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EFFECTS OF WATER IN SYNTHETIC LUBRICANT SYSTEMS AND CLATHRATE FORMATION

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ABSTRACT

An extensive literature search and a confidential survey were critically analyzed to determine the effects of water on the stability of hydrofluorocarbon/synthetic lubricant systems and to identify key areas requiring further investigation. Following are highlights from the analysis:

- Clathrate hydrates are solid solutions formed when water molecules are linked through hydrogen bonding creating cavities that can enclose various guest molecules from hydrate formers, such as hydrofluorocarbons R-32, R-125, R-134a, R-407C and R-410A. The four methods for preventing clathrate formation were drying the gas, heating it, reducing its pressure, or using inhibitors.
- The hydrolysis of polyolester lubricants was mostly acid-catalyzed and its reaction rate constant typically followed the Arrhenius equation of an activated process. Hydrolytic stability improved with hindered molecular structures, and with the presence of acid catcher additives and desiccants. Water vapor can effect the adsorption of long-chain fatty acids and the chemistry of formation of protective oxide film. However, these effects on lubrication can be either positive or negative.
- Fifty to sixty percent of the moisture injected into an air-conditioning system remained in the refrigerant and the rest mixed with the compressor oil. In an automotive air-conditioning system using R-134a, ice would form at 0°C evaporating temperature when the water content in the vapor refrigerant on the low-pressure side was more than 350 ppm.
- Moisture would cause the embrittlement of polyethylene terephthalate and the hydrolysis of polyesters, but would reduce the effect of amine additives on fluoroelastomer rubbers. The reactions of water with refrigerants and lubricants would cause formicary and large-pit corrosion in copper tubes, as well as copper plating and sludge formation. Moreover, blockage of capillary tubes increased rapidly in the presence of water.
- Twenty-four companies responded to the survey. From the responses, the water concentrations specified and expected for different refrigerant/lubricant systems varied depending on the products, their capacities and applications, and also on the companies. Among the problems associated with high moisture level, lubricant breakdown was of greatest concern, followed by acid formation, compressor failure and expansion valve sticking.

The following research topics are suggested:

1. The air-conditioning and refrigeration industry needs to measure and record the water content and total acid number of the lubricant of newly installed systems as well as operating systems that are shutdown for service or repair. The reason for the shutdown needs to be documented. A database can then be established to correlate water content with type and cause of breakdown.
2. Detailed studies on the distribution of water in refrigeration and air-conditioning systems should be conducted to pinpoint problem areas associated with free water.
3. Research is needed to validate the current theories and mechanisms of formicary corrosion. Corrosion inhibitors need to be developed.
4. The conditions for clathrate formation and decomposition of other alternative refrigerants, such as R-23, R-41, R-116, R-125, R-143a, R-404A and R-507C, and water should be determined to avoid possible problems associated with tube plugging.
5. The mechanism by which water facilitates or hinders lubrication needs to be studied.
INTRODUCTION

Moisture is a universal contaminant of refrigeration systems and a scientific understanding of the effects of water in these systems is needed for their proper design, efficient operation, and reliable service. The effects of water on chlorofluorocarbons (CFC) and mineral oil have been extensively studied (Walker 1962; Nippon Reito Kyokai 1981). However, the phase-out of CFC/mineral oil systems and the introduction of alternative hydrofluorocarbon (HFC) refrigerants and their compatible synthetic lubricants have once more raised concerns about the effects of water on the stability of refrigeration systems. The HFC/synthetic lubricant systems are polar and have good solubility for moisture, thus present reduced risk of free water with its associated problems. Because of the different types of synthetic lubricants and system designs encountered in the refrigeration and air-conditioning industry, initial investigations into the effects of excess water with the HFC/synthetic lubricant working fluids are limited, proprietary, or of a screening nature. There has not been a reported in-depth study of the effects of moisture on the long-term stability of the HFC/synthetic lubricant systems. Such a study would assist the equipment manufacturers in defining allowable maximum limits of water concentration for satisfactory long-term operation of the HFC/synthetic lubricant systems, and evaluating potential difficulties associated with the presence of excessive water.

An extensive literature search was conducted to compile and critically evaluate the current state of knowledge of the effects of water on the stability of HFC/synthetic lubricant systems, and to identify key areas requiring further investigation. A confidential survey was prepared and sent to compressor, lubricant, desiccant and filter-drier manufacturers to determine the industry specifications on the amount of water allowable in the HFC/synthetic lubricant systems and to identify the problems associated with high moisture levels.

CLATHRATE FORMATION AND DECOMPOSITION IN HFC-WATER SYSTEMS

Clathrate hydrates first discovered in 1810, are solid solutions formed when water molecules, linked through hydrogen bonding, create cavities that can be occupied by various guest molecules also known as hydrate formers. Englezos (1993) reviewed the formation, structures and properties of clathrate hydrates, described their phase equilibria and thermodynamic models, and discussed their nucleation, growth and decomposition. Clathrate compounds have been found under the evaporating pressure condition of a refrigeration unit using R-407C and R-410A (Matsuo, Tagashira and Yoshida 1996). The critical decomposition temperature, which is the maximum temperature for the existence of the clathrate, of the HFC-32/water mixture was reported at 17.6 °C (Davidson 1973), and that of the HFC-134a/water mixture was 10 °C (Oowa et al. 1990). Tanii et al. (1997) recorded the critical decomposition temperature of HCFC-141b clathrate as 8.5 °C and showed that the addition of 0.05% by weight of surfactant increased the clathrate formation rate while the addition of ethylene glycol lowered the clathrate formation/decomposition temperature. Akiya et al. (1999) studied the formation conditions of clathrates between HFC refrigerants and water. Curves of Pressure (P) versus temperature (T) before the formation of the clathrate were called condensation curves, while curves of P versus T between clathrate formation and clathrate decomposition were clathrate formation curves. Condensation and clathrate formation curves, which were linear with a logarithmic pressure scale and linear temperature scale, were obtained for each of the following refrigerants and water: HFC-32, HFC-125, HFC-134a, and refrigerant blends R-407C and R-410A. The critical decomposition temperature T_c and the critical decomposition pressure P_c were obtained from the intersection of the condensation line and clathrate formation line. From their studies, the authors concluded that R-407C and R-410A form clathrate compounds with water under the evaporating temperature condition in the refrigeration cycle of air-conditioners and heat pumps, operating below 14 °C.

Englezos (1993) cited four methods for preventing the formation of clathrates, including drying the gas, heating it to a temperature above the equilibrium hydrate formation temperature at a given pressure, reducing the gas pressure to below the hydrate formation pressure at a given temperature, or injecting inhibiting substances. Known clathrate inhibitors include methanol, ethanol, ethylene glycol, diethylene glycol, butanone, acetone, or electrolytes such as NaCl, KCl, CaCl_2, and NH_3 (Holder, Zetts and Pradhan 1988; Gubbins 1993; Koga, Tanaka and Nakamishi 1994). In addition to alcohols, glycols, and electrolytes, which are known as thermodynamic inhibitors, water-soluble polymers are found to have inhibiting potential (Englezos 1992; Lederhos et al. 1996). These inhibitors, also
called kinetic inhibitors, generally are effective at less than one weight percent in the aqueous phase whereas methanol is used between 10 and 60%.

**WATER IN REFRIGERANT AND LUBRICANT SYSTEMS**

In describing the water absorption of synthetic lubricants, Echin, Novosartov and Popova (1981) stated that hygroscopicity of oils based on esters increased with increasing relative humidity of the air (according to Henry’s law) and with increasing temperature. Kussi (1985) reported that water absorption is dependent on the content of ethylene oxide in the polyether molecule, the degree of polymerization, and the temperature. In similar studies, the water solubility of polyalkylene glycol was seen to be reduced by end-capping the hydroxyl group on the molecular structure with an alkyl group (Idoux, McCurry and Aminabhavi 1994). Sheiretov, Glabbeek and Cusano (1996) reported that the approximate saturation limit of polyalkylene glycol is 18,000 ppm and that of polyolester is between 2000 and 4500 ppm. Fukui, Sanechika and Ikeda (2000) remarked that moisture absorption of fluorinated alkyl aryl ethers is much slower and reaches a lower equilibrium water content of around 200 ppm.

Tazaki, Konishi and Nagamatsu (1998) noted that moisture enters into the refrigeration and air-conditioning systems during installation or repair and is quite difficult to eliminate by vacuuming. Both polyvinylether and polyolester lubricants are hygroscopic, but polyolesters hydrolyze in the presence of water, while polyvinylethers do not. Sealed tube tests of R-134a/polyester in the presence of iron, copper, and aluminum and controlled amounts of water indicated that hydrolysis activity tends to increase with high water content or residual carboxylic acid (Jolley 1991). Bailey (1999) stated that in lubricant service applications, acid-catalysed hydrolysis occurred more frequently than base-catalysed hydrolysis. The hydrolysis reaction rate constants typically showed temperature dependence consistent with an activated process following the Arrhenius equation. The activation energy for hydrolysis of aromatic esters is higher than that for simple polyolesters and diesters, and polyolesters generally had lower rates of hydrolysis than analogous diesters. In polyolesters, branching at the 2 or 3 position relative to the ester carbon drastically reduces the rate of hydrolysis compared with analogous linear esters. High acid value and high hydroxyl value in the esters also resulted in faster hydrolysis reactions. The use of acid catcher additives, such as epoxides, could significantly improve the hydrolytic stability of ester lubricants. Similarly, Dick et al. (1996) showed that hindered polyolester is more resistant to hydrolysis than the conventional polyolester and both molecular sieve desiccant and hydrolysis inhibiting chemicals markedly enhance the stability of unadditized and additized lubricants. Epoxy-type acid catchers were shown to be good hydrolysis inhibitors (Iizuka et al. 1996).

Lancaster (1990) reviewed the effect of humidity on the friction and wear of metals. In general, under lubricated conditions, water vapor can modify the adsorption of long-chain fatty acids that act as boundary lubricants, thus influencing friction and wear. Water can also affect the chemistry of protective film formation by oxygen. However, depending on the lubricants tested and the conditions of the tests, the effects can be either positive or negative. A detailed study by Sheiretov, Glabbeek and Cusano (1996) on the effect of dissolved water on the tribological properties of polyalkylene glycol and polyolester lubricants showed that the lubricant, the contact metals (steel pin on aluminum plate or steel pin on cast iron plate), the atmosphere (whether refrigerant R-134a or air), and the moisture content, all have an effect on friction and wear, as shown in Table 1. A positive effect corresponds to a decrease in wear with increasing water content and a negative effect corresponds to an increase in wear with increasing water content.

The water solubility of hydrochlorofluorocarbons (HCFC) and HFC refrigerants, including R-22, R-123, R-124, R-125, R-134a, R-141b, R-142b, R-152a has been reported by McLinden (1989), while Thrasher et al. (1994) studied the moisture solubility in R-123 and R-134a. According to Gehring (1995), water is the single most deleterious contaminant in air-conditioning and refrigeration systems.

Cohen and Tucker (1998) stated that, for molecular sieve desiccants, the maximum water capacity is achieved when the refrigerant is excluded from the molecular sieve micropores, because the refrigerant and water molecules compete for the available adsorption sites. They showed that molecular sieve type 3A can be modified to exclude refrigerant R-32, and reported the partitioning of water between refrigerants R-410A and R-407C and molecular sieves at 52 °C. Cohen and Tucker measured the drydown rate of the molecular sieves in R-407C and R-410A and concluded that both 3A-6 or 3A-11 would dry the refrigerants very fast in about two hours and almost completely in about six hours. Rohatgi et al. (2000) studied the distribution of moisture between R-134a, polyalkylene glycol, and desiccant, and concluded that at equilibrium, some moisture from the PAG is redistributed between the refrigerant and the desiccant with the larger fraction going to the desiccant. In addition, the study of moisture dynamics showed that under steady operation, moisture is distributed between R-134a and the PAG lubricant after twenty-four hours. The amount of moisture varies according to the total system moisture and, if desiccant is present, on the degree of desiccant saturation. Goswami et al. (1996) investigated the effect of moisture
on the performance of an air-conditioning system and determined that approximately 50 to 60% of the moisture injected into the system remains in the refrigerant and the rest mixes with the compressor oil. Kitamura et al. (1993) conducted a detailed study of the water distribution in an automotive air-conditioning system using R-134a. They determined that ice would form in the refrigerating cycle at 0 °C evaporating temperature when the water content in the vapor refrigerant on the low-pressure side is more than 350 ppm.

EFFECT OF WATER ON MATERIALS OF CONSTRUCTION

The presence of moisture was observed to cause the embrittlement of the polyethylene terephthalate (PET) found in Mylar and Melinex sheet and sleeving insulations (Korleski 1991; Sundaresan and Finkenstadt 1991; Doerr and Waite 1996). Polyester material (used as screen for orifice tube in automotive air-conditioners) is hydrolyzed by humidity, and Hunter et al. (2000) have developed a model to express the rate of polyester hydrolysis in terms of the relative humidity and to connect the degree of hydrolysis to hardness. Kumagai and Yoshimura (2000) reported that absorbed water in cycloaliphatic epoxies (used as electrical insulating material for motors) caused hydrolysis of ester linkages leading to decreased tracking resistance or surface resistivity. On the positive side, the presence of water was shown to reduce the effect on fluoroelastomer (FKM) rubbers of amine additives, which can cross-link with the rubbers thus changing their properties (Smith 1960; Dinzburg 1995).

Campbell (1972) described the forms of corrosion encountered in heat exchangers for air conditioning and heating and indicated that corrosion can be avoided by correct choice of alloys, design of components, and equipment operation. The hydrolysis of organic solvents and lubricants or the reactions of refrigerants with water have been shown to cause formicary and large-pit corrosion in copper tubes (Nagata and Kawano 1994; Lenox and Hough 1995), as well as copper plating and sludge formation in refrigeration systems. Elliott and Corbett (2001) described formicary or ant-nest corrosion as a particular form of localized corrosion of a submicroscopic nature. The morphology of the corrosion damage within the metal includes a series of minute interconnecting tunnels, starting from the tube surface and propagating rapidly into the tube wall. The corrosion product (copper oxide Cu$_2$O) is usually found in the micro channels. The mechanism of formicary corrosion generally involves the presence of moisture, oxygen and a corrosive agent such as an organic acid. Herbe and Lundqvist (1997) reviewed the experiences of companies with refrigerant and heat pump equipment that have converted from R-12/mineral oil to R-134a/polyolester. They concluded that all the companies surveyed believed that the problems with copper plating and formation of acid could be avoided if residual mineral oil was kept at less than one percent and moisture at less than fifty parts per million.

The presence of water in refrigeration systems leads to loss of performance, ice deposition, corrosion of metals, blockage of expansion devices, copper plating, and poor lubrication. Goswami et al. (1996) investigated the effect of moisture on the performance of an air-conditioning system using R-22. They reported that cooling capacity of the system is not affected until about 100 ppm of injected moisture. Beyond that point, the capacity and COP of the system begin to drop with increasing moisture, decreasing by 10-15% at 1000 ppm injected moisture (around 700 ppm moisture in the refrigerant). Moreover, studies of blockage of capillary tubes showed that blockage is low in dry systems, but increases rapidly in the presence of water or when the system is doped with carboxylic acid (Herbe and Lundqvist 1997).

SUMMARY OF INDUSTRY SURVEY

Twenty-four companies responded to the survey, including four companies producing or servicing equipment in commercial refrigeration, two in residential air-conditioning, and three in commercial air-conditioning. Two companies manufacture flow controls, and two manufacture commercial icemakers. Of the remaining eleven companies, two have products in commercial refrigeration and residential air-conditioning, four in residential and commercial air-conditioning, and five in commercial refrigeration as well as residential and commercial air-conditioning. As shown in Figure 1, R-22/mineral oil is still the refrigerant/lubricant system most in used. In the survey, a larger number of companies reported the use of R-22/mineral oil in residential or commercial air-conditioning than in commercial refrigeration, where more companies reported the use of R-134a/POE or R-404A/POE. Fewer companies with products in commercial refrigeration indicated the use of R-410A/POE than in residential or commercial air-conditioning. While more commercial air-conditioners than residential air-conditioners or commercial refrigerators reportedly use R-407-C/POE, R-22/alkylbenzene is found in all the three types of
equipment. A few products also use R-134a/PAG, R-410A/POE, R-507A/polyolester, R-507C/PVE, and R-401A/POE. Two commercial refrigeration companies reported using R-22/POE with scroll and screw compressors. The water concentrations specified and expected for different refrigerant/lubricant systems vary depending on the products, their capacities and applications, and also on the companies. In flow controls, the specified values for new field-erected or factory-sealed equipment are less than 50 ppm for HCFC as well as HFC. The expected values after service and re-assembly are also less than 50 ppm, but the actual measured values in the field can be as high as 300 ppm. In residential air-conditioning, for HCFC refrigerants, the specified water contents ranged from 10 ppm to 1.5 weight percent (reported by one company that did not specify whether the percentage was based on refrigerant, lubricant or refrigerant plus lubricant weight), while the expected water contents are from 10 to 150 ppm. For HFC refrigerants, the specified values are from 10 to 50 ppm, while the expected values are between 50 and 150 ppm. The measured moisture for both HCFC and HFC is between 13 and 700 ppm. In commercial refrigeration and commercial air-conditioning, the specified values for HCFC and HFC are 100 ppm on the low side or 1.5 weight percent on the high side. The expected values are between 20 and 100 ppm, while the measured numbers are as high as 700 ppm. Among the problems that would most likely result from the presence of high moisture level in the refrigeration systems, lubricant breakdown is of greatest concern, as shown in Table 2. Next in importance is acid formation, followed by compressor failure and expansion valve sticking. Elastomeric seal failure and sticking of suction valve cause fewer concerns. Of the twenty-four companies that responded to the survey, seventeen (71%) use filter driers and six (25%) employ acid catchers.

**CONCLUSIONS**

Since the introduction and use of HFC/synthetic lubricant systems in air-conditioning and refrigeration, there has been active research in the area of water content in the new operating fluids and its effect on system components and performance, as evidenced by the number of references cited in this review. However, much remains to be investigated. Based on the literature reviewed, the following research topics are suggested for future investigation, in the order of their importance, practicality and ease of implementation:

1. The air-conditioning and refrigeration industry needs to measure and record the water content and total acid number of the lubricant in newly installed systems as well as operating systems that are shutdown for service or repair. The reason for the shutdown and repair needs to be documented. A database can then be established to correlate water content in systems with type of breakdown or problems encountered. This research project is easy to implement and has practical application, because the database, combined with detailed studies on the distribution of water in refrigeration and air-conditioning systems, would help the industry in setting meaningful limits on the allowable water content in newly installed equipment, either field-erected or factory-sealed.

2. Along with the database, detailed studies on the distribution of water in refrigeration and air-conditioning systems should be conducted to pinpoint problem areas associated with free water, and to help in the formulation and implementation of effective solutions to these problems.

3. Although formicary corrosion is a real phenomenon leading to copper tube failures, it is less well known than other forms of corrosion. Formicary corrosion has been successfully replicated in the laboratory, but research is still needed to validate the current theories and mechanisms for this type of corrosion. Studies are needed to determine the rate of pit formation and propagation, the conditions of temperature, water content, acid content, and oxygen content needed to initiate the corrosion process. Corrosion inhibitors need to be developed and evaluated.

4. Although studies have been conducted on a number of hydrate formers including hydrofluorocarbon refrigerants, the conditions for formation and decomposition of clathrate hydrates of other alternative refrigerants under consideration for use in refrigeration and air-conditioning systems and water should be determined to avoid possible problems associated with tube plugging. These alternative refrigerants may include R-23, R-41, R-116, R-125, R-143a, and refrigerant blends such as 404A and 507C. A research project, built on the work of Akiya et al. (1999), can be conducted to study the formation and decomposition of clathrate hydrates of R-125, R-143a, and their blends R-404A (44% R-125, 52% R-143a, and 4% R-134a) and R-507C (50% R-125 and 50% R-143a). Such a research, in addition to providing additional thermodynamic data, would verify the theory that it is possible to determine the clathrate decomposition conditions of a blend of HFC refrigerants from the data of its individual components.
5. The mechanism by which water facilitates or hinders lubrication is not known and needs to be studied and characterized in order to formulate more effective lubricants and lubricant additives.

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Contact metals</th>
<th>Atmosphere</th>
<th>Water Effect on Wear</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAG</td>
<td>Steel/Aluminum</td>
<td>R-134a</td>
<td>Positive from 200 ppm up to 5000 ppm moisture. After that, no effect</td>
</tr>
<tr>
<td>PAG</td>
<td>Steel/Cast Iron</td>
<td>R-134a</td>
<td>Negative</td>
</tr>
<tr>
<td>PAG</td>
<td>Steel/Aluminum</td>
<td>Air</td>
<td>Positive</td>
</tr>
<tr>
<td>PAG</td>
<td>Steel/Cast Iron</td>
<td>Air</td>
<td>Slightly positive</td>
</tr>
<tr>
<td>POE1</td>
<td>Steel/Aluminum</td>
<td>R-134a</td>
<td>No effect</td>
</tr>
<tr>
<td>POE1</td>
<td>Steel/Cast Iron</td>
<td>R-134a</td>
<td>No effect</td>
</tr>
<tr>
<td>POE1</td>
<td>Steel/Aluminum</td>
<td>Air</td>
<td>Positive</td>
</tr>
<tr>
<td>POE2 (higher viscosity)</td>
<td>Steel/Aluminum</td>
<td>R-134a</td>
<td>No effect</td>
</tr>
<tr>
<td>POE2</td>
<td>Steel/Cast Iron</td>
<td>R-134a</td>
<td>No effect</td>
</tr>
<tr>
<td>POE2</td>
<td>Steel/Aluminum</td>
<td>Air</td>
<td>Positive</td>
</tr>
<tr>
<td>POE2</td>
<td>Steel/Cast Iron</td>
<td>Air</td>
<td>Slightly positive (wear is small at either high or low water content)</td>
</tr>
</tbody>
</table>

**Table 2. Possible Problems Caused by High Water Contents**

<table>
<thead>
<tr>
<th>Types of problems</th>
<th>Number of responses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lubricant breakdown</td>
<td>22</td>
</tr>
<tr>
<td>Acid formation</td>
<td>21</td>
</tr>
<tr>
<td>Compressor failure</td>
<td>19</td>
</tr>
<tr>
<td>Copper plating</td>
<td>16</td>
</tr>
<tr>
<td>Expansion valve sticking</td>
<td>16</td>
</tr>
<tr>
<td>Refrigerant breakdown</td>
<td>13</td>
</tr>
<tr>
<td>Degradation of motor insulation material</td>
<td>13</td>
</tr>
<tr>
<td>Metal Corrosion</td>
<td>12</td>
</tr>
<tr>
<td>Ice formation in the evaporator</td>
<td>11</td>
</tr>
<tr>
<td>Deterioration of wire coating</td>
<td>9</td>
</tr>
<tr>
<td>Plugging of suction filter or heat-exchanger (clathrate formation)</td>
<td>7</td>
</tr>
<tr>
<td>Elastomeric seal failure</td>
<td>6</td>
</tr>
<tr>
<td>Suction/discharge valve sticking</td>
<td>4</td>
</tr>
<tr>
<td>Plugging of liquid line filter-drier</td>
<td>1</td>
</tr>
</tbody>
</table>

**Figure 1: Refrigerant/Lubricant Usage from Industry Survey**

- ■ Comm. Refrig.
- □ Resid. A/C
- □ Comm. A/C
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