ester-type base fluids seem to offer the greatest number of advantages, followed by the polyalkyleneglycols and amides. Since compressor durability is the primary function for which these fluids were created, it would appear that esters, amides, and PAGs hold the greatest promise of providing an acceptable fluid. It is also probable that the use of additives in these fluids will be necessary to provide the amount of protection needed to achieve acceptable compressor durability for the industry. Various additive approaches are presently being evaluated Lubrizol and may be the subject of a future paper.

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Appendix

Table 1
Lubricant Solubility *

Lubricant	Lower Limit -°C (°F)	Upper Limit -°C (°F)
1. Mineral Oil (R-12)	≃-25 (-13)	>90 (195)
2. PAG	<-40 (-40)	≃40 (104)
3. Sulfur Oxide	-35 (-31)	>90 (195)
4. Phosphorus Oxide	-10 (14)	>90 (195)
5. Nitro	-35 (-31)	>90 (195)
6. Ester A	-30 (-22)	>90 (195)
7. Ester B	<-40 (-40)	>90 (195)
8. Amide A	-20 (- 5)	>90 (195)
9. Amide B	<-60 (-75)	>90 (195)
10. Cyclic Nitrogen A	<-60 (-75)	>90 (195)
11. Cyclic Nitrogen B	<-40 (-40)	>90 (195)

*Evaluations run in a sealed tube at 10% weight of Lubricant in R-134a

Table 2

Lubricant Thermal Stability[2]

Lubricant	Oil Rating	Fe	Al	Cu	%R-134a Decomp.
1. Mineral Oil (ISO 100)	1-2	2	0	3	0.3-1.5
2. PAG	0	0	0	0	<0.01
3. Sulfur Oxide[1]	3	4	4	3	<0.01
4. Phosphorus Oxide	4	3	2	0	<0.01
5. Nitro[1]	4	3	1	3	<0.01
6. Ester A	1	1	0	1	-
7. Ester B	1	1	0	1	-
8. Amide A	1	1	0	1	-
9. Amide B	1	0	0	0	-
10. Cyclic Nitrogen A	2	0	0	1	0.02
11. Cyclic Nitrogen B[1]	2	4	0	1	<0.01

[1] Thermal stability evaluated at 205°C (400°F). All other parameters were the same.

[2] Rating scale: 0 = excellent, 4 = poor

Table 3

Lubricant Viscosity

Lubricant	cSt 40°C	SUS (104°F)	cSt 100°C (212°F)	VI	Pour Point °C (°F)
Mineral Oil	≃30	(150)	≃4	≃100	<-25 (-13)
PAG	26.8	124	5.78	230	<-50 (-59)
Sulfur Oxide	24.8	115	4.30	62	≃-12 (10)
Phosphorus Oxide	42.7	198	6.02	78	<-50 (-59)
Nitro	28.7	133	3.73	-125	-42 (-44)
Ester A	116	537	12.3	97	-33 (-27)
Ester B	28.2	130	4.95	97	-48 (-54)
Amide A	105.8	490	9.0	33	-39 (-38)
Amide B	19.0	88	3.20	-50	-39 (-38)
Cyclic NA	242	1120	33.4	183	-12 (10)
Cyclic NB	51.8	240	6.84	82	-42 (-44)

Table 4

Lubricity

Lubricant	Failure Load, lbs (Kg)
Mineral oil [1]	300 (135)
PAG	450 (200)
Sulfur Oxide	650 (300)
Phosphorus Oxide	450 (200)
Nitro	150 (70)
Ester A [1]	250 (110)
Ester B	200 (90)
Amide B	150 (70)
Cyclic N A [1]	650 (300)
Cyclic N B	650 (300)

[1] High viscosity fluids (≃ 100 cSt (500 SUS) @ 40°C (100°F))

Table 5
Lubricant Strengths vs Weaknesses

	Viscosity	R-134a Solubility	Thermal Stability	Water adsorption	Seal [1] Compatability	Lubricant Compatability	Lubricity [2]
Mineral Oil	+	-	+	++	+	NA	NA
PAG	+	-?	+	-	+	-	+
Sulfur Oxide	+	+	-	+	-	+	+
Phosphorus Oxide	+	-?	-	-	-	+	+
Nitro	+	+	-	NA	-	+	-
Ester A	+	+	+	+	+	+	-
Ester B	+	+	+	++	+	+	-
Amide A	+	+	+	-	+	+	NA
Amide B	+	+	+	-	-	+	-
Cyclic Nitrogen A	+	+	+	--	+	-	+
Cyclic Nitrogen B	+	+	-	--	+	-	+

1 Depends on elastomer used, based on preliminary data
2 Performance based on each lubricant vs mineral oil in Falex 6 test
NA Not evaluated

Figure 1
Water Adsorption