EXECUTIVE SUMMARY

FINAL REPORT ARTI-21CR/610-50035-01
STUDY OF THE EFFECTS OF WATER IN SYNTHETIC LUBRICANT SYSTEMS AND CLATHRATE FORMATION

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 and mineral oil have been extensively studied. In these non-polar systems with low solubility for water, moisture levels are usually controlled to twenty five parts per million or less to avoid free water and the associated corrosion of metals, compatibility problems with polymeric materials, and possible ice formation in expansion valves, capillary tubes, or evaporators. The phase-out of chlorofluorocarbon/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. The current common practice of equipment manufacturers is to allow moisture levels of 50-100 parts per million (ppm) or less in new equipment with HFC and synthetic lubricants. However, service practices are not well controlled and may lead to high levels of water in the refrigeration system. 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.

Under ARTI 21-CR Project 610-50035-01, Spauschus Associates, Inc. has compiled and critically evaluated the current state of knowledge of the effects of water on the stability of HFC/synthetic lubricant systems to identify key areas requiring further investigation. An extensive literature search was conducted and 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. Following are highlights from the extensive literature review and analysis of the survey:

- Clathrate hydrates, first discovered in 1810, are solid solutions formed when water molecules are linked through hydrogen bonding creating cavities that can enclose various guest molecules also know as hydrate formers. The formation, nucleation, growth, decomposition, structures, properties, and thermodynamic phase equilibria have been reported for a number of hydrate formers, including HFC refrigerants such as R-32, R-125, R-134a, R-407C and R-410A. Four methods for preventing the formation of clathrate hydrates were cited, including drying the gas, heating it to a temperature above the equilibrium formation temperature at a given pressure, reducing the gas pressure to below the hydrate formation pressure at a given temperature, or injecting inhibiting substances.

- Polyolester (POE) lubricants hydrolyzed in the presence of water while polyvinylethers (PVE) do not. Hydrolysis activity of POE was more frequently acid-catalyzed than base-catalyzed and tended to increase with high water content and high residual carboxylic acids. The hydrolysis reaction rate constants typically showed temperature dependence consistent with an activated process following the Arrhenius equation. Hydrolytic stability of POE was shown to improve with hindered POE , and with the presence of acid catcher additives and molecular sieve desiccant. 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 positive effect corresponds to a decrease in wear with increasing water content while a negative effect corresponds to an increase in wear with increasing water content.
- In the study of the distribution of moisture between R-134a, polyalkylene glycol (PAG) and desiccant, it was concluded that at equilibrium, some moisture from the PAG 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 state operation, moisture is distributed between the refrigerant and the 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. It was also determined that approximately fifty to sixty percent of the moisture injected into an air-conditioning system remains in the refrigerant and the rest mixes with the compressor oil. In an automotive air-conditioning system using R-134a, it was discovered that ice would form in the refrigerating cycle at 0 ^{o}C evaporating temperature when the water content in the vapor refrigerant on the low-pressure side is more than 350 ppm.

- The presence of moisture was observed to cause the embrittlement of polyethylene terephthalate and the hydrolysis of polyester materials. On the positive side, water was shown to reduce the effect of amine additives on fluoroelastomer rubbers. The reactions of water with refrigerants or the hydrolysis of organic solvents and lubricants have been shown to cause formicary and large-pit corrosion in copper tubes, as well as copper plating and sludge formation in refrigeration systems. 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.
- The responses from the twenty-four companies that participated in the survey suggested that 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. 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, followed by acid formation, compressor failure and

expansion valve sticking. Elastomeric seal failure and sticking of suction valve cause fewer concerns.

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 of 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 R-404A and R-507C.
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.