**ACCELERATED SCREENING METHODS FOR DETERMINING CHEMICAL
AND THERMAL STABILITY OF REFRIGERANT-LUBRICANT MIXTURES
PART II: EXPERIMENTAL COMPARISON AND
VERIFICATION OF METHODS**

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ABSTRACT

The initial research has focused primarily on conductivity measurements to perform *in situ* degradation measurements of CFC-12/mineral oil and HCFC-22/mineral oil mixtures heated at 175°C (347°F) in sealed glass tubes. Tungsten rods were sealed into the round bottoms of the sealed tubes to provide electrical connections for the *in situ* conductivity measurements. Different metals (steel, copper, and tungsten) have been used as catalysts as well as conductivity probes. The conductivity measurements have been made with both ac and dc voltage inputs.

The preliminary results indicate that the *in situ* conductivity measurements correlate with refrigerant/lubricant degradation as determined by other analytical techniques (color and gas chromatographic measurements). Some of the continuous conductivity measurement tests appear to accelerate as well as monitor the refrigerant/lubricant degradation. Tungsten posts with a valve steel catalyst appear to be the optimum combination for conductivity measurements.

Experiments with ferric fluoride catalysts and differential thermal analysis measurements have also been performed. Initial tests indicate that the ferric fluoride catalyst has potential for testing lubricant stability at temperatures lower than 175°C (347°F). The differential thermal analysis measurements have minimal potential for *in situ* measurements of long-term refrigerant/lubricant degradation processes.

SCOPE

This report describes the research performed during Part II of the MCLR Project Number 655-51500 entitled, "Accelerated Screening Methods for Determining Chemical and Thermal Stability of Refrigerant-Lubricant Mixtures." The research was performed from March 1, 1993 to June 30, 1993. The research described in this report was performed to evaluate analytical techniques for development into accelerated compatibility tests. The candidate techniques were identified in Part I of the MCLR Project Number 655-51500 performed from October 15, 1992 to January 15, 1993.

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SIGNIFICANT RESULTS

INTRODUCTION

Three different thermal analytical techniques were studied during the past four months for development into accelerated screening methods for determining the chemical and thermal stabilities of refrigerant/lubricant mixtures. The thermal analytical techniques employed differential temperature analysis (temperature difference between the sample and reference), conductivity measurements, and catalyst additions (iron fluoride) to accelerate/monitor the degradation mechanisms. All of the studied thermal analytical techniques used sealed glass tubes constructed in accordance with ANSI/ASHRAE Standard 97-1989 [1]. Refrigerants, CFC-11, CFC-12, and HCFC-22, were tested in combination with naphthenic mineral oil and refrigerant HFC-134a was tested in combination with pentaerythritol ester oils, mixed acid and branched acid, for up to 7 days at 175°C (347°F). Appendix A contains the commercial sources and brand names of the refrigerants and oils used in this study.

Differential Thermal Analysis (DTA)

During Part I [2] of this project, a DTA technique detected small temperature differences [2°C (4°F)] between heated tubes filled with CFC-12/mineral oil and HCFC-22/mineral oil combinations. The tubes were placed into the wells of a heated, graphite block and the temperatures of the tubes were measured during the analysis using thermocouples placed between the tubes and the walls of the heating block.

To improve the temperature sensing capabilities of the DTA method, the temperature sensors were placed into direct contact with the heated refrigerant/lubricant mixtures. The only sealed tube modification required for performing *in situ* temperature measurements was the sealing of two tungsten wires (Figure 1) into the round bottom of the sealed tube. Thermocouples and glass thermistors were then spot welded to the inside ends of the tungsten wires to make the *in situ* measurements.

To initially evaluate the potential of DTA for development into an accelerated screening test, a sealed tube shown in Figure 1 prepared with a thermocouple was filled with a CFC-12/mineral oil combination. Due to refrigerant interactions and other factors (glass conductivity), the thermocouple was not sensitive to temperature changes, i.e., the voltage output was independent of temperature.

MODIFIED SEALED GLASS TUBE

Figure 1. Schematic of Modified Sealed Glass Tube. Tube Dimensions According to ANSI/ASHRAE Standard 97-1989.

Therefore, a second sealed tube was prepared with a glass thermistor spot welded to the tungsten posts. The sealed glass tube was filled with a CFC-12/mineral oil combination and placed into the well of a graphite block. A second glass thermistor was placed into an empty well of the block and the block was then placed into an oven heated to 175°C (347°F). The outputs of the thermistors inside the glass tube and an empty well of the graphite block were measured and recorded every five minutes by a data logger interfaced to a microcomputer. During the initial warm-up period [the block required two hours to reach 175°C (347°F)], the temperature of the sealed tube was 1 to 5°C (1.8 to 9°F) lower than the block temperature. After the initial 2 hour warm-up period, the temperatures of the block and sealed tube containing CFC-12/mineral oil differed less than 1°C (1.8°F) during the entire 120 hour test at 175°C (347°F). The color of the CFC-12/mineral oil mixture darkened (ASTM color = 1.0) during the test indicating that slight degradation had occurred.

Since the CFC-12/mineral oil combination is expected to be more reactive than HCFC or HFC/oil combinations and only minor temperature differences were measured for the CFC-12/mineral oil mixture, the initial test results indicate that the DTA is unsuitable for development into an accelerated screening test, i.e., lower reactivities of HCFC and HFC systems will produce smaller temperature differences than CFC-12 systems.

Ferric Fluoride Additions

In an attempt to accelerate the refrigerant/lubricant degradation, ferric fluoride was added to the sealed tubes in place of the valve steel coupons. Studies with fluorinated ether lubricants have shown that the lubricant degradation rate was minimal until fluorides formed on the steel surface. Since all of the current and proposed refrigerants contain fluorine, ferric fluoride (ferrous fluoride not available) was chosen as a possible catalyst for the refrigerant/lubricant mixtures.

For this study, 0.05 grams of ferric fluoride was added to the sealed tubes after the addition of the mineral oil. The sealed tubes containing the CFC-12/mineral oil and HCFC-22/mineral oil mixtures were then prepared according to ANSI/ASHRAE Standard 97-1989 and heated for 3 days at 175°C (347°F). After aging, the refrigerant/lubricant mixtures were brown for the CFC-12 tubes and black for the HCFC-22 tubes. However, the gas chromatographic analyses detected only minor refrigerant degradation indicating that the color changes were not proportional to refrigerant decomposition. The aged refrigerant gases had a strong acid smell and turned blue litmus paper red indicating the production of acids (presumably hydrofluoric acid).

Consequently, the ferric fluoride catalyzed reactions appear to be more dependent on lubricant degradation than on refrigerant degradation, i.e., HCFC-22 tubes underwent reactions similar to the CFC-12 tubes. At lower test temperatures which are more representative of compressor operating temperatures, ferric fluoride additions may have the potential for development into accelerated screening methods for lubricant stability.

Conductivity Measurements

To initially evaluate the potential of *in situ* conductivity measurements for development into an accelerated screening method for refrigerant/lubricant combinations, modified sealed tubes (Figure 1) containing CFC-11/mineral oil, CFC-12/mineral oil, and HCFC-22/mineral oil mixtures were placed into the wells of an aluminum block. The aluminum block was then placed inside an oven preheated to 175°C (347°F).

In the first set of experiments, the tungsten wires in Figure 1 were replaced with iron wires and a 9V dc voltage was applied to the iron wires with a 9V battery. The current (nanoamp range) was measured and recorded by a data logger interfaced to a microcomputer. The current readings versus heating time at 175°C (347°F) for sealed tubes containing CFC-12/mineral oil and HCFC-22/mineral oil mixtures are shown in Figure 2.

Although the sealed tubes are at temperature after two hours, the conductivities of the heated HCFC-22/mineral oil and CFC-12/mineral oil mixtures continue to increase for 4 and 12 hours, respectively. The conductivity of a tube containing mineral oil increased during the two hour warm-up period and then became constant, i.e., no chemical reaction. After the initial conductivity increases are complete, the conductivities of the heated refrigerant/oil mixtures decrease with increasing time. The slight increase in conductivity of the CFC-12/mineral oil mixture after 20 hours of heating (Figure 2) was caused by reversing the positive and negative leads of the 9V battery, i.e., polarity of iron wires reversed.

Since an increase in conductivity (after warmup) is indicative of an increase in the degradation product concentration, the conductivity plots in Figure 2 indicate that the degradation products increase initially then decrease (deposit onto glass walls, coat the metal wires, etc.) with further heating.

Since the measured conductivities decrease with heating time (conductivity expected to increase due to increasing degradation) and the more stable HCFC-22/mineral oil undergoes a larger conductivity increase than the less stable CFC-12/mineral oil, the conductivity

Figure 2. Current (Arbitrary Units) Versus Heating Time at 175°C (347°F) for Conductivity Measurements (Using Iron Posts and 9V Battery) of CFC-12/Mineral Oil and CFC-22/Mineral Oil Mixtures in Modified Sealed Glass Tubes.

measurements using iron or iron-copper wire combinations and a dc voltage do not appear to be suitable for development into an accelerated screening test. The initial reactions of the CFC-12 and HCFC-22 mixtures detected by the conductivity measurement in Figure 2 may be responsible for the temperature differences detected previously by DTA [1].

To investigate the possibility that coatings were forming on the metal wires causing the conductivity decreases observed in Figure 2, the dc voltage source was replaced with a triangular waveform generator. The voltage output of the generator continuously cycled between -15V and 15V (i.e., 9 V dc replaced with 15V ac). Tungsten wires (Figure 1) were used in place of the iron wires to further decrease the possibility of coatings forming on the metal surfaces. No metal catalyst (valve steel or copper) was used for this series of tests. The current readings versus heating time at 175°C (347°F) for sealed tubes containing CFC-11/mineral oil, CFC-12/mineral oil, and HCFC-22/mineral oil mixtures are shown in Figure 3.

The current versus heating time plots for the heated CFC-12 and HCFC-22 mixtures in Figure 3 are fairly constant for the first 40 hours of heating indicating minimal refrigerant/lubricant/metal surface reactions. In contrast to the CFC-12 and HCFC-22 mixtures, the current readings for the CFC-11/mineral oil mixture (Figure 3) increase dramatically with heating time and are off-scale after only 9 hours of heating. The heated CFC-11/mineral oil tube was removed after 10 hours of heating and was very dark in color (ASTM color = 4.0) indicating the CFC-11/mineral oil mixture had undergone severe degradation.

After 40 hours of heating, the current readings of the CFC-12/mineral oil mixture begin to increase at an accelerated rate. The current readings of the HCFC-22/mineral oil mixture remain constant up to 120 hours of heating at 175°C (347°F) (Figure 3). The heated CFC-12/mineral oil and HCFC-22/mineral oil tubes were removed after 120 hours of heating. The heated CFC-12/mineral oil tube was darker (ASTM color = 1.5) than the heated HCFC-22/mineral oil tube (ASTM color = 0.5).

Consequently, the conductivity and color increases for the heated refrigerant/mineral oil mixtures are in full agreement, and the conductivity measurements rank the thermal and chemical stabilities of the mixtures (in order of decreasing stability)

$$\text{HCFC-22} > \text{CFC-12} \gg \text{CFC-11},$$

in full agreement with the literature.

Figure 3. Current (Arbitrary Units) Versus Heating Time at 175°C (347°F) for Conductivity Measurements (Using Tungsten Posts and ±15V Waveform Generator) of CFC-11/Mineral Oil, CFC-12/Mineral Oil, and HCFC-22/Mineral Oil Mixtures in Modified Sealed Glass Tubes.

When the tungsten wires were replaced with iron-copper, iron-iron, copper-tungsten, and iron-tungsten wires the conductivity measurements were similar to those in Figure 2. When copper was present, the second post was covered with copper (greater than 10 microns thick) at the end of the heating periods. Also, the refrigerant/oil mixtures underwent less color change when heated in the presence of the non-tungsten posts, i.e., more degradation with tungsten wires (increased conductivity) than with iron and copper containing wires (decreased conductivity).

To determine if the modified sealed tube tests affect the degradation mechanisms of refrigerant/lubricant mixtures, CFC-12/mineral oil and HCFC-22/mineral oil mixtures were heated for 7 days in unmodified (ANSI/ASHRAE Standard 97-1989 [1]) and modified [tungsten posts (Figure 1) - monitored (i.e., $\pm 15V$ power applied) continuously and unmonitored (i.e., no $\pm 15V$ power applied)] sealed tubes in the presence of valve steel catalysts. The plots of conductivity measurements versus heating time at $175^{\circ}C$ ($347^{\circ}F$) for the modified sealed tube tests are shown in Figure 4. The unmonitored sealed tubes showed no change in conductivity and thus were not plotted in Figure 4. The ASTM colors of the heated tubes, the concentrations of the volatile degradation products and the trace metals in the residues of the CFC-12 and HCFC-22 sealed tubes are listed in Table 1.

The results in Figure 4 and in Table 1 indicate that the application of 15V accelerates the degradation rates of the CFC-12/mineral oil and HCFC-22/mineral oil mixtures, i.e., color, volatile degradation products, trace metal concentrations, and conductivity measurements are increased by application of 15V power. The fact that the types of volatile degradation products are the same with and without the applied 15V (Table 1) indicates that the degradation mechanisms are accelerated without mechanism changes. It is interesting to note in Table 1 that the continuous *in situ* conductivity measurements increase the metal interactions (increased Fe concentration) and decrease the glass interactions (decreased Na concentration) with the refrigerant/mineral oil mixtures.

The results in Figures 3 and 4 also indicate that the conductivity measurements increase at a slower rate in the presence of steel catalysts. The slower conductivity increases indicate that the degradation products (responsible for increased conductivity) are coating/reacting with the metal catalyst decreasing the species in solution for conductivity measurements. The results in Figures 3 and 4 are in agreement with the decreasing conductivity measurements in Figure 2 determined by the iron wire posts. Further study will be required to determine if the presence of metal catalysts are beneficial or detrimental for accelerated refrigerant/lubricant compatibility evaluations.

Figure 4. Current (Arbitrary Units) Versus Heating Time at 175°C (347°F) for Continuous and Delayed (At End of Test) Conductivity Measurements (Using Tungsten Posts, A Valve Steel Catalyst, and $\pm 15V$ Waveform Generator) of CFC-12/Mineral Oil and CFC-22/Mineral Oil Mixtures in Modified Sealed Glass Tubes.

Table 1

Experimental Results for Sealed Tube Tests [175°C (347°F) for 7 days] of CFC-12/Lubricant and HCFC-22/Lubricant Mixtures (see Figure 4)

<u>Refrigerant</u>	<u>Tube Style</u>	<u>ASTM Color</u>	<u>% Volatile Degradation Products</u>	<u>Trace Metals in Residue (ppm)</u>	
				<u>Fe</u>	<u>Na</u>
CFC-12	ASHRAE Standard	1.0	0.06 ^a	2.3	0.7
	Modified ^c - Unmonitored	1.0	0.09	3.2	3.4
	Modified ^c - Monitored	2.0	0.42	7.1	1.1
HCFC-22	ASHRAE Standard	0.5	0.03 ^b	0.5	1.8
	Modified ^c - Unmonitored	0.5	0.04	0.6	3.2
	Modified ^c - Monitored	1.0	0.07	1.5	0.6

^a HCFC-22 -- Main Degradation Product

^b HFC-23, HFC-32 -- Main Degradation Products

^c As shown in Figure 1

SUMMARY

The initial research has shown that *in situ* conductivity measurements have the best potential for development into accelerated screening methods for evaluating the chemical and thermal stability of refrigerant/lubricant mixtures. The research indicates that non-reactive (e.g., tungsten) metal probes and an ac voltage supply should be used for the conductivity measurements to reduce the possibility of coatings and other insulating deposits from forming on the probes. If required, catalysts (e.g., valve steel, copper, etc.) may be added separately. The stability rankings of the conductivity measurements for CFC and HCFC refrigerant/lubricant mixtures are in good agreement with the literature.

The initial research also indicates that ferric fluoride additions may have potential for testing lubricant stability at temperatures lower than 175°C (347°F). Initial results also indicate that DTA measurements are more sensitive to initial degradation reaction than to long-term refrigerant/lubricant degradation processes.

Future work will concentrate on *in situ* conductivity measurements of all the refrigerant/lubricant mixtures listed in the work statement. All lubricants will be dried and analyzed thoroughly prior to use. Modifications of the conductivity measurement electronics will be performed to ensure the technique is inexpensive and easy to operate and to negate the initial conductivity differences among the CFC, HCFC, and CFC/lubricant mixtures. The predictive capabilities of the conductivity measurements will be evaluated using different features of the conductivity plots, e.g., maximum conductivity readings, rate of conductivity increase, etc.

References

1. ANSI/ASHRAE Standard 97-1989, "Sealed Glass Tube Method to Test the Chemical Stability of Material for Use Within Refrigerant Systems," ASHRAE, Atlanta, GA (1989).
2. Kauffman, R. E., "Accelerated Screening Methods for Determining Chemical and Thermal Stability of Refrigerant-Lubricant Mixtures, Part I: Method Assessment," Final Report, Air-Conditioning and Refrigeration Technology Institute, April 1993.

COMPLIANCE WITH AGREEMENT

The University of Dayton Research Institute has complied with all aspects of the agreement.

PRINCIPAL INVESTIGATOR EFFORT

Mr. Robert Kauffman was the principal investigator for Part II of this research effort. Mr. Kauffman devoted 50% of his available work hours on the project.

APPENDIX A

CHEMICALS UTILIZED IN THE RESEARCH

Naphthenic Mineral Oil: Suniso 3GS (32 cSt) purchased from Witco Corp., Sonneborn Div., New York, NY.

Refrigerants: CFC-11, CFC-12, and HCFC-22 purchased from PCR Incorporated, Gainesville, FL.

END

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