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ACCELERATED SCREENING METHODS FOR DETERMINING CHEMICAL AND THERMAL STABILITY OF REFRIGERANT-LUBRICANT MIXTURES PART I: METHOD ASSESSMENT

Final Report

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<u>ABSTRACT</u>

This report presents the results of a literature search performed to identify the analytical techniques suitable for development into accelerated screening tests for evaluating the chemical and thermal stabilities of different refrigerant/lubricant combinations. The literature search focused on three main areas of research: (1) chemical stability data of HFC-134a and other non-chlorine containing refrigerant candidates, (2) chemical stability data of CFC-12, HCFC-22, and other chlorine containing refrigerants and (3) accelerated thermal analytical techniques. The identified literature was catalogued by area and an abstract was written for each journal article or technical report for the formation of a bibliography.

The literature search identified several thermal analytical techniques as candidates for development into accelerated screening tests. The candidates are easy to operate, are common to most laboratories, and are expected to produce refrigerant/lubricant stability evaluations which are in agreement with the current stability test ANSI/ASHRAE (American National Standards Institute/American Society of Heating, Refrigerating, and Air-Conditioning Engineers) Standard 97-1989, "Sealed Glass Tube Method to Test the Chemical Stability of Material for Use Within Refrigerant Systems" ***[1]***.

The initial results of one accelerated thermal analytical candidate, differential thermal analysis, are presented for CFC-12/mineral oil and HCFC-22/mineral oil combinations.

Also described is the research which will be performed during the first three months of Part II to optimize the selected candidate for development into an accelerated screening test.

<u>SCOPE</u>

This report describes the research performed during Part I 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 October 15, 1992 to January 15, 1993. The literature search described in this report was performed to identify analytical techniques for development into accelerated compatibility tests. The candidate techniques will be evaluated in Part II of the MCLR Project Number 655-51500 to be performed from January 15, 1993 to February 15, 1994.

SIGNIFICANT RESULTS

TASK 1- LITERATURE SEARCH

A literature search was performed to identify the analytical techniques suitable for development into accelerated chemical and thermal stability tests for screening refrigerant/lubricant combinations. The majority of the literature search was computer-aided and focused on several databases, e.g., Chemical Abstracts, Defense Technical Information Center, Engineering Abstracts, etc. The key words used by the computer search included: refrigerant (CFC-12, HCFC-22, HFC-134a, E-134 and their chemical names), lubricant, oil, chemical stability, thermal stability, compatibility tests, thermal analysis, high pressure sealed-tube tests, and liquid-gas systems.

In addition to the computer search, published searches such as the NTIS® Alert (National Technical Information Service) were searched weekly for recently published government reports of interest to this research. Current Contents® (Institute for Scientific Information®, Inc.) was also searched weekly to identify articles published during the past three months in pertinent journals, e.g., Analytical Chemistry, Analytica Chimica Acta, ASHRAE Transactions, International Journal of Refrigeration, Journal of Thermal Analysis, Lubrication Engineering, Thermal Decomposition, etc.

The literature search also obtained the published proceedings of recent American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) Meetings and Technology Conferences. The literature search also included Chapter 6 (Refrigerant System Chemistry) of the 1990 ASHRAE Handbook. The literature search was completed by obtaining the ARTI Refrigerant Database which contains unpublished presentations, MCLR progress reports, etc. This database was printed and searched manually to ensure identification of all the pertinent articles contained in the database.

TASK 2 - DOCUMENTATION

As the identified journal articles, scientific reports, presentations, etc. were received, they were categorized into three main areas:

(1) Non-chlorine Containing Refrigerant (e.g., HFC-134a) Analyses
(2) Chlorine Containing Refrigerant (e.g., CFC-12 and HCFC-22) Analyses
(3) Accelerated Thermal Analytical Techniques

An abstract containing information pertinent to this research project was prepared for each obtained article or report for presentation in the Bibliography. Articles or reports which were identified but did not pertain to this research project are listed in Appendix A.

The information derived from the sealed tube tests and analyses of chlorine (CFC-12 and HCFC-22) and non-chlorine (HFC-134a) containing refrigerants, described in Sections 1 and 2 of the Bibliography, respectively, will be used primarily in Part II of the research program. The reported refrigerant data will be used to evaluate the accuracy of the stability rankings determined by the developed screening test for current and candidate refrigerant/lubricant combinations: The information in Sections 1 and 2 of the Bibliography will also be used to design the developed screening test, e.g., metal catalysts, degradation products of refrigerants and lubricants to be monitored, temperatures, constituent contaminants in new refrigerants and lubricants, etc.

The information derived from the accelerated thermal analytical techniques described in Section 3 of the Bibliography was used in Part I of this research program to identify and initially evaluate candidates for development into chemical and thermal stability tests for refrigerant/lubricant combinations.

TASK 3 - METHOD PROPOSAL

To evaluate the identified analytical techniques (Section 3 of Bibliography) for development into an accelerated compatibility test for different refrigerant/lubricant combinations, the most important requirement was that the candidate test produce stability rankings which correlate with the rankings determined by the current compatibility test ANSI/ASHRAE Standard 97-1989 ***[1]***. The evaluation criteria listed in Table 1 were also used to rank the identified techniques.

Table 1
Evaluation Criteria for Candidate Compatibility Tests

- Is commercially available, common to most laboratories or easily constructed
- Requires small amounts of refrigerant and lubricant
- Employs metal catalysts similar to ANSI/ASHRAE Standard 97-1989
- Allows incorporation of various construction materials, additives, etc.
- Reduces safety hazards of ASHRAE Standard 97-1989
- Uses temperatures which accelerate, without altering, degradation mechanisms
- Is easy to operate and gives reproducible results
- Provides continuous monitoring of degradation process
- Incorporates quantitative methods for measuring degradation which are independent of the chlorine content of the refrigerant and which allow degradation products and mechanisms to be identified

The techniques identified during the literature search with the most potential for development into accelerated compatibility tests- were thermal analytical techniques. The majority o. the identified thermal analytical techniques (Section 3 of Bibliography) are designed to analyze single phase systems under minimal pressures, and consequently are not well suited for high pressure, two-phase systems such as refrigerant/lubricant combinations heated to 200°C (392°F).

The sample container of the thermal analytical technique must be a design that allows known quantities of refrigerant and lubricant to be combined for thermal aging in the presence of metal catalysts, construction materials, etc. Thermal analytical techniques such as high pressure-differential scanning calorimetry (HP-DSC) *[2]* heat a lubricant in an aluminum pan in a chamber under high pressure for thermal (nitrogen) or oxidative (oxygen) stability tests. Although HP-DSC is suitable for high pressure analyses, large quantities of refrigerant would need to be flushed through the system prior to filling the chamber with refrigerant gas and the aged refrigerant gas would be exhausted into the hood after analysis. Since the solubility of the refrigerant into the lubricant (solubility controls reaction rates between refrigerant/lubricant) and the toxicity of the refrigerant (before and after aging) may be unknown, the HP-DSC and similar thermal analytical techniques using high pressure chambers were deemed unsuitable for development into compatibility tests.

Of the sample containers identified during the literature search, the containers constructed from sealed glass tubes or miniature metal bombs with appropriate fittings were deemed the most suitable for refrigerant/lubricant compatibility studies.

In addition to the sealed glass tubes utilized by ANSI/ASHRAE Standard 97-1989 ***[1]*** a thermal analysis technique has been reported ***[3]*** which uses flat bottom, four millimeter diameter glass tubes. When sealed properly, the tubes can withstand internal pressures of 4560 kPa (45 atmospheres) and external temperatures over 500°C (932°F). The thermal analysis technique ***[3]*** monitors the temperatures (thermocouple in contact with flat bottom of tube) of the sealed glass tubes containing the sample and a reference material (thermally stable) during heating to detect the temperature (range) at which the sample undergoes thermal degradation or reaction. When the sample and reference tubes are initially heated isothermally or using a temperature ramp [e.g. 20°C(68°F)/minute from 25-400°C (77-752°F)], the temperatures of the sealed tubes remain very similar [±0.2°C(±0.4°F)]. When the temperature (ramped temperatures) or time (isothermal temperature) of the thermal analysis exceeds the stability of the sample, the sample undergoes degradation reactions. If the degradation reactions are exothermic, the sample tube temperature increases, and if the degradation reactions are endothermic, the sample tube temperature decreases, with respect to the reference tube temperature. If the sample does not undergo reaction in the temperature range of the thermal analysis, the plot of the ΔT (sample temperature minus reference temperature) versus temperature of the reference tube (Figure 1) is flat.

Thermograms showing the ΔT plotted versus temperature of the reference tube are shown in Figure 1 for theoretical exothermic and endothermic reactions. If multiple, successive reactions occur, the thermogram will contain multiple peaks occurring at different temperatures. If multiple, simultaneous reactions occur, the peaks will represent the sum of the reactions. Consequently, simultaneous exothermic and endothermic reactions will tend to cancel out producing one diminished peak.

Thermal analysis techniques which measure differences between sample and reference temperatures are referred to as differential thermal analytical (DTA) techniques. One important characteristic of the DTA technique is that the outside temperature of the sealed tube is measured. Consequently, thermocouples could be added to the walls of the aluminum block used

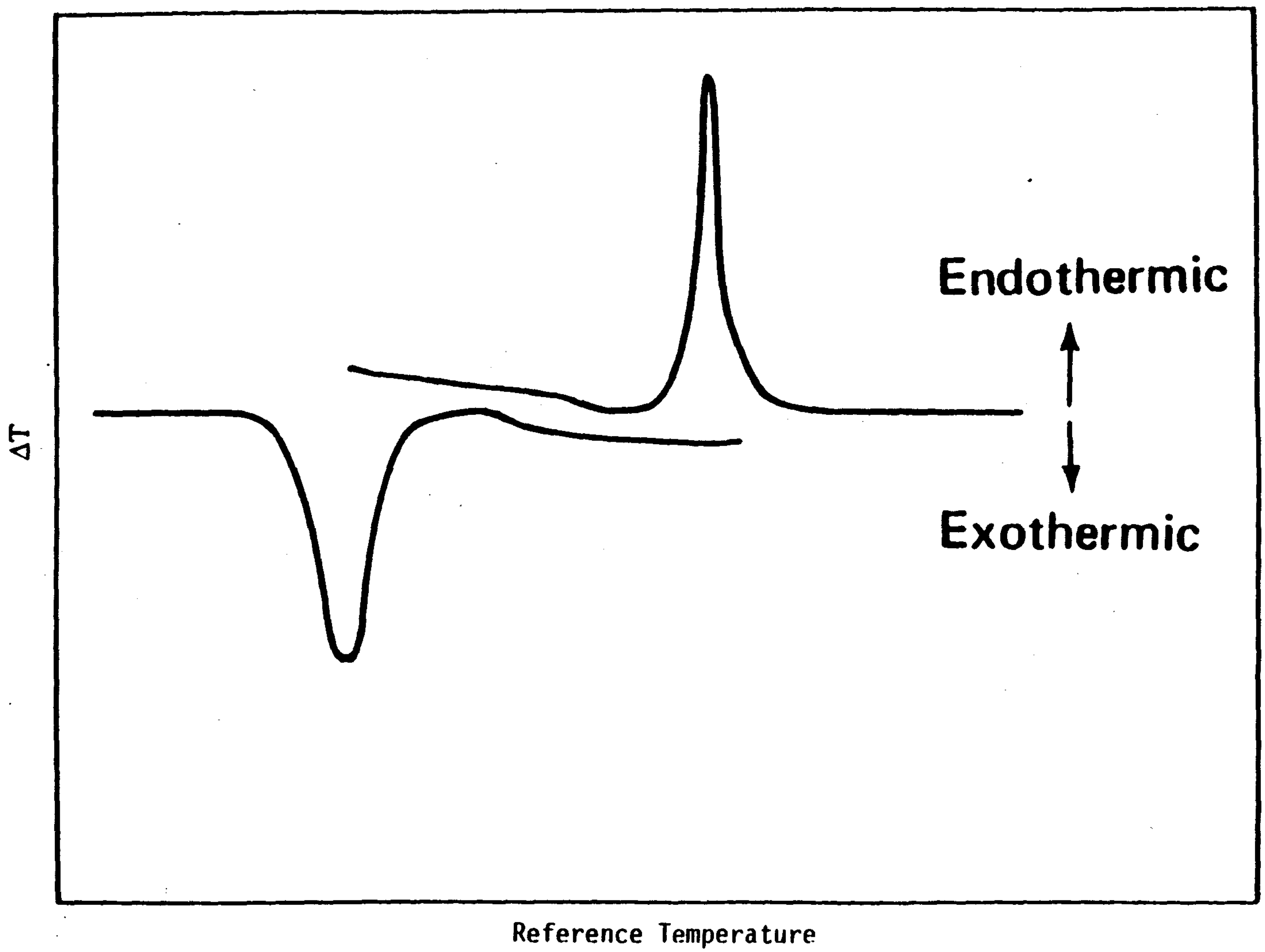

Figure 1. Theoretical DTA Thermogram Demonstrating Endothermic and Exothermic Reactions (ΔT = Sample Temperature - Reference Temperature).

to heat the sealed tubes of the ANSI/ASHRAE Standard 97-1989 *[1]* or other thermal analysis techniques to convert the methods into DTA techniques capable of simultaneously analyzing and comparing the stabilities of several different refrigerant/lubricant combinations. However, the heat transfer through the glass walls of the sealed glass tubes is slow, decreasing the sensitivity of the DTA technique to the low energy, multiple step degradation reactions of heated refrigerant/lubricant combinations.

One modification to improve the heat transfer of the sealed glass tube would be to incorporate a glass thermocouple well into the sealed glass tube. By making the walls of the thermocouple well thinner than the walls of the sealed tube, the heat transfer would be faster through the well's walls than the sealed tube walls. The thermocouples built into the heating block would slide up into the thermocouple wells as the sealed tube tests are inserted into the wells of the heating block. A modification to further reduce the poor heat transfer of the sealed glass tube would be to use miniature metal bombs with appropriate fittings. Although metal bombs would increase the sensitivity of the DTA technique, they would also greatly increase the cost and time of analysis while decreasing the ease of operation. Also, the interior walls of the metal bombs may be harder to clean than the interior walls of glass tubing making the results less reproducible.

The modification that would completely eliminate the poor heat transfer through the glass walls would be to seal the thermocouple and electrical leads (using glass-to-metals seals directly into the bottom of the glass tube. The process of sealing an electrical lead into the bottom of the glass tube would complicate and increase the cost of the production of the sealed tubes but would have little effect on the DTA technique. With the thermocouple directly in contact with the liquid phase, of the refrigerant/lubricant system, the DTA technique would be extremely sensitive to slow, low energy reactions.

The modification of sealing wires directly into the glass tubes also allows several different techniques to be used for detecting and monitoring the thermal reactions of refrigerant/lubricant combinations. Conductivity measurements could be made if two closely spaced wires were sealed into the glass tubes. The production of hydrochloric or hydrofluoric acid, fluorinated or chlorinated oil, polar organic compounds, etc. from degradation of the refrigerant/lubricant combinations *[4-6]* would be detected by conductivity measurements.

If two dissimilar, closely spaced wires (e.g., steel/copper or steel/aluminum employed as catalysts *[1, 4-6]*) were sealed into the glass tube, voltage production *[7- 9]* caused by interactions between the refrigerant/lubricant combination and metal surfaces could be used as a low cost, simple compatibility test. The voltage production technique has been estimated to be at least ten times more sensitive to thermal degradation than DTA techniques *[7]*. Applying a voltage to the dissimilar wire pair could be used to accelerate the interactions of the metal surfaces and refrigerant/lubricant combinations *[8]*. The dissimilar metals could also be inserted into construction materials to evaluate the effects of lubricant/refrigerant combinations on candidate elastomers, varnishes, etc. The thermal degradation of nylon has been studied using voltaic production between dissimilar metal plates *[9]*.

If multiple, closely spaced wires are sealed into the glass tubes, then DTA, conductivity, and voltage production techniques can be used in various combinations to improve the detection of different type reactions. For instance, if thermal degradation was endothermic and corrosion of metal surfaces by the produced acids was exothermic (temperature of the tube would remain fairly constant), the DTA would be insensitive, while the conductivity and voltage production techniques would be sensitive, to the degradation reactions. However, if thermal degradation occurred without corrosion or production of polar compounds, the DTA would be sensitive, while the conductivity and voltage production techniques would be insensitive, to the degradation reactions. The main disadvantage of multiple leads is the complex manufacture of the sealed tubes.

Although less practical and more expensive, in situ viscosity measurements using surface acoustic wavelength (SAW) devices *[10]* could be used to detect the lubricant degradation. It has been reported that the viscosity of a lubricant increases when aged in the presence of a refrigerant *[11]*. If coated with the correct polymer, the SAW devices could be situated in the gas or liquid phase of the sealed tube to detect degradation products common to all refrigerant/lubricant reactions, e.g., inorganic acids *[12]*.

TASK 4 . METHOD ASSESSMENT

Of the thermal analytical techniques discussed in Task 3, the DTA techniques which employ a sealed tube with a flat bottom or with a thermocouple well best meet the criteria listed in Table 1. Although the elimination of glass vessels would be desirable for safety purposes, the use of sealed glass tubes which are miniaturized with respect to the sealed tubes employed by ANSI/ASHRAE Standard 97-1989 *[1]* and the elimination of visual observations decrease the safety hazards of glass vessels.. Also, correlation between the accelerated thermal analytical technique and Standard 97-1989 results will be enhanced by employing sin-War sample encapsulation procedures.

To initially evaluate the capability of DTA techniques to evaluate the chemical and thermal stabilities of refrigerant/lubricant combinations, two flat bottom [4 millimeter (0.16 inches) in diameter, 2 centimeters (0.08 inches) in length] tubes were prepared as described in the literature ***[3]***. Using the procedure described in ANSI/ASHRAE Standard 97-1989, one tube was filled with equal amounts of CFC-12 and mineral oil [50 mg (0.0018 ounces) total] and the other tube was filled with equal amounts of HCFC-22 and mineral oil. The tubes were placed into the wells of a small (7.5 cm (3.0 inches) diameter and 7.5 cm (3.0 inches) height) aluminum heating block and heated at 10°C(50°F)/minute from room temperature to 200°C (392°F) (analysis time approximately 20 minutes). The produced DTA thermogram (ΔT = CFC-12 tube temperature-HCFC-22 tube temperature) is shown in Figure 2.

The thermogram in Figure 2 indicates that the CFC-12/oil combination is undergoing a temperature increase (exothermic reaction) with respect to the HCFC-22/oil combination. Although small, the temperature difference of 2°C(4°F) at 190°C(374°F) is much greater than the 0.2°C (0.4°F) difference (slight difference due to temperature imbalance between reference and sample tubes) obtained for a blank run performed with empty sealed tubes. It is interesting to note that temperature differences between the CFC-12/oil and HCFC-22/oil combinations were detected at temperatures below 150°C (302°F) indicating that accelerated thermal analytical techniques will not require extreme temperatures to evaluate different refrigerant/lubricant combinations. Finally, the thermogram in Figure 2 indicates that HCFC-22 is more stable than CFC-12 (i.e., CFC-12 reaction more exothermic than CFC-22 reaction) in the presence of mineral oil which is in agreement with the literature ***[4-6]***.

Due to the requirements for ease of operation, low cost, commercial availability, independence of refrigerant/lubricant composition, etc. and due to the results in Figure 2, the DTA technique with a flat bottom or thermocouple well was evaluated to have the most potential for development into an accelerated chemical and thermal stability test for refrigerant/lubricant mixtures.

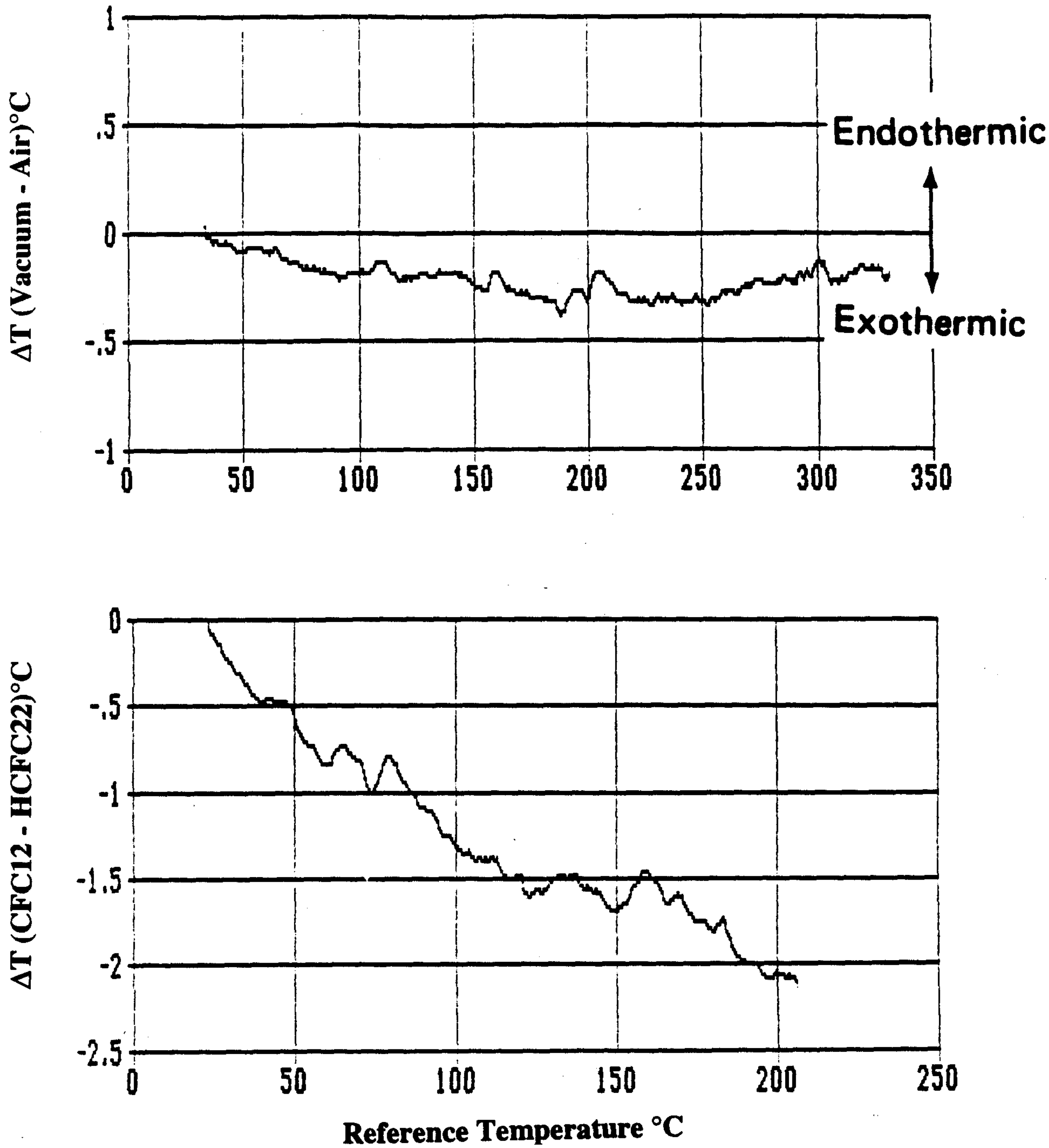

Figure 2. DTA Thermograms of Empty Sealed Tubes (Vacuum vs. Air) and Sealed Tubes Containing R- 12/Oil and R-22/Oil Combinations.

PROPOSED APPROACH of PART II

Two DTA techniques will be evaluated in Part II of this project. The first DTA technique will be highly accelerated and will be performed as described above. The aged glass tubes will be opened and analyzed for decomposition products by gas chromatography, for trace metals (if catalysts used) and silicon (from reaction with glass walls) in the residue, and color. The second DTA technique will be ANSI/ASHRAE Standard 97-1989 ***[1]*** in which the aluminum heating block will be fitted with thermocouples to monitor the sealed tube temperatures. The standard method will also be used to ensure correlation between the accelerated DTA and current compatibility tests. Information from the literature search will also be used in evaluating the DTA techniques. The sealed tubes will be opened and analyzed for degradation products as previously described. The refrigerant/lubricant combinations selected by the ARTI monitoring committee will be studied, with and without the presence of metal catalysts. Great care and pretest analyses will be employed to ensure the purity of the refrigerants and lubricants used during Part II.

If the DTA techniques are not sensitive to all of the proposed refrigerant/lubricant combinations, accelerated thermal analytical techniques which employ conductivity (similar wires) and voltaic (dissimilar wires) monitoring techniques will be evaluated. Again short-term, accelerated and longer-term (ANSI/ASHRAE Standard 97-1989 ***[1]***) thermal analytical techniques will be performed to evaluate the capabilities of conductivity and voltaic monitoring techniques for development into chemical and stability tests for refrigerant/lubricant mixtures.

Accelerated analytical techniques which employ sealed glass tubes incorporating thermocouples, SAW devices, *in situ* viscosity measurements, etc. and miniaturized metal bombs with proper fittings will be studied only if the initial two approaches fail to correlate with ANSI/ASHRAE Standard 97-1989.

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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 I of this research effort. Mr. Kauffman devoted 50% of his available work hours on the project.

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ALTERNATIVE REFRIGERANTS

Carrier Corporation. *Sealed-Tube Stability Test Results: Alternative Refrigerants,* September 1989 (1 page with 1 table, ARTI database number RDB0020)

This report describes sealed tube tests of R-134a with mineral oils (Suniso 3GS and Mobil DTE 26) and alkyl benzene lubricants (Zerol 150 and 300). No R-134a decomposition was detected.

Carrier Corporation. *Polyglycol Sealed-Tube Tests,* September 1989 (1 page with 1 table, ARTI database number RDB0021)

This report describes sealed tube tests of R-12 and R-134a with two polyalkylene glycol lubricants (Nippon RS680 and Glygoyle 11). The R-134a was stable while the R-12 decomposed up to 90% in the presence of the polyalkylene glycol lubricants.

G. Doerr, D. Lambert, R. Schafer, and D. Steinke. *Stability and Compatibility Studies of R-245a, $CHF_2CF_2CH_2F$, A Potential Low-Pressure Refrigerant,* **Proceedings of the International CFC and Halon Alternatives Conference** (Washington, DC), Alliance for Responsible CFC Policy, Arlington, VA, pp. 147-152, September 1992. (6 pages with 1 figure and 4 tables. ARTI database number RDB2A10)

This report describes sealed tube tests of R-245a with various lubricants at 175°C for 500 hours. Decomposition of R-245a was not detected in the aged R-245a/lubricant combinations.

M. Fukuda, H. Tomizawa, M. Ohta, and H. Osaka. *Esters as Lubricants for a Haloalkane Refrigerant,* **Europe Patent Application,** 1991

This patent describes the development of ester-based lubricating oils for use with R-134a. Of interest to this project are the refrigerant stability tests performed by adding the ester candidates and R-134a in a 2:1 ratio into an autoclave. Steel-aluminum-copper catalysts were added to the R-134a/ester mixtures and the mixtures were heated at 175°C for 20 days. Copper plating and acid number were used to evaluate degradation of the R-134a/ester mixture. Sealed glass tubes were also prepared containing a 1:1 ratio of R-134a/ester and steel-aluminum-copper catalysts. After 14 days at 175°C, the sealed tubes were visually inspected for color change and copper plating. Although the autoclave method ranked the stability of the R-134a/ester combinations in the same order as the sealed tube tests, the autoclave method was a more severe test and was able to rank the more stable oils which passed the sealed tube tests.

D. L. Harmon, W. J. Rhodes, and L. Weitzman. *Mobile Air Conditioner Refrigerant Evaluation,* Government Report Announce Index (US) 1989, Vol 89, No. 22, Report EPA/600/D-89/064, AEERL-P-527; 1989

This report describes research to determine the contaminants present in used R-12 samples removed from operating and failed automotive air conditioners. The used R-12 samples were tested for water content, acidity, residue quantity, refrigerant decomposition, and inorganic chlorides and fluorides. Of the 227 samples obtained and analyzed, only water and residue (lubricating oil) contents exceeded new refrigerant levels. The information described in this report was used in the development of recycling programs for used R-12 supplies obtained from automotive air conditioners.

D. F. Huttenlocker. *Chemical and Thermal Stability of Refrigerant-Lubricant Mixtures with Metals,* Report No. DOE/CE/23810-3B, Air-Conditioning and Refrigeration Technology Institute, Inc. (ARTI), July 1992. (64 pages with 37 figures and 24 tables - ARTI database number RDB2802)

This report describes sealed glass tube tests performed at 150, 175, and 200°C for R- 134a in the presence of valve steel catalysts and three different pentaerythritol esters. Gas chromatography, fluoride ion, total acid number, and infrared spectrometric analyses were used to evaluate the stabilities of the R-134a/lubricant combinations. The R-134a was stable at the temperatures tested and in the presence of the different ester lubricants. One of the ester lubricants decomposed by decarboxylation at 200°C.

J. G. Johnson. *R-134a, R-123, and Mineral Oil Compatibility with Steel, Aluminum, and Copper,* September 1990. (4 pages with 1 figure and 1 table - ARTI database number RDB0902)

This report describes sealed tube tests of R-134a/Suniso 4GS mineral oil at 175°C for 14 days in the presence of steel, copper, and aluminum catalyst. R-134a was much more stable than R-12 and R-500. R-123 was found to be unstable under the described conditions. Visual analyses and gas chromatography were used to evaluate the stabilities of the refrigerant/lubricant mixtures.

K. S. Sanvordenker. *Durability of HFC134a Compressors - The Role of the Lubricant,* **Proceedings of the 42nd Annual International Appliance Technical Conference,** University of Wisconsin, May 1991. (8 pages with 2 figures and 2 tables - ARTI database RDB2216)

This paper describes sealed tube tests of R-134a/lubricant combinations in the temperature range of 177-260°C with steel-copper-aluminum catalysts. It was reported that polyalkylene glycol lubricants were unstable in the 177-204°C sealed tube tests. It was also reported that the catalytic effect of steel on the decomposition of pentaerythritol ester type lubricants (204-260°C) could be inhibited by metal passivators.

K. S. Sanvordenker. *Materials Compatibility of R-134a in Refrigerant Systems,* **CFCs: Time of Transition**, ASHRAE Publication 90315, pp. 211-216, 1989.

This paper summarizes a wide range of compatibility research performed on R-134a. Of interest to this project are the sealed tube test results of R-134a with various types of soluble lubricants. Although no test results are presented, it is stated that if peroxides, acids, and other contaminants are removed from the lubricants prior to testing, the R-134a was found to be stable with numerous types of oils. (14 references)

H. O. Spauschus. *HFC 134a as a Substitute Refrigerant for CFC12*, **CFCs: Time of Transition**, ASHRAE Publication 90315, pp. 123-127, 1989.

This paper states that the thermal decomposition temperature of R-134a (above 1170°K) was well above the temperatures realized in refrigeration systems and compressors. Sealed tube tests performed at 175°C for 21 days in the presence of steel-copper-aluminum catalysts did not produce detectable amounts of R-134a degradation products. However, several lubricant candidates underwent significant decomposition. (20 references)

H. O. Spauschus, G. Freeman, and T. L. Starr. *Surface Analysis of Glass from Sealed Tubes After Aging with HFC-134a,* presentation charts, ASHRAE Annual Meeting, Baltimore, MD, June 1992. (21 pages with 7 figures and 2 tables - ARTI database number RDB2729)

This paper presents X-ray Photoelectron spectrometric results of glass (surface pieces and inner walls of sealed tubes) exposed to R-134a/lubricant mixtures at temperatures up to 200°C. The glass surfaces did not contain detectable amounts of fluorides (hydrofluoric acid attack). These results indicate that reactions did not occur between R-134a (and its reaction products) and the glass surfaces. Consequently, glass sealed tube tests appear to be suitable for stability testing of R- 134a/lubricant combinations.

CFC REFRIGERANTS

ANSI/ASHRAE 97-189. ASHRAE Standard. *Sealed Glass Tube Method to Test the Chemical Stability of Material for Use Within Refrigerant Systems,* **ASHRAE**, Atlanta, GA, 1989

This standard describes the sealed tube test used by most researchers. It describes the preparation of the sealed glass tubes, the procedure for charging the tubes with refrigerant, and the procedures for including metal catalysts or construction materials in the sealed tubes. The standard also describes methods for opening the aged sealed tubes for gas analysis. The standard also states that color, chloride analysis, gas chromatography, infra-red spectroscopy, and mass spectrometry have been used the most frequently for refrigerant/lubricant degradation determinations. (11 references)

ASHRAE Handbook. *Refrigeration Systems and Applications,* Chapter 6. Refrigerant System Chemistry, pp. 6.5-6.7, 1990

This review presents a comprehensive discussion of sealed tube tests performed on numerous refrigerant/lubricant combinations. The chemical stability of CFC and HCFC refrigerants in the presence of oil increased in the order of: R-11, R-12, R-13, R-14, R-113, R-114, and R-115. Review discusses color, chloride ion, gas chromatography and copper plating as degradation measuring techniques. (34 references)

H. J. Borchardt. *New Findings Shed Light on Reactions of Fluorocarbon Refrigerants,* **Journal of Refrigeration and Air Conditioning**, Vol. 6, No. 2, pp 48-51, 1975

This paper reports findings in three main areas. Pyrolysis reactions of R-11, R-12, R-13, R-22, R-114 and R-115 were studied by passing refrigerant gas through a hot platinum tube. Reported that in the absence of oil, R-22 has lowest thermal stability (maximum use temperature of 800°F). Also reported that thermal reaction between aluminum and R-12/oil mixture in sealed tube test was minimal until the oil was black and 2-3% R-12 had been decomposed to R-22. Stated that during sealed tube tests at 400°F for 5 days using steel/copper/aluminum catalysts, R-12/alkyl benzene oil mixtures unchanged in color, R-12/mineral oil mixture black. (7 references)

H. J. Borchardt. *Effect of Metals on the Reaction of Refrigerant 12 with* Oils, **ASHRAE Bulletin**, LO-73-5, 1973

This paper describes sealed tube tests performed at 400°F to study chemical reactions of R-12 with Suniso 3GS refrigerant grade oil in the presence of different metal catalysts. Color, R-12 to R-22 conversion (gas chromatographic analysis) and X-ray Photoelectron Spectroscopy were used to evaluate the effects of metals on the R-12/oil decomposition reaction. Steel (No. 1020 cold rolled) after three days accelerated the R-12/decomposition reaction. Aluminum (No. 1100) had minor effects and copper (soft annealed) had no effect on the R-12/decomposition reaction. Steel and aluminum pairs caused the most R-12 decomposition and copper containing pairs tended to be passivated due to copper coating of the other metals' surfaces. (11 references).

G. C. Doderer and H. O. Spauschus. A *Sealed Tube-Gas Chromatograph Method for Measuring Reaction of Refrigerant 12 with Oil,* **ASHRAE Transactions**,Vol. 72, No. 2, pp. IV 4.1 - IV 4.6, 1966

This paper describes a gas chromatographic technique to quantitate R-22 production by R-12/oil decomposition reaction during sealed tube tests. Sealed tube tests performed at 175°C for 14 days with valve steel catalyst showed color was unreliable for estimating degree of R-12 decomposition. The refrigerant oils in order of decreasing reactivity were: conventional pale oils > special pale oils and white oils with additives > white oils and highly refined pale oils. (6 references)

J. L. Glajch and W. G. Schindel. *Column Packing for On-Line GC Analysis of Fluorocarbons in the Presence of Reactive Gases,* **LC-GC**, Vol. 4 No. 6, 1986

This paper describes a gas chromatography column (60/80 mesh Carbopack B and Carbopack BHT- Supelco, Bellefonte, PA) capable of separating refrigerant mixtures into the individual components in the presence of hydrochloric and hydrofluoric acids. The refrigerants 12, 22, and 134a were among those studied. (6 references)

D. F. Huttenlocher. *Chemical and Thermal Stability of Refrigerant-Lubricant Mixtures with Metal,* MCLR Quarterly Report No. DOE/CE/23810-2B, March 1992

This report describes results for sealed tube tests at 105°, 150°, and 175°C for R-22, R-32, R-123, R-124, R-125, R-134a, and R-142b with mineral oil, alkyl benzene, and ester lubricants in the presence of valve steel. Except for the R-123/mineral oil combination which decomposed to form R-133a and R-143a, the tested refrigerant/lubricant mixtures were extremely stable. Gas chromatography and specific ion (chloride and fluoride) analyses were used to evaluate the stablilities of the refrigerant/lubricant mixtures. (no references)

R. E. Kauffman. *Sealed Tube Tests of Refrigerants from Field Systems Before and After Recycling,* ASHRAE Research Project 683-RP, Final Report, January 1993

This report describes results for sealed tube tests performed at 105° for R-11/lubricant combinations and at 175°C for R-12, R-22, and R-502/lubricant combinations. New and recycled refrigerants were aged in sealed tube tests. Results demonstrate that used refrigerants must be recycled prior to reuse to ensure the health of the charged system. Gas chromatography, trace metal analyses, color, and copper plating were used to evaluate the stabilities of the aged refrigerant/lubricant combinations. (11 references)

D. E. Kvalnes. *The Sealed Tube Test for Refrigeration Oils,* **ASHRAE Transactions,** Vol. 71, Part I, pp. 138-142, 1965

This paper describes results for a series of sealed tube tests performed by different groups. Describes various experimental parameters that may lead to inconsistent results. Sealed tube tests of R-12 run at 347°F for 8 and 16 days in presence of different metal catalysts. Presents a procedure to obtain uniform sealed tube tests. (12 references)

D. E. Kvalnes and H. M. Parmelee. *Behavior of Refrigerants 12 and 22 in Sealed-Tube Tests,* **Refrigeration Engineering**, Vol. 65, No. 11, pp. 40-42, 1957

This paper describes results from sealed tube tests of R-12 and R-22 at 250° and 300°F in the presence of various oils and oil additives. The paper reports that R-22 was more stable than R-12, and that significant R-22 decomposition (>0.04%) was only obtained after 450 days at 300°F. Oil additives such as hindered phenol antioxidants, tricresyl phosphate antiwear agent, and silicone antifoam agent did not affect refrigerant/lubricant stability. Water also had no effect on refrigerant/oil stability. Aluminum-copper-mild steel and copper-mild steel combinations were used in this study. (7 references)

K. Mall. *Studies on Aged Refrigerating-Machine Oils and Gaseous Reaction Products from Motor Compressors,* **Kaeltetechnik-Klimatisierung**, Vol. 23, No. 2, pp. 58-63, 1971

This paper describes analytical results using gas chromatograph-mass spectrometric analysis of gaseous products, pyrolysis gas chromatographic analysis of residues, and infrared spectrometric and acid number measurement analyses of used lubricating oils obtained from operating compressors. Significant amounts of oxygenated (CO, $C0_2$, acids, ketones, etc.) and dechlorinated (methane, ethane, R-23, R-32, etc.) compounds were detected in the used R-22/lubricant systems. (9 references)

H. M. Parmelee. *Sealed-Tube Stability Tests on Refrigeration Materials,* **ASHRAE Transactions**, Vol. 71, No. 1, pp. 154-161, 1965

This paper reports sealed tube tests of R-11, R-12, R-22, R-113, R-114, R-115, R-C318, R-124, R-216, and R-502 under a wide variety of test conditions. This paper reports that R-12 produces R-22, R-22 produces R-32, and R-115 produces R-125 during sealed tube tests. The stability of the refrigerants in the presence of naphthenic oil and copper/iron catalysts increases in the order R-11, R-113, R-114, R-12, R-22, R-115, and R-C318. Also reports that azeotropic refrigerants are slightly less stable than the constituent refrigerants. Of great importance to this work, it was reported that temperatures up to 450°F accelerated, but did not alter the degradation reactions of R-22/lubricant mixtures. The paper also reports that air accelerates, while water has little effect on the decomposition rates of R-12 and R-22/lubricant combinations. Aluminum/copper/steel combination was the most effective catalyst for refrigerant decomposition in the presence of oil. Copper oxides had both inhibitory and catalytic effects on refrigerant/lubricant degradation depending on the refrigerant and the method used to incorporate the copper oxide into the sealed tube test. Paper reports that antioxidants, tricresyl phosphate and other oil additives decrease the stability of the refrigerant/lubricant system. (4 references)

D. D. Rudy. *Correlation of Sealed-Tube Data for Freon® 22 and Freon® 12 Refrigerants,* FREON Products Laboratory Report No. KSS-6425, December 1968.

This report describes attempts to correlate sealed tube test results for R-12 and R-22/lubricant combinations between 250-450°F in the presence of aluminum/copper/steel catalysts. The reactions in the sealed tube tests were reported to be autocatalytic for both R-12 and R-22. The degradation mechanisms were found to be accelerated, but not altered, by temperatures up to 450°F. Equations were developed to correlate the decomposition rates of the R-12 and R-22/oil sealed tube tests with reaction time and temperature. (no references)

K. S. Sanvordenker. *Mechanism of Oil R-12 Reaction - The Role of Iron Catalyst in Glass Sealed Tubes,* **ASHRAE Transactions**, Vol. 91, No. 1A, pp. 356-363 (1985)

This paper describes results to study the effects of glass surfaces on the R-12/lubricant degradation mechanism. Infrared spectrometry was used to monitor the degradation products. The appearance of a gas (postulated to be SiF_4) with an infrared absorbance at 1030 cm^{-1} was used to indicate the participation of the glass surface in the R-12/lubricant reaction. An absorbance at 1680-1690 cm^{-1} (postulated to be an oil-iron complex) was recorded for the aged oil after the sealed tube tests were completed. The infrared spectrometric technique was also used to quantitate the production of R-22 for monitoring the R-12/lubricant reaction in the absence and presence of valve steel (participant not catalyst): to produce 1.7% of R-22 took 24 hours at 200°C in the presence of valve steel and 6 months in the absence of valve steel. (2 references)

H. O. Spauschus. *Factors Affecting Reliability of Hermetic Compressors,* **Proceedings of the Purdue Compressor Technical Conference**, July 21-23, 1982

This paper summarized work performed to evaluate refrigerant/lubricant combinations using sealed tube stability tests. The paper reports that the reaction rate is higher for R-12 than for R-22 and that the degradation mechanism is not affected by temperature up to 250°C. (5 references)

H. O. Spauschus and G. C. Doderer. *Reactions of Refrigerant 12 with Petroleum* Oils, **ASHRAE Transactions,** Vol. 3, No. 2, pp 65-69, 1961

This paper describes sealed tube tests of R-12/lubricant combinations at 175 and 200°C. Mass spectrometry was used to monitor the production of the degradation gases: R-22, hydrochloric acid, carbon dioxide and monoxide, methane, and hydrogen. Valve steel was used as a catalyst. A highly refined, white oil produced much lower degradation products than a medium refined naphthenic oil when in combination with R-12. (12 references)

H. O. Spauschus and G. C. Doderer. *Chemical Reactions of Refrigerant 22,* **ASHRAE Transactions**, Vol. 71, pp. 162-167, 1965

This paper describes sealed tube tests of R-22/lubricant combinations at 200° and 250°C in the presence of aluminum, copper, and steel catalysts. The degradation products were monitored by color, copper plating, gas chromatography, and mass spectrometry. The R-22/oil combination produced R-32, R-23, carbon monoxide and dioxide, methane, and hydrogen. The stability of the tested oils decreased in the order: white oil > n-undecane > pale oil. Effects of metals were reported to be independent of metal composition. The log of percent R-22 decomposed increased linearly with temperature up to 250°C. (12 references)

P. Srinivasan, S. Devotta, and F. A. Watson. *Thermal Stability of R-11, R-12B1, R-113 and R-114 and Their Compatibility with Some Lubricating Oils,* **Chemical Engineering Research Des**, Vol. 63, pp. 230-234, 1985

This paper reports sealed tube tests of R-11, R-12B1, R-113, and R-114 between 180-280°C in combination with naphthenic mineral oil, alkyl benzene oil, and polyalphaolefin based synthetic hydrocarbon oil in the presence of copper-steel catalysts. Viscosity measurements of the aged lubricants were correlated with the degree of refrigerant decomposition (gas chromatography). The refrigerants in order of increasing stability in the presence of oil were: R-12B1, R-11, R-113, and R-114. Mineral oil was reported to be less stable than alkyl benzene oil. The stability of the polyalphaolefin oil was dependent on the refrigerant. A flowing test which impinged refrigerant on a copper target heated to 350 to 450°C was also described. The stability rankings produced by the flowing test agreed with the stability rankings of the sealed tube tests.

W. O. Walker, S. L. Levy, and S. Rosen. *Stability of Mixtures of Refrigerants and Refrigerating* Oils, **ASHRAE Transactions**, Vol. 68, pp. 360-389, 1962

This paper reports sealed tube tests for R-11, R-12, R-22, R-113, R-114, R-114a, and R-500 in combination with naphthenic and paraffinic oils at 250° and 350°F. Metal catalyst combinations of copper-valve steel, copper-aluminum, steel-bronze, and copper-steel-aluminum were used in the sealed tube tests. Decomposition evaluations were made using color, viscosity change (visual), sediment, wall deposit, corrosion of metals, and copper plating. The effects of various contaminants on the refrigerant/lubricant decomposition reactions were studied. The presence of liquid water increased corrosion of the metal specimens and copper plating but had little effect on color and wall deposits. The presence of air increased the refrigerant/lubricant degradation as treasured by all of the evaluation techniques. Paraffinic oils were reported to be more stable than naphthenic oils. For increased color and copper plating, the steel-copper-aluminum combination had the largest effects, while for corrosion and wall deposits, the bronze-steel combination had the largest effects.

THERMAL ANALYSIS

R. Danforth, H. Krakauer, and J. Sturtevant. *Differential Calorimetry of Thermally Induced Processes in Solution,* **Review of Scientific Instrumentation**, Vol. 38, No. 4, pp 484-488, 1967

This paper describes a differential thermal analytical technique for small (1.7 mL) samples of solutions. The technique gains sensitivity to low-energy reactions by employing platinum cylinders sealed with gold. (12 references)

S. E. R. Hiscocks. *Liquid Encapsulation Technique for the Determination of Melt Vapor Pressures,* **Journal of Scientific Instrumentation**, Vol. 2, No. 5, pp 417-418, 1969

This paper describes a thermal analytical technique for determining the equilibrium vapor pressures above volatile melts. Modifications for allowing differential thermal analytical and visual analyses of the heated sample are described. (2 references)

C. Juhasz and J. L. Gil-Zambrano. *Spontaneous Electric Currents from Nylon Films,* **Journal of Physics D: Applied Physics**, Vol. 15, pp. 327-336, 1982

This paper describes differential thermal analytical and thermally stimulated discharge technique studies of nylon heated to 160°C. The results of the differential thermal analytical and thermally stimulated discharge techniques were in good agreement for the temperatures studied. A DuPont 900 differential thermal analyzer and simple electrical circuits were used to perform the described tests. (19 references)

D. A. Nissen and D. C. MacMillan. *Apparatus for the Measurement of the Physical Properties of Liquids at Elevated Temperature and Pressure,* **Review of Scientific Instrumentation,** Vol. 54, No. 7, pp. 861-867, 1983

This paper describes a thermal analytical technique which employs a harmonic oscillator to measure the viscosity, surface tension, and density of fluids in the 250-400°C range under elevated pressures (up to 1 MPa). The technique employs stainless steel tubes to contain the samples to be analyzed. (13 references)

A. V. Santoro, E. J. Barrett, and H. Hoyer. *Differential Thermal Analysis Studies of Chemical Systems in Sealed Cells,* **Journal of Thermal Analysis,** Vol. 2, No. 4, pp 461-468, 1970

This paper describes a technique for producing small sealed glass tubes for analysis on the DuPont Model 900 Differential Thermal Analyzer or other suitable instruments. The sealed tubes are reported to withstand pressures up to 45 atmospheres at temperatures up to 500°C. The sealed tubes can hold wires or thin slices of polymers, can hold up to 100 milligrams of material and the aged tubes can be broken open for post-test analysis with gas chromatography, mass spectrometry, infrared spectrometry, etc. (9 references)

W. W. Wendlandt. *Thermalvoltaic Detection. V. An Improved Apparatus,* **Thermochimica Acta**, Vol. 99, pp 49-53, 1986

This paper describes an improved apparatus for performing thermovoltaic detection analyses of thermal decomposition reactions for solid samples situated between dissimilar metal surfaces. The improved apparatus allows replacement of metal surfaces between analyses. Slower heating rates of 1-2°C/minute were used to improve the sharpness of the voltage peaks produced by the thermovoltaic analysis. (4 references)

W. W. Wendlandt. *The Development of Thermal Analysis Instrumentation 1955-1985,* **Thermochimica Acta**, Vol. 100, No. 1-22, 1986

This review paper describes the research performed during thirty years in the author's laboratory. The paper describes development and optimization of the following thermal analytical techniques: thermogravimetric analysis, differential thermal analysis, evolved gas detection and analysis, emission thermophotometry, thermovoltaic detection, electrical conductivity in high pressure-stainless steel vessels (withstand up to 170 atmospheres), and automated systems. (54 references)

W. W. Wendlandt. *Electrothermal Analysis: A Neglected Thermal Analysis Technique,* **Thermochimica Acta**, Vol. 72 No. 1-2, pp 1-9, 1992

This review paper describes thermal analytical techniques which employ d.c. or a.c. conductivity measurements between similar metal electrodes or thermovoltaic detection measurements between dissimilar metal electrodes. Sample holders that can withstand high pressures are described. The paper states that conductivity and thermovoltaic detection instruments measure signals in the 0.1-10 volt range and consequently are 10-100 times more sensitive and can be constructed from simpler, less expensive electronic components than other thermal analytical techniques which measure signals in the microvolt to millivolt range. (20 references)

H. Wohltjen and R. Dessy. *Surface Acoustic Wave Probe for Chemical Analysis. I. Introduction and Instrument Description,* **Analytical Chemistry**, Vol. 51, No. 9, pp. 1458-1464, August 1979

This paper describes the production and fundamental principles of the surface acoustic wave probe. Initial thermal studies performed with the surface acoustic probe are described. The capabilities of the surface acoustic wave probe to monitor pressure changes, changes in the molecular weight of the gas environment, and temperature changes are demonstrated.

H. Wohltjen and R. Dessy. *Surface Acoustic Wave Probe for Chemical Analysis. III. Thermomechanical Polymer Analyzer,* **Analytical Chemistry**, Vol. 51, No. 9, pp. 1470-1475, August 1979

This paper describes the capabilities of the surface acoustic wave probe to monitor thermomechanical properties of heated polymers. Polymers were clamped to the surface of the surface acoustic wave probe and heated from room temperature to 200°C. Changes in the thermomechanical properties of polyethylene terephthalate, polycarbonate, polysulfone, teflon, and acrylate polymer films versus temperature were successfully monitored. Speculation of using polymer films to convert the surface acoustic wave probe into a selective organic vapor sensor are also discussed.

APPENDIX A

ALTERNATIVE REFRIGERANTS

J. L. Boot. *Overview of Alternatives to Chlorofluorocarbons (CFCs) for Domestic Refrigerators and Freezers,* **International Journal of Refrigeration**, Vol. 13, No. 2, pp 100-105, 1990

H. J. Borchardt. *The Reaction of Fluorohydrocarbon Refrigerants with Refrigeration Machinery* Oils, **Ki, Kaeltetechnik-Kilmatisierung. Heiz**, Vol. 7, No. 9, pp 345-347, 1979

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S. Devolta and S. Gopichand. *Theoretical Assessments of HFC 134A and Alternatives to CFC12 as Working Fluids for Heat Pumps,* **Applied Energy**, Vol. 41, N4, pp 285-299, 1992

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C. J. Feldmanis. *Performance Evaluation of a Refrigeration Cycle with Non-Azeotropic Refrigerant Mixtures*, Air Force Wright Aeronautical Labs, Wright-Patterson AFB, OH, January 1987.

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APPENDIX B

CHEMICALS UTILIZED IN THE RESEARCH

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

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

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