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

Volume I

Final Report

Robert Kauffman

University of Dayton Research Institute
300 College Park
Dayton, Ohio 45469-0160

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ABSTRACT

The research reported herein was performed to develop an accelerated screening method for determining the chemical and thermal stabilities of refrigerant/lubricant mixtures. The developed screening method was designed to be safe and to produce accelerated stability rankings that are in agreement with the rankings determined by the current test, Sealed Glass Tube Method to Test the Chemical Stability of Material for Use Within Refrigerant Systems, ANSI/ASHRAE Method 97-1989 ***[1]***. The accelerated screening test developed was designed to be independent of refrigerant and lubricant compositions and to be used with a wide variety of construction materials. The studied refrigerants included CFC-11, CFC-12, HCFC-22, HFC-134a, and HFC-32/HFC-134a (zeotrope 30:70 by weight). The studied lubricants were selected from the chemical classes of mineral oil, alkylbenzene oil, polyglycols, and polyolesters.

The work reported herein was performed in three phases. In the first phase, previously identified thermal analytical techniques ***[2]*** were evaluated for development into an accelerated screening method for refrigerant/lubricant mixtures. The identified thermal analytical techniques used *in situ* measurements of color, temperature, or conductivity to monitor the degradation of the heated refrigerant/lubricant mixtures. The identified thermal analytical techniques also used catalysts such as ferric fluoride to accelerate the degradation of the heated refrigerant/lubricant mixtures. The thermal analytical technique employing *in situ* conductivity measurements was determined to be the most suitable for development into an accelerated screening method.

In the second phase of the research reported herein, glass sealed tubes were prepared with valve steel catalysts and refrigerant/oil mixtures as described in ANSI/ASHRAE Method 97-1989 ***[1]***. The sealed tubes were placed in aluminum blocks and heated in an oven for 14 days at 175°C (347°F) for the CFC-12 refrigerant/oil mixtures and for 28 days at 175°C (347°F) for the HCFC-22, HFC-134a, and HFC-32/HFC-134a refrigerant/oil mixtures.

In the third phase of the research reported herein, modified sealed tubes, with and without steel catalysts present, were used to perform *in situ* conductivity measurements on the refrigerant/lubricant mixtures. The sealed tubes were aged at 175°C (347°F) for up to one week (ANSI/ASHRAE Method 97-1989 uses two to four weeks) using a modified aluminum block containing heating cartridges. The *in situ* conductivity measurements were compared with the ANSI/ASHRAE Method 97-1989 degradation measurements, e.g., color measurements, gas

chromatography, and trace metals, to evaluate the capabilities of *in situ* conductivity measurements for determining the chemical and thermal stabilities of refrigerant/lubricant mixtures.

Other sets of tests were performed using ramped temperature conditions from 175°C (347°F) to 205°C (401°F) to evaluate the capabilities of *in situ* conductivity measurements for detecting the onset of rapid degradation (i.e., thermal breakpoint) of different CFC-12, HCFC-22 and HFC-134a refrigerant/oil mixtures aged with and without steel catalysts present.

Additional sets of tests were performed using isothermal conditions of 175°C (347°F) for one week to evaluate the capabilities of *in situ* conductivity measurements for studying the effects of additives on the chemical and thermal stabilities of HCFC-22 refrigerant/polyolester oil mixtures with steel catalysts present.

The results presented herein demonstrate that *in situ* conductivity stability evaluations are in some agreement with those of ANSI/ASHRAE Method 97-1989 and are very useful in screening refrigerant/oil mixtures of unknown stabilities by detecting unstable mixtures prior to tube explosions. The *in situ* conductivity measurements may be more sensitive to degradation than traditional measurements and are capable of detecting degradation rate changes during extended aging tests. However, the *in situ* conductivity tests should be regarded as a supplement, not a replacement, of ANSI/ASHRAE Method 97-1989 until further testing and correlation studies are performed.

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 15, 1994. 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 ***[2]*** of the MCLR Project Number 655-51500 performed from October 15, 1992 to January 15, 1993.

SIGNIFICANT RESULTS

INTRODUCTION

The research reported herein was performed to develop an accelerated screening test for determining the chemical and thermal stabilities of refrigerant/lubricant mixtures. The refrigerants selected for this study included CFC-11, CFC-12, HCFC-22, HFC-134a, and HFC-32/HFC-134a (zeotrope 30:70). The lubricants used in this study were selected from the chemical classes of mineral oils, alkylbenzene oils, polyglycols, and polyolesters.

The most important feature of the developed accelerated test is that the stability rankings of the accelerated test must be in agreement with the stability rankings of the current stability test, Sealed Glass Tube Method to Test the Chemical Stability of Material for Use Within Refrigerant Systems, ANSI/ASHRAE Method 97-1989 ***[1]***. Other important features of the developed accelerated test include the following:

(1) Requires shorter aging times and equal or lower aging temperatures compared to ANSI/ASHRAE Method 97-1989

(2) Less hazardous than ANSI/ASHRAE Method 97-1989

(3) Performs stability rankings independent of refrigerant/lubricant mixture composition

(4) Easy and inexpensive to operate

(5) Small scale

(6) Incorporates commercially available equipment

(7) Allows testing of a wide variety of refrigerant system construction materials

(8) More sensitive to degradation of high stability refrigerant/lubricant mixtures than ANSI/ASHRAE Method 97-1989

During Part I of this research program ***[2]***, thermal analytical techniques were identified that met most or all of the important features listed above. Prior to evaluation, all of the identified techniques were modified to incorporate containers capable of withstanding the high pressures and temperatures involved in aging refrigerant/lubricant mixtures. To improve the ease and cost of operation and to improve agreement with ANSI/ASHRAE Method 97-1989 ***[1]***, sealed glass tubes were selected instead of metal containers for the developed accelerated test. The safety factors involved in handling glass containers were reduced by employing *in situ* monitoring techniques to eliminate the handling of heated tubes and to make optional the breaking open of glass tubes for post test analyses of the aged mixtures.

The research was performed in three phases. In the first phase, the previously identified thermal analytical techniques ***[2]*** were optimized and evaluated for development into an accelerated screening test. In the second phase of research, the various refrigerant/lubricant mixtures were aged using ANSI/ASHRAE Method 97-1989 ***[1]*** to determine the stability rankings by the current test method. In the third phase of research, the various refrigerant/lubricant mixtures were aged with the optimized accelerated screening method to evaluate the method's capabilities for routine use with different refrigerant/lubricant mixtures. The results of the developed accelerated screening test (with and without a steel coupon) were then compared to those of the ANSI/ASHRAE Method 97-1989 ***[1]*** to evaluate the agreement between the stability rankings determined by the two methods.

The research described herein is organized into the three phases of research. Representative gas chromatograms of the aged refrigerant/lubricant mixtures are organized by refrigerant in Appendix A. The *in situ* measurements of the accelerated screening method are organized by refrigerant in Appendix B. The suppliers and brand names of the refrigerants and lubricants used in this study and the analytical results of the lubricants are listed in Appendix D. In Volume II of this report are listings of the data points (plotted in Appendix B) obtained from the *in situ* measurements for all the refrigerant/lubricant mixtures tested.

EVALUATION OF IDENTIFIED THERMAL ANALYSIS TECHNIQUES - PHASE I

Introduction

Four different thermal analytical techniques were studied during the first phase of research for development into an accelerated screening method 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), color measurements, catalyst additions (iron fluoride), and conductivity measurements to accelerate/monitor the degradation mechanisms. Analyses (gas chromatography - mass spectrometry) were performed to ensure the degradation mechanisms were not altered by the developed techniques in comparison to the ANSI/ASHRAE Method 97-1989. All of the studied thermal analytical techniques used sealed glass tubes instead of metal containers for lower cost of operation and improved ease of operation. The capabilities of the different analytical techniques were evaluated using CFC-11, CFC-12, and HCFC-22 refrigerants combined with naphthenic mineral oil and refrigerant HFC-134a combined with pentaerythritol ester oils, mixed acid and branched acid. The refrigerant/oil mixtures were heated for up to 7 days at 175°C (347°F).

Differential Thermal Analysis (DTA)

During Part I ***[2]*** of this project, a DTA technique was performed by placing sealed tubes into the wells of a heated, graphite block and measuring the temperatures of the tubes using thermocouples placed between the tubes and the walls of the heating block. The 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

To improve the temperature sensing capabilities of the DTA method for this research phase, 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 glass 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 modified sealed tube (Figure 1) was prepared with a thermocouple and 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.

Therefore, a second modified sealed tube (Figure 1) 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 temperature difference between the block and sealed tube containing CFC-12/mineral oil never exceeded 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 (from ASTM color < 0.5 to ASTM color = 1.0) during the test indicating that slight degradation had occurred.

MODIFIED SEALED GLASS TUBE

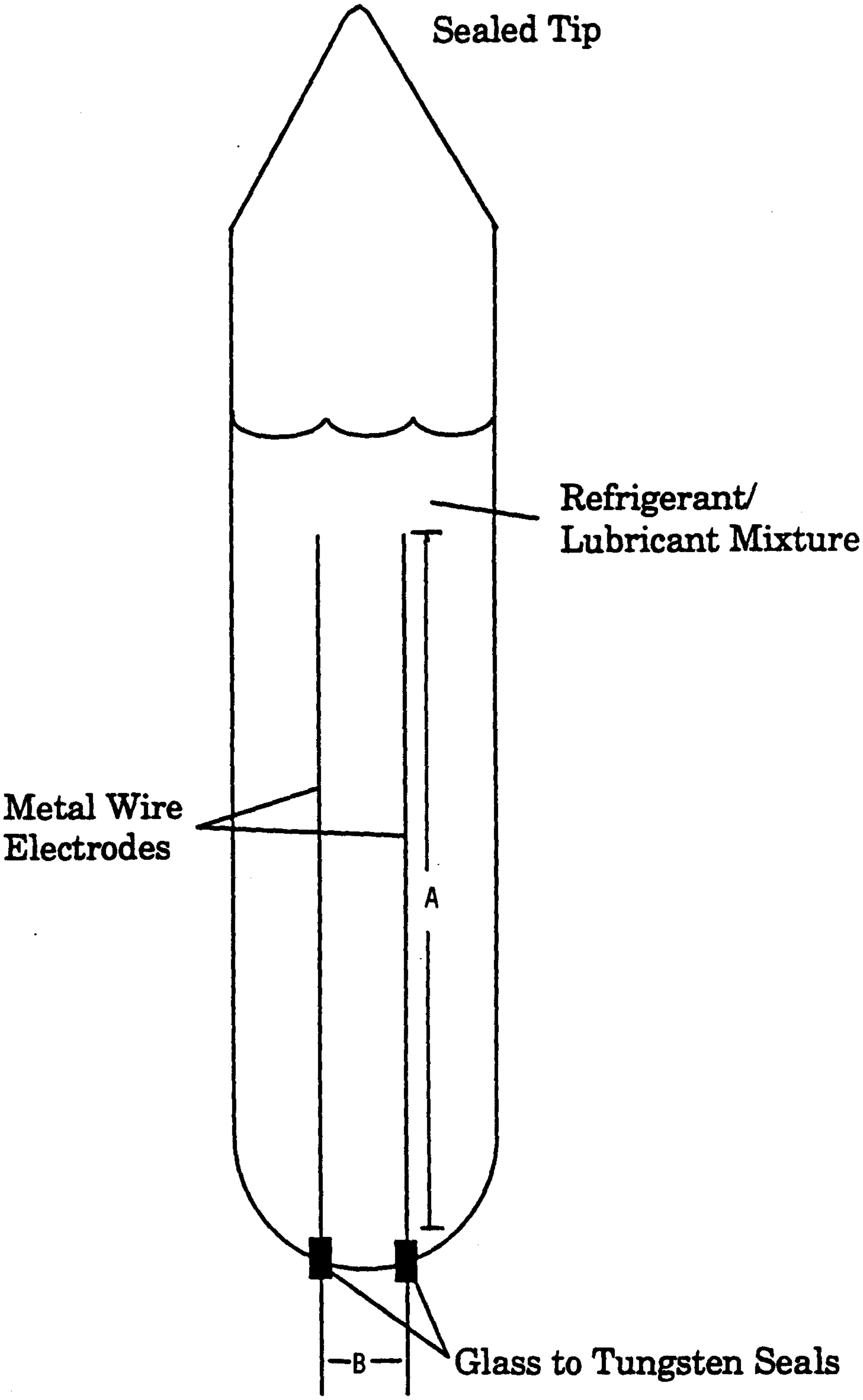


Figure 1. Schematic of Modified Sealed Glass Tube. Tube Dimensions [150 mm (l) x 9 mm (O.D.)] According to ANSI/ASHRAE Standard 97-1989. Wire Dimensions: Diameter = 0.5 mm, A = 10 mm, and B = 2 mm.

Since the CFC-12/mineral oil combination is expected to be more reactive than HCFC or HFC/oil combinations and insignificant temperature differences were measured for the CFC-12/mineral oil mixture, the initial test results indicated 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.

In Situ Color Measurements

Since the refrigerant/oil mixtures are heated in glass tubes and color is one of the degradation evaluation techniques most often used by ANSI/ASHRAE Standard 97-1989 ***[1]***, a short study was performed to evaluate *in situ* color measurements for development into an accelerated screening method. An aluminum block used to hold the glass tubes during heating was modified by drilling a 6.3 millimeter (0.25 inch) diameter bore perpendicular to, and intersecting with one of the wells used to hold the sealed glass tubes. To protect the light source and detector (entire visible spectrum monitored) from thermal stressing, the aluminum block was placed on a hot plate instead of inside an oven. A sealed glass tube containing a CFC-11/naphthenic mineral oil mixture was placed into the modified well of the heated aluminum block. The modified aluminum block was then placed onto a hot plate and heated to 175°C (347°F) [block temperature reached 175°C (347°F) in 30 minutes]. The amount of light reaching the detector decreased rapidly as the temperature reached 150°C (302°F). The sealed tube was removed and the refrigerant/oil mixture was inspected for color change. No color change was perceptible indicating the decrease in light transmission was most likely due to a change in the refractive index of the refrigerant/oil mixture caused by the increased temperature.

The tube was reinserted into the block and heated at 175°C for 1 hour. The light transmission remained constant (~70%) for the heating period indicating that the color of the refrigerant/oil mixture was unchanged. After 1 hour the tube was removed and reinspected for a color change. A perceptible color change had occurred (increased from below 0.5 to above 1.0), i.e., refrigerant/oil mixture degradation increased. Consequently, the *in situ* color measurement was insensitive to the initial refrigerant/oil degradation.

The experiment was repeated several times with different interference filters placed in front of the detector to select wavelength regions (400 to 450 nanometers: yellow) more susceptible to refrigerant/oil color changes. In all cases, the transmission was more dependent on temperature than on refrigerant/oil mixture color changes.

In addition to temperature dependence, the transmission of the tungsten light changed between experiments. Although double beam (sample beam and reference beam) set ups can be constructed to negate output fluctuation of light sources (and possibly refractive index changes), the associated electronics greatly increase the complexity of operation and the cost of the test equipment.

Consequently, the initial study indicated that the *in situ* color measurements were judged to be unsuited for development into an accelerated screening test.

Ferric Fluoride Additions

In an attempt to accelerate the refrigerant/lubricant degradation, a chemical catalyst was added to the sealed tubes in place of the valve steel coupons. Since all of the current and proposed refrigerants contain fluorine, ferric fluoride (which simulates hydrofluoric attack of steel surfaces) 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 (<0.05%) 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 since the inner walls of the glass tube were etched.

Consequently, the ferric fluoride catalyzed reactions appear to be more dependent on lubricant degradation than on refrigerant degradation, i.e., even though HCFC-22 is more stable than CFC-12, the HCFC-22 tubes underwent reactions similar to the CFC-12 tubes. However, 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. Further testing would be needed to quantitate the catalytic effect of ferric fluoride on lubricant degradation.

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 heated to 175°C (347°F).

Initial attempts to determine the conductivities (using ±1V, square wave, 60 thousand cycles per minute) of the refrigerant/oil mixtures failed due to the low conductivities of the mixtures and the small surface areas of the tungsten wires (Figure 1). Reducing the spacing between the tungsten wires or attaching electrodes with greater surfaces to the tungsten wires would increase the sensitivity of the *in situ* conductivity measurements. However, reducing the wire spacing or increasing the surface areas would decrease the reliability of the conductivity measurements and greatly increase the cost of producing modified sealed tubes.

Therefore, the voltage waveform applied to the tungsten electrodes was modified to improve the sensitivity of the conductivity measurements. Due to the low conductivity of the refrigerant/oil mixture, the voltage peaks were increased to 9V (dc - battery) or ±15V (ac - triangular waveform) to increase the current flow between the electrodes, and consequently, the sensitivity of the conductivity measurements. Reducing the cycle rate to less than 1 cycle per minute also improved the current flow between the electrodes. It is postulated that the slower cycle rate was required to allow movement of the ions between the electrodes situated in the low conductivity/relatively high viscosity mixtures of refrigerant and oil.

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. Sealed tubes containing CFC-12 and HCFC-22 refrigerant/oil mixtures and the iron wires were heated at 175°C (347°F) for 2 days. Although the sealed tubes reached 175°C (347°F) after 2 hours, the *in situ* conductivities, measured continuously, of the heated HCFC-22/mineral oil and CFC-12/mineral oil mixtures continued to increase for 4 and 12 hours, respectively. The conductivity of a tube containing just mineral oil increased during the 2 hour warm-up period and then became constant, i.e., no chemical reaction occurred. After the initial conductivity increases were complete, the *in situ* conductivities of the heated refrigerant/oil mixtures decreased with increasing time for the remainder of the aging time.

The conductivity increases indicated polar species (degradation products) were being produced by refrigerant/oil reactions caused by mixture instability, since the conductivity of heated oil remained constant. Whereas, the conductivity decreases indicate the produced polar species are being removed from solution through reactions with other polar species to produce nonpolar species, through reaction with solid surfaces such as the metal wires or glass surfaces, etc. Surface analyses of the iron wires were performed and high levels of chlorides were detected on the wires' surfaces indicating the conductivity decreases were at least in part caused by reaction species coating the iron wires.

Since the measured conductivities decreased with heating time (conductivity expected to increase due to increasing degradation) and the more stable HCFC-22/mineral oil underwent a larger conductivity increase than the less stable CFC-12/mineral oil, the conductivity measurements using iron wire combinations and a dc voltage did not appear to be suitable for development into an accelerated screening test.

To reduce the formation of coatings on the metal wires, 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) at a rate of 1V/second. The current (nanoamp range) was measured and recorded by a data logger interfaced to a microcomputer. 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. Plots of the current readings, which are proportional to conductivity, versus heating time at 175°C (347°F) for sealed tubes containing mixtures of CFC-11, CFC-12, and HCFC-22 refrigerant mixtures with naphthenic mineral oil are shown in Figure 2.

The *in situ* conductivity (current) versus heating time plots for the heated CFC-12/oil mixture in Figure 2 is fairly constant for the first 40 hours of heating indicating minimal refrigerant/lubricant/metal surface reactions. The small conductivity increase for the HCFC-22/oil mixture in comparison to the CFC-12/oil mixture in Figure 2 may be caused by the same reaction responsible for the temperature differences detected previously by DTA ***[1]***. In contrast to the CFC-12 and HCFC-22 mixtures, the current readings for the CFC-11/mineral oil mixture (Figure 2) 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.

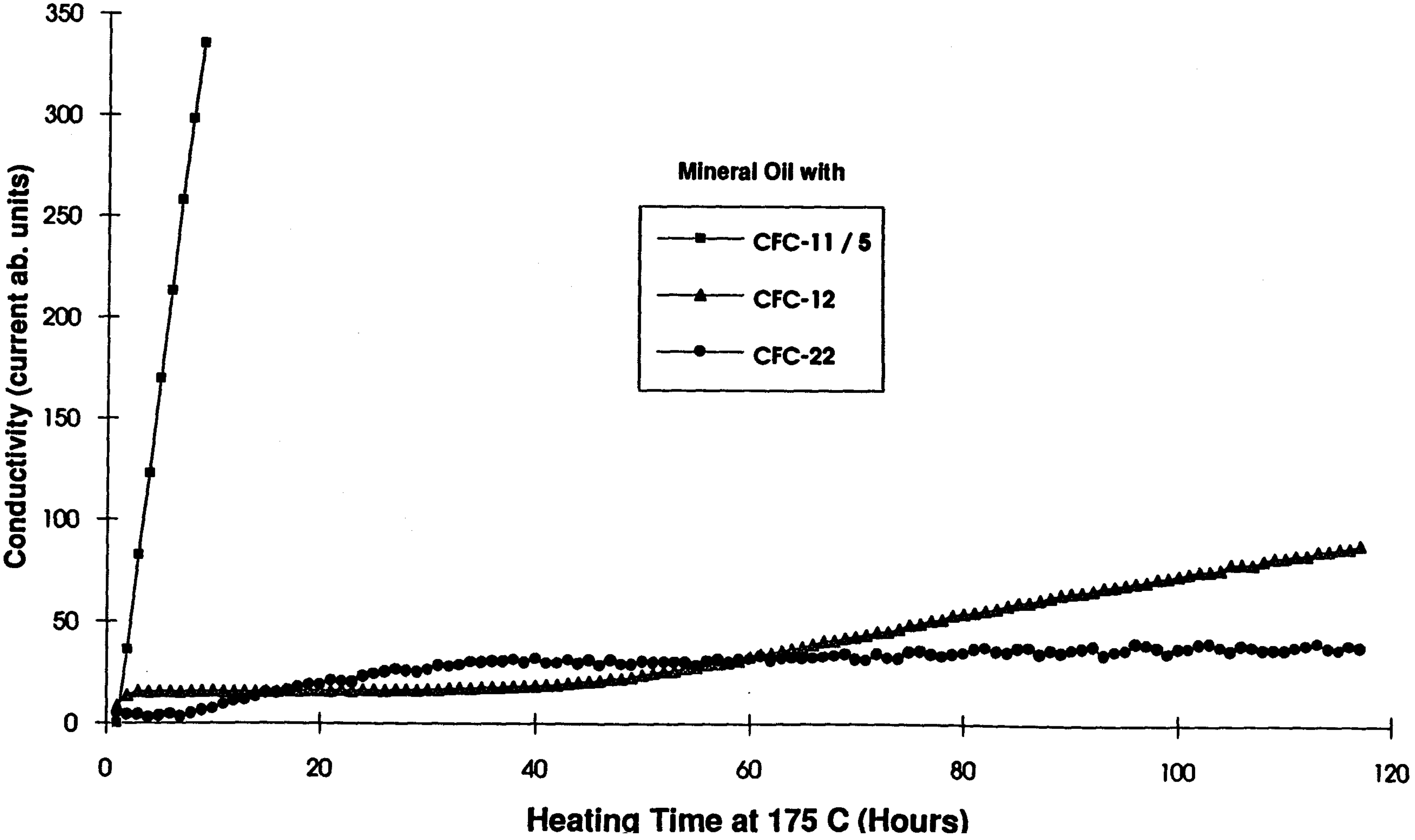


Figure 2. Current (Arbitrary Units) Versus Heating Time at 175°C (347°F) for Conductivity Measurements (Using Tungsten Posts and ±15V Waveform Generator) of CFC-11/Mineral Oil, CFC-12/Mineral Oil, and HCFC-22/Mineral Oil Mixtures in Modified Sealed Glass Tubes.

After 40 hours of heating, the current readings of the CFC-12/mineral oil mixture begin to increase at an accelerated rate (Figure 2). A similar acceleration in degradation has been previously reported for CFC-12/mineral oil mixtures ***[3]*** heated in sealed glass tubes. The *in situ* conductivity readings of the HCFC-22/mineral oil mixture remain constant up to 120 hours of heating at 175°C (347°F) (Figure 2). 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)

HCFC-22 > CFC- 12 >> CFC-11,

in full agreement with the literature ***[3,4]***. *In situ* conductivity readings (Figure 2) also provide time resolved degradation measurements allowing the tests to be stopped once degradation has accelerated (10 hours for CFC-11 and 100 hours for CFC-12) and allowing stable mixtures (HCFC-22) to continue undisturbed.

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)] sealed tubes in the presence of valve steel catalysts. The ASTM colors of the heated tubes, the concentrations of the volatile degradation products (calculations in Appendix C) and the trace metals in the residues of the CFC-12 and HCFC-22 sealed tubes are listed in Table 1.

The results 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 and trace metal concentrations 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 valve steel interactions (increased Fe concentration) and decrease the glass interactions (decreased Na concentration) with the refrigerant/mineral oil mixtures. The higher metal interactions (metal surface of valve steel coupon activated or kept residue free by voltage

Table 1

Experimental Results for Sealed Tube Tests [175°C (347°F) for 7 days With Valve Steel Catalysts] of CFC-12/Mineral Oil (1:1 By Weight) and HCFC-22/Mineral Oil (1:1 By Weight) Mixtures

Refrigerant	Tube Style	ASTM Color	% Increase of Volatile Degradation Products	Trace Metals in Residue (ppm) [f]	
				Fe	Na
CFC-12	ASHRAE Standard	1.0	0.06 [a]	2	0.7
	Modified [c] - Unmonitored [d]	1.0	0.09	3	3
	Modified [c] - Monitored [e]	2.0	0.4	7	1
HCFC-22	ASHRAE Standard	0.5	0.03 [b]	0.5	2
	Modified [c] - Unmonitored [d]	0.5	0.04	0.6	3
	Modified [c] - Monitored [e]	1.0	0.07	2	0.6

[a] HCFC-22 -- Main Degradation Product

[b] HFC-23, HFC-32 -- Main Degradation Products (Unresolved)

[c] As shown in Figure 1

[d] No power applied

[e] Continuously applied ±15V

[f] Fe from steel catalyst
Na from glass tube walls

waveform) would help explain why the monitored tubes in Table 1 produce more degradation products than the unmonitored tubes.

In Situ Conductivity Measurements of HFC-134a/Oil Mixtures

To further evaluate the potential of the *in situ* conductivity measurements for development into an accelerated screening method, modified sealed tubes (Figure 1) were prepared containing HFC-134a mixtures with three different ester based oils (branched acids 1 and 2 and mixed acid 2 in Appendix D). The oils were used as received (without prior drying or other purification). The oils were used as received since the research was more concerned with test development than oil evaluation. A sample of one oil (branched acid 1) was allowed to sit on a window sill in a closed glass bottle for 24 hours prior to testing. The hydroperoxide content of the oil sample increased (0.05 to 0.8 mmoles of hydroperoxide/liter of oil) upon exposure to sunlight and is referred to as "branched acid 1 exposed" in Figure 3. The prepared tubes were placed into the wells of an aluminum block which was placed into an oven and heated at 175°C (347°F) for two days.

The *in situ* conductivity measurements of the four HFC-134a/oil mixtures were made continuously during the test using a different electronics board and data logger input/output pair for each heated tube. A triangular waveform (oscillating between ±15V) was applied to the tungsten posts (Figure 1) at a rate of 1V/second to make the *in situ* conductivity measurements. The current readings of each tube were averaged over one hour of heating by the data logger. The resulting conductivity (average current) measurements versus heating time at 175°C (347°F) plots for the different HFC-134a/oil mixtures are shown in Figure 3.

The conductivity measurement versus heating time at 175°C plots in Figure 3 indicate that the HFC-134a/oil mixtures (as received) are stable at 175°C (in agreement with literature ***[4]***). After small, rapid changes in the first ten hours of heating (block reaches 175°C after two hours of heating), the conductivity measurements of the aged HFC-134a/fresh oil mixtures decrease or increase 76 to 312 (arbitrary current units) during the remaining 40 hours of heating at 175°C (347°F). Increases in conductivity measurements (increases in polar species) indicate that the HFC-134a/oil mixture is undergoing increased degradation. Decreases in conductivity measurements indicate that the concentration of polar species in the HFC-134a/oil mixture is decreasing or that the surfaces of the electrodes are being coated by degradation species or other reactive species present in the HFC-134a/oil mixtures.

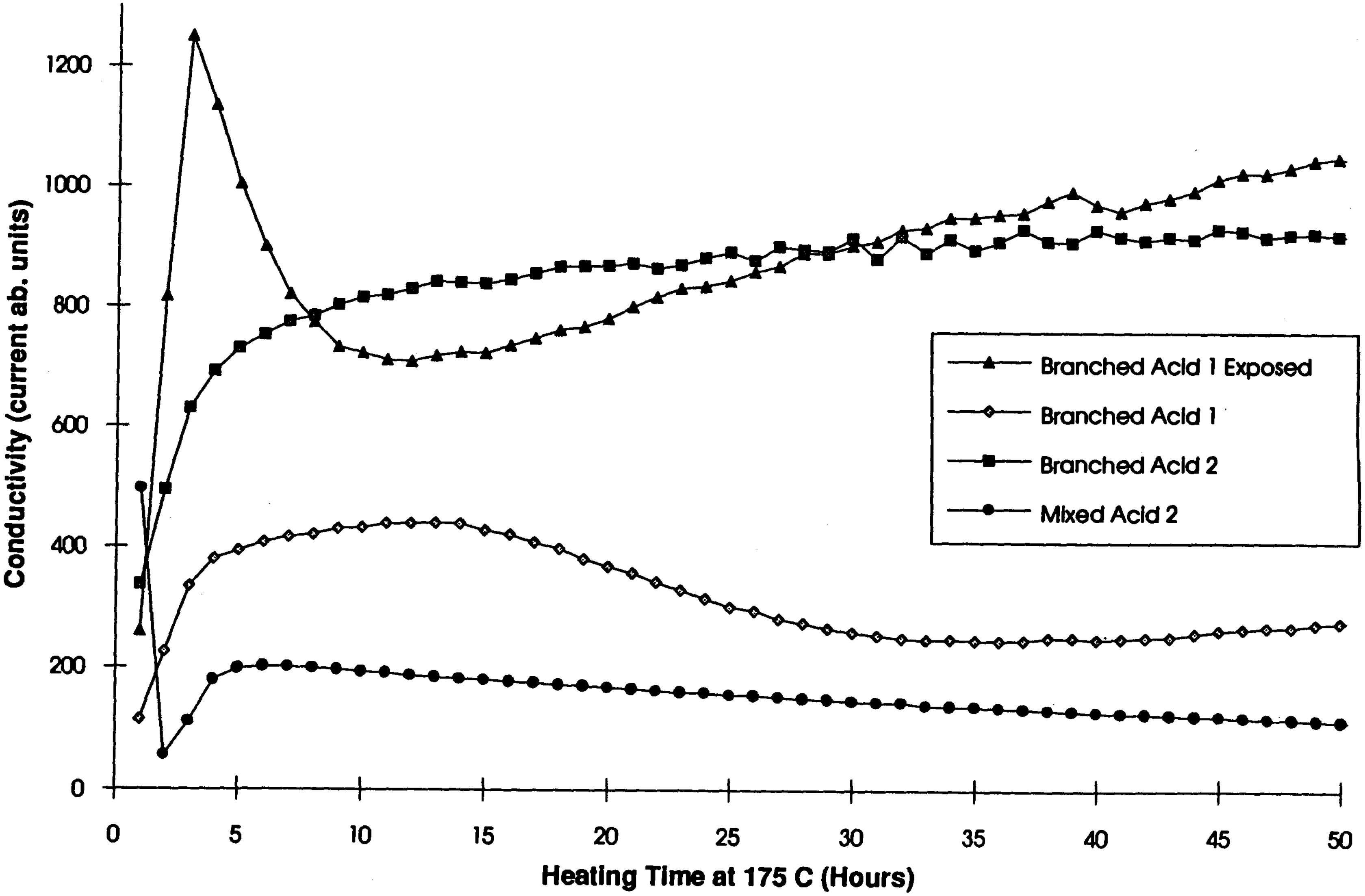


Figure 3. Plots of Conductivity Measurements (Current in Arbitrary Units) Versus Heating Time at 175°C (347°F) for HFC-134a/Ester Oil (Exposed and As Received) Mixtures Heated in Modified Sealed Glass Tubes (Figure 1).

In contrast to the as received ester oil mixtures, the conductivity of the exposed branched acid 1 oil mixture (Figure 3) increases dramatically during the first three hours of heating with HFC-134a, decreases during the next seven hours of heating, and then increases again during the remaining forty hours of heating at 175°C (347°F). The large conductivity changes in Figure 3 indicate that the exposed oil is less thermally stable (contains hydroperoxides which are free radical initiators) than the as received oil.

To better interpret the relationships between the conductivity changes and the degradation of the HFC-134a/oil mixtures, ASTM color and infrared spectrophotometric analyses of the aged oils (remaining in the opened sealed tubes) were performed and gas chromatographic analyses of the aged HFC-134a were performed. The results of the analytical tests for the aged HFC-134a and oils were compared with those of the unaged fluids to quantitate the degradation of the aged HFC-134a and oils.

The gas chromatograms of the unaged and aged HFC-134a refrigerants indicated that volatile degradation products of the HFC-134a were below detection limits (below 0.005 percent) in full agreement with the literature ***[4]***. The infrared spectra of the unaged and aged oils were identical (i.e., differences are smaller than experimental error) indicating that the nonvolatile degradation products are below the detection capabilities of the infrared spectrophotometer (in agreement with literature ***[4]***).

Of the analytical tests performed, only the ASTM color measurements detected degradation products in the aged oils with respect to the unaged oils (Table 2). The increase in color was greatest for the branched acid 1 oil and least for the branched acid 2 oil. For the branched acid 1 oil, the exposed oil showed greater increases in color during aging than the unexposed oil.

Comparison of the conductivity versus heating time plots in Figure 3 with the analytical results listed in Table 2 indicate that the conductivity changes that occur after the first ten hours of aging at 175°C (347°F) are related to the degradation evaluations made by the ASTM color measurements. Since the gas chromatographic analyses indicate that the HFC-134a had not undergone degradation, the conductivity increases are most likely related to degradation of the aged oils as detected by the color measurements. The dramatic conductivity changes that occur during the first ten hours of aging are most likely related to the metal wire (tungsten) surface-refrigerant-oil interactions, decomposition of reactive species in the unaged oil, and other short - term reactions that occur during the initial heating of the modified sealed tubes (Figure 1).

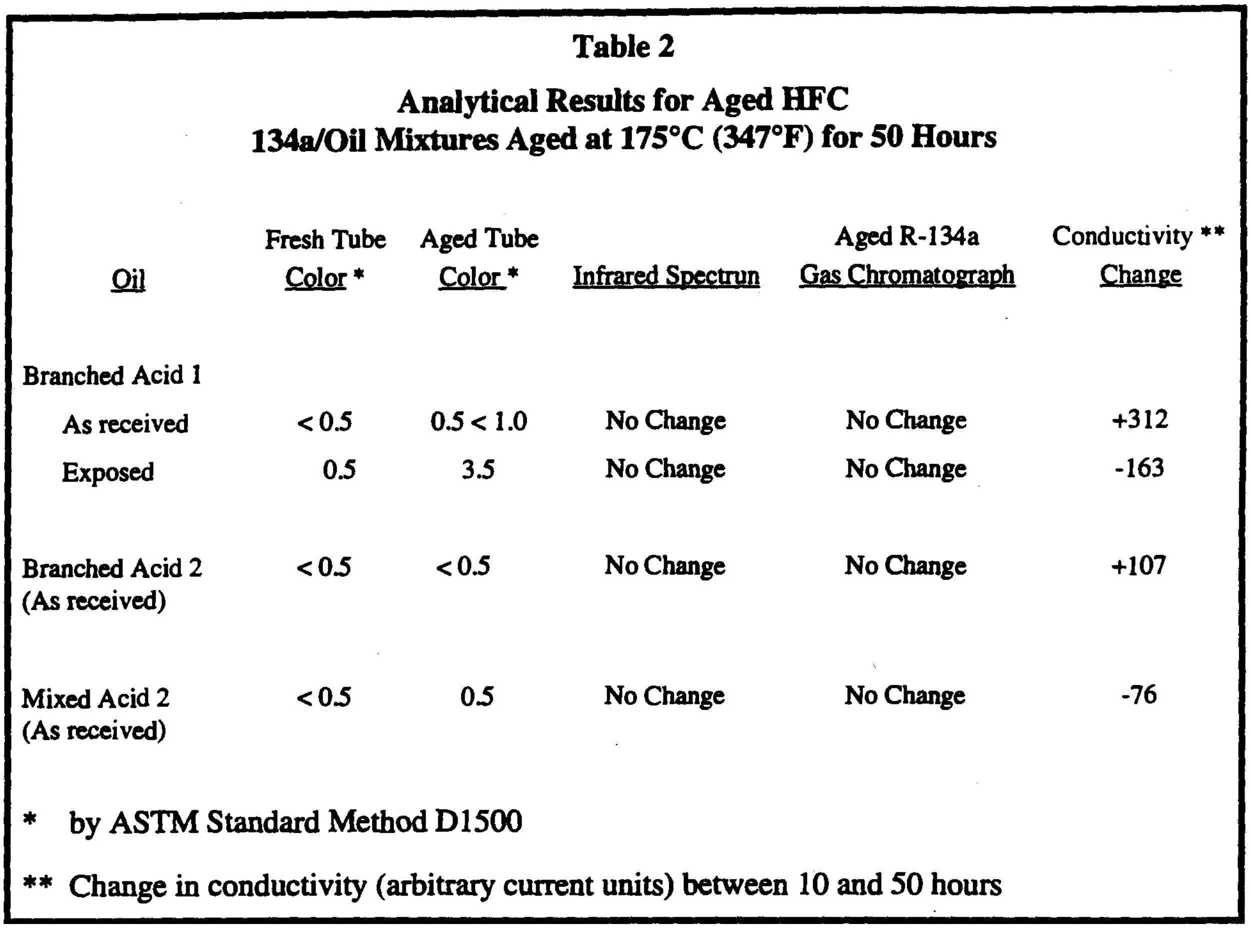


Table 2

Analytical Results for Aged HFC 134a/Oil Mixtures Aged at 175°C (347°F) for 50 Hours

Oil	Fresh Tube Color *	Aged Tube Color *	Infrared Spectrun	Aged R-134a Gas Chromatograph	Conductivity ** Change
Branched Acid 1					
As received	< 0.5	0.5 < 1.0	No Change	No Change	+312
Exposed	0.5	3.5	No Change	No Change	-163
Branched Acid 2 (As received)	< 0.5	< 0.5	No Change	No Change	+107
Mixed Acid 2 (As received)	< 0.5	0.5	No Change	No Change	-76

* by ASTM Standard Method D1500

** Change in conductivity (arbitrary current units) between 10 and 50 hours

Consequently, the relationship between degradation evaluation and the conductivity changes for the HFC-134a/ester oil mixtures (Figure 3) are not as straight forward as for the CFC-11, CFC-12, and HCFC-22 mixtures with naphthenic mineral oil, where refrigerant and oil degradations are reported to occur ***[3,4]***.

It is not known why mixed acid 2 ester oil after the first six hours of heating continually decreased in conductivity (Figure 3). However, unlike the other polyolesters, the mixed acid 2 ester oil contained phosphorous (Appendix D) indicating additives may affect the direction of the conductivity changes measured for refrigerant/lubricant mixtures.

In Situ Conductivity Measurement Dimensions

Traditionally, conductivity measurements are expressed in the terms of inverse resistance, i.e., ohms^{-1} or mhos. The conductivity measurement is made by applying a square voltage waveform (±lV) to two closely spaced calibrated square electrodes. For this research the conductivity is expressed in arbitrary current units since a triangular waveform (±15V) is applied to two closely spaced, uncalibrated tungsten wires. The reported current is equal to the average current (updated each hour) that flows between the wires at +15V and -15V. The current readings are made in arbitrary current units since the tungsten wires are uncalibrated. For current (I) readings of 10-1000 (10^{-10} amp range) in Figure 3, an approximate conductivity reading would be calculated as follows:

Conductivity (C) = 1/R : 1/C = R

V = IR = I/C

Since V=15, C=1/15

For a Current Reading of 10 in Figure 3: $C = \frac{10x10^{-10}}{15} = 6.7 \text{ x } 10^{-11} \text{ ohms}^{-1}$

For a Current Reading of 1000 in Figure 3: $C = \frac{1000x10^{-10}}{15} = 6.7 \text{ x } 10^{-9} \text{ ohms}^{-1}$

Summary

The initial results indicate that of the evaluated thermal analytical techniques, the *in situ* conductivity measurements have the best potential for development into an accelerated screening method for determining the chemical and thermal stabilities of CFC, HCFC, and HFC refrigerant mixtures with different lubricating oils. The addition of ferric fluoride to the sealed tube tests may be used to provide insight into the chemical stabilities of different lubricants. However, the ferric fluoride is unsuitable for refrigerant/lubricant stability evaluations. The *in situ* color measurements and DTA techniques would require complicated electronics and would provide stability rankings which are in poor agreement with rankings of the ANSI/ASHRAE Standard 97-1989 test.

ANSI/ASHRAE STANDARD 97-1989 AGING TESTS - PHASE 2

Introduction

One of the most important criteria of any accelerated screening test for refrigerant/lubricant mixtures is that the compatibility rankings of the developed accelerated screening test and ANSI/ASHRAE Standard 97-1989 test must be in good agreement. Therefore, the refrigerant/oil mixtures to be studied with the developed accelerated screening test were first aged using the ANSI/ASHRAE Standard 97-1989 test at 175°C (347°F) in the presence of a valve steel catalyst for two weeks (CFC-12 refrigerant/oil mixtures) or for four weeks [HCFC-22, HFC-134a, HFC-32/HFC-134a (30/70) refrigerant/oil mixtures]. The oils aged in this study were dried to less than 30 ppm moisture for the mineral oils and to less than 50 ppm moisture for the polypropylene glycols and polyolester (Appendix D). The dried oils were stored under dry nitrogen in amber glass bottles to inhibit degradation during storage. The ANSI/ASHRAE Standard 97-1989 test results (representative gas chromatograms in Appendix A and % volatile degradation product calculations in Appendix C) for the CFC-12, HCFC-22, HFC-134a, and HFC-32/HFC-134a (30/70) refrigerant mixtures aged with the various mineral, alkylbenzene, polypropylene glycol, and polyolester oils are listed in Tables 3-6, respectively.

CFC-12/Oil Mixtures

The results in Table 3 (degradation indicated by increases in color, volatile degradation products and trace metals) indicate that for CFC-12/oil mixtures, the compatibility rankings of mixtures decrease in the following order as identified by the oil:

Mineral Oils > Polyolesters >> Polypropylene glycols

The results in Table 3 also indicate that within each class of oil, there is a wide range of compatibility rankings for CFC-12/oil mixtures. For example, the CFC-12 refrigerant mixtures are much more stable with the mixed acid #1 and branched acid #2 polyolesters than with the mixed acid #2 and branched acid #1 polyolesters (Table 3). Since the polyolester oils contain varying amounts of different additives (Appendix D, Table D-2), the stability rankings within the polyolester class are more likely dependent on the basestock/additive combination stability than on the stability of the basestock alone.

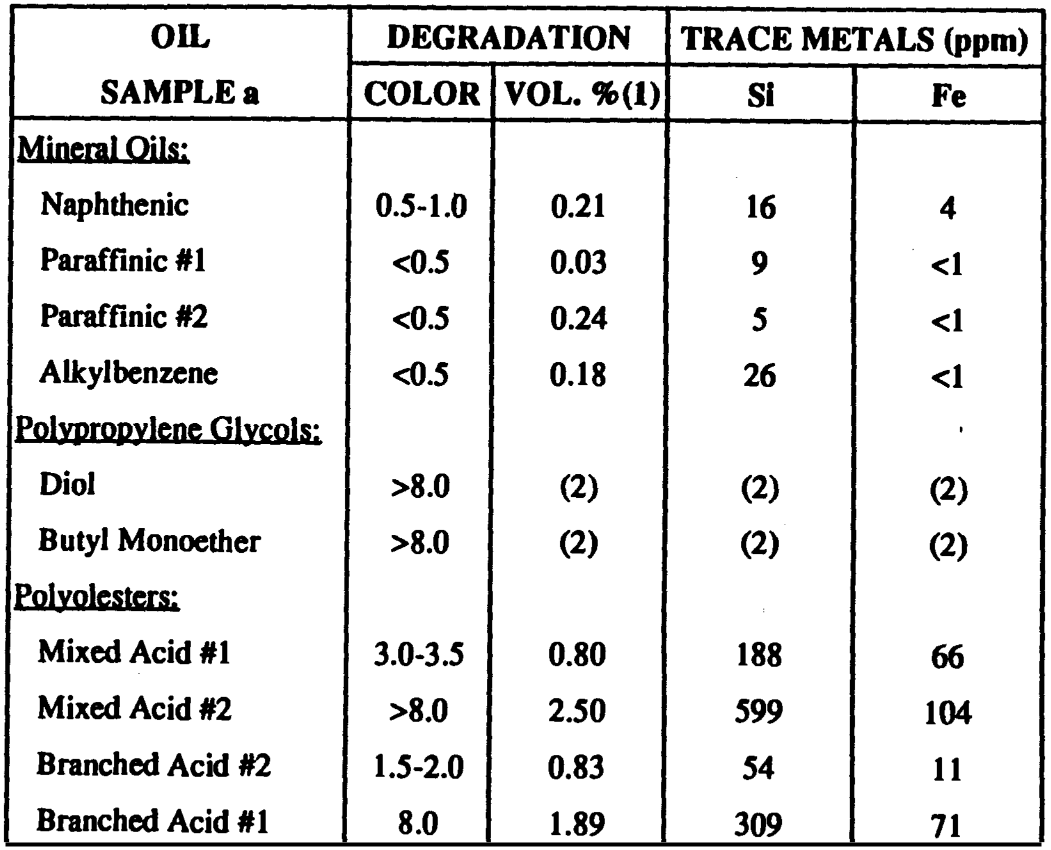
HCFC-22/Oil Mixtures

The color and volatile degradation product measurements in Table 4 indicate that the HCFC-22 refrigerant is more stable with the mineral and polyolester oils than the CFC-12 refrigerant (Table 3). Only mixed acid #2 and branched acid #1 polyolesters with HCFC-22 refrigerant produce detectable levels of degradation during aging at 175°C (347°F).

In contrast to the mineral and polyolester oils, the HCFC-22 refrigerant is unstable with the polypropylene glycols in Table 4 producing detectable levels of degradation during aging at 175°C (347°F). Although the color and degradation product measurements in Table 4 detect minimal levels of degradation in the aged refrigerant/oil mixtures, the trace metal analyses of the aged oils (remaining after removal of refrigerant for gas chromatographic analysis) detect differences in the mixtures' stabilities and degradation mechanisms. The silicon (hydrofluoric

TABLE 3

Color, Volatile Degradation Product, and Trace Metal Measurements for CFC-12 Refrigerant/Oil Mixtures (1:1 By Weight) Aged for Two Weeks at 175°C (347°F) with Valve Steel Catalysts According to ANSI/ASHRAE Standard 97-1989



OIL SAMPLE a	DEGRADATION		TRACE METALS (ppm)	
	COLOR	VOL. % (1)	Si	Fe
<u>Mineral Oils:</u>				
Naphthenic	0.5-1.0	0.21	16	4
Paraffinic #1	<0.5	0.03	9	<1
Paraffinic #2	<0.5	0.24	5	<1
Alkylbenzene	<0.5	0.18	26	<1
<u>Polypropylene Glycols:</u>				
Diol	>8.0	(2)	(2)	(2)
Butyl Monoether	>8.0	(2)	(2)	(2)
<u>Polyolesters:</u>				
Mixed Acid #1	3.0-3.5	0.80	188	66
Mixed Acid #2	>8.0	2.50	599	104
Branched Acid #2	1.5-2.0	0.83	54	11
Branched Acid #1	8.0	1.89	309	71

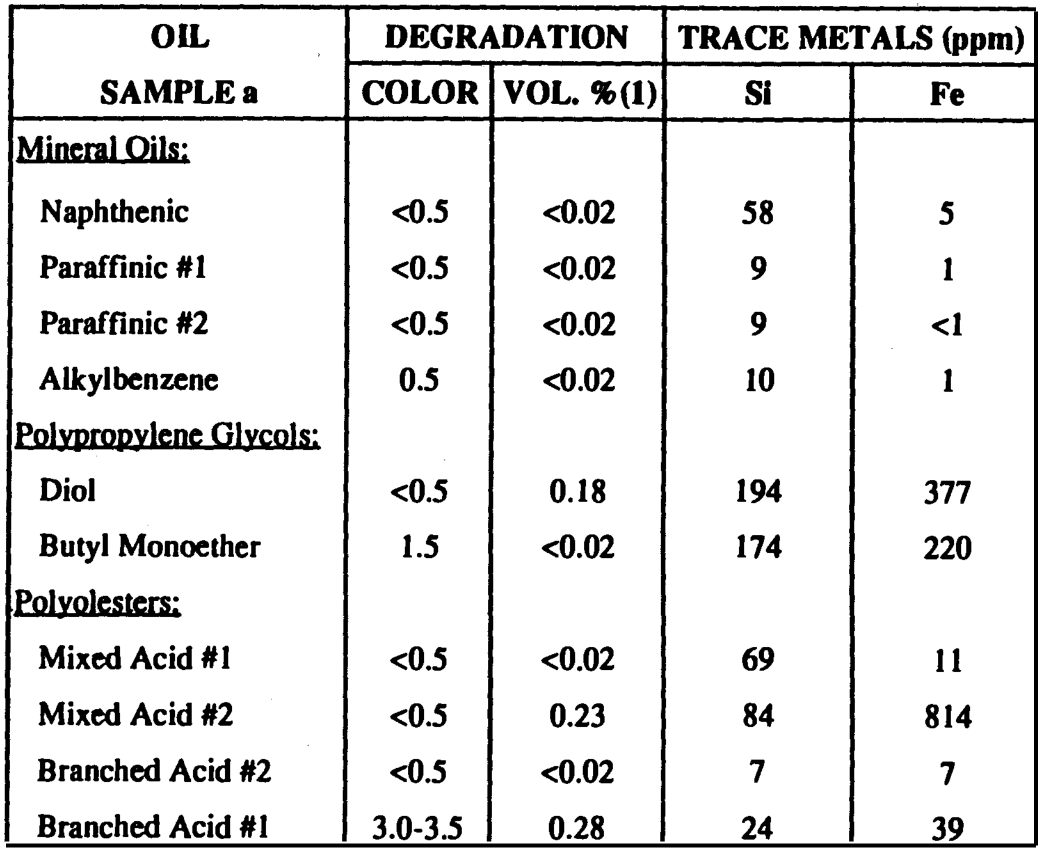
a All Oils Dried Prior to Use (Table D-2)

(1) % Volatile degradation product (HCFC-22) produced during aging.

(2) Solid mass, unable to analyze.

TABLE 4

Color, Volatile Degradation Product, and Trace Metal Measurements for HCFC-22 Refrigerant/Oil Mixtures (1:1 By Weight) Aged for Four Weeks at 175°C (347°F) with Valve Steel Catalysts According to ANSI/ASHRAE Standard 97-1989



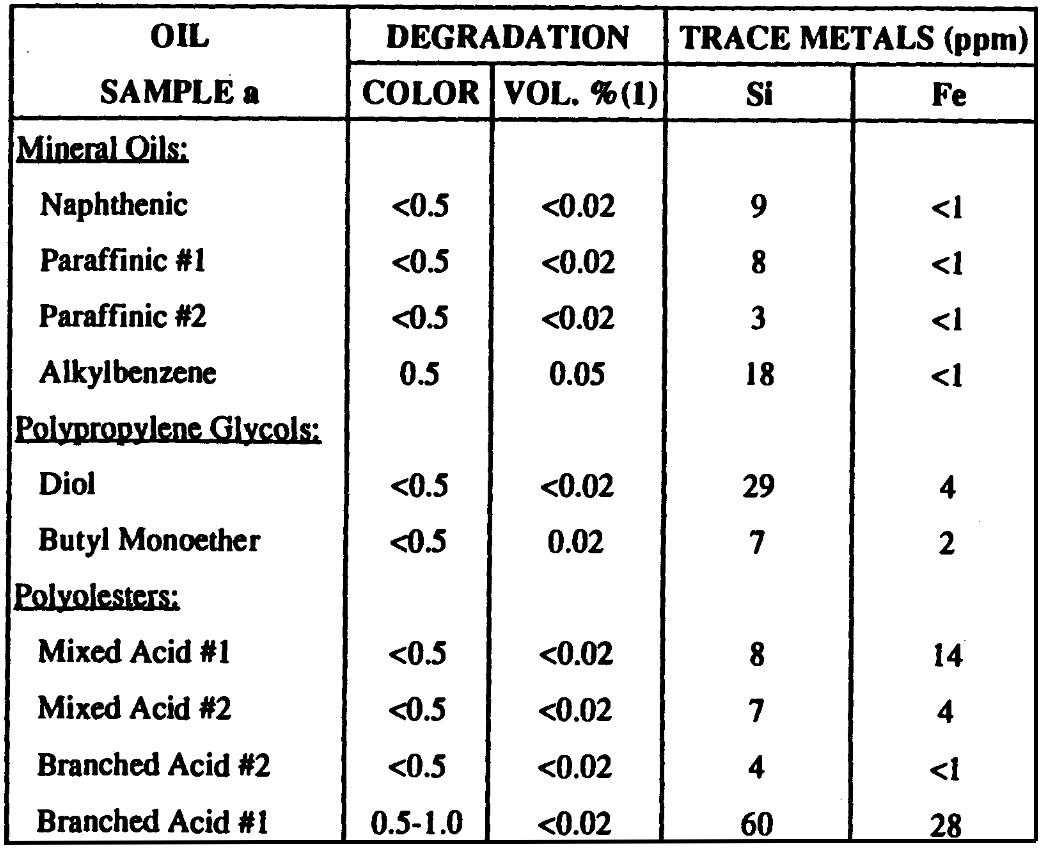
OIL SAMPLE a	DEGRADATION		TRACE METALS (ppm)	
	COLOR	VOL. %(1)	Si	Fe
<u>Mineral Oils:</u>				
Naphthenic	<0.5	<0.02	58	5
Paraffinic #1	<0.5	<0.02	9	1
Paraffinic #2	<0.5	<0.02	9	<1
Alkylbenzene	0.5	<0.02	10	1
<u>Polypropylene Glycols:</u>				
Diol	<0.5	0.18	194	377
Butyl Monoether	1.5	<0.02	174	220
<u>Polyolesters:</u>				
Mixed Acid #1	<0.5	<0.02	69	11
Mixed Acid #2	<0.5	0.23	84	814
Branched Acid #2	<0.5	<0.02	7	7
Branched Acid #1	3.0-3.5	0.28	24	39

a All Oils Dried Prior to Use (Table D-2).

(1) % Volatile degradation product (HFC-23 and HFC-32) produced during aging (Appendix A).

TABLE 5

Color, Volatile Degradation Product, and Trace Metal Measurements for HFC-134a Refrigerant/Oil Mixtures (1:1 By Weight) Aged for Four Weeks at 175°C (347°F) with Valve Steel Catalysts According to ANSI/ASHRAE Standard 97-1989



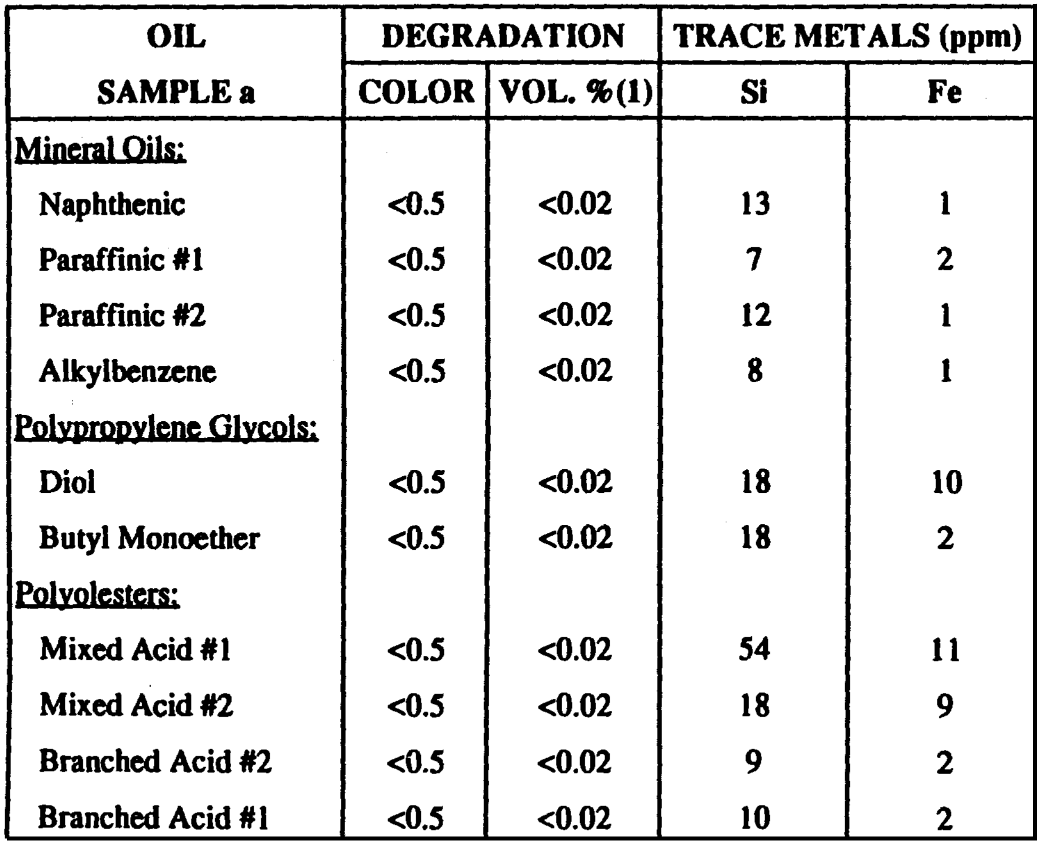
OIL	DEGRADATION		TRACE METALS (ppm)	
SAMPLE a	COLOR	VOL. %(1)	Si	Fe
Mineral Oils:				
Naphthenic	<0.5	<0.02	9	<1
Paraffinic #1	<0.5	<0.02	8	<1
Paraffinic #2	<0.5	<0.02	3	<1
Alkylbenzene	0.5	0.05	18	<1
Polypropylene Glycols:				
Diol	<0.5	<0.02	29	4
Butyl Monoether	<0.5	0.02	7	2
Polyolesters:				
Mixed Acid #1	<0.5	<0.02	8	14
Mixed Acid #2	<0.5	<0.02	7	4
Branched Acid #2	<0.5	<0.02	4	<1
Branched Acid #1	0.5-1.0	<0.02	60	28

a All Oils Dried Prior to Use (Table D-2).

(1) % Volatile degradation product (unknown) produced during aging (Appendix A).

TABLE 6

Color, Volatile Degradation Product, and Trace Metal Measurements for HFC-32/HFC-134a Refrigerant/Oil (1:1 By Weight) Mixtures Aged for Four Weeks at 175°C (347°F) with Valve Steel Catalysts According to ANSI/ASHRAE Standard 97-1989



OIL	DEGRADATION		TRACE METALS (ppm)	
SAMPLE a	COLOR	VOL. %(1)	Si	Fe
<u>Mineral Oils:</u>				
Naphthenic	<0.5	<0.02	13	1
Paraffinic #1	<0.5	<0.02	7	2
Paraffinic #2	<0.5	<0.02	12	1
Alkylbenzene	<0.5	<0.02	8	1
<u>Polypropylene Glycols:</u>				
Diol	<0.5	<0.02	18	10
Butyl Monoether	<0.5	<0.02	18	2
<u>Polyolesters:</u>				
Mixed Acid #1	<0.5	<0.02	54	11
Mixed Acid #2	<0.5	<0.02	18	9
Branched Acid #2	<0.5	<0.02	9	2
Branched Acid #1	<0.5	<0.02	10	2

a All Oils Dried Prior to Use (Table D-2).

(1) % Volatile degradation product (unknown) produced during aging (Appendix A).

acid attack of glass wall)/iron (hydrochloric or organic acid attack of valve steel coupon) concentration ratio also indicates differences in the degradation mechanisms of the aged refrigerant/oil (additive) mixtures (Table 4). For instance, the silicon concentration is greater than the iron concentration for the HCFC-22/mixed acid #1 polyolester mixture, implying glass attack is dominant, while the iron concentration is greater than the silicon concentration for the HCFC-22/branched acid #1 polyolester mixture, implying that here steel attack is dominant. The trace metal measurements also indicate that the polypropylene glycols and mixed acid #2 polyolester oil mixtures with HCFC-22 are extremely corrosive toward the valve steel catalyst (i.e., high iron concentrations).

The trace metal concentrations in Table 4 indicate that the branched acid #2 polyolester oil is the most stable polyolester oil and the paraffinic oils are slightly more stable than the alkylbenzene and naphthenic oils for the HCFC-22 refrigerant/oil mixtures.

Overall, the compatibility rankings for the different HCFC-22/oil mixtures decrease in the following order:

Mineral Oils > Polyolesters >> Polypropylene glycols

Since the polyolester and glycol oils contain varying amounts of different additives (Appendix D, Table D-2), the stability rankings within the classes of oils are more likely dependent on the basestock/additive combination stability than on the stability of the basestock alone.

HFC-134a/Oil Mixtures

In contrast to the CFC-12/oil and HCFC-22/oil results in Tables 3 and 4, the color and volatile degradation product measurements in Table 5 indicate that the HFC-134a refrigerant is very stable with the mineral oils, polyolester oils, and polypropylene glycols. Only the alkyl benzene, butyl monoether polypropylene glycol, and branched acid #1 polyolester mixtures produce detectable levels of degradation products during aging at 175°C (347°F) with HFC-134a refrigerant.

Although the color and degradation product measurements in Table 5 detect minimal levels of degradation in the aged refrigerant/oil mixtures, the trace metal analyses of the aged oils (remaining after removal of refrigerant for gas chromatographic analysis) detect small differences in the mixtures' stabilities. The silicon/iron concentration ratio also indicates differences in the degradation mechanisms of the aged refrigerant/oil mixtures (Table 5). For instance, the silicon concentration is greater than the iron concentration for the HCFC-134a/branched acid #1 polyolester mixture, implying glass attack is dominant, while the iron concentration is greater than the silicon concentration for the HFC-134a/mixed acid #1 polyolester mixture, implying here that steel attack is dominant.

The trace metal concentrations in Table 5 indicate that the branched acid #2 polyolester oil is the most stable polyolester oil and the paraffinic oils are slightly more stable than the alkylbenzene and naphthenic oils for the HFC-134a refrigerant/oil mixtures.

Overall, the compatibility rankings for the different HFC-134a/oil mixtures are fairly similar for the different classes of oils:

Mineral Oils ≈ Polyolesters ≈ Polypropylene glycols

The results for the HFC-134a/oil mixtures are in good agreement with the literature ***[4]***, i.e., no refrigerant degradation, but varying amounts of degradation products from oils. Since the polyolester and glycol oils contain varying amounts of different additives (Appendix D, Table D-2), the stability rankings within the classes of oils are more likely dependent on the basestock/additive combination stability than on the stability of the basestock alone.

HFC-32/HFC-134a/Oil Mixtures

In contrast to the CFC-12/oil and HCFC-22/oil results in Tables 3 and 4 and in agreement with the HFC-134a/oil results in Table 5, the color and volatile degradation product measurements in Table 6 indicate that the HFC-32/HFC-134a (30:70 ratio by weight) refrigerant is very stable with the mineral oils, polyolester oils, and polypropylene glycols.

Although the color and degradation product measurements in Table 6 detect minimal levels of degradation in the aged refrigerant/oil mixtures, the trace metal analyses of the aged oils (remaining after removal of refrigerant for gas chromatographic analysis) detect small differences in the mixtures' stabilities. The silicon/iron concentration ratio also indicates differences in the degradation mechanisms of the aged refrigerant/oil mixtures (Table 6). For instance, the silicon concentration is greater than the iron concentration for the HCFC-32/HFC-134a/branched acid #1 polyolester mixture, implying glass attack is dominant, while the iron concentration is greater than the silicon concentration for the HFC-32/HFC-134a/branched acid #2 polyolester mixture, implying that here steel attack is dominant.

Overall, the compatibility rankings for the different HFC-32/HFC-134a/oil mixtures are fairly similar for the different classes of oils:

Mineral Oils ≈ Polyolesters ≈ Polypropylene glycols

The results for the HFC-32/HFC-134a/oil mixtures are in good agreement with the literature ***[4]***, i.e., no refrigerant degradation, but varying amounts of degradation products from oils. Since the polyolester and glycol oils contain varying amounts of different additives (Appendix D, Table D-2), the stability rankings within the classes of oils are more likely dependent on the basestock/additive combination stability than on the stability of the basestock alone.

IN SITU CONDUCTIVITY AGING TESTS - PHASE 3

Introduction

The third phase of research focused on modifying the ANSI/ASHRAE Standard 97-1989 ***[1]*** for development into an accelerated screening method for determining the chemical and thermal stabilities of refrigerant/lubricant mixtures. Three aluminum blocks (Figure 4), containing one, three, and five wells, were constructed with built-in cartridge heaters and electrical connections for monitoring the modified sealed tubes depicted in Figure 1. A separate programmable temperature controller/data logger combination was used for each aluminum block to control the block temperature and to monitor the *in situ* conductivity measurements of the modified tubes during the accelerated screening test.

For the *in situ* conductivity measurements to be suitable for development into a routine compatibility test, the *in situ* conductivity versus aging time plots (Appendix B) must be reducible to a single value, e.g., color measurements (0.5 to 8.0 color scale), trace metals (ppm of dissolved metal), gas chromatography (percent volume of volatile degradation products as . described in Appendix C), etc. Previous attempts (Table 2) of expressing the conductivity change using the following formula

Conductivity Change = Final Conductivity Reading - First Conductivity Reading

succeeded in evaluating linear or constantly increasing or decreasing plots (Figure 2). However, plots such as HFC-134a/exposed branched acid #1 in Figure 3 where the conductivity increases, decreases, and then increases with aging time are incorrectly evaluated by the above equation.

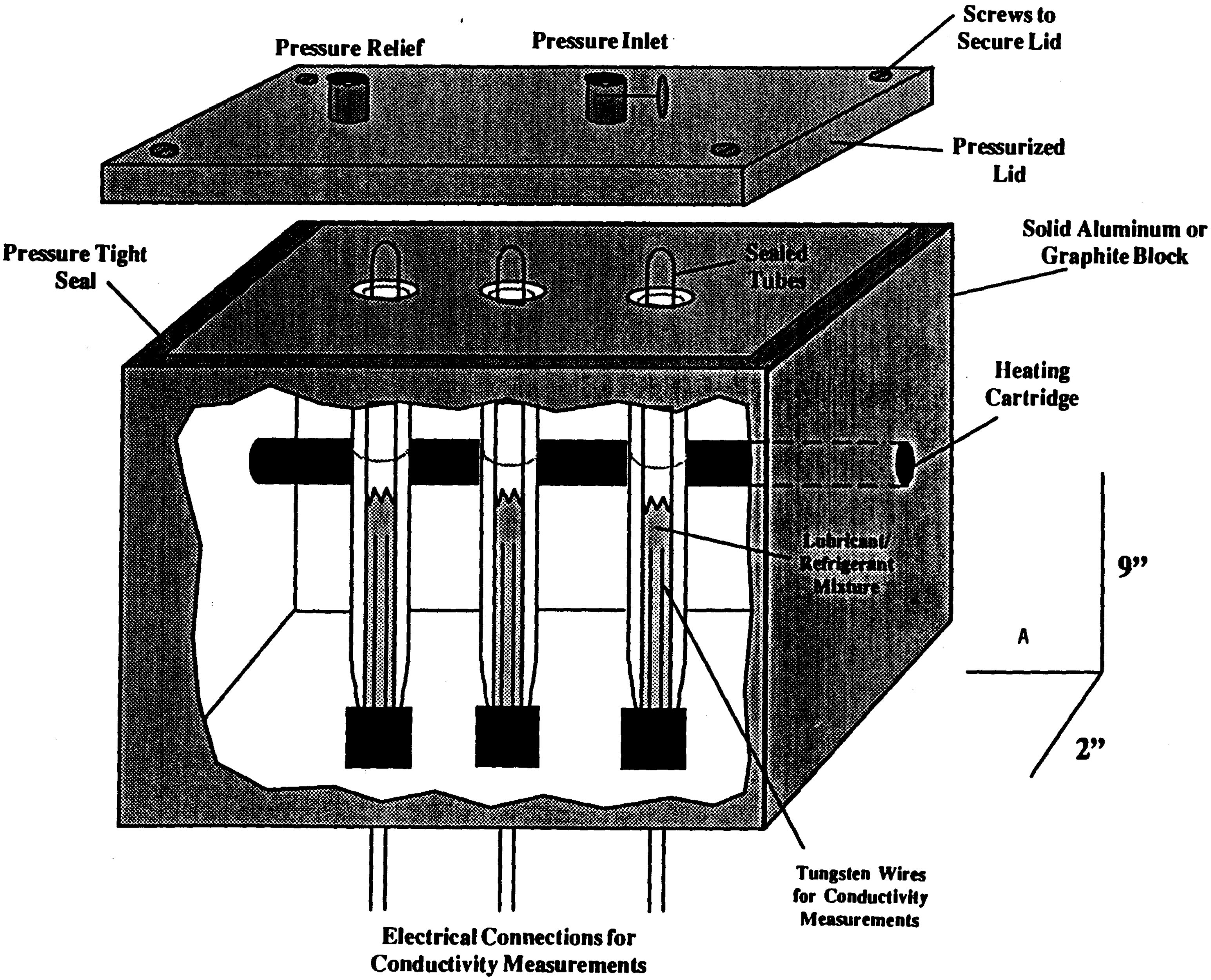


Figure 4. Design of Aluminum Block Heaters. (Three Well Heater Shown for Reference). A = 2" for One Well Heater; A = 3 1/2" for Three Well Heater, and A = 9" for Five Well Heater.

Therefore, the total conductivity changes for aged refrigerant/lubricant mixtures were determined using the following equation:

$$\textit{Total Conductivity Change} = \sum_{n=o}^{n=at} \textit{absolute value} \left(CR_{n+1} - CR_n\right)$$

where

CR: conductivity reading
n=o: time when aluminum block reaches temperature equilibrium (approximately 2 hours)
n=at: test time t (hours) X a (where a is the number of conductivity readings made every hour)

The total conductivity increases when polar species are produced *(in situ* conductivity increases) by refrigerant/oil reactions indicating mixture instability. The total conductivity also increases when polar species are removed *(in situ* conductivity decreases) from solution through reaction with other polar species to produce nonpolar species, through reaction with solid surfaces such as the metal coupon or glass surfaces. Therefore, the total conductivity change equation treats conductivity increases and decreases as positive changes so that *in situ* conductivity plots that increase then decrease will produce significant values. Also, the total conductivity has time resolution so that conductivity changes during different periods of the aging test can be calculated and compared.

To evaluate the *in situ* conductivity techniques for development into an accelerated screening method, CFC-12, HCFC-22, HFC-134a, and HFC-32/HFC-134a refrigerant mixtures with the dried oils listed in Appendix D were heated at 175°C (347°F) for less than 1 week with and without metal catalysts. The total conductivity (1 and 7 days), color, volatile degradation product (Appendix C), and trace metal measurements of the CFC-12, HCFC-22, HFC-134a, and HFC-32/HFC-134a/oil mixtures aged at 175°C (347°F) without and with valve steel catalyst present are listed in Tables 7 -14, respectively. The *in situ* conductivity versus aging time plots of the CFC-12, HCFC-22, HFC-134a, and HFC-32/HFC-134a/oil mixtures are presented in Appendix B.

TABLE 7

Color, Volatile Degradation Product, Trace Metal, and Total Conductivity Measurements of CFC-12 Refrigerant/Oil Mixtures (1:1 By Weight) Aged at 175°C (347°F) for One Week Without Valve Steel Catalysts in the Three Channel Aluminum Block Heater

OIL	DEGRADATION		TOTAL CONDUCTIVITY		TRACE METALS (ppm)	
SAMPLE a	COLOR	VOL. %(1)	1 DAY	7 DAYS	Si	Fe
<u>Mineral Oils:</u>						
Naphthenic	<0.5	<0.003	2,000	2,500	4	<1
Paraffinic #1	<0.5	<0.003	2,000	2,900	5	<1
Paraffinic #2	<0.5	<0.003	200	500	3	<1
Alkylbenzene	<0.5	<0.003	2,000	2,400	5	<1
<u>Polypropylene Glycols:</u>						
Diol	<0.5	0.01	66,400	196,000	9	<1
Butyl Monoether (2)	<0.5	<0.02	(2)	(2)	7	<1
<u>Polyolesters:</u>						
Mixed Acid #1	<0.5	<0.003	200	500	6	<1
Mixed Acid #2	<0.5	0.003	5,900	14,900	4	<1
Branched Acid #2	<0.5	<0.003	400	1,000	28	<1
Branched Acid #1	<0.5	<0.003	6,600	53,600	6	<1

a All Oils Dried Prior to Use (Table D-2).

(1) % Volatile degradation product (HCFC-22) produced during aging (Appendix A).

(2) Heated for only 0.8 day.

TABLE 8

Color, Volatile Degradation Product, Trace Metal, and Total Conductivity Measurements of CFC-12 Refrigerant/Oil Mixtures (1:1 By Weight) Aged at 175°C (347°F) for One Week With Valve Steel Catalysts in the Three Channel Aluminum Block Heater

OIL SAMPLE a	DEGRADATION		TOTAL CONDUCTIVITY		TRACE METALS (ppm)	
	COLOR	VOL. %(1)	1 DAY	7 DAYS	Si	Fe
Mineral Oils:						
Naphthenic	1.5	0.31	1,600	8,400	25	3
Paraffinic #1	<0.5	0.03	100	600	4	<1
Paraffinic #2	<0.5	0.09	200	600	8	1
Alkylbenzene	<0.5	0.08	600	1,500	11	1
Polypropylene Glycols:						
Diol	b	b	(2)	(2)	b	b
Butyl Monoether	>8.0	2.31	(3)	(3)	964	58
Polyolesters:						
Mixed Acid #1	0.5-1.0	0.96	20,900	147,900	158	44
Mixed Acid #2	5.5	2.13	(4)	(4)	795	1640
Branched Acid #2	<0.5	0.35	21,600	36,500	7	5
Branched Acid #1	5.5	0.58	(5)	(5)	357	132

a All Oils Dried Prior to Use (Table D-2). b Exploded after 0.8 day, no analysis performed.

(1) % Volatile degradation product (HCFC-22) produced during aging (Appendix A).

(2) Offscale after 0.1 day.

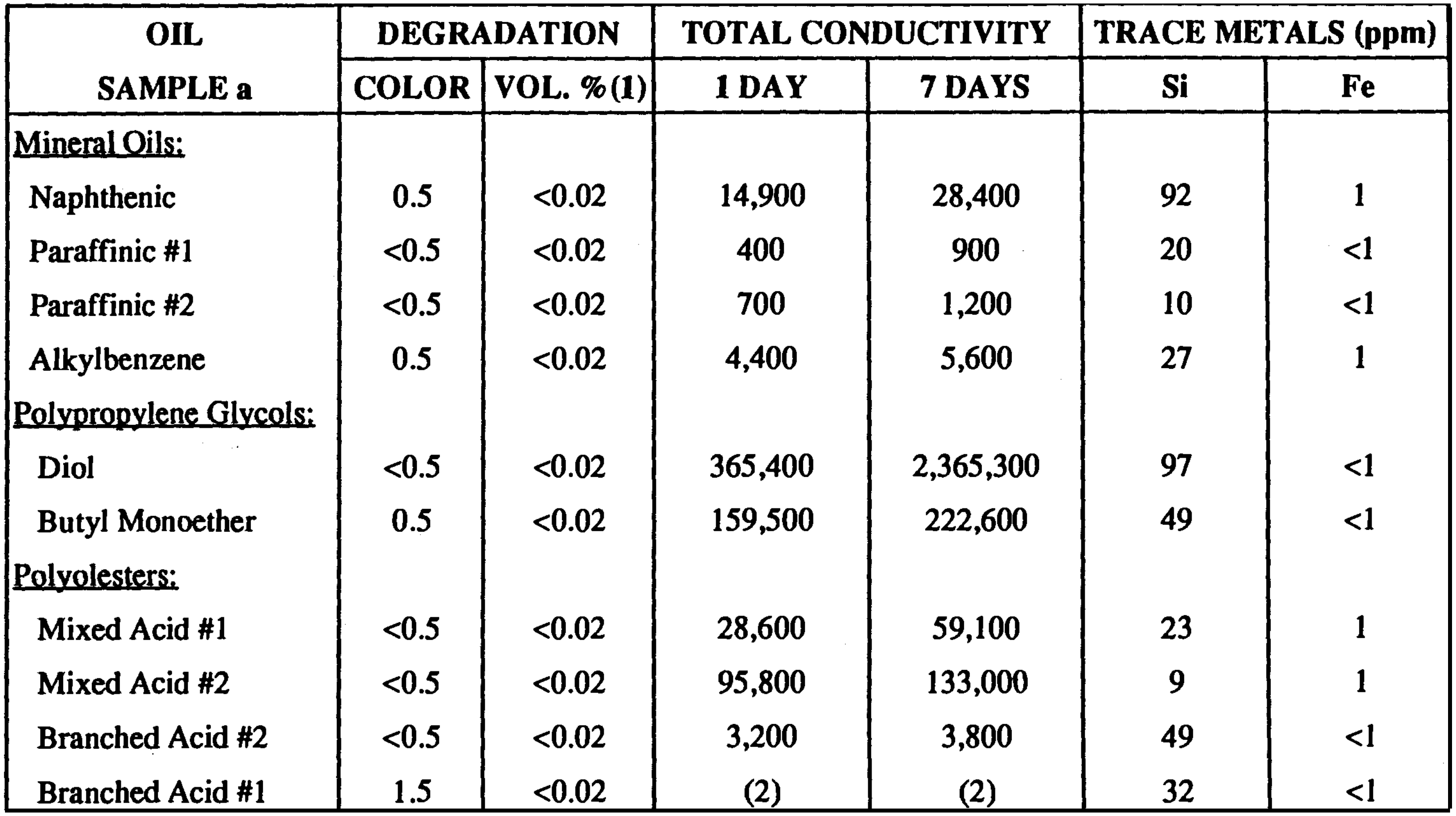
(3) Offscale soon after heating, then removed.

(4) Offscale after 0.8 day.

(5) Offscale after 0.4 day.

TABLE 9

Color, Volatile Degradation Product, Trace Metal, and Total Conductivity Measurements of HCFC-22 Refrigerant/Oil Mixtures (1:1 By Weight) Aged at 175°C (347°F) for One Week Without Valve Steel Catalysts in the Three Channel Aluminum Block Heater



OIL	DEGRADATION		TOTAL CONDUCTIVITY		TRACE METALS (ppm)	
SAMPLE a	COLOR	VOL. %(1)	1 DAY	7 DAYS	Si	Fe
Mineral Oils:						
Naphthenic	0.5	<0.02	14,900	28,400	92	1
Paraffinic #1	<0.5	<0.02	400	900	20	<1
Paraffinic #2	<0.5	<0.02	700	1,200	10	<1
Alkylbenzene	0.5	<0.02	4,400	5,600	27	1
Polypropylene Glycols:						
Diol	<0.5	<0.02	365,400	2,365,300	97	<1
Butyl Monoether	0.5	<0.02	159,500	222,600	49	<1
Polyolesters:						
Mixed Acid #1	<0.5	<0.02	28,600	59,100	23	1
Mixed Acid #2	<0.5	<0.02	95,800	133,000	9	1
Branched Acid #2	<0.5	<0.02	3,200	3,800	49	<1
Branched Acid #1	1.5	<0.02	(2)	(2)	32	<1

a All Oils Dried Prior to Use (Table D-2).

(1) % Volatile degradation product (HFC-23 and HFC-32) produced during aging (Appendix A).

(2) Offscale after 3 hours.

TABLE 10

Color, Volatile Degradation Product, Trace Metal, and Total Conductivity Measurements of HCFC-22 Refrigerant/Oil Mixtures (1:1 By Weight) Aged at 175°C (347°F) for One Week With Valve Steel Catalysts in the Three Channel Aluminum Block Heater

OIL SAMPLE a	DEGRADATION		TOTAL CONDUCTIVITY		TRACE METALS (ppm)	
	COLOR	VOL. %(1)	1 DAY	7 DAYS	Si	Fe
<u>Mineral Oils:</u>						
Naphthenic	<0.5	<0.02	6,100	6,800	21	1
Paraffinic #1	<0.5	<0.02	500	900	62	2
Paraffinic #2	<0.5	<0.02	1,000	1,500	9	2
Alkylbenzene	<0.5	<0.02	6,600	9,000	23	2
<u>Polypropylene Glycols:</u>						
Diol	0.5	0.053	(2)	(2)	34	313
Butyl Monoether	1.5	<0.02	19,900	252,500	23	852
<u>Polyolesters:</u>						
Mixed Acid #1	<0.5	<0.02	8,900	18,700	11	2
Mixed Acid #2	<0.5	<0.02	63,100	121,400	12	37
Branched Acid #2	<0.5	<0.02	50,000	85,200	33	20
Branched Acid #1	0.5	<0.02	(3)	(3)	48	15

a All Oils Dried Prior to Use (Table D-2).

(1) % Volatile degradation product (HFC-23 and HFC-32) produced during aging (Appendix A).

(2) Offscale after 0.5 day.

(3) Offscale after 2.7 days.

TABLE 11

Color, Volatile Degradation Product, Trace Metal, and Total Conductivity Measurements of HFC-134a Refrigerant/Oil Mixtures (1:1 By Weight) Aged at 175°C (347°F) for One Week Without Valve Steel Catalysts in the Three Channel Aluminum Block Heater

OIL SAMPLE a	DEGRADATION		TOTAL CONDUCTIVITY		TRACE METALS (ppm)	
	COLOR	VOL. % (1)	1 DAY	7 DAYS	Si	Fe
Mineral Oils:						
Naphthenic	<0.5	<0.02	100	300	49	1
Paraffinic #1	<0.5	<0.02	200	900	9	1
Paraffinic #2	<0.5	<0.02	100	700	8	<1
Alkylbenzene	<0.5	<0.02	100	700	7	<1
Polypropylene Glycols:						<1
Diol	<0.5	<0.02	415,300	910,200	13	<1
Butyl Monoether	<0.5	<0.02	23,700	49,400	10	<1
Polyolesters:						
Mixed Acid #1	<0.5	<0.02	300	700	5	<1
Mixed Acid #2	<0.5	<0.02	14,400	28,800	8	<1
Branched Acid #2	<0.5	<0.02	200	800	7	<1
Branched Acid #1	<0.5	<0.02	4,700	27,600	7	<1

a All Oils Dried Prior to Use (Table D-2).

(1) % Volatile degradation product (unknown) produced during aging (Appendix A).

TABLE 12

Color, Volatile Degradation Product, Trace Metal, and Total Conductivity Measurements of HFC- 134a Refrigerant/Oil Mixtures (1:1 By Weight) Aged at 175°C (347°F) for One Week With Valve Steel Catalysts in the Three Channel Aluminum Block Heater

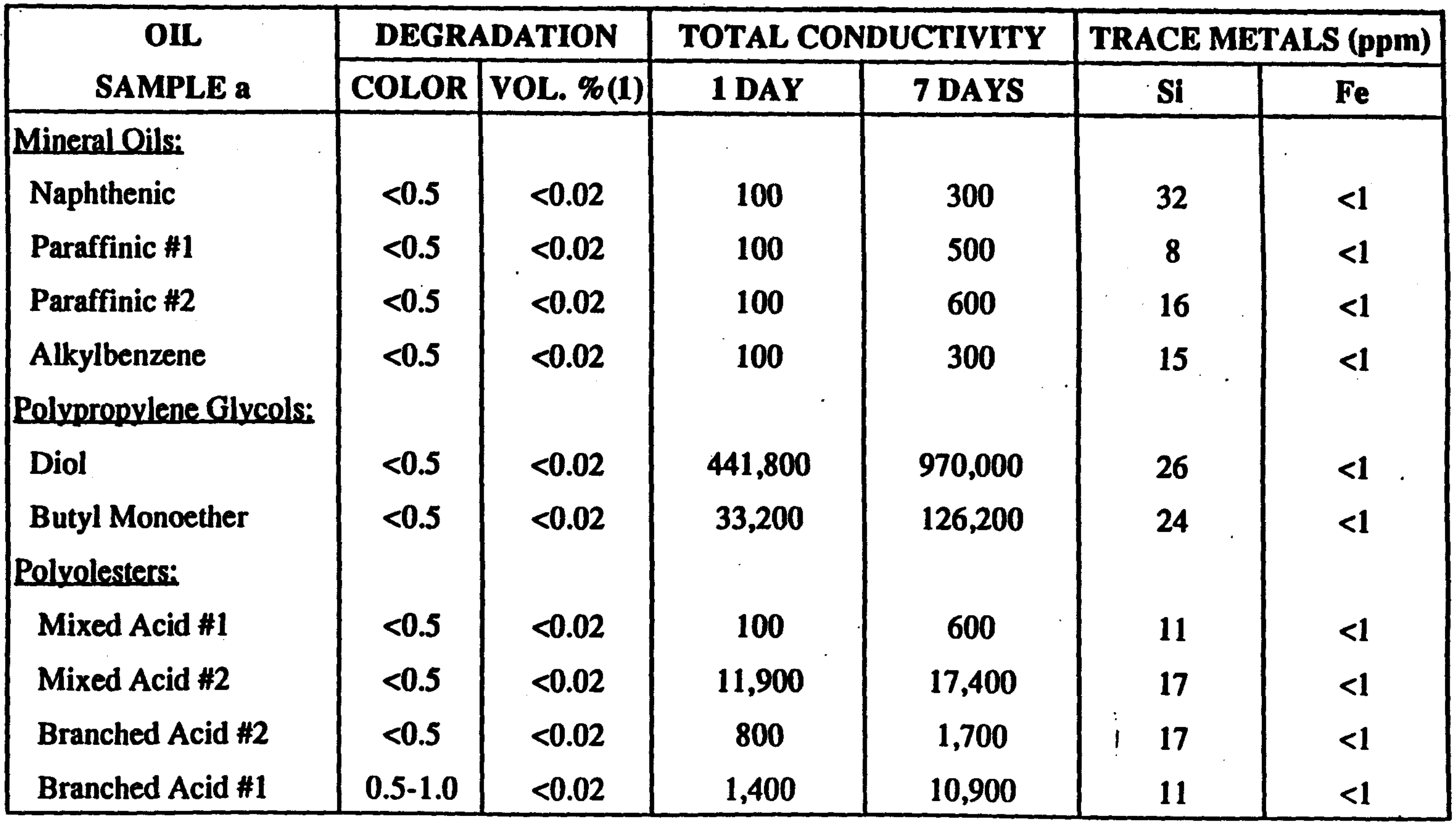
OIL	DEGRADATION		TOTAL CONDUCTIVITY		TRACE METALS (ppm)	
SAMPLE a	COLOR	VOL. %(1)	1 DAY	7 DAYS	Si	Fe
Mineral Oils:						
Naphthenic	<0.5	<0.02	100	200	8	<1
Paraffinic #1	<0.5	<0.02	100	600	15	<1
Paraffinic #2	<0.5	<0.02	100	300	9	<1
Alkylbenzene	<0.5	<0.02	100	300	22	1
Polypropylene Glycols:						
Diol	<0.5	<0.02	554,800	1,890,200	20	17
Butyl Monoether	<0.5	<0.02	35,500	47,600	10	2
Polyolesters:						
Mixed Acid #1	<0.5	<0.02	2,500	4,300	10	5
Mixed Acid #2	<0.5	<0.02	16,300	33,600	9	2
Branched Acid #2	<0.5	<0.02	900	1,500	4	<1
Branched Acid #1	<0.5	<0.02	4,100	11,600	12	2

a All Oils Dried Prior to Use (Table D-2).

(1) % Volatile degradation product (unknown) produced during aging (Appendix A).

TABLE 13

Color, Volatile Degradation Product, Trace Metal, and Total Conductivity Measurements of HFC-32 (70%)/HFC-134a (30%) Refrigerant/Oil Mixtures (1:1 By Weight) Aged at 175°C (347°F) for One Week Without Valve Steel Catalysts in the Three Channel Aluminum Block Heater



OIL SAMPLE a	DEGRADATION		TOTAL CONDUCTIVITY		TRACE METALS (ppm)	
	COLOR	VOL. %(1)	1 DAY	7 DAYS	Si	Fe
Mineral Oils:						
Naphthenic	<0.5	<0.02	100	300	32	<1
Paraffinic #1	<0.5	<0.02	100	500	8	<1
Paraffinic #2	<0.5	<0.02	100	600	16	<1
Alkylbenzene	<0.5	<0.02	100	300	15	<1
Polypropylene Glycols:						
Diol	<0.5	<0.02	441,800	970,000	26	<1
Butyl Monoether	<0.5	<0.02	33,200	126,200	24	<1
Polyolesters:						
Mixed Acid #1	<0.5	<0.02	100	600	11	<1
Mixed Acid #2	<0.5	<0.02	11,900	17,400	17	<1
Branched Acid #2	<0.5	<0.02	800	1,700	17	<1
Branched Acid #1	0.5-1.0	<0.02	1,400	10,900	11	<1

a All Oils Dried Prior to Use (Table D-2).

(1) % Volatile degradation product (unknown) produced during aging (Appendix A).

TABLE 14

Color, Volatile Degradation Product, Trace Metal, and Total Conductivity Measurements of HFC-32 (70%)/HFC-134a (30%) Refrigerant/Oil Mixtures (1:1 By Weight) Aged at 175°C (347°F) for One Week With Valve Steel Catalysts in the Three Channel Aluminum Block Heater

OIL SAMPLE a	DEGRADATION		TOTAL CONDUCTIVITY		TRACE METALS (ppm)	
	COLOR	VOL. %(1)	1 DAY	7 DAYS	Si	Fe
Mineral Oils:						
Naphthenic	<0.5	<0.02	<100	400	13	<1
Paraffinic #1	<0.5	<0.02	100	500	10	<1
Paraffinic #2	<0.5	<0.02	100	600	15	<1
Alkylbenzene	<0.5	<0.02	100	300	14	<1
Polypropylene Glycols:						
Diol	<0.5	<0.02	332,200	1,514,800	21	13
Butyl Monoether	<0.5	<0.02	46,500	56,500	7	3
Polyolesters:						
Mixed Acid #1	<0.5	0.02	1,300	3,300	11	<1
Mixed Acid #2	<0.5	<0.02	38,900	85,100	12	6
Branched Acid #2	<0.5	<0.02	2,000	3,500	15	<1
Branched Acid #1	0.5	<0.02	5,400	19,700	64	2

a All Oils Dried Prior to Use (Table D-2).

(1) % Volatile degradation product (unknown) produced during aging (Appendix A).

CFC-12/Oil Mixtures

The results in Tables 7 and 8 indicate there is agreement between the total conductivity values for the aged CFC-12/oil mixture and the traditional degradation evaluations using the color, volatile degradation, and trace metal measurements. The total conductivity values and traditional degradation evaluations (Tables 7 and 8) both indicate that (1) the presence of valve steel catalyzes the degradation mechanisms of the aged CFC-12/polyolester and propylene glycol oil mixtures, (2) the CFC-12 refrigerant/naphthenic oil mixture is the least stable of the mineral oil mixtures in the presence of steel, (3) the CFC-12 refrigerant/mixed acid #2 oil mixture is the least stable polyolester oil (additive, Table D-2) mixture in the presence of steel, and (4) overall the CFC-12 refrigerant/polyolester mixtures are less stable than the CFC-12 refrigerant/mineral oil mixtures in the presence of valve steel.

The results in Tables 7 and 8 also indicate for oils with low levels of degradation (paraffinic and alkylbenzene oils), the presence of valve steel generally reduces the conductivity readings of the aged refrigerant/oil mixtures. Surface analyses of the removed steel coupons detected chloride, fluoride, and other polar species on the metal surfaces. Consequently, the conductivity decreases appear to be due to removal of polar species from solution by the metal coupon surface.

The *in situ* conductivity measurements in Table 8 indicate that for CFC-12/oil mixtures in the presence of valve steel, the compatibility rankings of the different classes of oils decrease in the following order:

Mineral Oils > Polyolesters >> Polypropylene Glycols

Consequently, the *in situ* conductivity measurements (Table 8) and degree of degradation measurements for the ANSI/ASHRAE 97-1989 test (Table 3) show good agreement for ranking the stability of general classes of lubricants with CFC-12/oil mixtures in the presence of valve steel.

The results in Tables 3 and 8 indicate that the total conductivity values and *in situ* conductivity aging test have several advantages with respect to the traditional degradation evaluation methods and ANSI/ASHRAE 97-1989 aging test. The total conductivity values detected the unstable CFC-12/oil mixtures with the steel catalyst in less than one day and detected the change in the degradation rate for the CFC-12/mixed acid #1 oil mixture with respect to the CFC-12/branched acid #2 mixture. Although, the traditional evaluation methods could also detect degradation in the early stages of aging, only color measurements could be made without tube breakage. Sets of tubes would be required to provide degradation measurements throughout the entire aging process. *In situ* conductivity monitoring eliminates visual monitoring and shortens aging times for unstable refrigerant/oil mixtures decreasing safety risks, e.g., *in situ* monitoring would have indicated CFC-12 refrigerant/polypropylene glycol oil mixtures were unstable prior to tube explosions and hazardous tube openings.

HCFC/Oil Mixtures and HFC/Oil Mixtures

The traditional degradation evaluations using color or volatile degradation products indicate that the majority of the HCFC-22/oil mixtures (Tables 9 and 10), HFC-134a/oil mixtures (Tables 11 and 12), and HFC-32/HFC-134a/oil mixtures (Tables 13 and 14) are stable and not affected by the presence of valve steel. Only the HCFC-22/propylene glycol mixtures with valve steel catalyst present (Table 10) undergo color changes and produce detectable levels of degradation products.

In contrast to the color and volatile degradation product measurements, the iron concentration analyses of the HCFC-22/oil mixtures (Table 10) indicate the stabilities of the propylene glycol and polyolester mixtures are decreased by the presence of valve steel. The iron concentrations for the propylene glycol mixtures (Table 10) are especially high indicating severe corrosion of the valve steel coupon.

In comparison to the HCFC-22/oil mixtures, the iron concentration analyses of the HFC-134a/oil mixtures and HFC-32/HFC-134a/oil mixtures indicate the stabilities of the polypropylene glycol and polyolester mixtures are decreased to a lesser degree by the presence of valve steel. Again, a polypropylene glycol (diol in Tables 12 and 14) causes the highest degree of valve steel corrosion, i.e., highest iron concentration.

The results in Table 10 (valve steel present), indicate there is good agreement between the *in situ* conductivity measurements and the iron concentrations of the HCFC-22/oil mixtures. In agreement with the iron concentrations, the *in situ* conductivity measurements indicate (1) polypropylene glycol diol produces the least stable oil mixture with HCFC-22, (2) the mineral oils produce the most stable oil mixtures with HCFC-22, and (3) the polypropylene glycols and the polyolesters produce unstable mixtures with HCFC-22, with and without valve steel present. Since the polypropylene glycol and polyolesters contain varying amounts of different additives, the stability rankings are for the oil/additive combinations not the stability of the basestock alone.

The results in Tables 12 and 14, also indicate there is some agreement between the *in situ* conductivity measurements and the iron concentrations of the HFC-134a/oil mixtures and HFC-

32/HFC-134a/oil mixtures. In agreement with the iron concentrations, the *in situ* conductivity measurements indicate that in the presence of the valve steel (1) propylene glycol diol produces the least stable oil mixtures with HFC-134a and HFC-32/HFC-134a, (2) the mineral oils produce the most stable oil mixtures with HFC-134a and HFC-32/HFC-134a, and (3) the HFC/oil mixtures are more stable then HCFC-22/oil mixtures (Table 10).

Previous research ***[4]*** using the ANSI/ASHRAE 97-1989 aging test ***[l]*** to evaluate HCFC and HFC/oil mixtures in the presence of steel for 14 days at temperatures between 150°C (300°F) and 200°C (392°F) reported that (1) no refrigerant decomposition was detected for HFC-134a and HFC-32, (2) polyolesters were stable at 175°C (347°F) but underwent significant decomposition at 200°C (347°F), (3) polyglycols underwent significant molecular weight changes at all tested temperatures, and (4) HFC-134a and HFC-32 are generally more stable than HCFC-22 in oil mixtures.

Consequently, the total conductivity values and *in situ* conductivity show some agreement with previously reported ANSI/ASHRAE 97-1989 results ***[4]*** and 97-1989 tests performed for this study (Tables 4 - 6).

The results in Tables 9 -14 indicate that the total conductivity values and *in situ* conductivity aging test have several advantages with respect to the traditional degradation evaluation methods and ANSI/ASHRAE 97-1989 aging test (Tables 4 - 6). The total conductivity values detected the most unstable HCFC and HFC mixtures with the polypropylene glycols and polyolester oils with or without the steel catalyst in less than one day and detected the change in the degradation rate for the HCFC-22/mixed acid #2 oil mixture with respect to the HCFC-22/branched acid #2 mixture. *In situ* conductivity monitoring eliminates the need for visual monitoring during the aging period and may shorten aging times for unstable refrigerant/oil mixtures, decreasing safety risks from tube explosions, and is more sensitive to the degradation products (as detected by trace metal analyses) of the aged HCFC and HFC/oil mixtures than the traditional evaluation methods.

In Situ **Conductivity Aging Tests - Ramped Temperature**

To further evaluate the development of the *in situ* conductivity method into an accelerated screening method for determining the thermal and chemical stabilities of refrigerant/lubricant mixtures, single channel tests were performed using ramped temperatures instead of isothermal [175°C (347°F)] temperatures. The single channel block was used for the ramped temperature test since its lower mass [compared to the three well block (see Figure 4)] would allow more rapid temperature ramps.

The ramped temperature tests of the single channel aluminum block heater were performed by aging CFC-12, HCFC-22, and HFC-134a refrigerant/naphthenic oil mixtures in the modified sealed tubes (Figure 1). The naphthenic mineral oil was soluble in the CFC-12 and HCFC-22 refrigerants and was insoluble in the HFC-134a refrigerant forming two separate layers. The tungsten wires were in contact with both layers in the HFC- 134a refrigerant/naphthenic oil mixture. The refrigerant/oil mixtures were aged with and without valve steel catalysts present to determine the effects of metal catalysts on the ramped temperature *in situ* conductivity measurements. The refrigerant/oil mixtures were heated from 175°C (347°F) to 205°C (401 °F) over periods of seven to thirteen days to determine the capabilities of *in situ* conductivity to detect the onset of rapid degradation. The temperature was raised in steps of 10°C (18°F) with each new higher temperature maintained for 2-5 days. The stair step temperature ramp was used instead of a continuous ramp because the stair step was less expensive (stair steps initiated manually). Also, the stair step ramp allowed the degradation rate *(in situ* conductivity measurements inspected) to be inspected prior to the next temperature increase so that unstable refrigerant/oil mixtures would not undergo additional heating at higher temperature possibly resulting in tube explosions.

The results in Table 15 show that the presence of the valve steel catalyst increases the degradation rate of the refrigerant/oil mixtures by differing degrees, i.e., color, volatile degradation products or trace metal concentration increase by differing degrees with the presence of valve steel.

The *in situ* conductivity versus aging time plots in Figures 5 and 7 also indicate that the presence of the valve steel catalyst increases the degradation rates of the refrigerant/oil mixtures by differing degrees, i.e., conductivity changes (positive or negative) increased in size with valve steel catalyst, especially CFC-12/mineral oil mixture (Figure 5). The *in situ* conductivity versus aging time plots in Figures 5 - 7 also indicate that increased temperatures up to 195°C (383°F) have little effect on the rate of degradation (rate of conductivity change) for the HCFC-22 and HFC-134a refrigerant/mineral oil mixtures (Figures 6 and 7). The rapid increases in conductivity due to temperature increases in Figures 6 and 7 are reversible, i.e., conductivity decreases when temperature decreases, and consequently are not indicative of rapid decomposition. The CFC-12/oil mixture with valve steel was not heated above 185°C (365°F) due to the rapid degradation (rapid conductivity change) detected by the *in situ* conductivity measurement at 175°C (347°F).

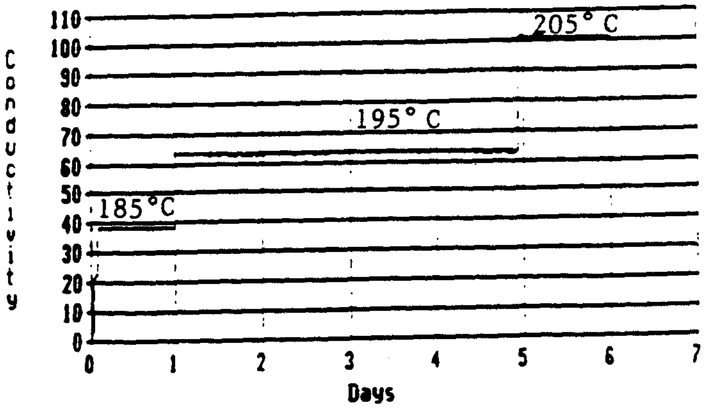
TABLE 15

Color, Volatile Degradation Product, and Trace Metal Measurements for CFC-12, HCFC-22, and HFC-134a Refrigerant/Naphthenic Oil Mixtures (1:1 by Weight) Aged With and Without Valve Steel Catalysts from 175°C (347°F) to 205°C (401°F) Using the Single Channel Aluminum Block Heater and *In Situ* Conductivity

OIL SAMPLE	REFRIGERANT/ METAL	DEGRADATION		TRACE METALS (ppm)	
		COLOR	VOL. %(1)	Si	Fe
Naphthenic	CFC-12/no steel	<0.5	<0.003	22	<1
Naphthenic	CFC-12/steel	1.5	0.17	17	3
Naphthenic	HCFC-22/no steel	<0.5	<0.02	16	<1
Naphthenic	HCFC-22/steel	<0.5	0.04	17	3
Naphthenic	HFC-134a/no steel	<0.5	<0.02	4.7	<1
Naphthenic	HFC-134a/steel	<0.5	<0.02	20	3

(1) % Volatile degradation product for CFC-12 is HCFC-22, for HCFC-22 HFC-23/32, and for HFC-134a is unknown (Appendix A).

Without Steel



With Steel

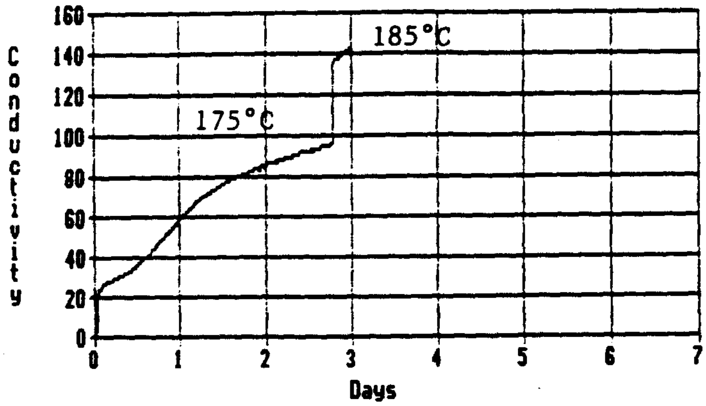
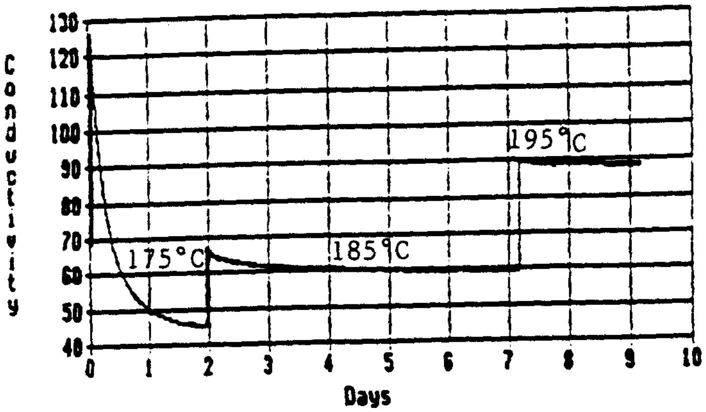


Figure 5. *In Situ* Conductivity Versus Aging Time Plots of CFC-12/Naphthenic Oil Mixtures Aged With and Without Valve Steel Catalysts from 175°C (347°F) to 205°C (401°F) in the Single Channel Aluminum Block Heater.

Without Steel



With Steel

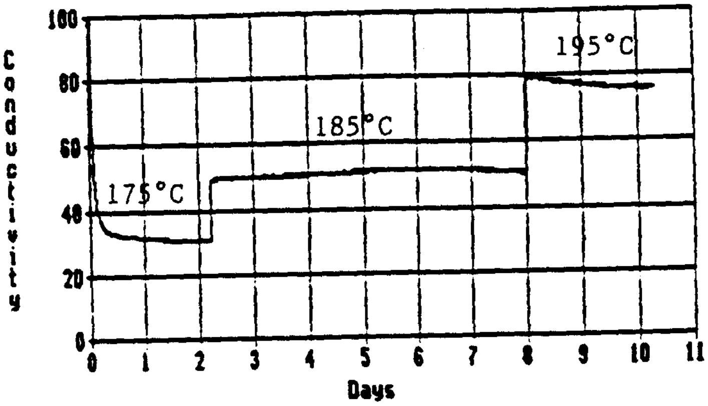
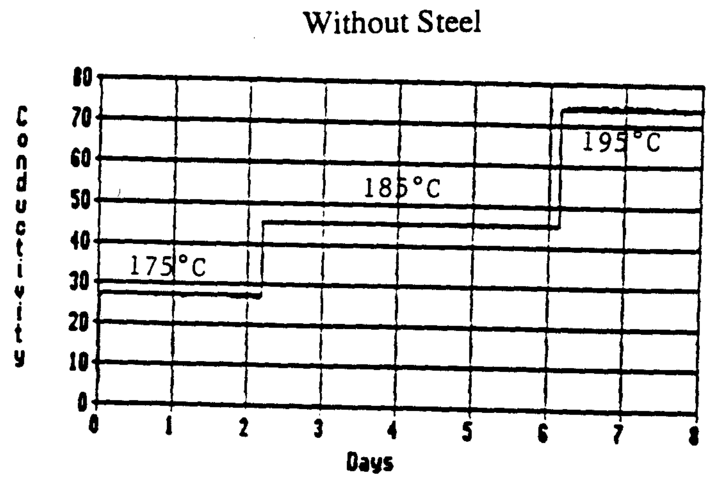
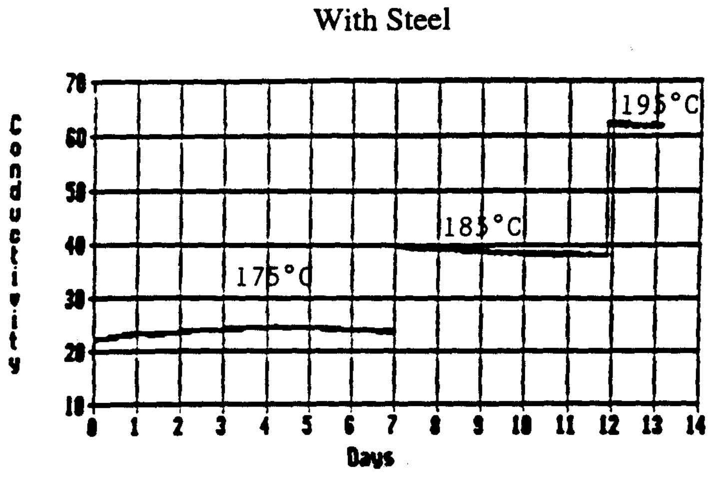


Figure 6. *In Situ* Conductivity Versus Aging Time Plots of HCFC-22/Naphthenic Oil Mixtures Aged With and Without Valve Steel Catalysts from 175°C (347°F) to 195°C (383°F) in the Single Channel Aluminum Block Heater.



Without Steel



With Steel

Figure 7. *In Situ* Conductivity Versus Aging Time Plots of HFC-134a/Naphthenic Oil Mixtures Aged With and Without Valve Steel Catalysts from 175°C (347°F) to 195°C (383°F) in the Single Channel Aluminum Block Heater.

Therefore, the initial results in Table 15 indicate that the *in situ* conductivity test can be used to monitor the degradation rates of refrigerant/oil mixtures up to 195°C (383°F). The capability to perform ramped temperature studies has the potential for rapid determinations of upper temperature limits for refrigerant/oil mixtures, construction materials, etc.

Effects of Oil Composition on *In Situ* Conductivity Readings

To determine if the changes in the *in situ* conductivity measurements for heated refrigerant/oil mixtures were due to oil instability, and not mixture instability, the branched acid #1 oil was sealed into a modified tube (Figure 1) and heated for 7 days at 175°C (347°F). The branched acid #1 oil was chosen since it produced higher than expected conductivities with all of the tested refrigerants. The *in situ* conductivity plot versus aging time plot for the branched acid #1 oil is shown in Figure 8. The *in situ* conductivity in Figure 8 has a low initial value and does not increase with aging (Figure 8). Consequently, the high conductivity values for the heated refrigerant/branched acid #1 oil mixtures (Appendix B) are due to refrigerant/oil instabilities, especially for chlorine containing refrigerants CFC-12 and HCFC-22.

In an initial attempt to determine if oil additives are responsible for the high conductivity readings and low stabilities of the refrigerant/polyolester mixtures, two common oil antioxidants (BHT and PANA) were added to branched acid #2 polyolester oil (no antioxidants detected, Table D-2). The additives were added to the oil at concentrations of ~500 ppm. Since the additives had larger effects for refrigerants containing chlorine, the effects of additives were evaluated in HCFC-22/oil mixtures. The *in situ* conductivity versus aging time plots for the HCFC-22/branched acid #2 polyolester oil mixtures with the different additives are shown in Figure 9 and the plot without additives is shown in Appendix B, Figure B-12.

The *in situ* conductivity plot in Figure 9 indicates that the phenolic type (BHT) antioxidant initially increases the conductivity of the HCFC-22/oil mixture (compared to Figure B-12). However, the effect of BHT on the mixture's conductivity decreases during the 7 day aging test. In contrast to BHT, in the presence of the aromatic amine type (PANA) antioxidant the conductivity of the HCFC-22/oil mixture (after the tube is at temperature) increases rapidly exceeding 2000 (off scale) after only 3 days of aging.

Therefore, the plots in Figure 9 indicate that HCFC-22/oil mixtures containing aromatic amine antioxidants are less stable than HCFC-22/oil mixtures containing phenolic type antioxidants. These results are in agreement with the ANSI/ASHRAE 97-1989 test results in Table 4 and *in situ* conductivity results in Table 10 [branched acid #1 which contains PANA is

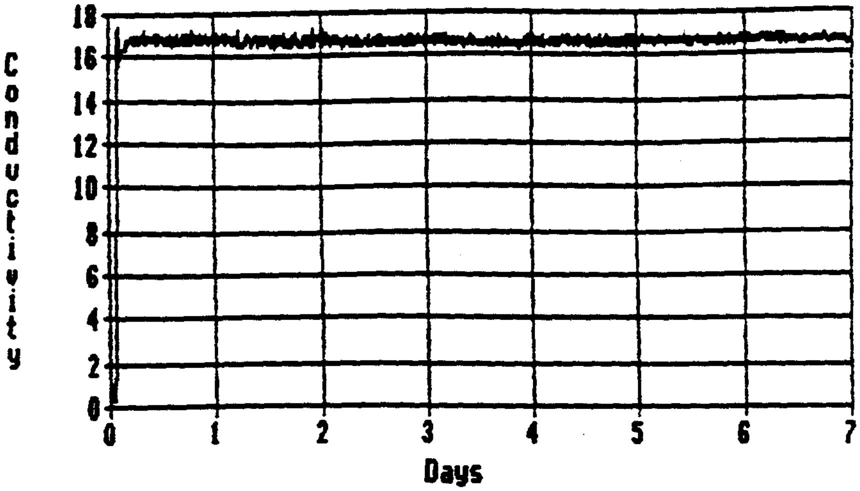


Figure 8. *In Situ* Conductivity Versus Aging Time Plots of Branched Acid #1 Polyolester Oil Aged With a Valve Steel Catalyst at 175°C (347°F) in the Single Channel Aluminum Block Heater.

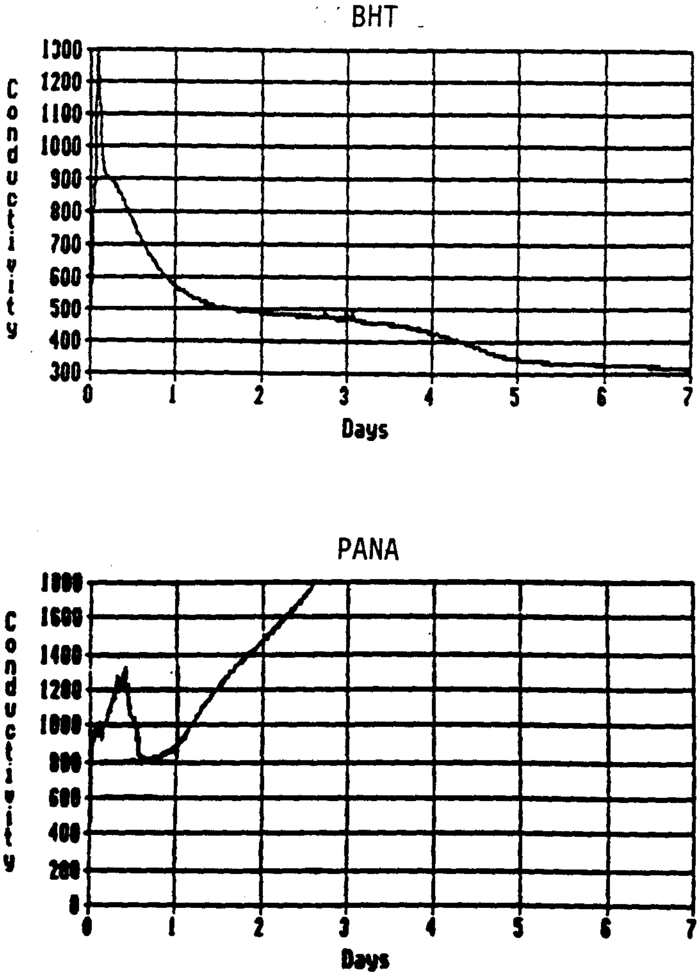


Figure 9. *In Situ* Conductivity Versus Aging Time Plots of HFC-22/Branched Acid #1 Polyolester Oil (Containing BHT and PANA Antioxidants) Mixtures Aged With a Valve Steel Catalyst at 175°C (347°F) in the Single Channel Aluminum Block Heater.

less stable than mixed acid #1 which contains BHT (Appendix D, Table D-2)] for HFC-22/polyolester oil mixtures. Further analyses, e.g., trace metal analyses, are required to determine the consequences of the increased conductivity changes caused by additives.

SUMMARY

The research reported herein has shown that *in situ* conductivity measurements may have potential for development into an accelerated screening test for determining the chemical and thermal stabilities of refrigerant/lubricant mixtures. The *in situ* conductivity method was used to evaluate a wide range of refrigerant/oil mixtures. The refrigerants tested in this study included CFC-11, CFC-12, HCFC-22, HFC-134a, and HFC-32/HFC-134a (zeotrope 30:70). The lubricants used in this study were selected from the chemical classes of mineral oils, alkylbenzene oils, polyglycols, and polyolesters.

The most important feature of a developed screening test is that the stability rankings of the screening test are in good agreement with the stability rankings of the current stability test, Sealed Glass Tube Method to Test The Chemical Stability of Material for Use Within Refrigeration Systems, ANSI/ASHRAE Method 97-1989 ***[1]***. The results presented herein have shown that the stability rankings of the *in situ* conductivity test are in general agreement with the rankings of Method 97-1989.

Other important advantages of the *in situ* conductivity test include the following:

(1) Less hazardous than ANSI/ASHRAE Method 97-1989 by eliminating tube explosions and handling of sealed tubes containing highly degraded materials

(2) May be more sensitive to degradation of high stability HCFC and HFC refrigerant/lubricant mixtures than ANSI/ASHRAE 97-1989 measurements

(3) Provides time resolved degradation measurements so that changes in degradation rates can be monitored *in situ* allowing for tests of unstable mixtures to be terminated early and for tests of highly stable mixtures to be extended

(4) Have potential to rapidly determine upper temperature limits of refrigerant/oil mixtures

Although the total conductivity values listed in Tables 9-14 provide a single value to rank the stabilities of tested refrigerant/oil mixtures, the total conductivities, and consequently the rankings, of the mixtures may be affected by the presence of additives and other impurities (water, peroxides, etc.). Therefore, time resolution during the initial hours of aging should be applied to the *in situ* conductivity plots to determine if the effects of the additives rapidly decrease with aging time (less likely to affect stability) or increase with time (more likely to affect stability) indicating the test should be terminated.

This research has shown that the valve steel catalyst used to accelerate the degradation of CFC and HCFC refrigerant/oil mixtures has little, if any effect, on the degradation rates of HFC refrigerant/oil mixtures.

This research reported herein has also shown that trace metal analyses are more useful in ranking the stabilities of HCFC and HFC/oil mixtures than the less sensitive color or volatile decomposition product concentration.

Therefore, the results presented herein demonstrate that *in situ* conductivity stability evaluations are in good agreement with those of ANSI/ASHRAE Method 97-1989 and are very useful in screening refrigerant/oil mixtures of unknown stabilities by detecting unstable mixtures prior to tube explosions. The *in situ* conductivity measurements may be more sensitive to degradation than traditional measurements and are capable of detecting degradation rate changes during extended aging tests. However, the *in situ* conductivity tests should be regarded as a supplement, not a replacement, of ANSI/ASHRAE Method 97-1989 until further testing and correlation studies are performed.

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 II: Experimental Comparison and Verification of Methods," Progress Report No. DOE/CE/23810-20D, Air-Conditioning and Refrigeration Technology Institute, October 1993.

3. Kauffman, R. E., "Sealed-Tube Tests of Refrigerants from Field Systems Before and After Recycling," ASHRAE Research Project 683-RP, June 1992 and ASHRAE Technical Data Bulletin Vol. 9, No. 5, 1993, Atlanta, GA, American Society of Heating, Refrigerating, and Air Conditioning Engineers, Inc. .

4. Huttenlocher, D. F., "Chemical and Thermal Stability of Refrigerant-Lubricant Mixtures with Metals," Final Report No. DOE/CE/23810-5, Air-Conditioning and Refrigeration Technology Institute, October 1992.

COMPLIANCE WITH AGREEMENT

The University of Dayton Research Institute has complied with all aspects of the agreement. Due to delays in obtaining electronic components purchased for constructing the accelerated testing instruments, a time extension of three months (at no extra cost) was obtained to complete the planned research.

PRINCIPAL INVESTIGATOR EFFORT

Mr. Robert Kauffman was the principal investigator for Part II of this research effort. Mr. Kauffman devoted 20% of his available work hours on the project.

APPENDIX A

GAS CHROMATOGRAMS OF FRESH REFRIGERANTS AND AGED REFRIGERANT/OIL MIXTURES

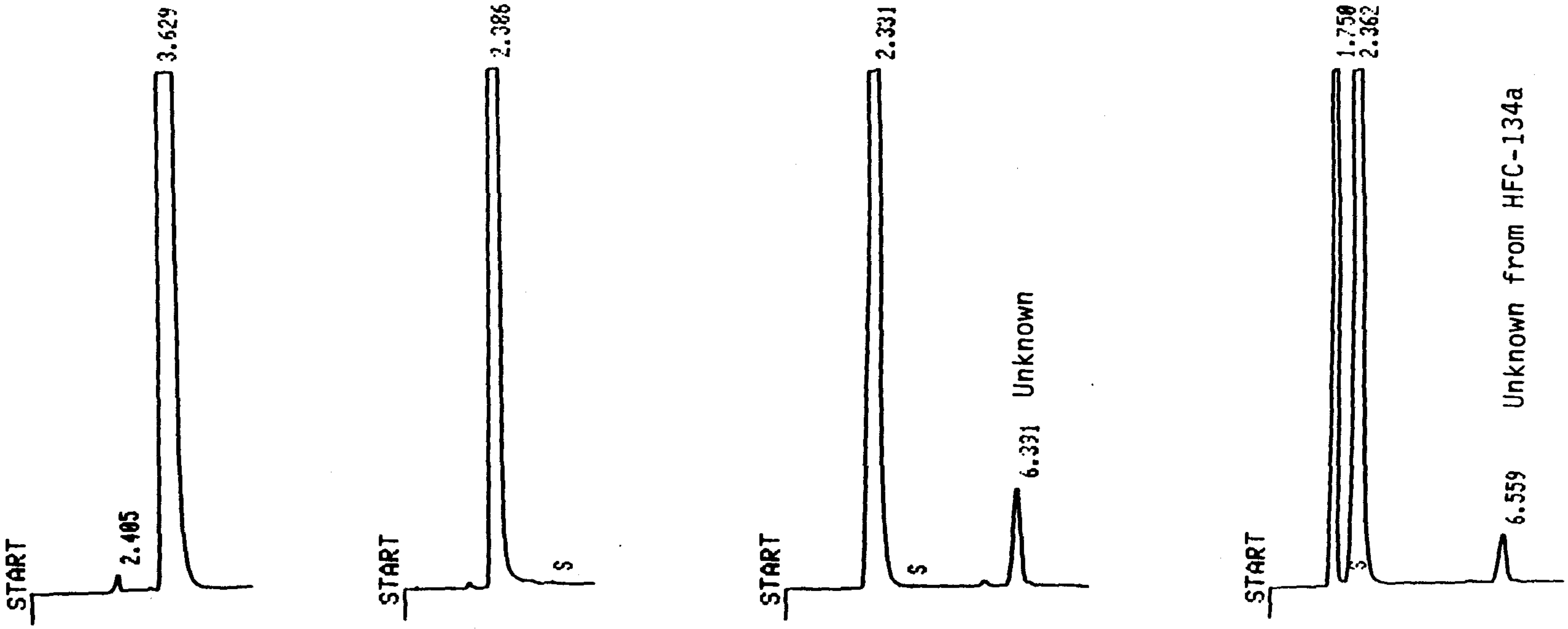
Purity Levels of Refrigerants

CFC-12: 99.9%

HCFC-22: 99.9+%

HFC-134a: 99.7%

HFC-32: 99.8%



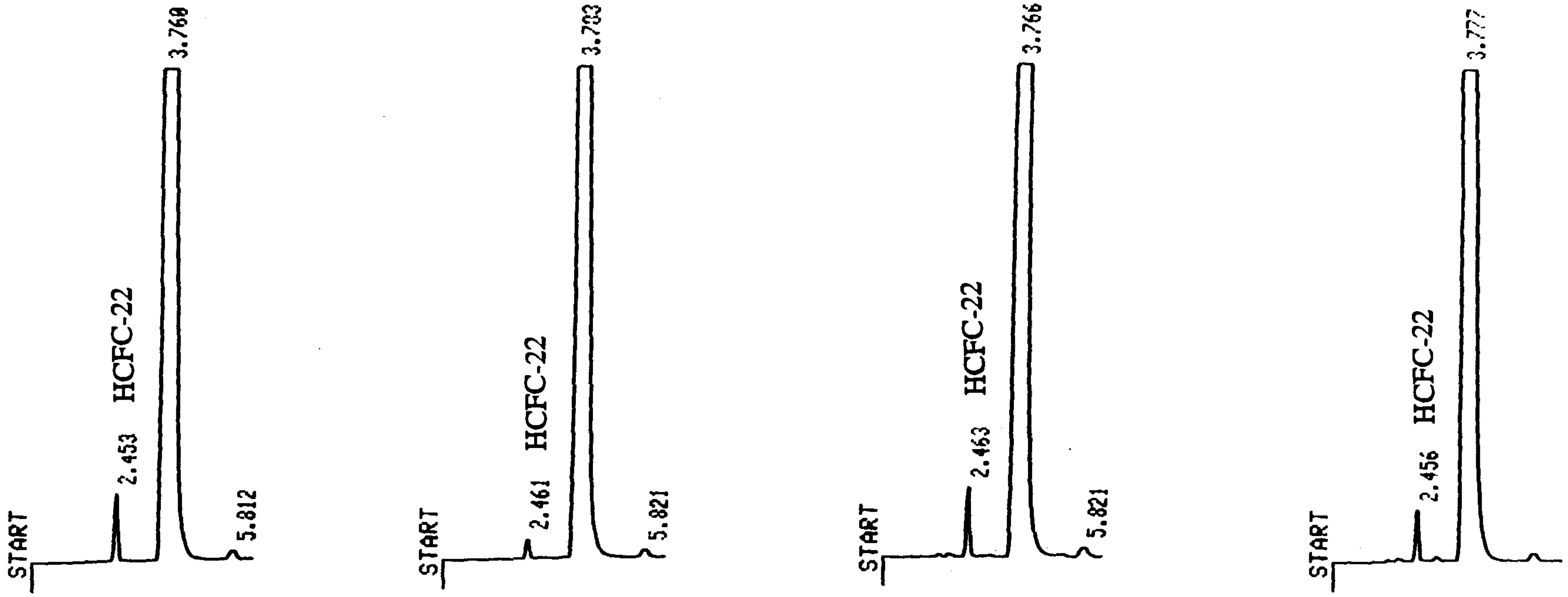
CFC-12

HCFC-22

HFC-134a

HFC-32 (30%)
HFC-134a (70%)

Figure A-1. Gas Chromatograms of Unaged Refrigerants.

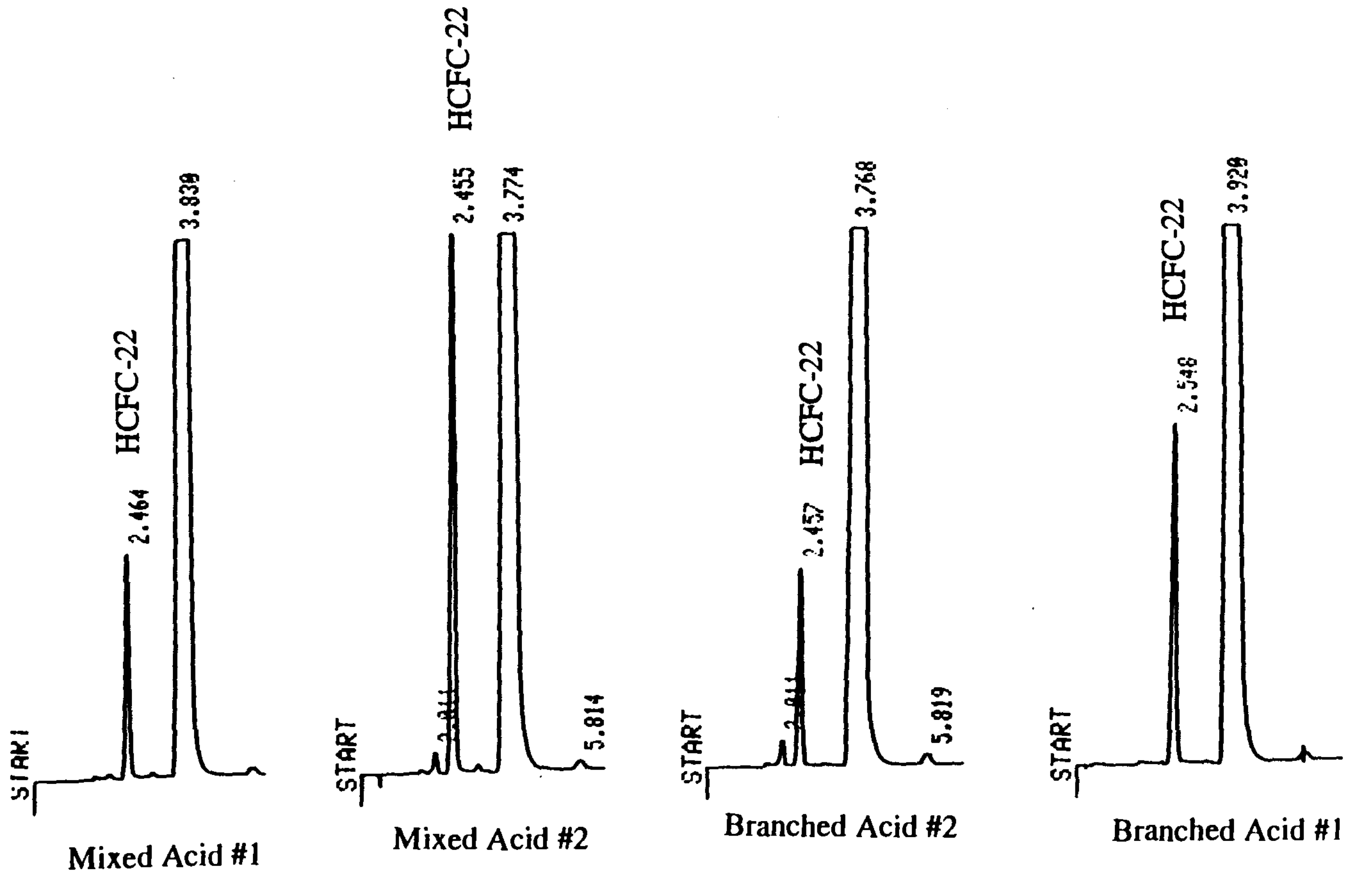


Naphthenic **Paraffinic #1** **Paraffinic #2** **Alkylbenzene**

Figure A-2. Gas Chromatograms of CFC-12/Mineral Oil Mixtures Aged at 175°C (347°F) for Two Weeks in the Presence of Valve Steel Catalysts. ANSI/ASHRAE Standard 97-1989 Test Method.

No Chromatograms Available Due to Sealed Tubes Disintegrating
During Gas Sampling Process

Figure A-3. Gas Chromatograms of CFC- 12/Polypropylene Glycol Mixtures Aged at 175°C (347°F) for Two Weeks in the Presence of Valve Steel Catalysts. ANSI/ASHRAE Standard 97-1989 Test Method.



Mixed Acid #1

Mixed Acid #2

Branched Acid #2

Branched Acid #1

Figure A-4. Gas Chromatograms of CFC- 12/Polyolester Oil Mixtures Aged at 175°C (347°F) for Two Weeks in the Presence of Valve Steel Catalysts. ANSI/ASHRAE Standard 97-1989 Test Method.

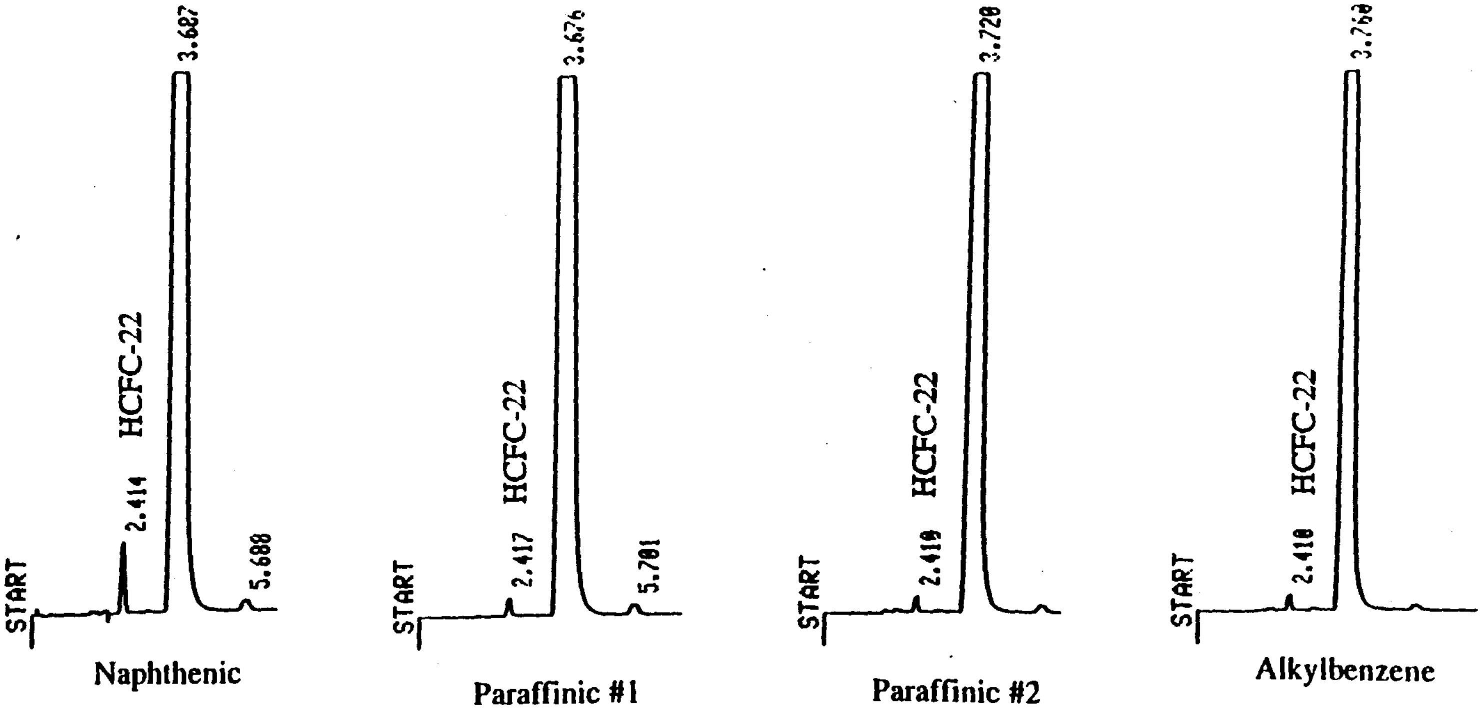
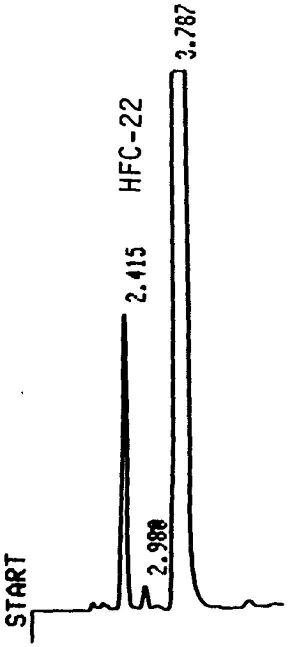


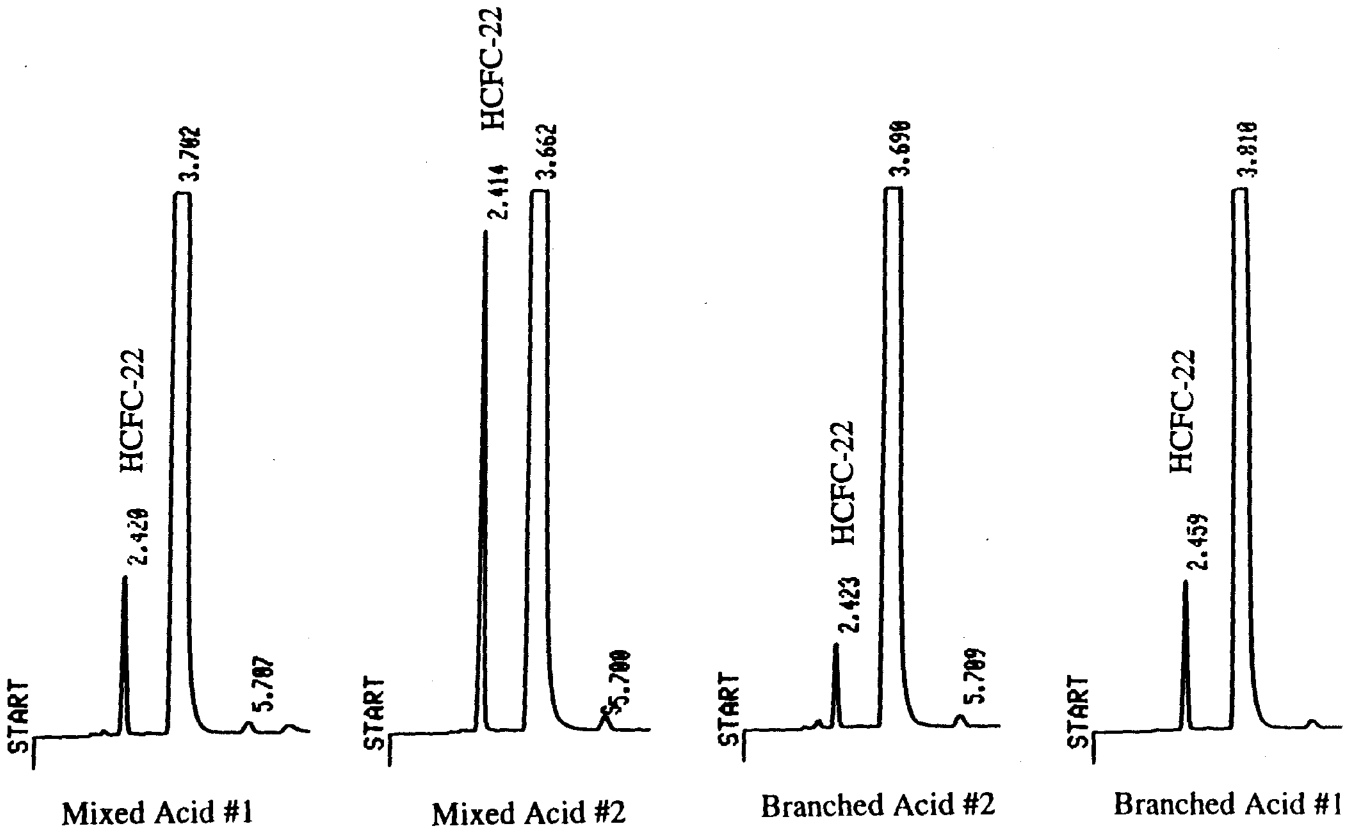
Figure A-5. Gas Chromatograms of CFC-12/Mineral Oil Mixtures Aged at 175°C (347°F) for One Week in the Presence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.

Diol Chromatogram
Not Available Due
to Sealed Tube
Disintegrating During
Gas Sampling Process



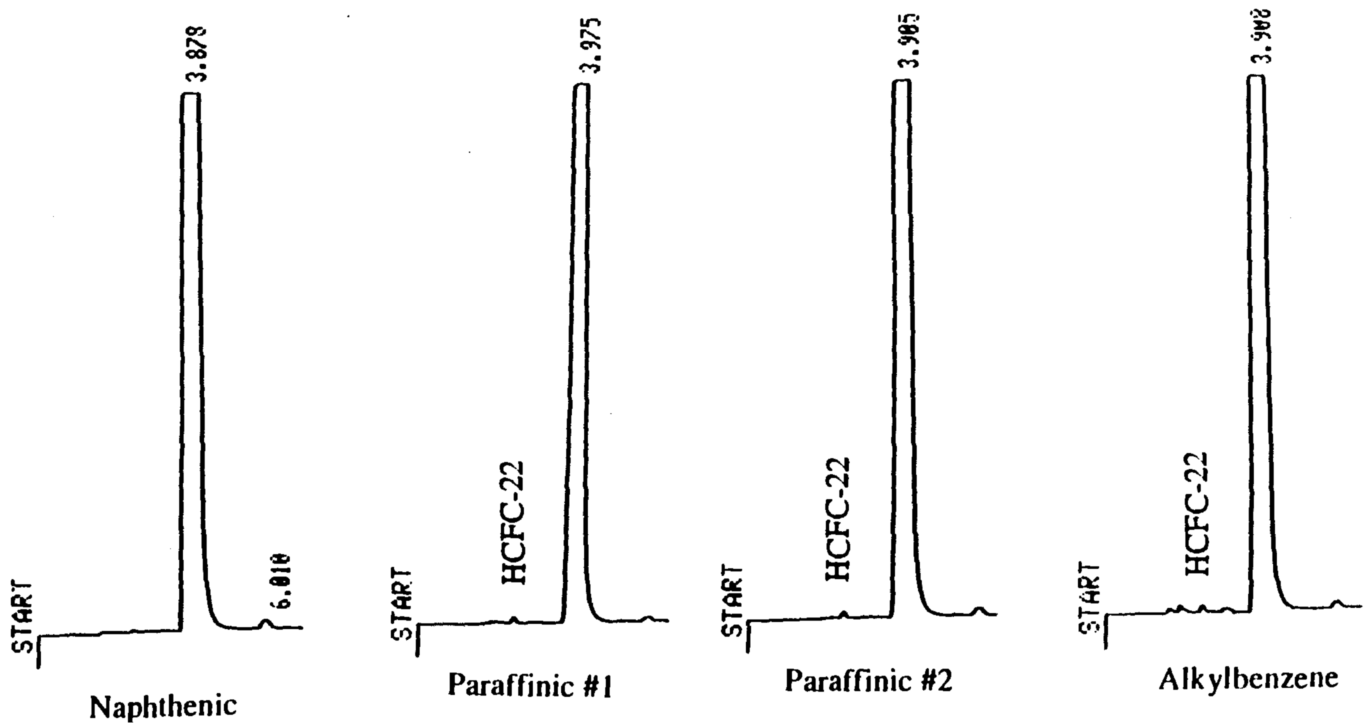
Butyl Monoether

Figure A-6. Gas Chromatograms of CFC-12/Polypropylene Glycol Mixtures Aged at 175°C (347°F) for One Week in the Presence of Valve Steel Catalysts. *In Situ* Conductivity Test Method.



Mixed Acid #1 Mixed Acid #2 Branched Acid #2 Branched Acid #1

Figure A-7. Gas Chromatograms of CFC-12/Polyolester Oil Mixtures Aged at 175°C (347°F) for One Week in the Presence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.



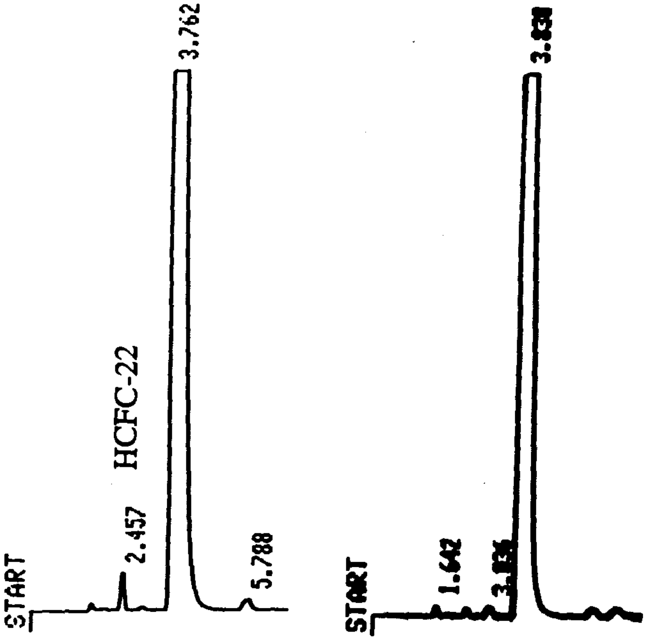
Naphthenic

Paraffinic #1

Paraffinic #2

Alkylbenzene

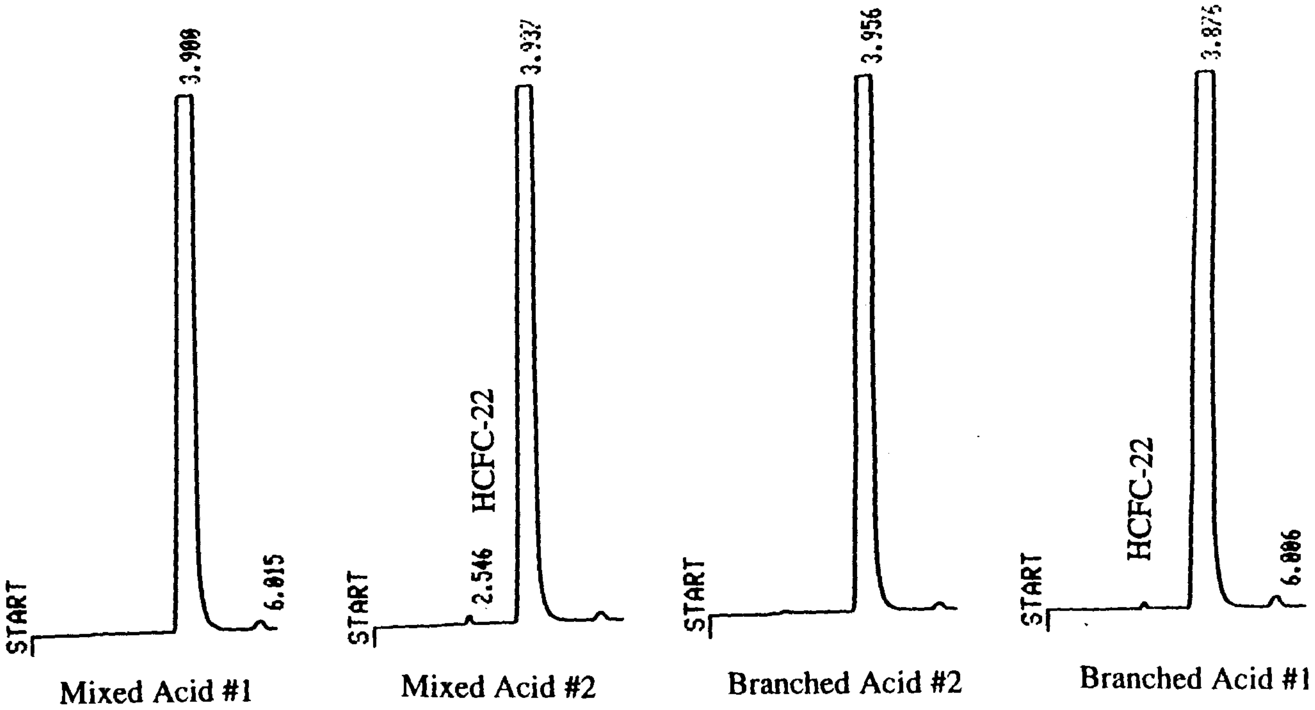
Figure A-8. Gas Chromatograms of CFC-12/Mineral Oil Mixtures Aged at 175°C (347°F) for One Week in the Absence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.



Diol

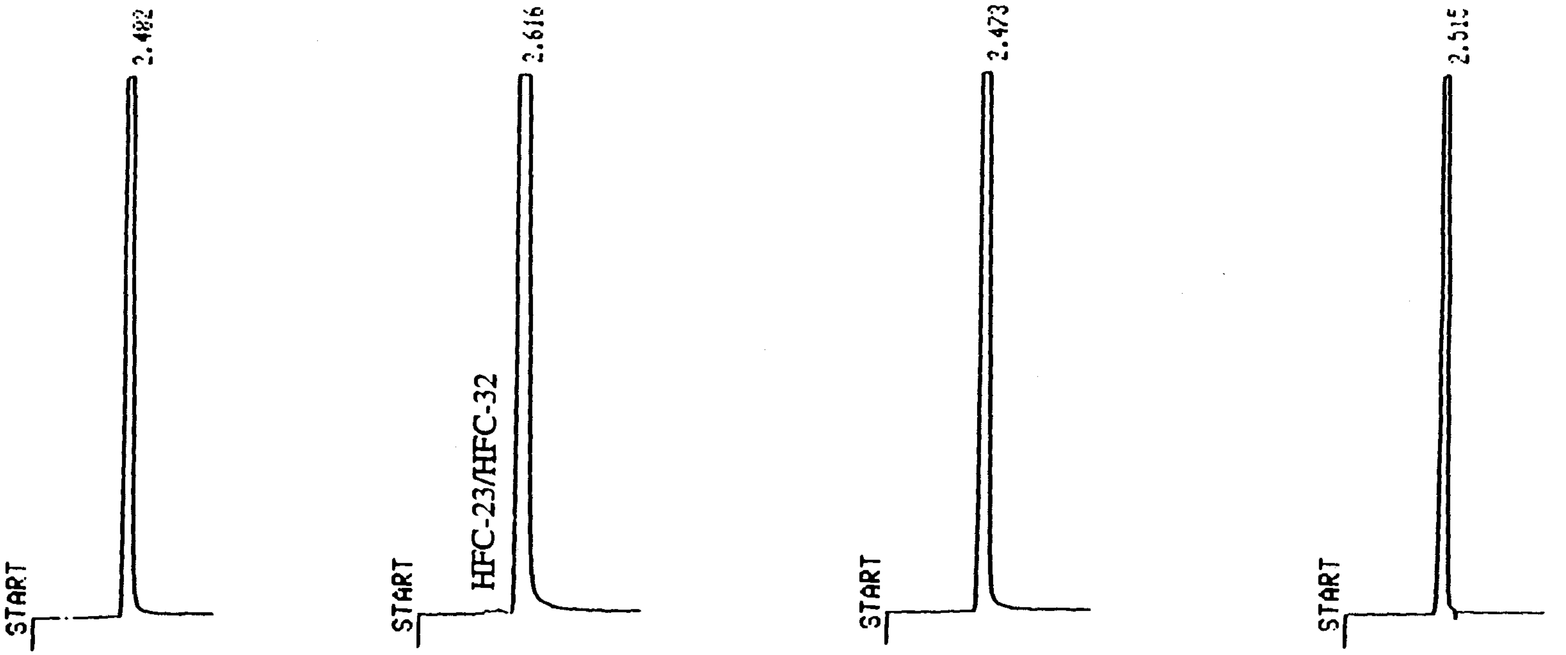
Butyl Monoether

Figure A-9. Gas Chromatograms of CFC-12/Polypropylene Glycol Mixtures Aged at 175°C (347°F) for One Week in the Absence of Valve Steel Catalysts. *In Situ* Conductivity Test Method.



Mixed Acid #1 **Mixed Acid #2** **Branched Acid #2** **Branched Acid #1**

Figure A-10. Gas Chromatograms of CFC-12/Polyolester Oil Mixtures Aged at 175°C (347°F) for One Week in the Absence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.



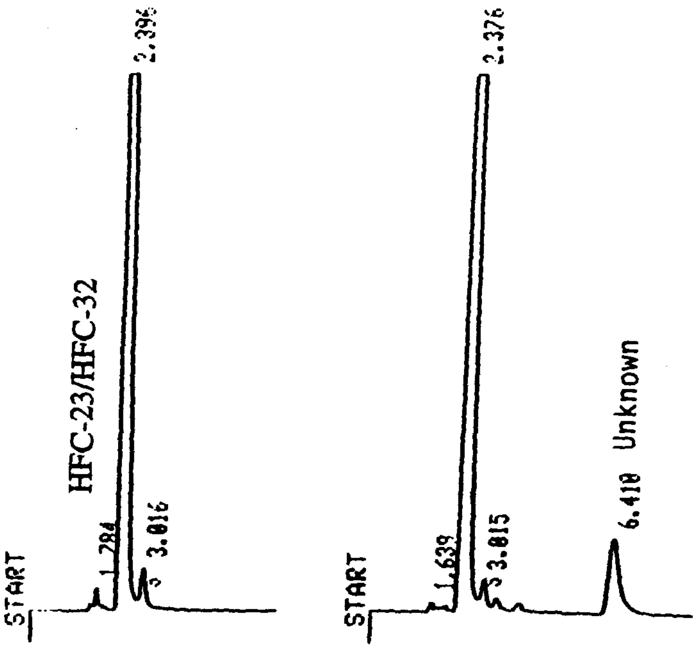
Naphthenic

Paraffinic #1

Paraffinic #2

Alkylbenzene

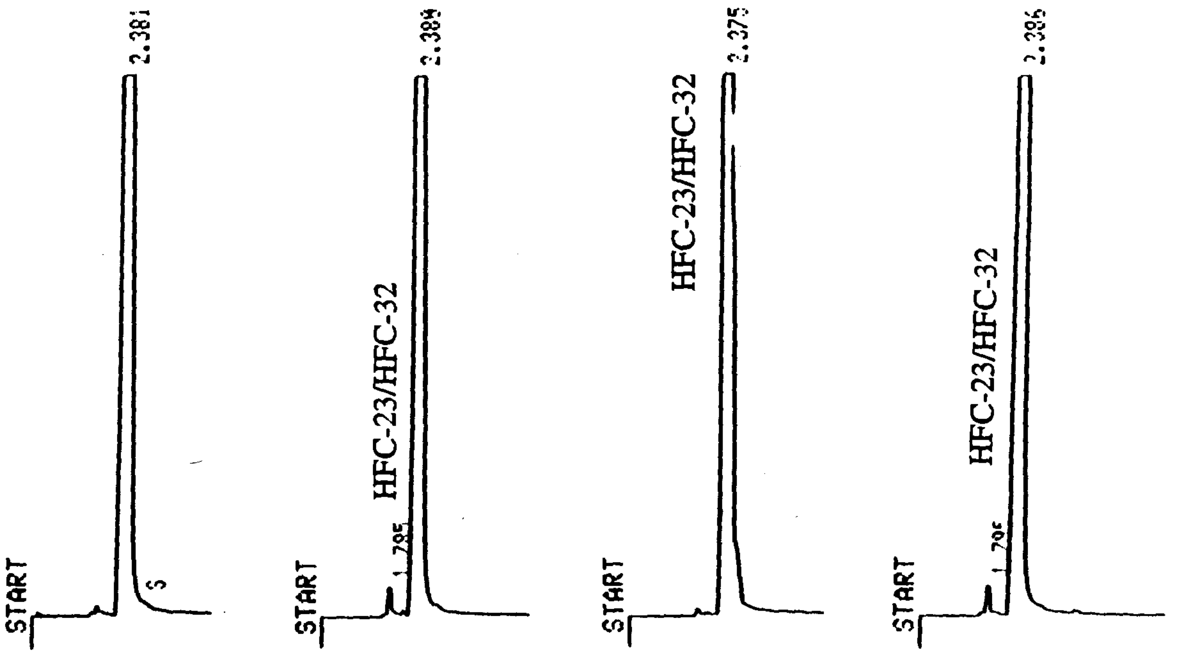
Figure A-11. Gas Chromatograms of HCFC-22/Mineral Oil Mixtures Aged at 175°C (347°F) for Two Weeks in the Presence of Valve Steel Catalysts. ANSI/ASHRAE Standard 97-1989 Test Method.



Diol

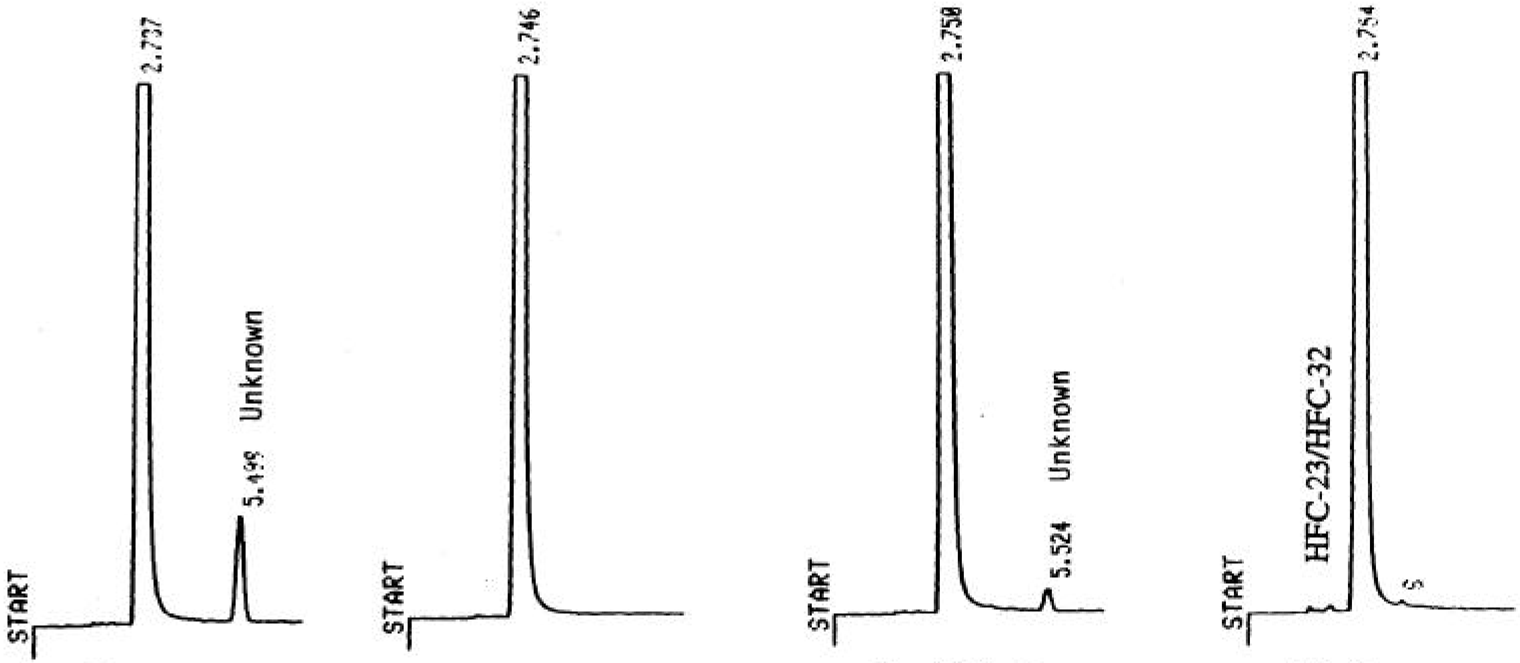
Butyl Monoether

Figure A-12. Gas Chromatograms of HCFC-22/Polypropylene Glycol Mixtures Aged at 175°C (347°F) for Two Weeks in the Presence of Valve Steel Catalysts. ANSI/ASHRAE Standard 97-1989 Test Method.



Mixed Acid #1 Mixed Acid #2 Branched Acid #2 Branched Acid #1

Figure A-13. Gas Chromatograms of HCFC-22/Polyolester Oil Mixtures Aged at 175°C (347°F) for Two Weeks in the Presence of Valve Steel Catalysts. ANSI/ASHRAE Standard 97-1989 Test Method.



Naphthenic   Paraffinic #1   Paraffinic #2   Alkylbenzene

Figure A-14. Gas Chromatograms of HCFC-22/Mineral Oil Mixtures Aged at 175°C (347°F) for One Week in the Presence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.

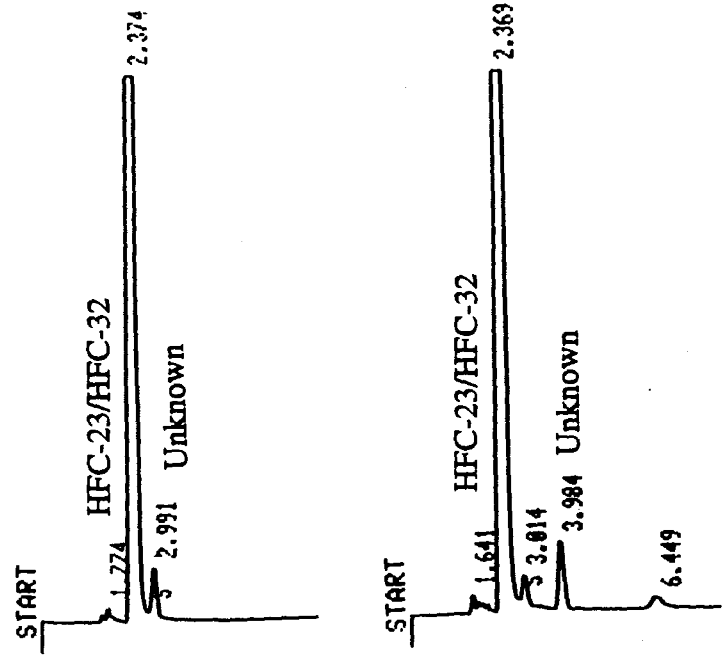
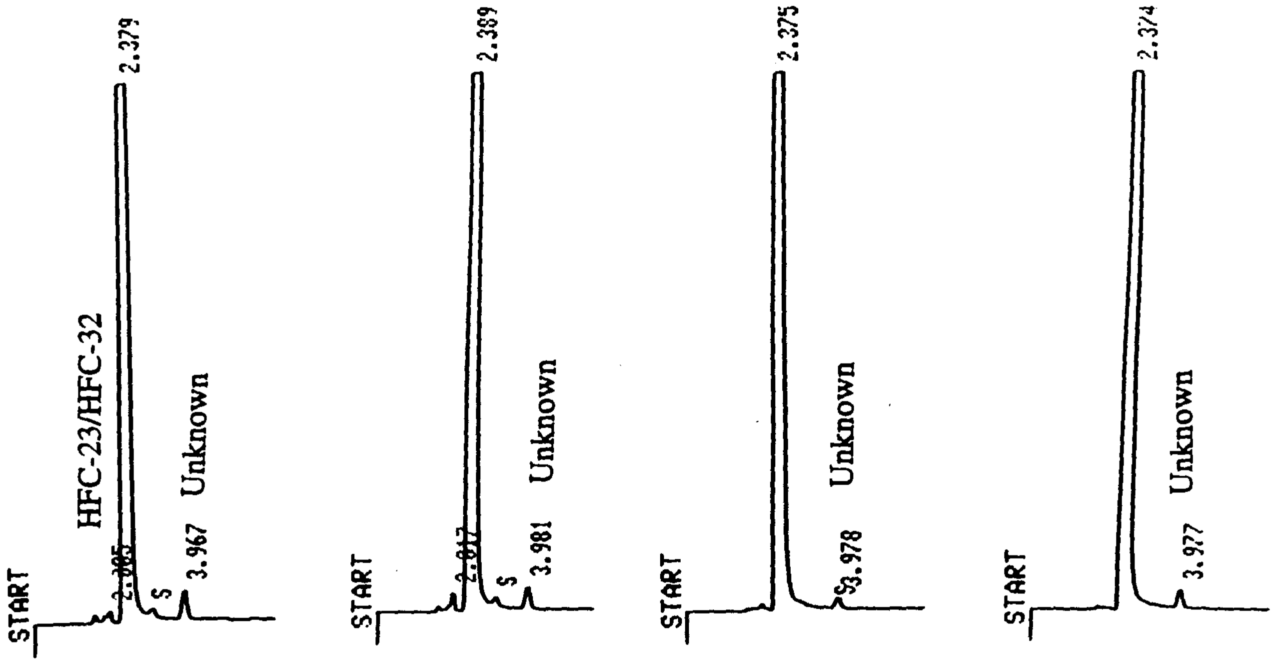
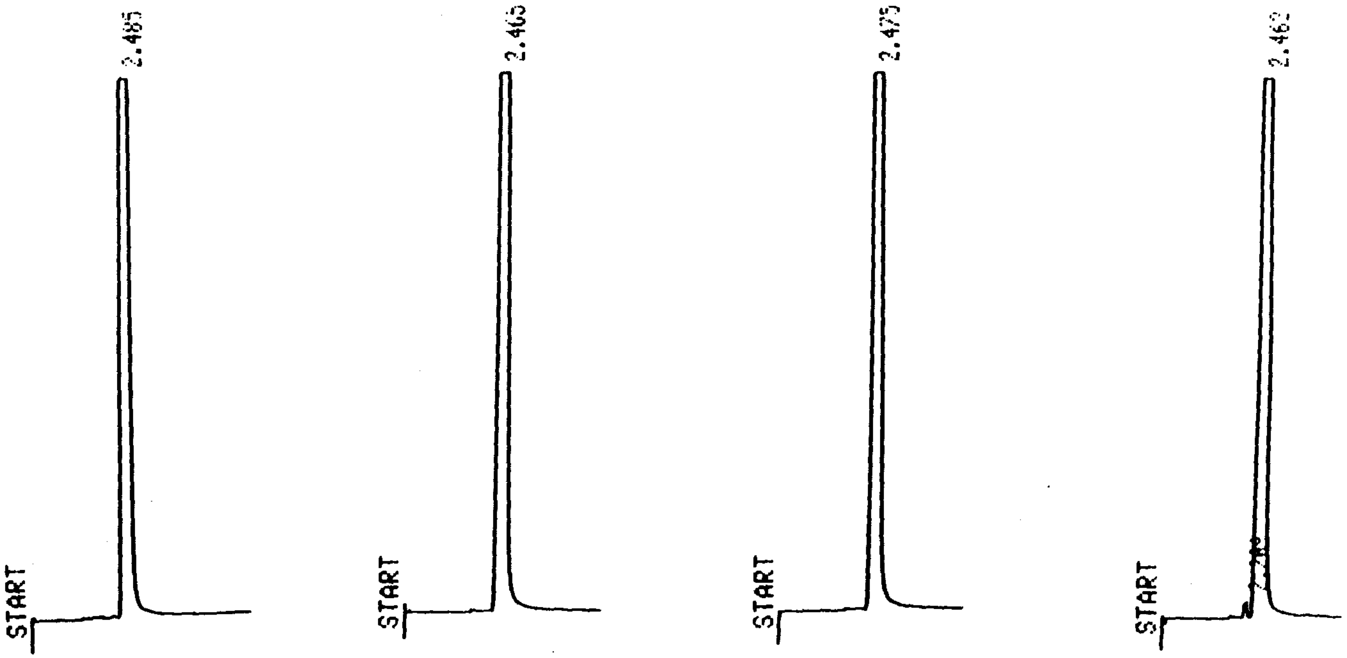


Figure A-15. Gas Chromatograms of HCFC-22/Polypropylene Glycol Mixtures Aged at 175°C (347°F) for One Week in the Presence of Valve Steel Catalysts. *In Situ* Conductivity Test Method.



Mixed Acid #1 Mixed Acid #2 Branched Acid #2 Branched Acid #1

Figure A-16. Gas Chromatograms of HCFC-22/Polyolester Oil Mixtures Aged at 175°C (347°F) for One Week in the Presence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.



Naphthenic **Paraffinic #1** **Paraffinic #2** **Alkylbenzene**

Figure A-17. Gas Chromatograms of HCFC-22/Mineral Oil Mixtures Aged at 175°C (347°F) for One Week in the Absence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.

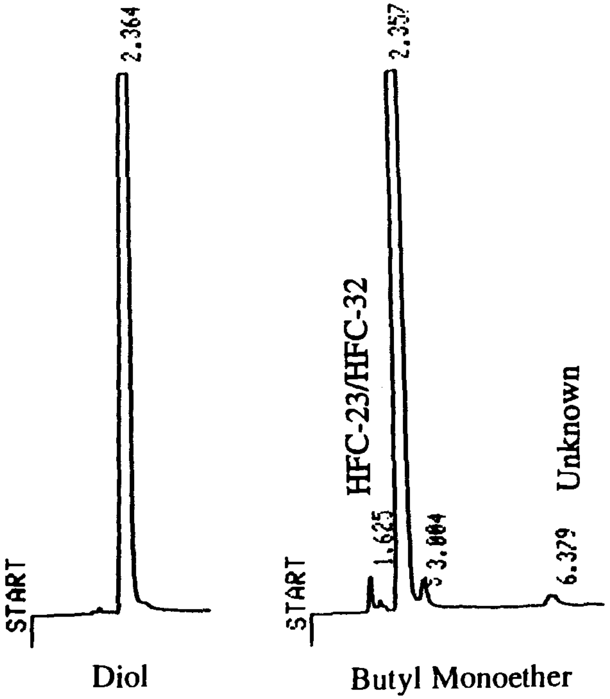
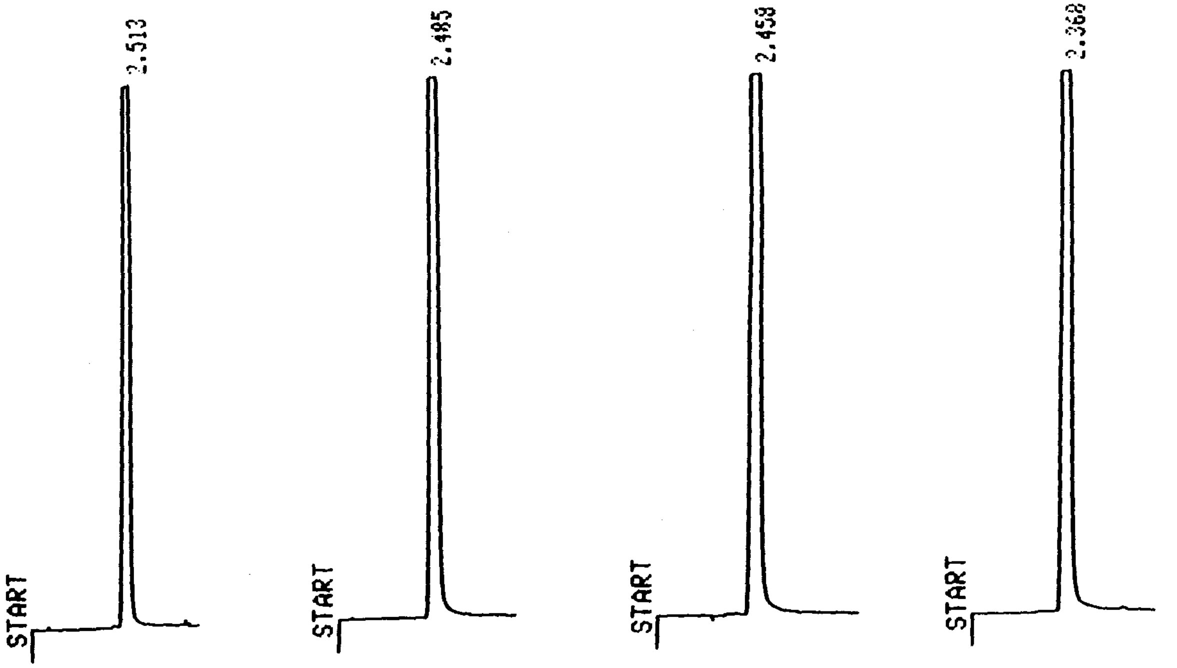
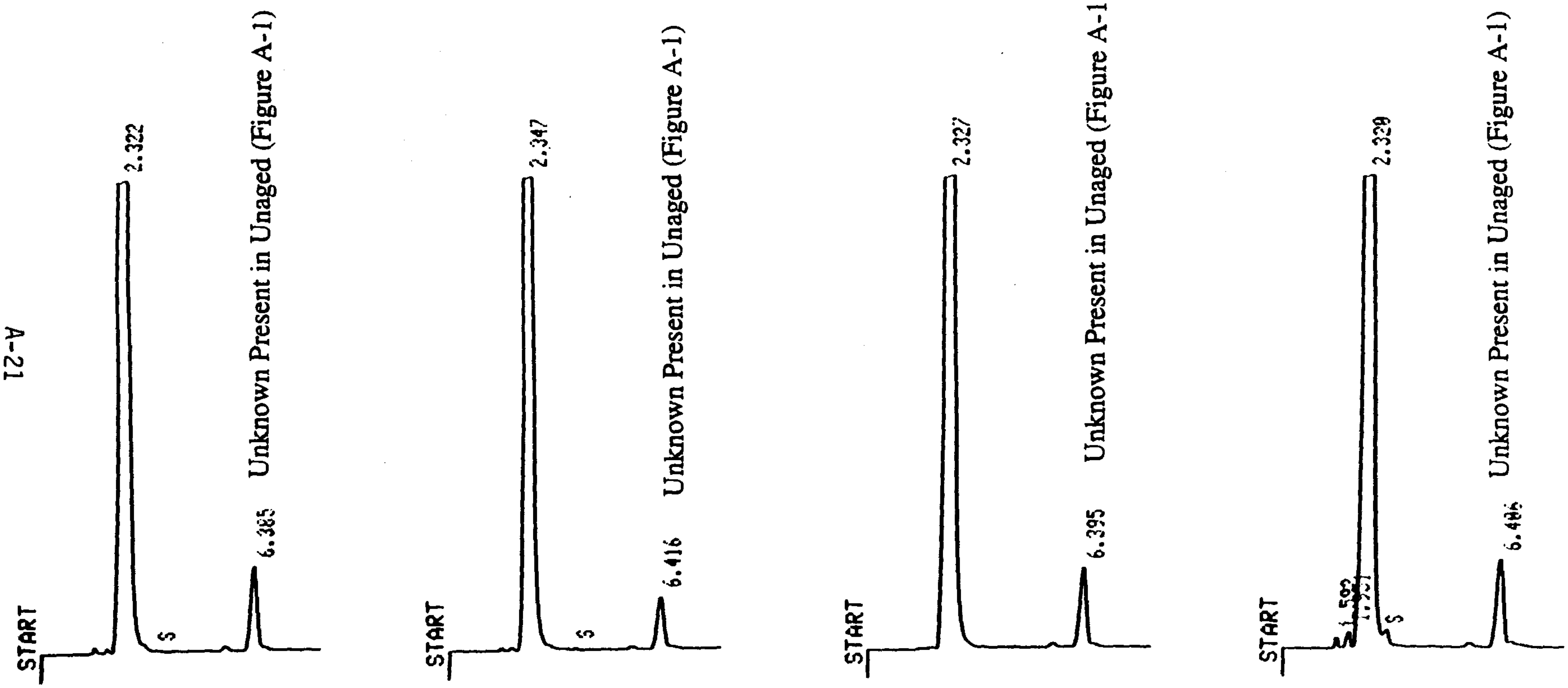


Figure A-18. Gas Chromatograms of HCFC-22/Polypropylene Glycol Mixtures Aged at 175°C (347°F) for One Week in the Absence of Valve Steel Catalysts. *In Situ* Conductivity Test Method.



Mixed Acid #1 Mixed Acid #2 Branched Acid #2 Branched Acid #1

Figure A-19. Gas Chromatograms of HCFC-22/Polyolester Oil Mixtures Aged at 175°C (347°F) for One Week in the Absence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.



Naphthenic **Paraffinic #1** **Paraffinic #2** **Alkylbenzene**

Figure A-20. Gas Chromatograms of HFC- 134a/Mineral Oil Mixtures Aged at 175°C (347°F) for Two Weeks in the Presence of Valve Steel Catalysts. ANSI/ASHRAE Standard 97-1989 Test Method.

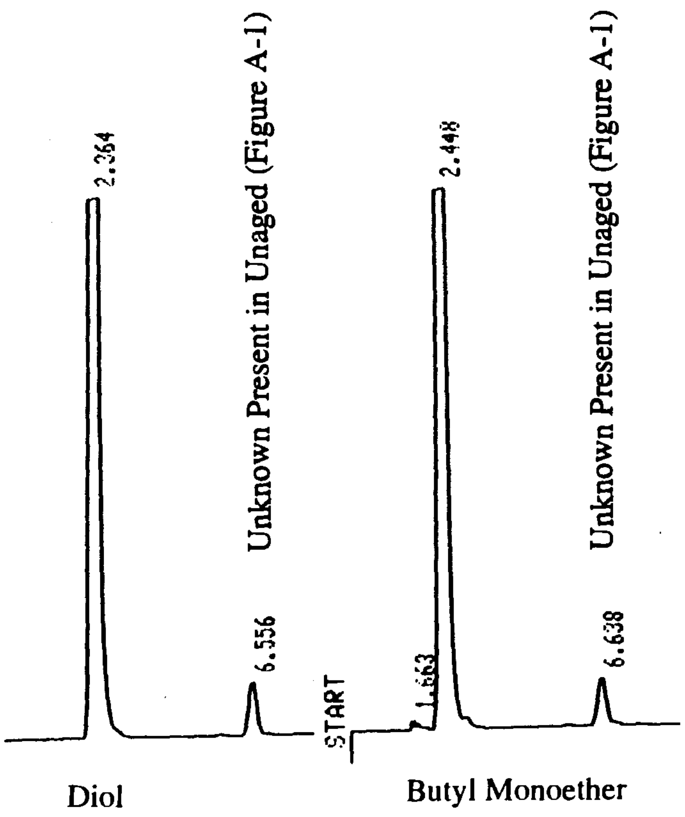
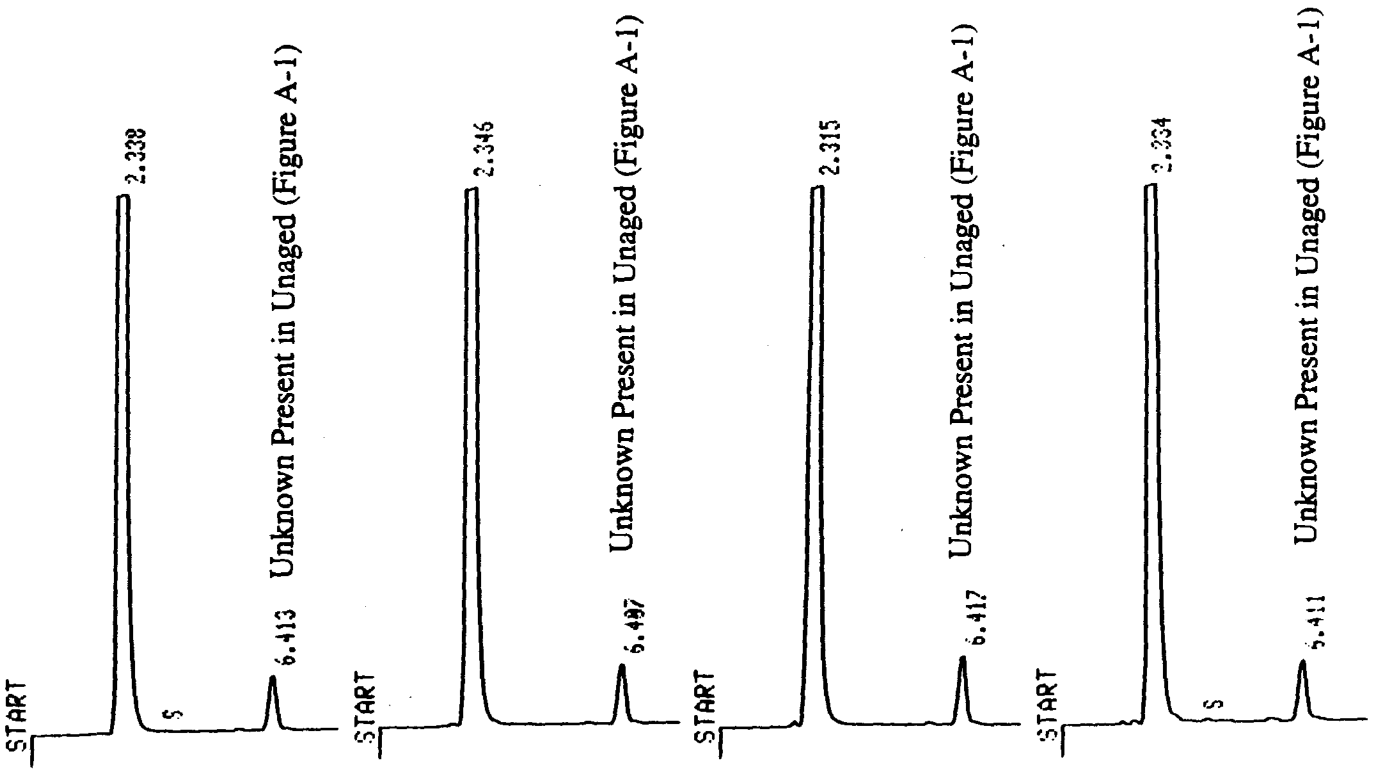


Figure A-21. Gas Chromatograms of HFC-134a/Polypropylene Glycol Mixtures Aged at 175°C (347°F) for Two Weeks in the Presence of Valve Steel Catalysts. ANSI/ASHRAE Standard 97-1989 Test Method.



Mixed Acid #1 Mixed Acid #2 Branched Acid #2 Branched Acid #1

Figure A-22. Gas Chromatograms of HFC-134a/Polyolester Oil Mixtures Aged at 175°C (347°F) for Two Weeks in the Presence of Valve Steel Catalysts. ANSI/ASHRAE Standard 97-1989 Test Method.

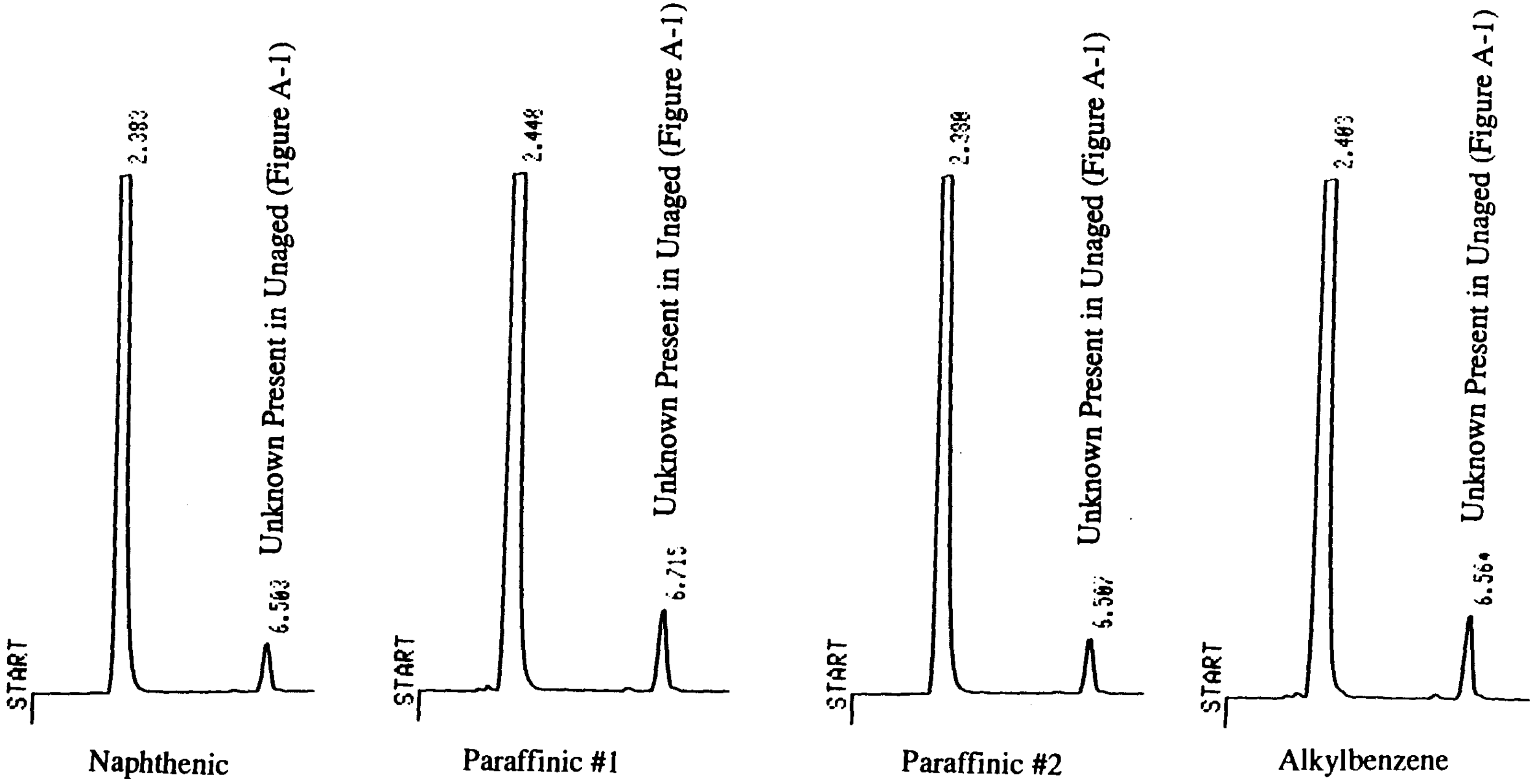


Figure A-23. Gas Chromatograms of HFC-134a/Mineral Oil Mixtures Aged at 175°C (347°F) for One Week in the Presence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.

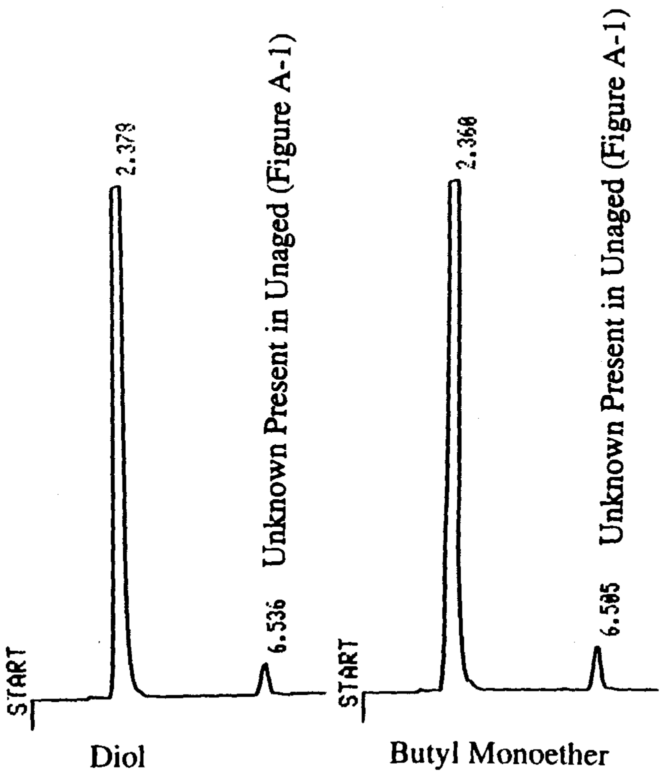
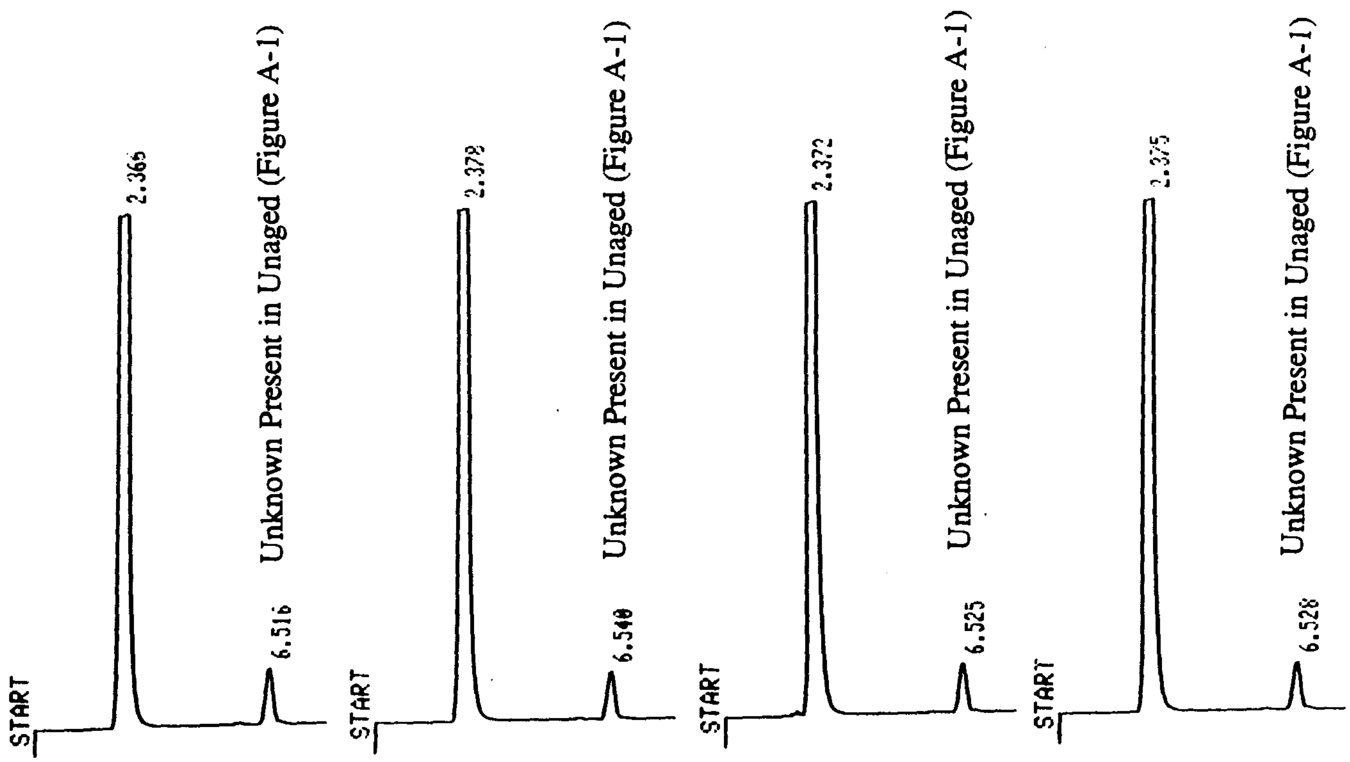
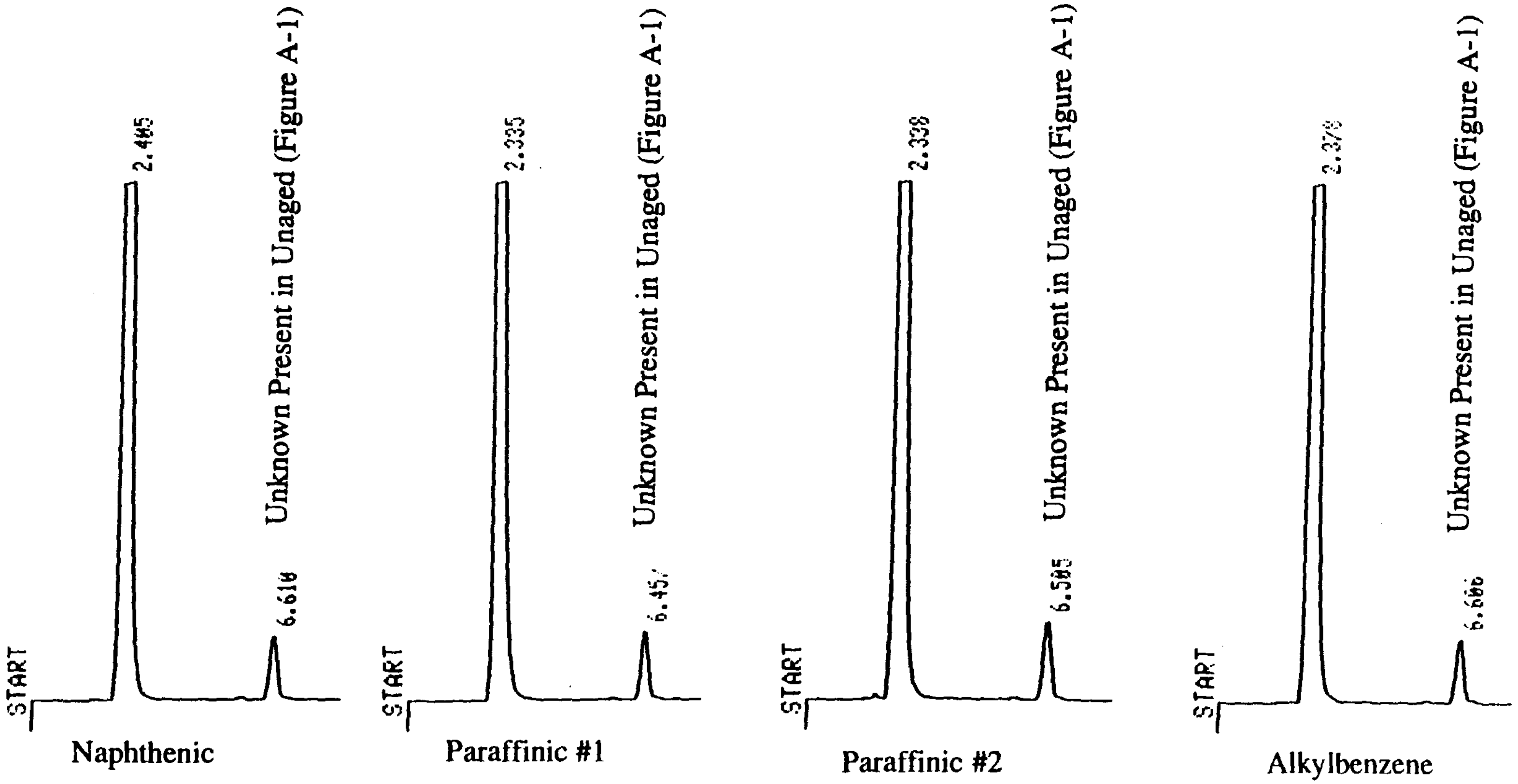


Figure A-24. Gas Chromatograms of HFC-134a/Polypropylene Glycol Mixtures Aged at 175°C (347°F) for One Week in the Presence of Valve Steel Catalysts. *In Situ* Conductivity Test Method.



Mixed Acid #1 **Mixed Acid #2** **Branched Acid #2** **Branched Acid #1**

Figure A-25. Gas Chromatograms of HFC-134a/Polyolester Oil Mixtures Aged at 175°C (347°F) for One Week in the Presence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.



Naphthenic **Paraffinic #1** **Paraffinic #2** **Alkylbenzene**

Figure A-26. Gas Chromatograms of HFC-134a/Mineral Oil Mixtures Aged at 175°C (347°F) for One Week in the Absence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.

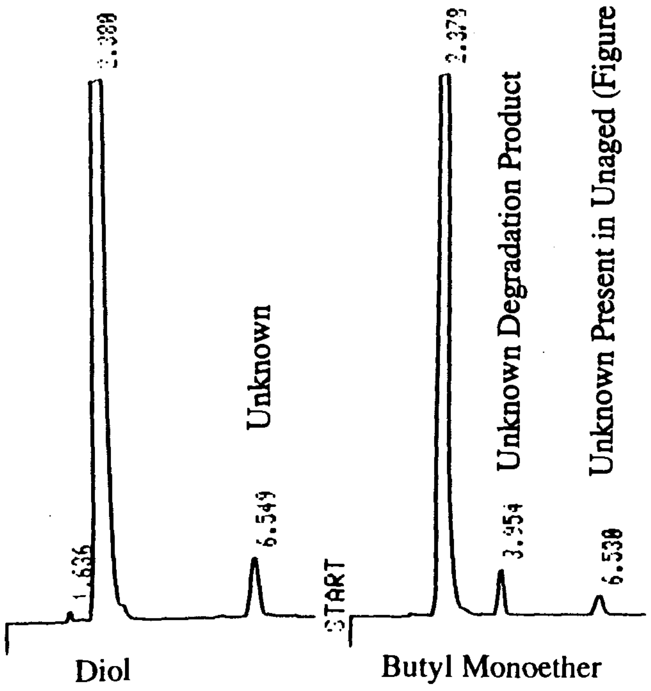


Figure A-27. Gas Chromatograms of HFC-134a/Polypropylene Glycol Mixtures Aged at 175°C (347°F) for One Week in the Absence of Valve Steel Catalysts. *In Situ* Conductivity Test Method.

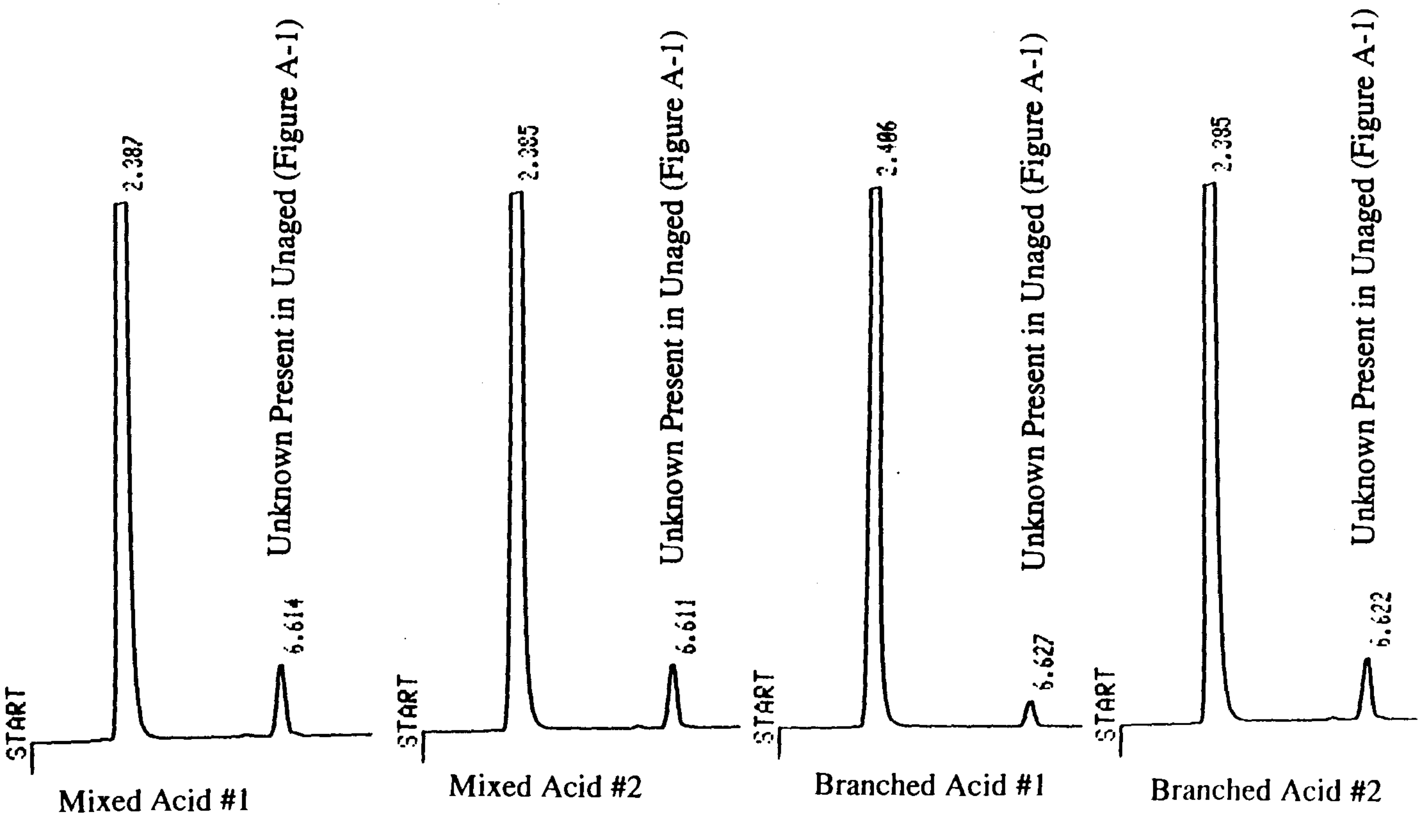
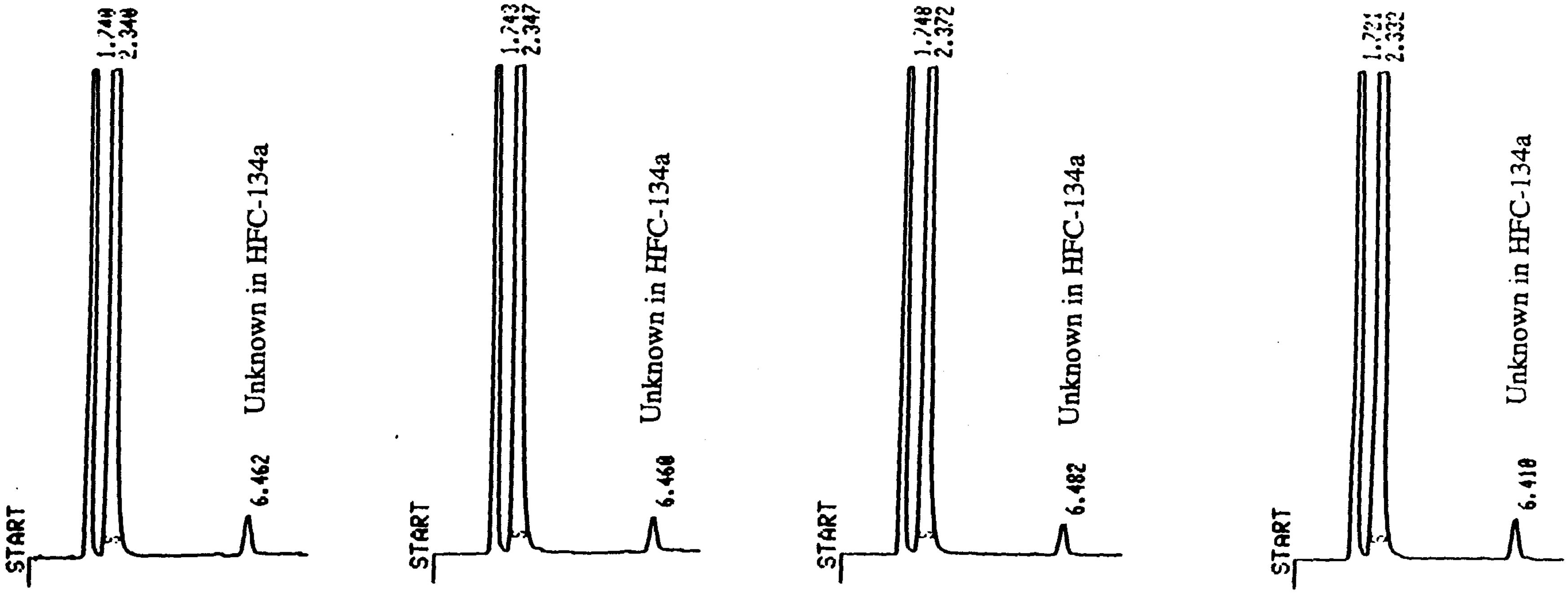


Figure A-28. Gas Chromatograms of HFC-134a/Polyolester Oil Mixtures Aged at 175°C (347°F) for One Week in the Absence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.



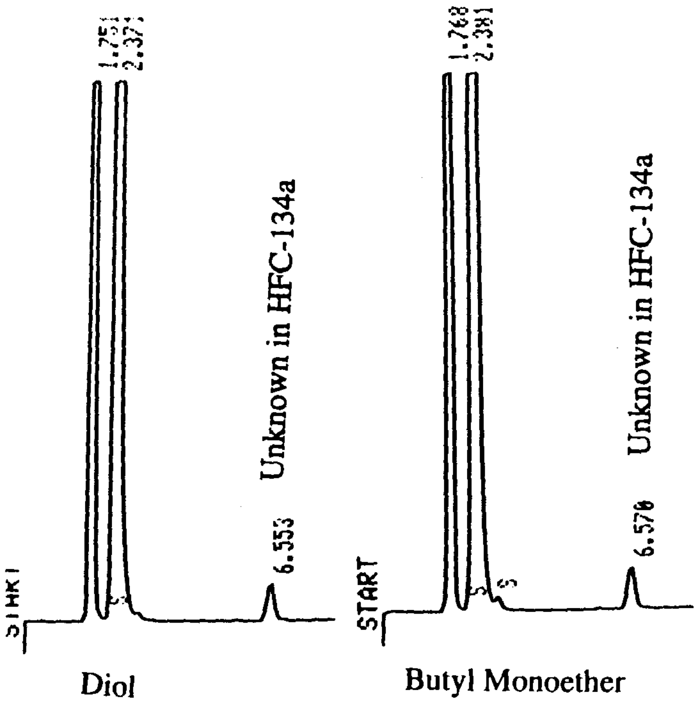
Naphthenic

Paraffinic #1

Paraffinic #2

Alkylbenzene

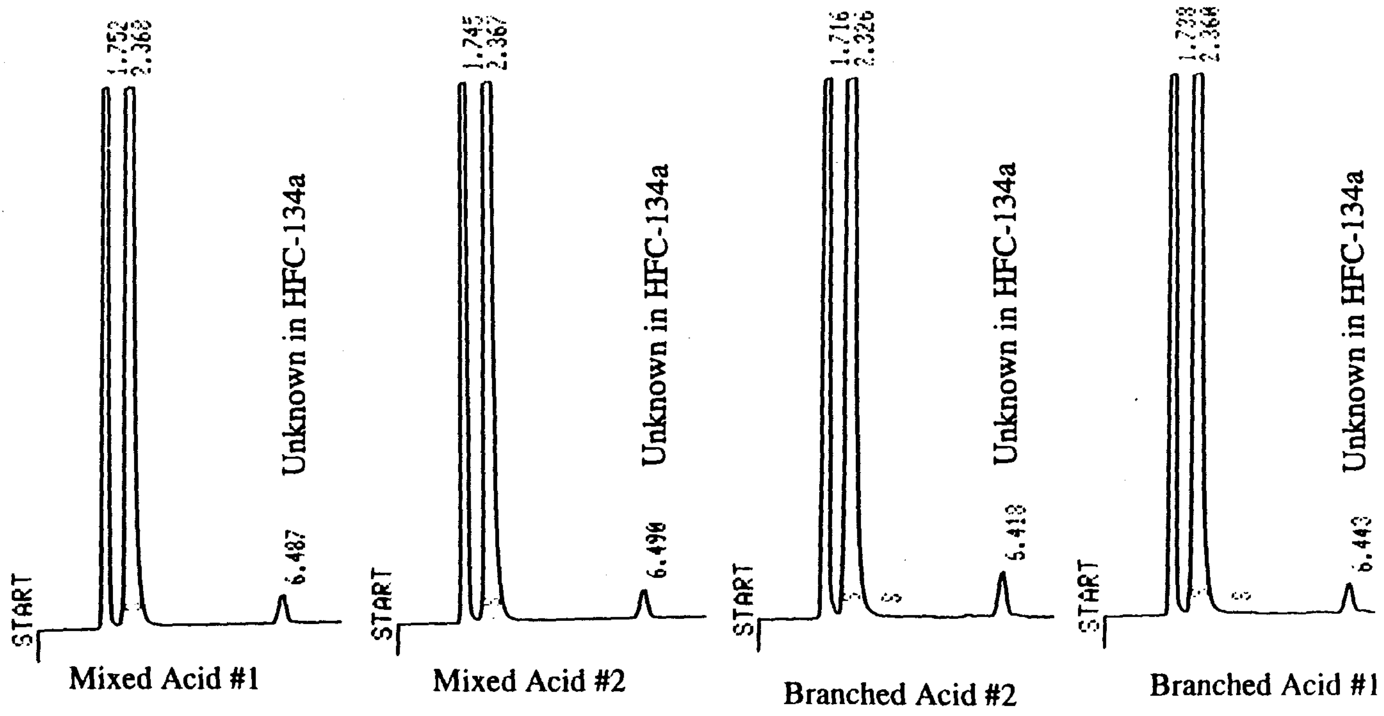
Figure A-29. Gas Chromatograms of HFC-32 (30%)/HFC-134a (70%)/Mineral Oil Mixtures Aged at 175°C (347°F) for Four Weeks in the Presence of Valve Steel Catalysts. ANSI/ASHRAE Standard 97-1989 Test Method.



Diol

Butyl Monoether

Figure A-30. Gas Chromatograms of HFC-32 (30%)/HFC-134a (70%)/Polypropylene Glycol Mixtures Aged at 175°C (347°F) for Four Weeks in the Presence of Valve Steel Catalysts. ANSI/ASHRAE Standard 97-1989 Test Method.



Mixed Acid #1

Mixed Acid #2

Branched Acid #2

Branched Acid #1

Figure A-31. Gas Chromatograms of HFC-32 (30%)/HFC-134a (70%)/Polyolester Oil Mixtures Aged at 175°C (347°F) for Four Weeks in the Presence of Valve Steel Catalysts. ANSI/ASHRAE Standard 97-1989 Test Method.

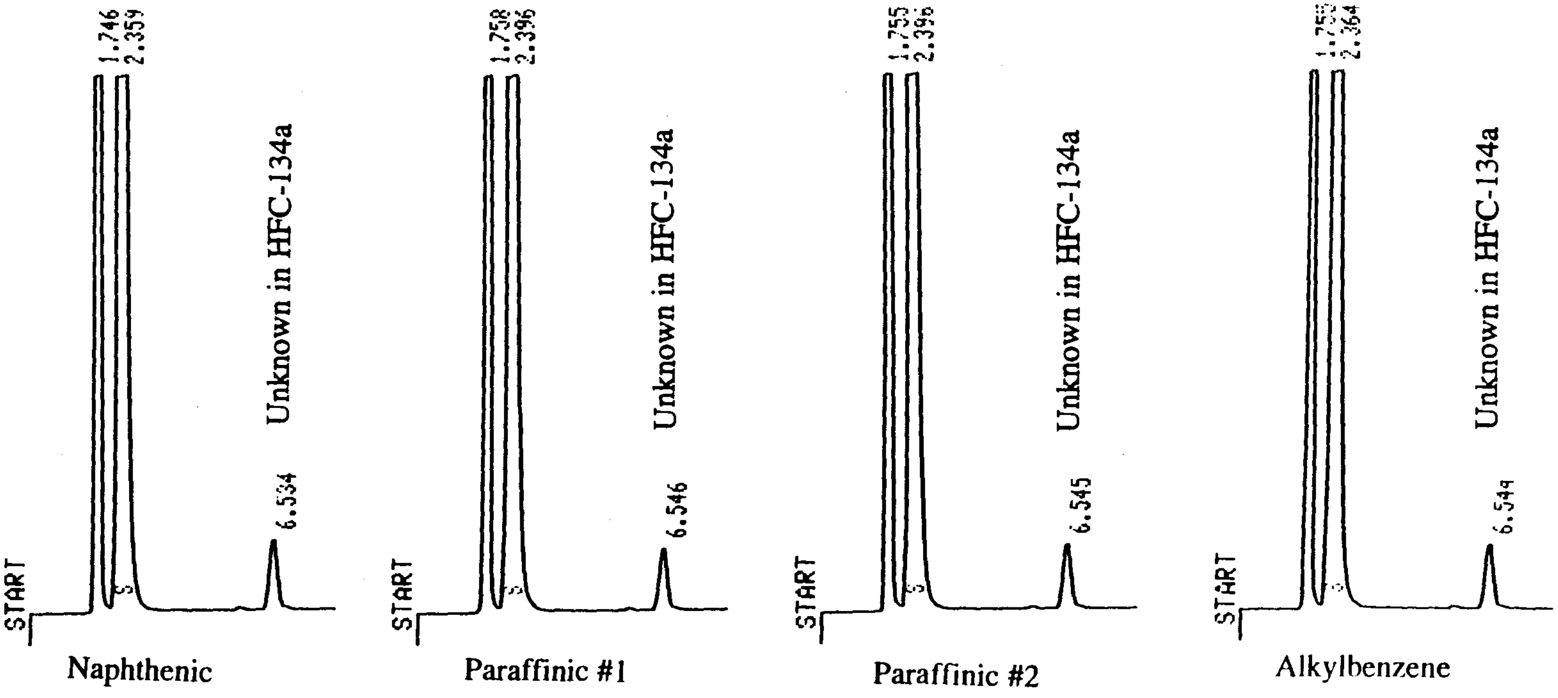
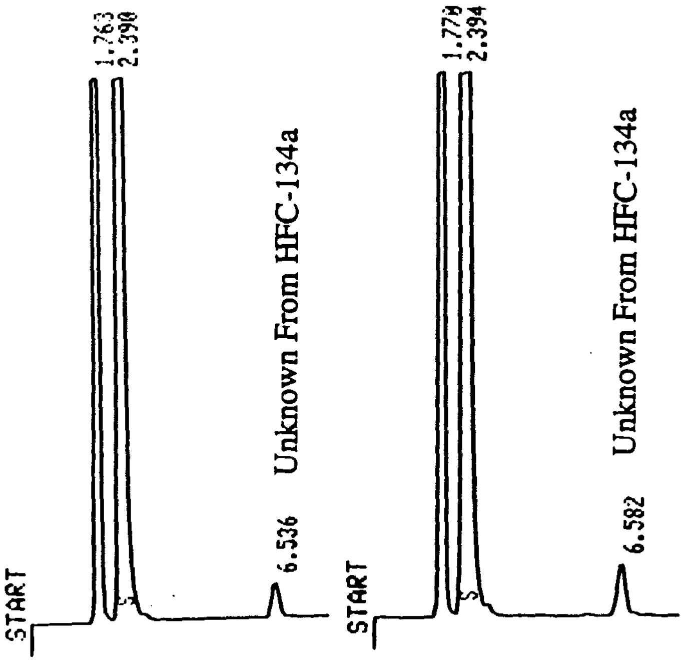
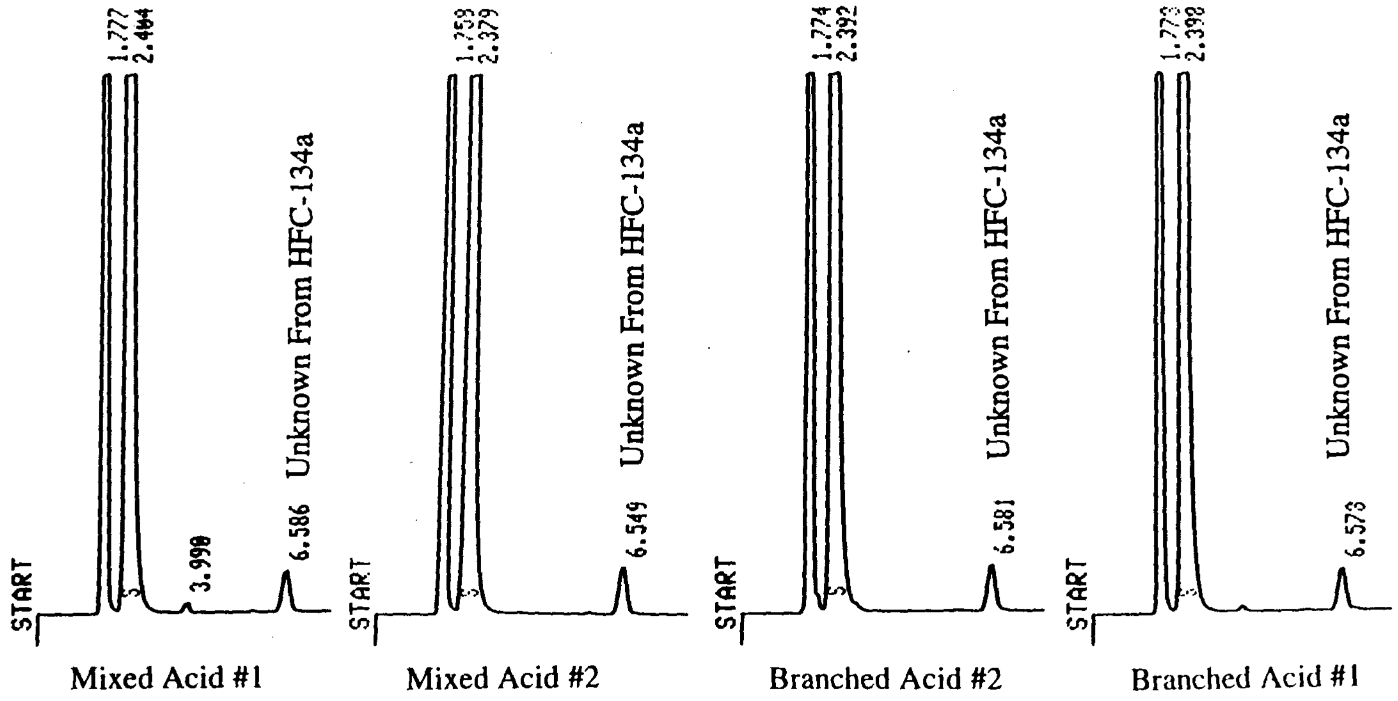


Figure A-32. Gas Chromatograms of HFC-32 (30%)/HFC-134a (70%)/Mineral Oil Mixtures Aged at 175°C (347°F) for One Week in the Presence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.



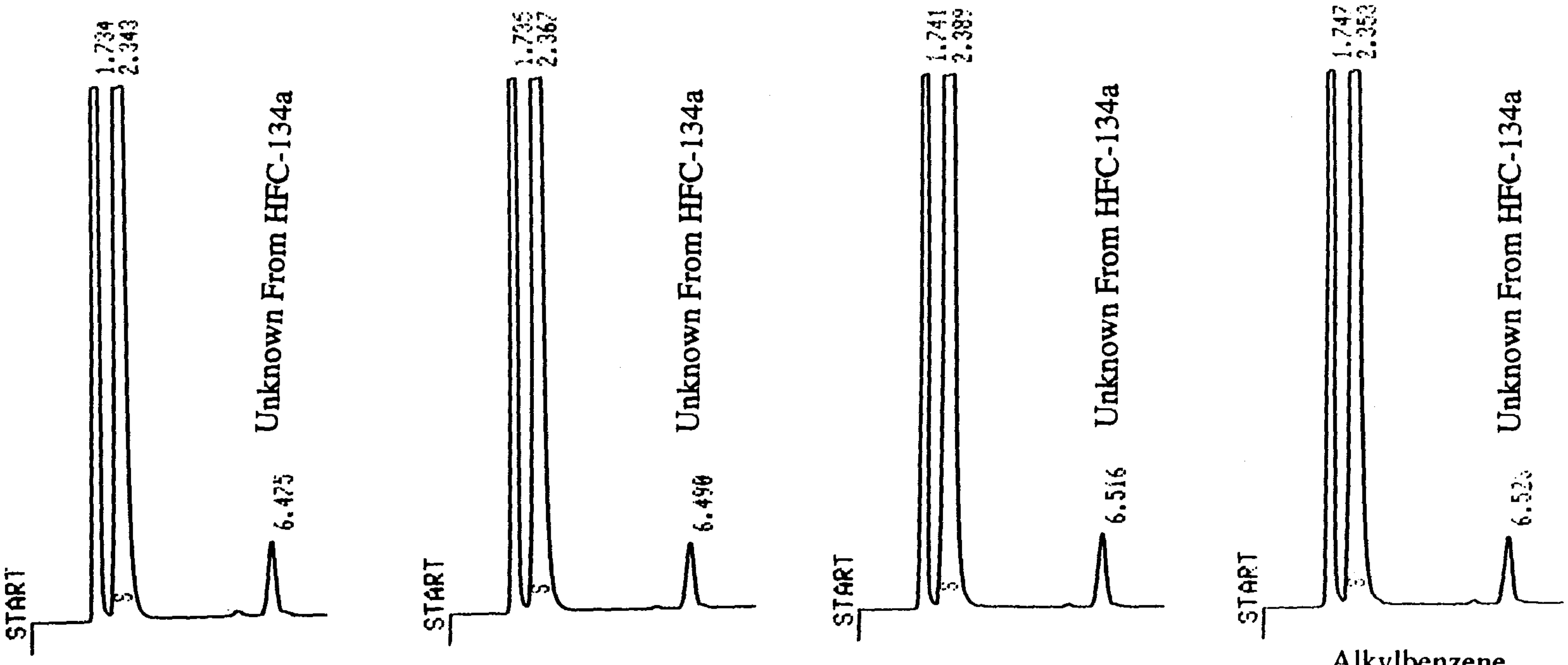
Diol **Butyl Monoether**

Figure A-33. Gas Chromatograms of HFC-32 (30%)/HFC-134a (70%)/Polypropylene Glycol Mixtures Aged at 175°C (347°F) for One Week in the Presence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.



Mixed Acid #1 Mixed Acid #2 Branched Acid #2 Branched Acid #1

Figure A-34. Gas Chromatograms of HFC-32 (30%)/HFC-134a (70%)/Polyolester Oil Mixtures Aged at 175°C (347°F) for One Week in the Presence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.



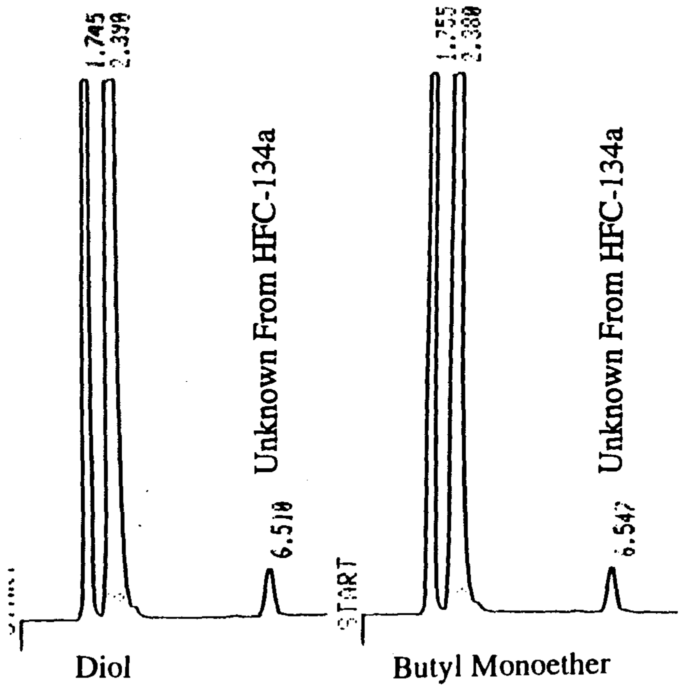
Naphthenic

Paraffinic #1

Paraffinic #2

Alkylbenzene

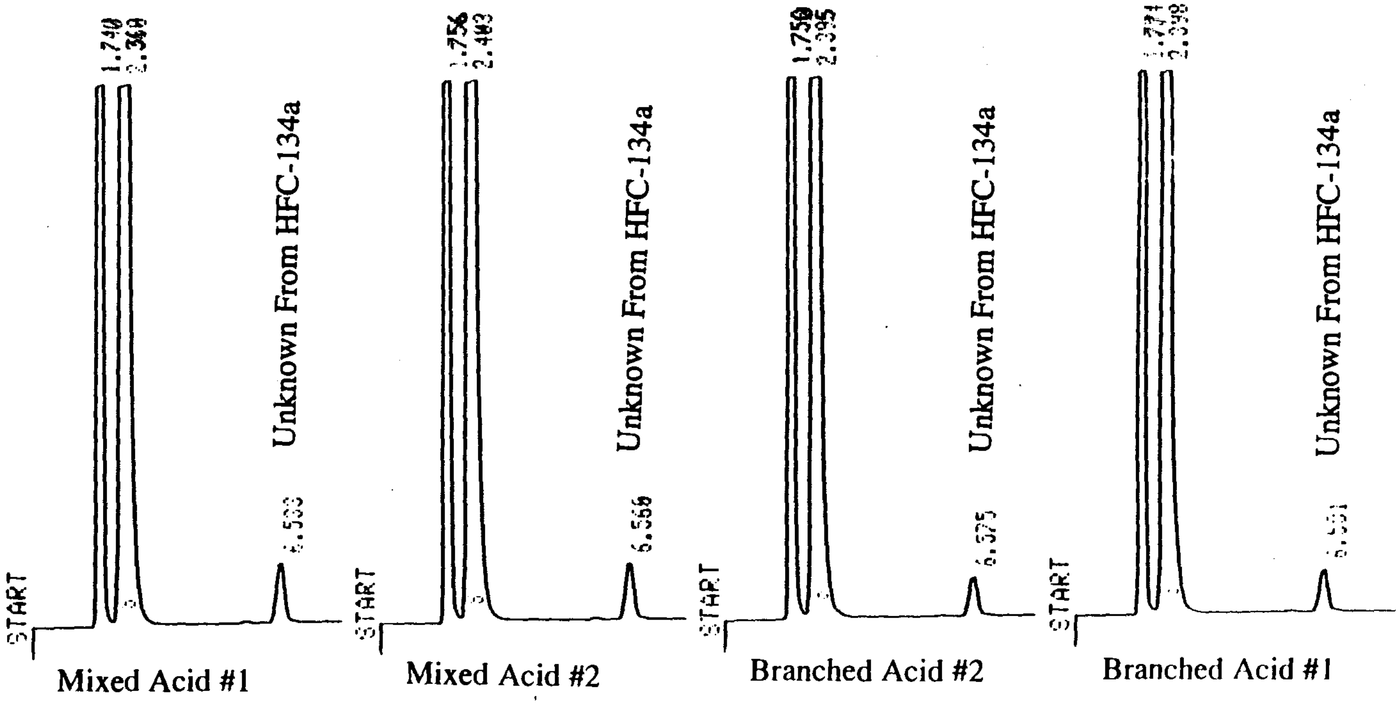
Figure A-35. Gas Chromatograms of HFC-32 (30%)/HFC-134a (70%)/Mineral Oil Mixtures Aged at 175°C (347°F) for One Week in the Absence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.



Diol

Butyl Monoether

Figure A-36. Gas Chromatograms of HFC-32 (30%)/HFC-134a (70%)/Polypropylene Glycol Mixtures Aged at 175°C (347°F) for One Week in the Absence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.

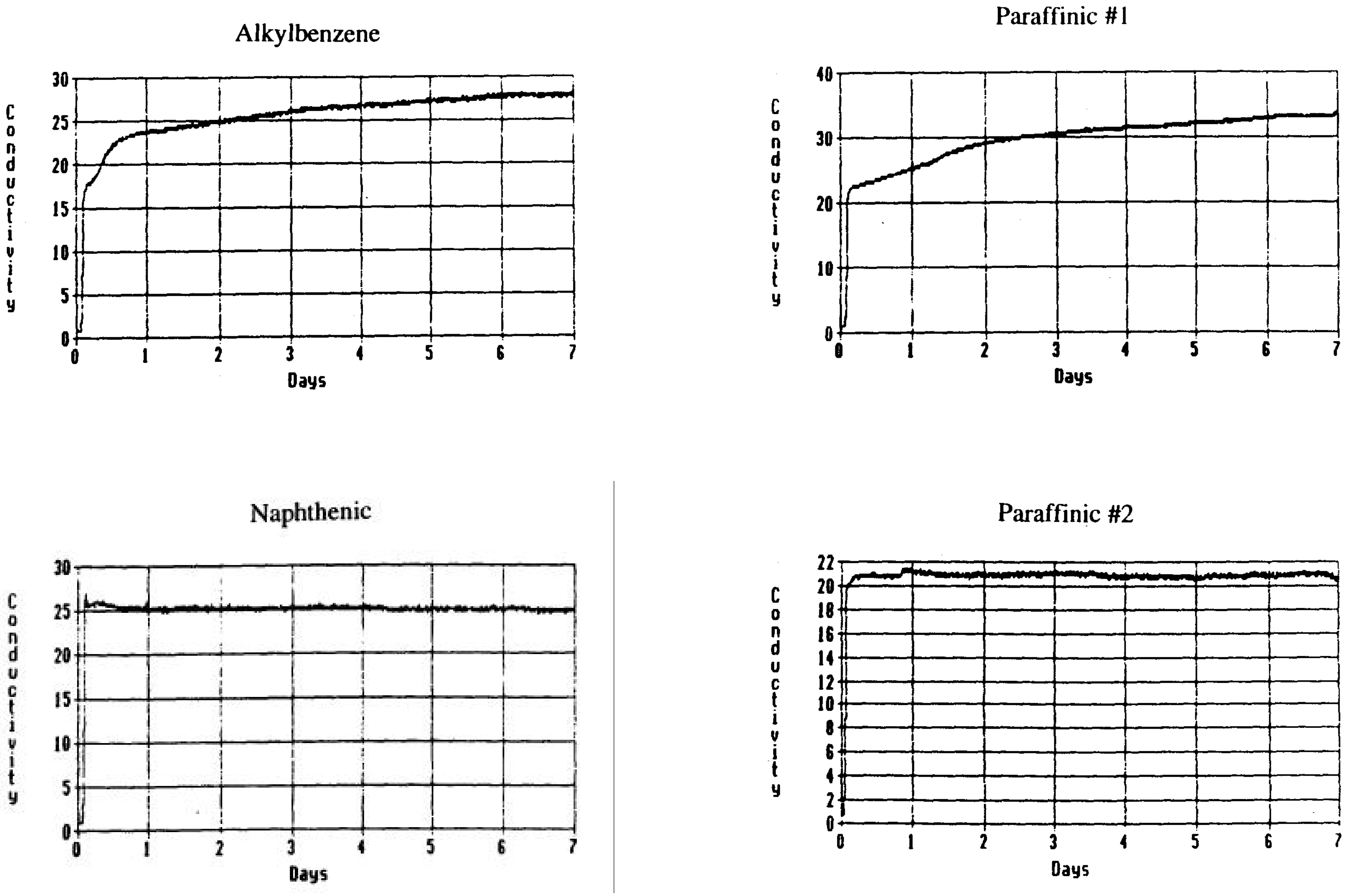


Mixed Acid #1 Mixed Acid #2 Branched Acid #2 Branched Acid #1

Figure A-37. Gas Chromatograms of HFC-32 (30%)/HFC-134a (70%)/Polyolester Oil Mixtures Aged at 175°C (347°F) for One Week in the Absence of Valve Steel Catalysts in the Multichannel Aluminum Block Heater. *In Situ* Conductivity Test Method.

APPENDIX B

IN SITU CONDUCTIVITY VERSUS AGING TIME PLOTS OF REFRIGERANT/OIL MIXTURES

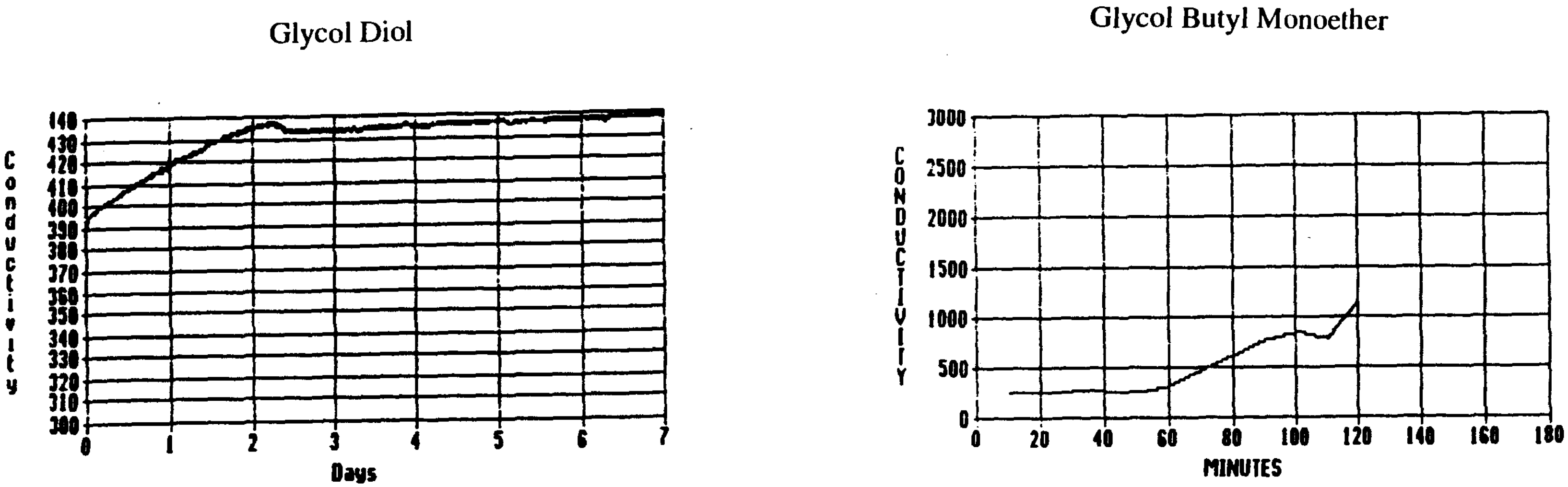

Alkylbenzene

Paraffinic #1

Naphthenic

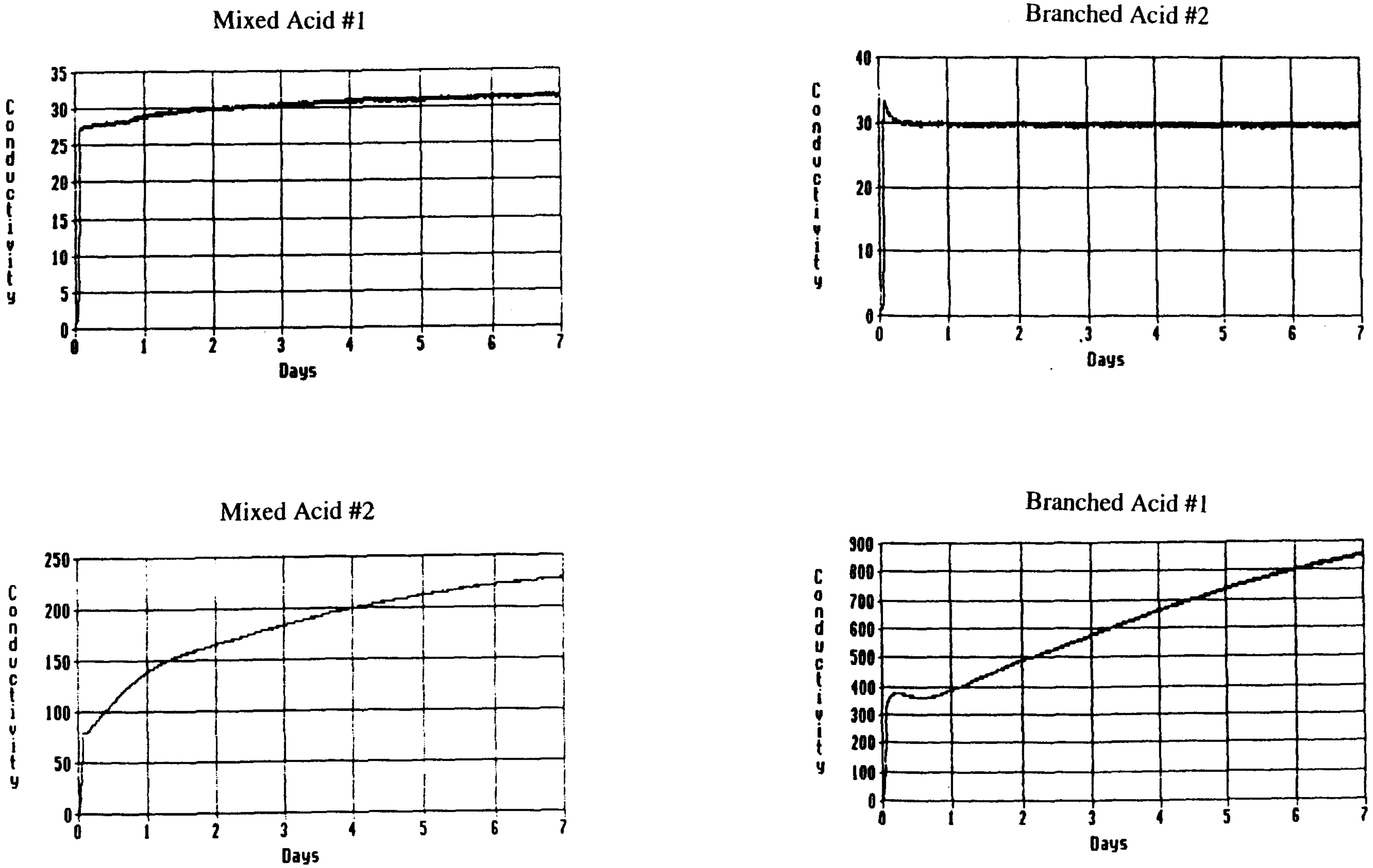
Paraffinic #2

Figure B-1. *In Situ* Conductivity Versus Aging Time Plots of CFC-12/Mineral Oil Mixtures (No Metal Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.


Glycol Diol

Glycol Butyl Monoether

Figure B-2. *In Situ* Conductivity Versus Aging Time Plots of CFC-12/Polypropylene Glycol Mixtures (No Metal Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.



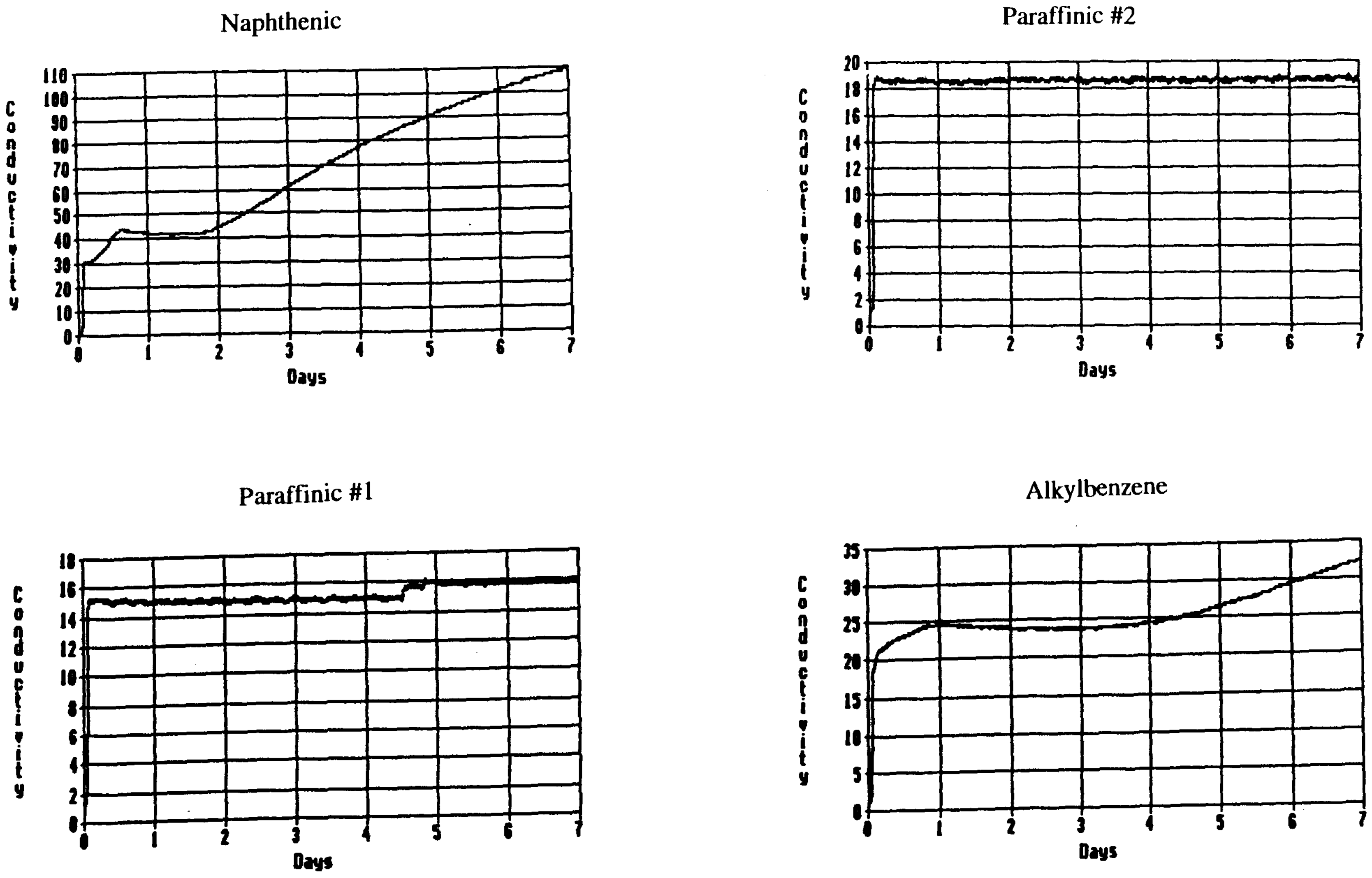
Mixed Acid #1

Branched Acid #2

Mixed Acid #2

Branched Acid #1

Figure B-3. *In Situ* Conductivity Versus Aging Time Plots of CFC-12/Polyolester Oil Mixtures (No Metal Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.


Naphthenic

Paraffinic #2

Paraffinic #1

Alkylbenzene

Figure B-4. *In Situ* Conductivity Versus Aging Time Plots of CFC-12/Mineral Oil Mixtures (Valve Steel Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

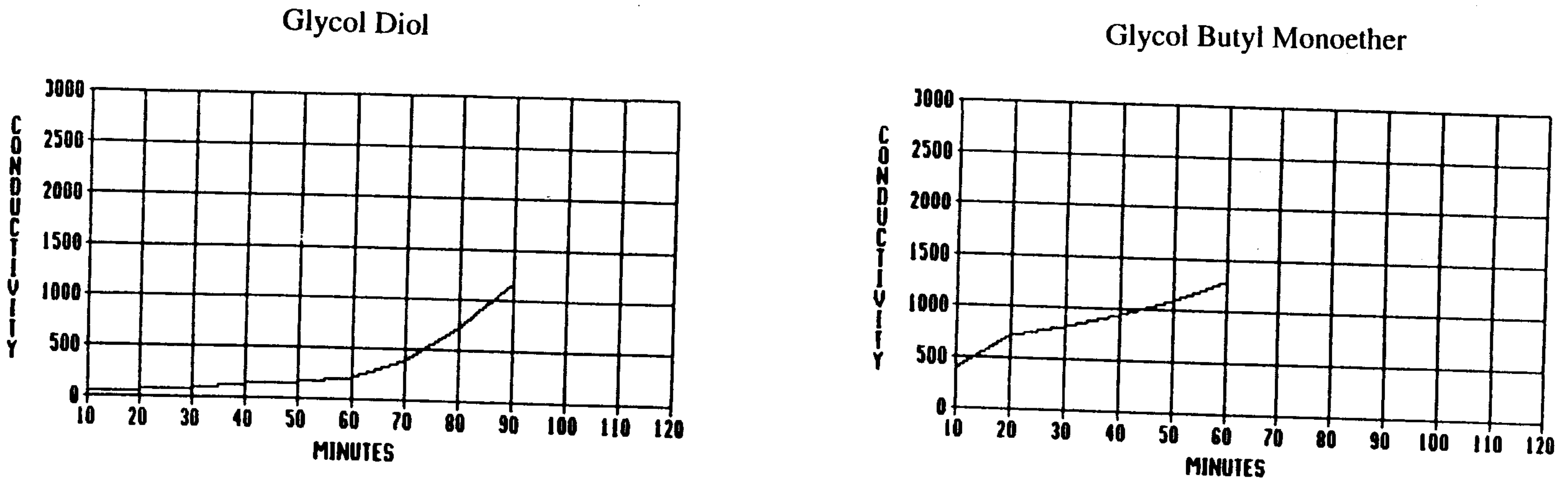


Figure B-5. *In Situ* Conductivity Versus Aging Time Plots of CFC-12/Polypropylene Glycol Mixtures (Valve Steel Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

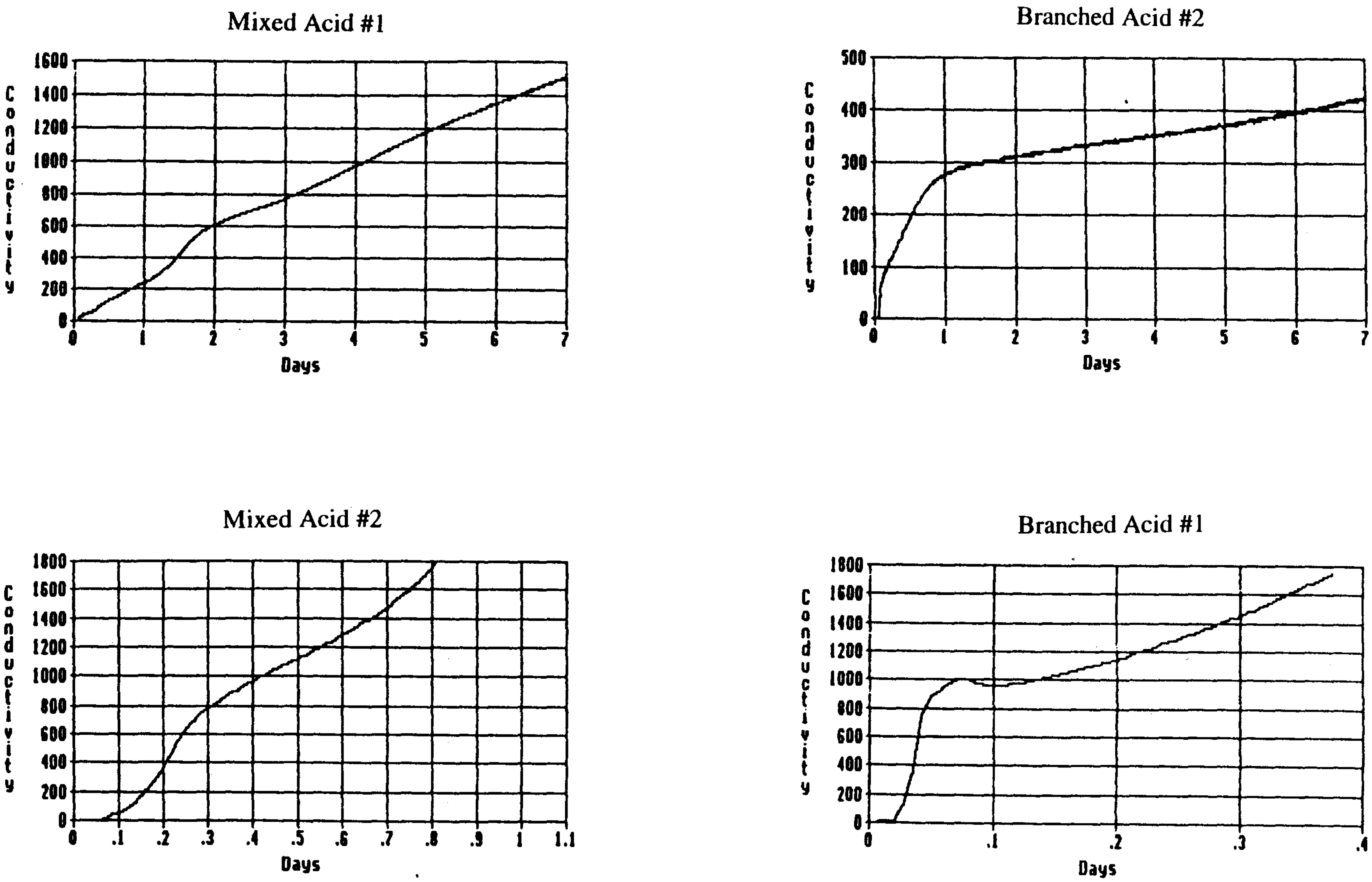


Figure B-6. *In Situ* Conductivity Versus Aging Time Plots of CFC-12/Polyolester Oil Mixtures (Valve Steel Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

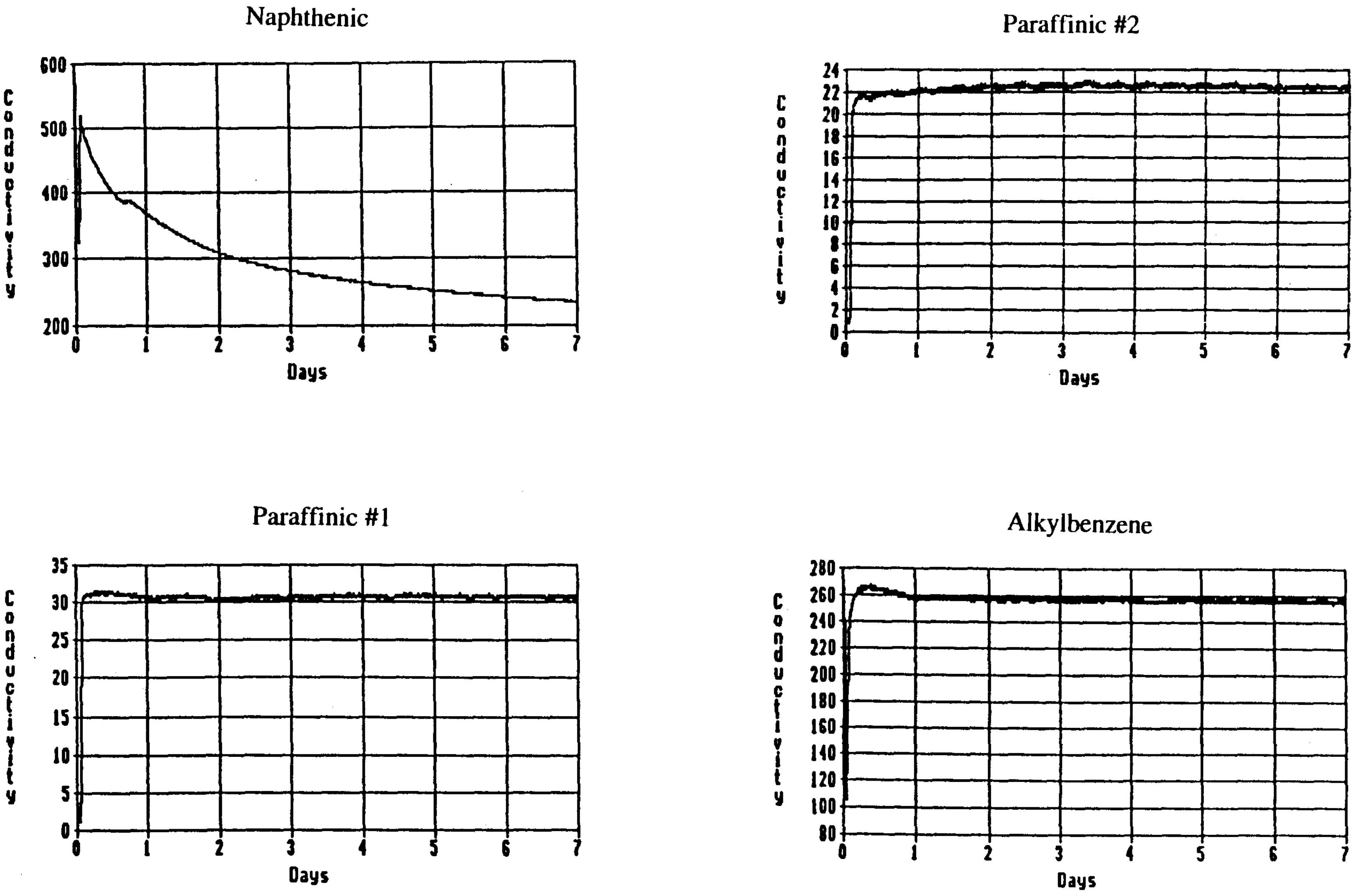
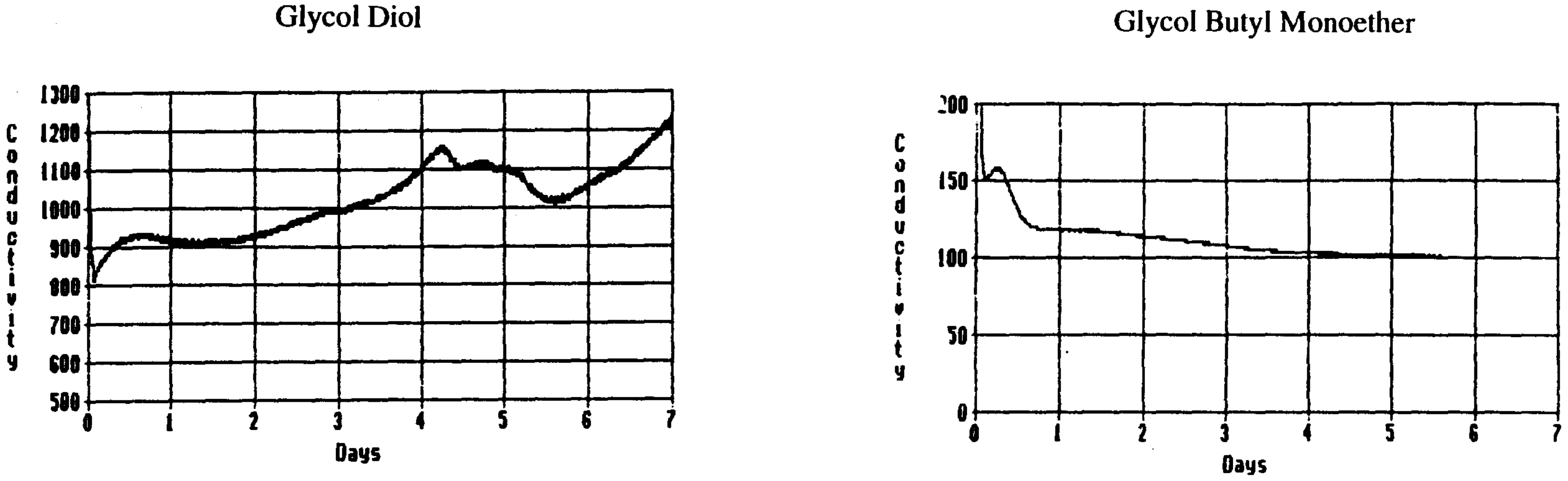
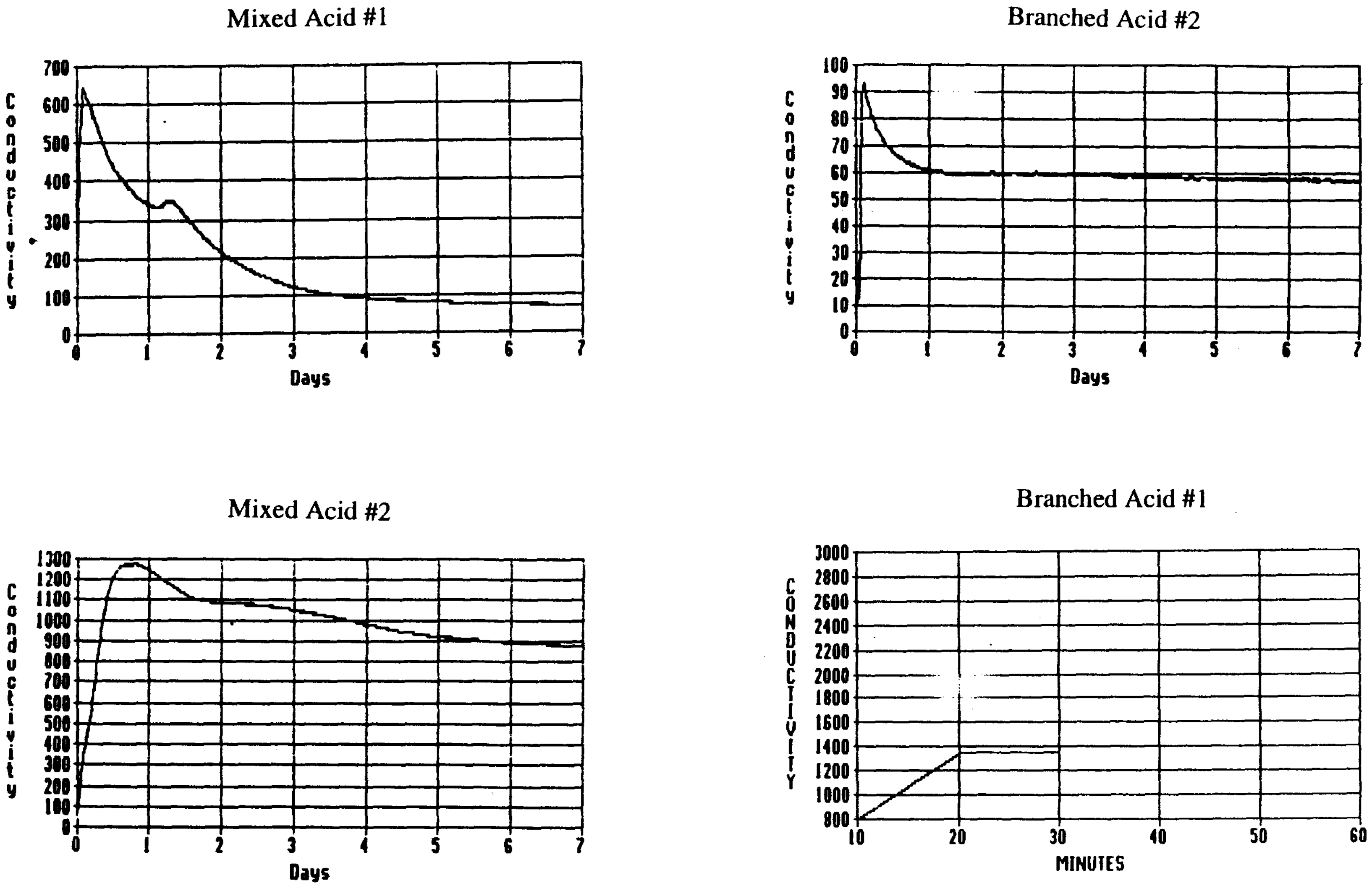


Figure B-7. *In Situ* Conductivity Versus Aging Time Plots of HCFC-22/Mineral Oil Mixtures (No Metal Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.


Glycol Diol

Glycol Butyl Monoether

Figure B-8. *In Situ* Conductivity Versus Aging Time Plots of HCFC-22/Polypropylene Glycol Mixtures (No Metal Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.


Mixed Acid #1

Branched Acid #2

Mixed Acid #2

Branched Acid #1

Figure B-9. *In Situ* Conductivity Versus Aging Time Plots of HCFC-22/Polyolester Oil Mixtures (No Metal Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

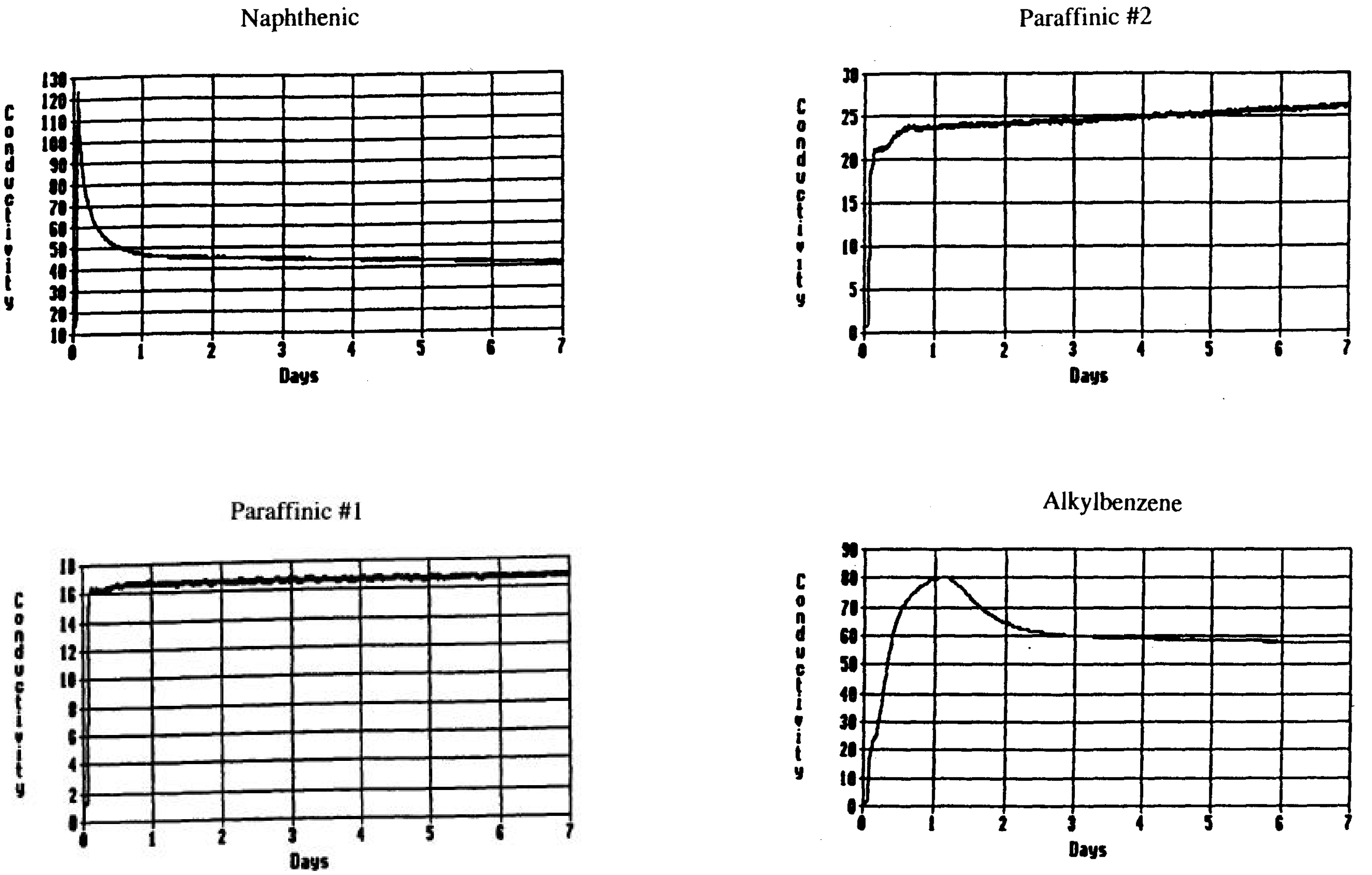


Figure B-10. *In Situ* Conductivity Versus Aging Time Plots of HCFC-22/Mineral Oil Mixtures (Valve Steel Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

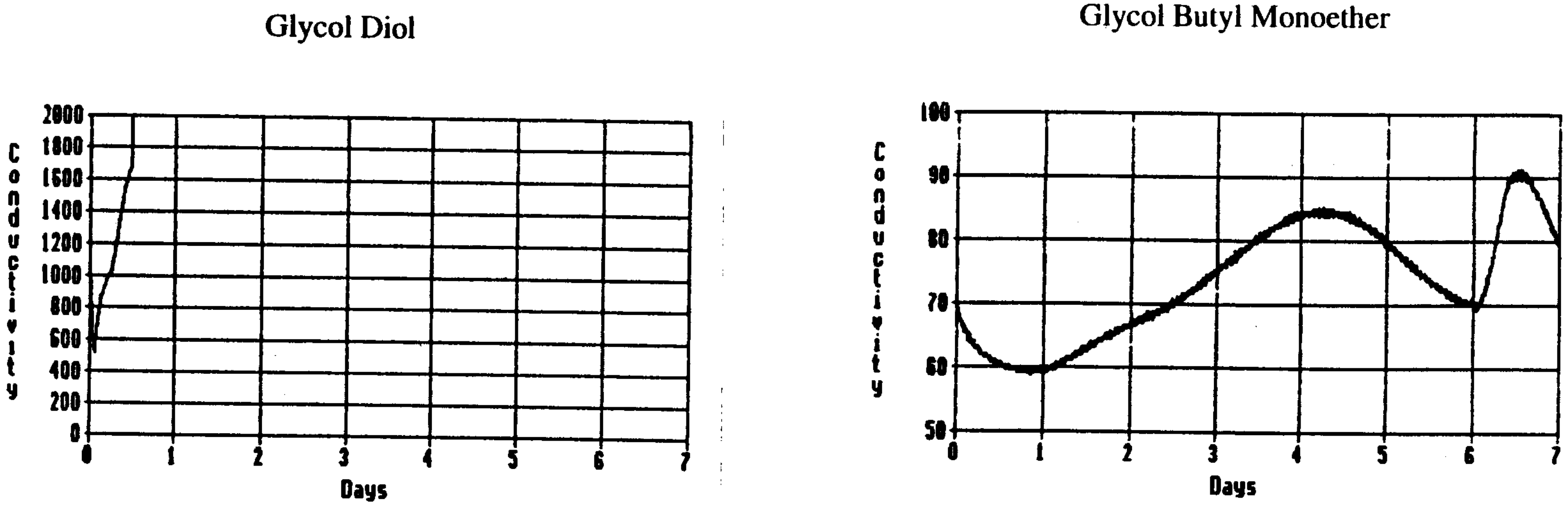
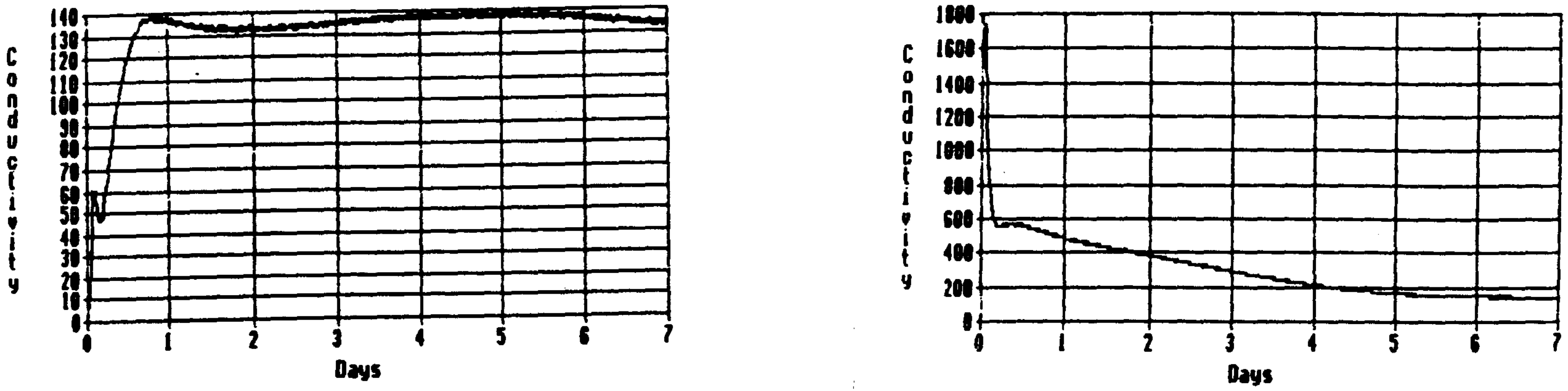
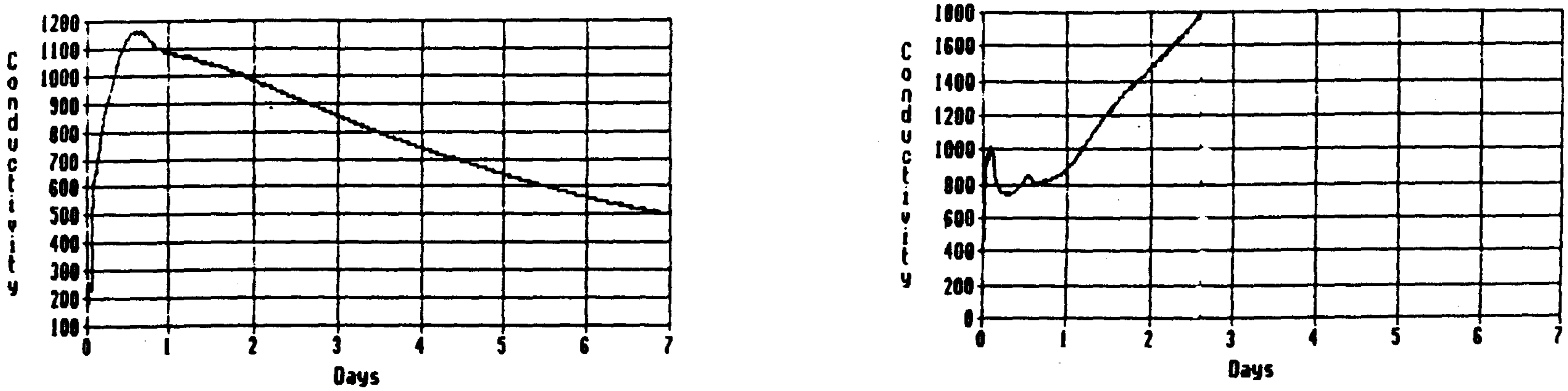


Figure B-11. *In Situ* Conductivity Versus Aging Time Plots of HCFC-22/Polypropylene Glycol Mixtures (Valve Steel Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.



Mixed Acid #1

Branched Acid #2



Mixed Acid #2

Branched Acid #1

Figure B-12. *In Situ* Conductivity Versus Aging Time Plots of HCFC-22/Polyolester Oil Mixtures (Valve Steel Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

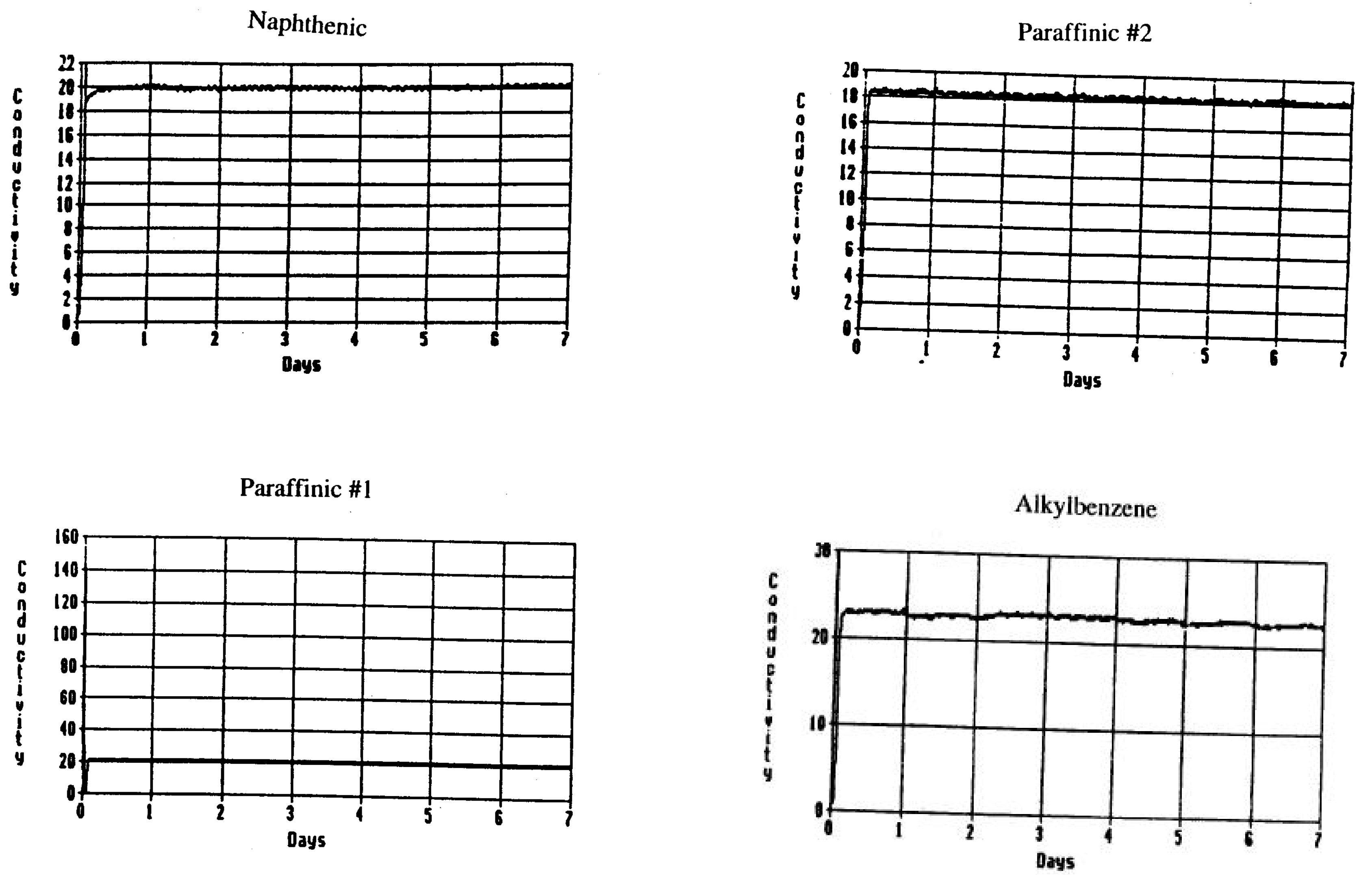
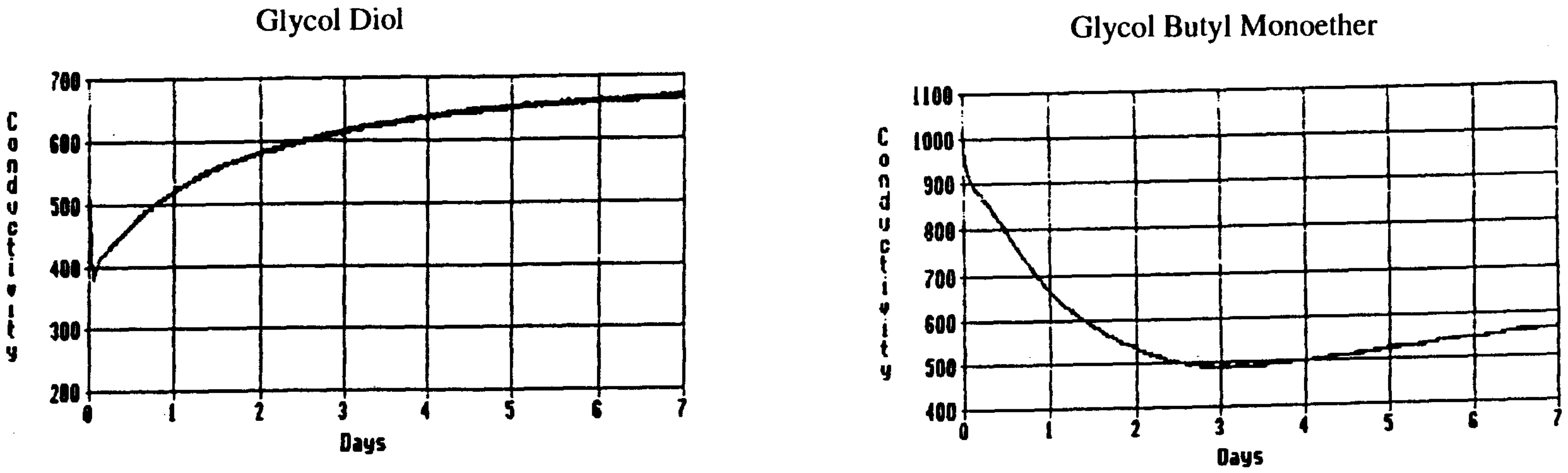


Figure B-13. *In Situ* Conductivity Versus Aging Time Plots of HFC-134a/Mineral Oil Mixtures (No Metal Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.



Glycol Diol

Glycol Butyl Monoether

Figure B-14. *In Situ* Conductivity Versus Aging Time Plots of HFC-134a/Polypropylene Glycol Mixtures (No Metal Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

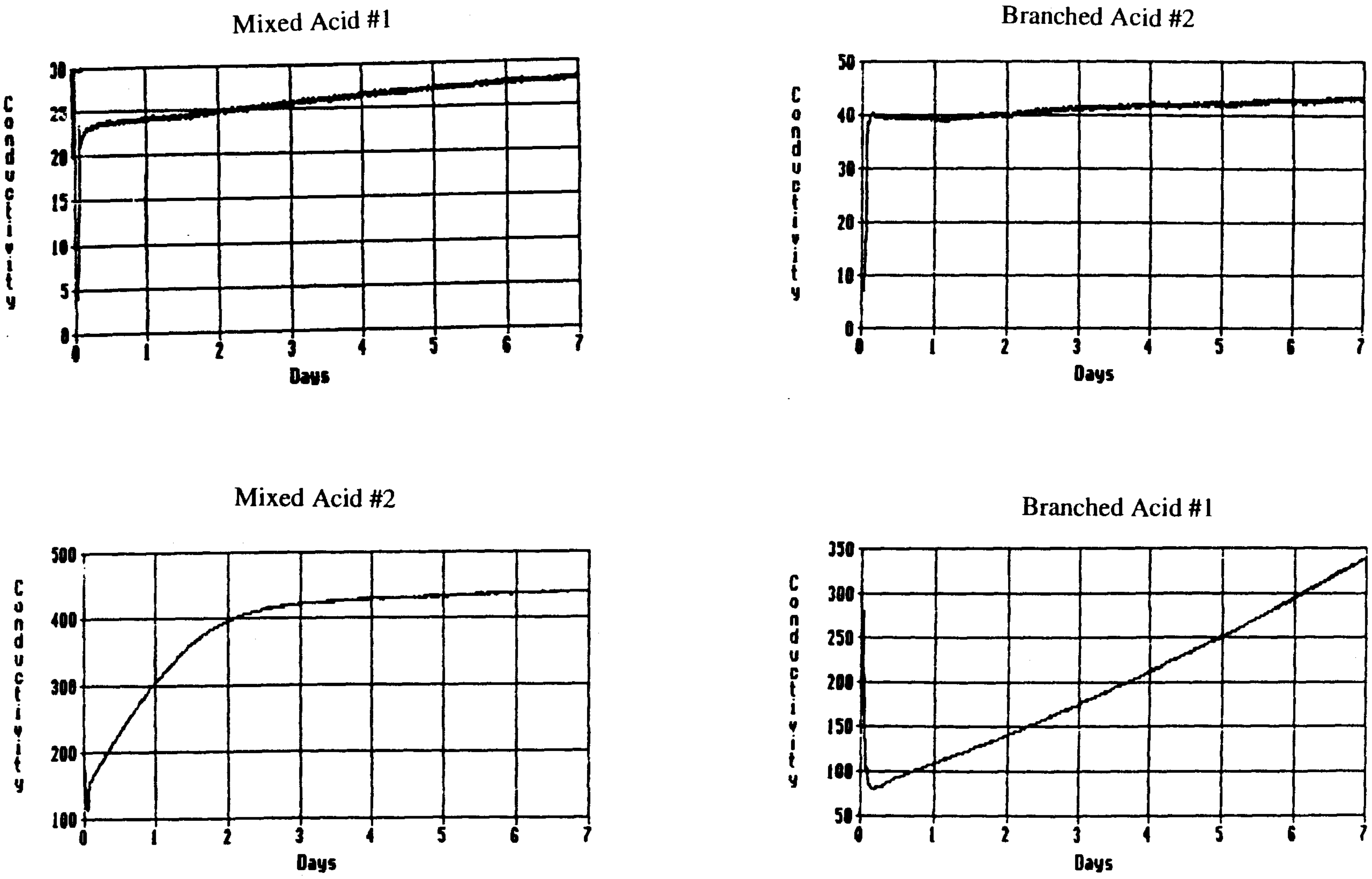
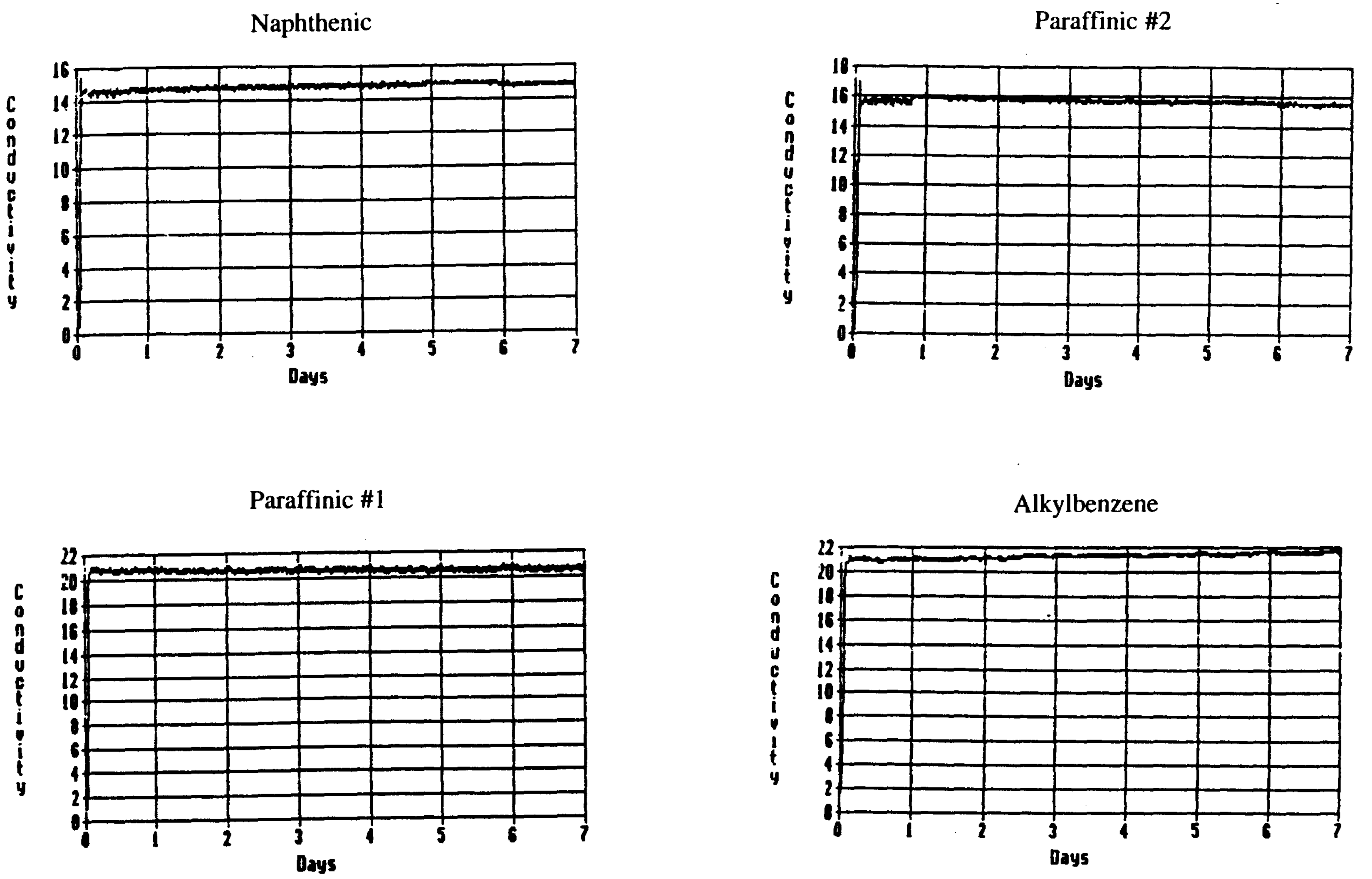


Figure B-15. *In Situ* Conductivity Versus Aging Time Plots of HFC-134a/Polyolester Oil Mixtures (No Metal Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.


Naphthenic

Paraffinic #2

Paraffinic #1

Alkylbenzene

Figure B-16. *In Situ* Conductivity Versus Aging Time Plots of HFC-134a/Mineral Oil Mixtures (Valve Steel Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

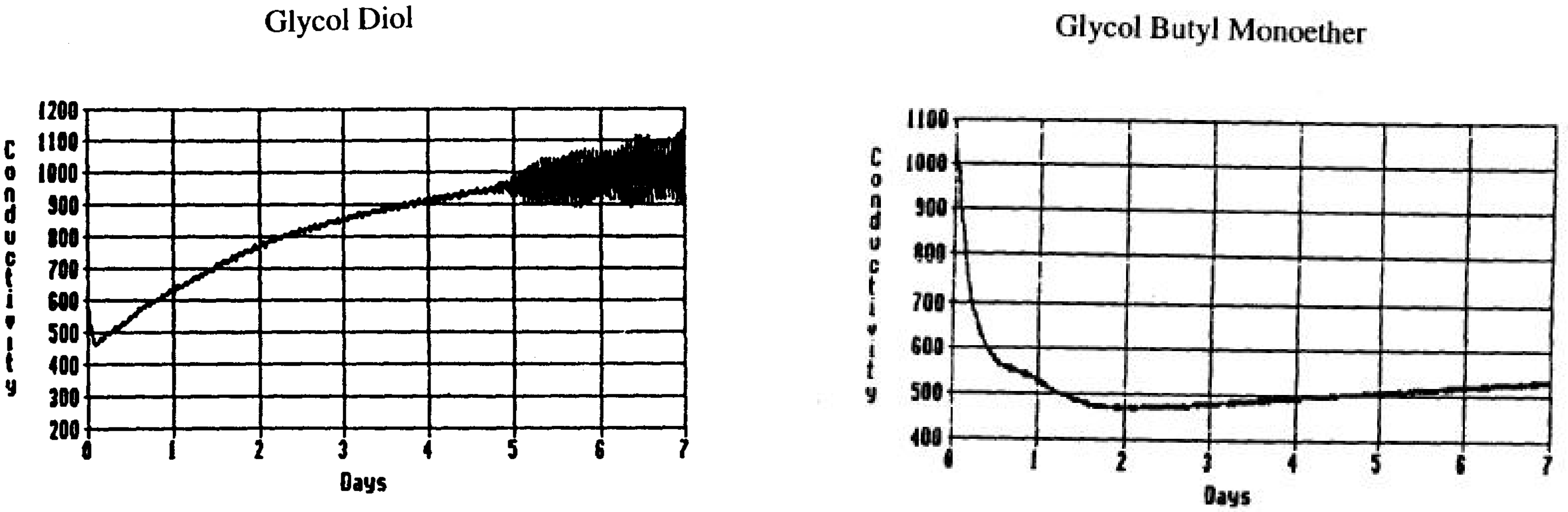


Figure B-17. *In Situ* Conductivity Versus Aging Time Plots of HFC-134a/Polypropylene Glycol Mixtures (Valve Steel Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

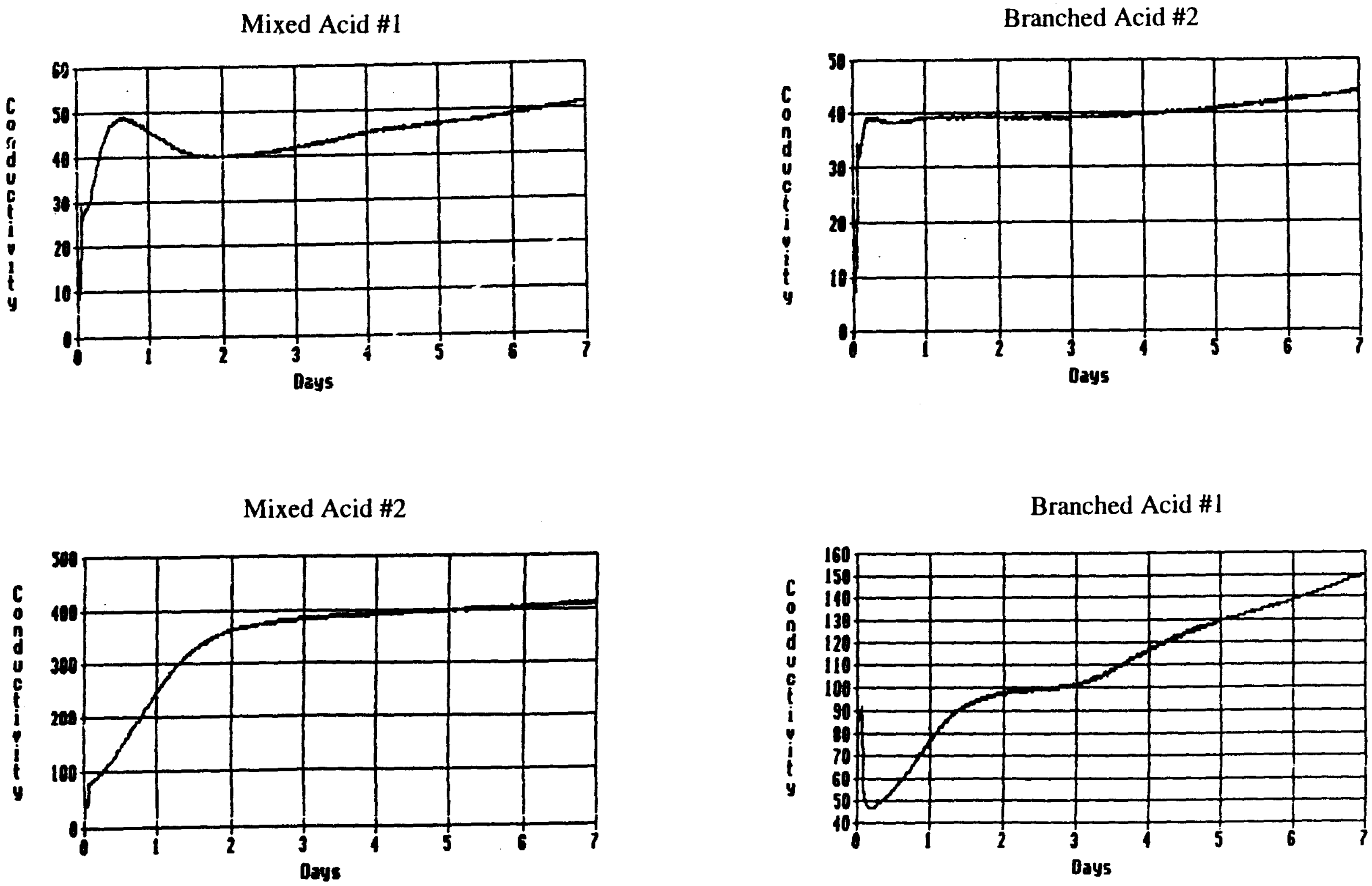


Figure B-18. *In Situ* Conductivity Versus Aging Time Plots of HFC-134a/Polyolester Oil Mixtures (Valve Steel Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

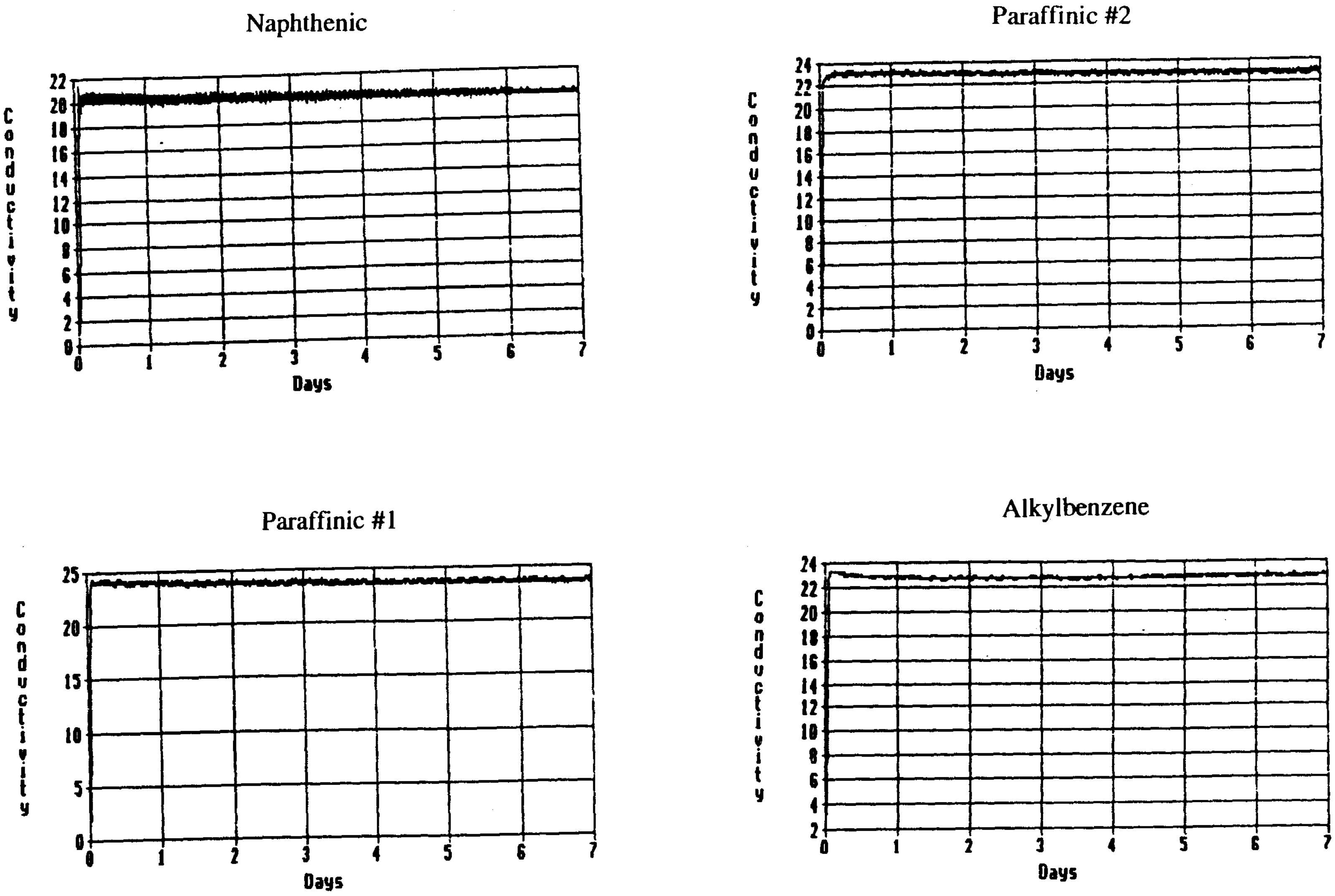


Figure B-19. *In Situ* Conductivity Versus Aging Time Plots of HFC-32 (30%)/HFC-134a (70%)/Mineral Oil Mixtures (No Metal Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

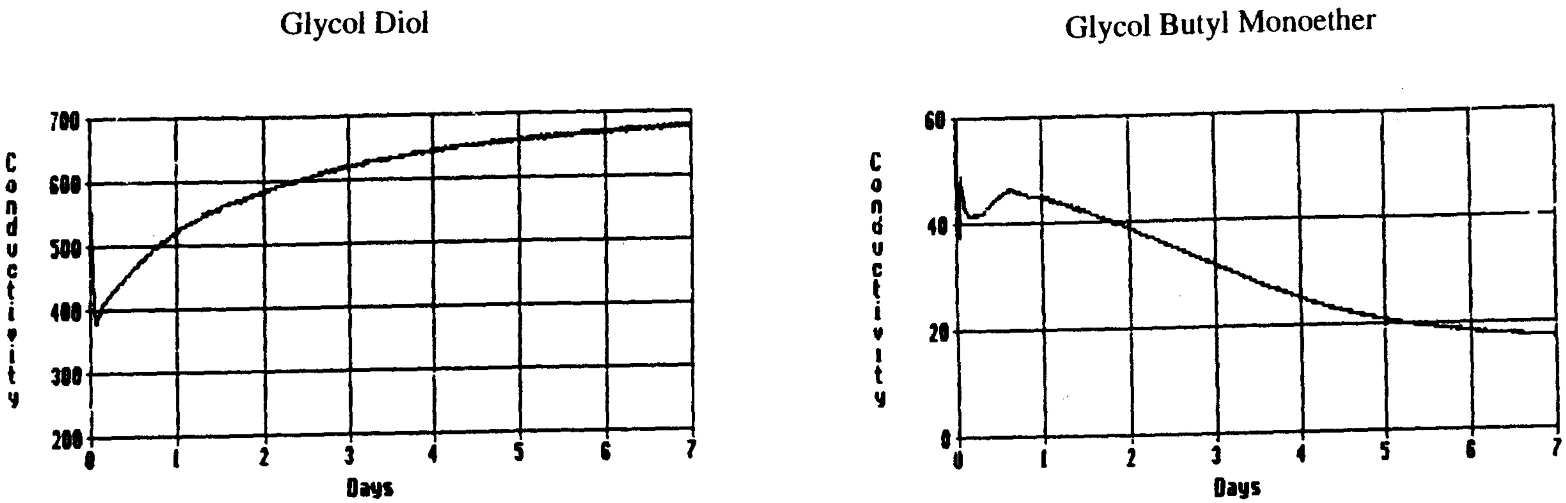
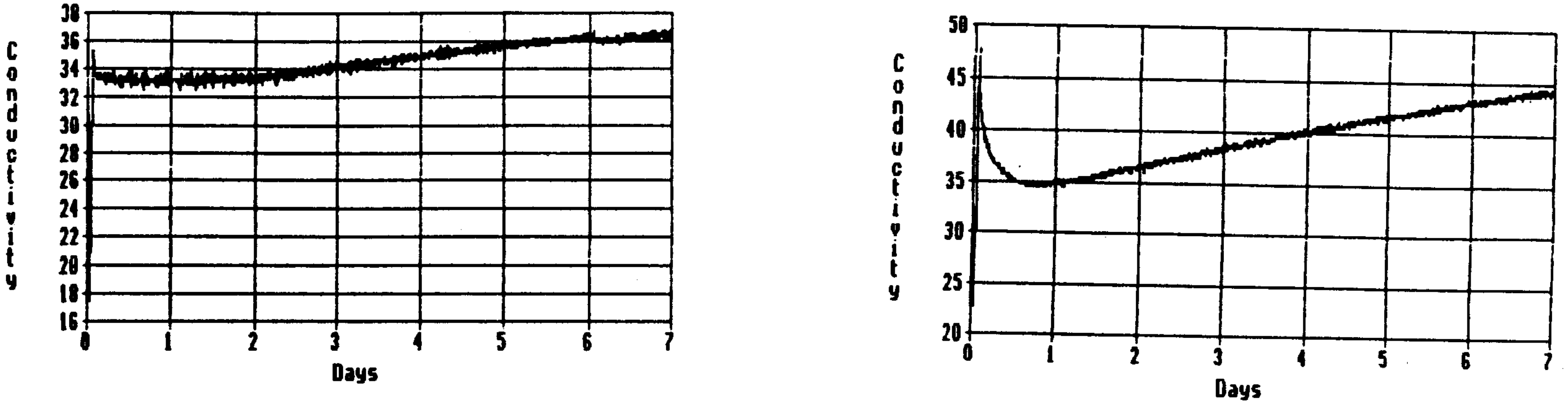
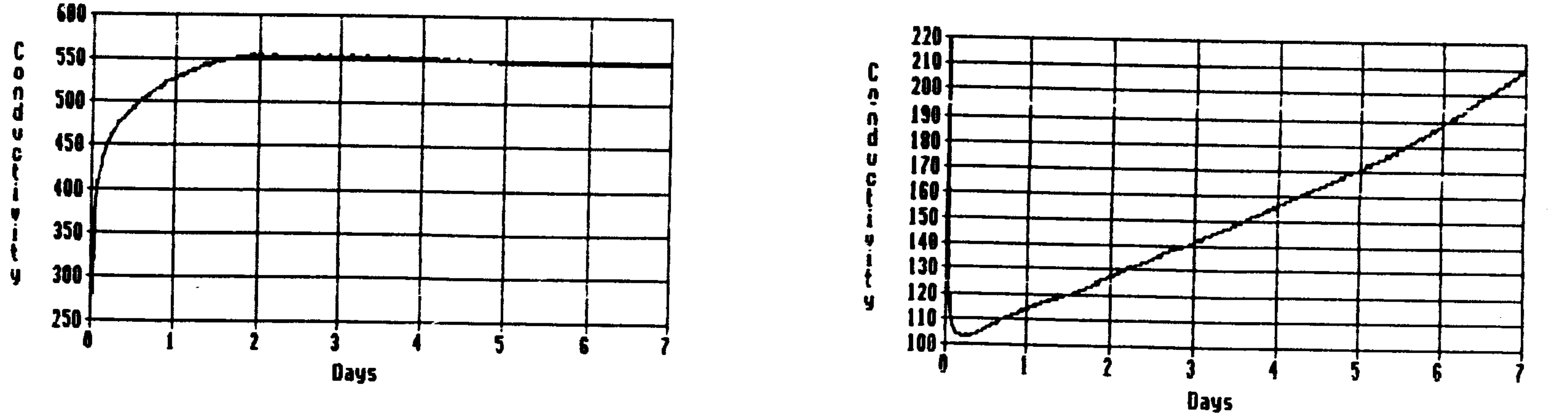


Figure B-20. *In Situ* Conductivity Versus Aging Time Plots of HFC-32 (30%)/HFC-134a (70%)/Polypropylene Glycol Mixtures (No Metal Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.


Mixed Acid #1

Branched Acid #2


Mixed Acid #2

Branched Acid #1

Figure B-21. *In Situ* Conductivity Versus Aging Time Plots of HFC-32 (30%)/HFC-134a (70%)/Polyolester Oil Mixtures (No Metal Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

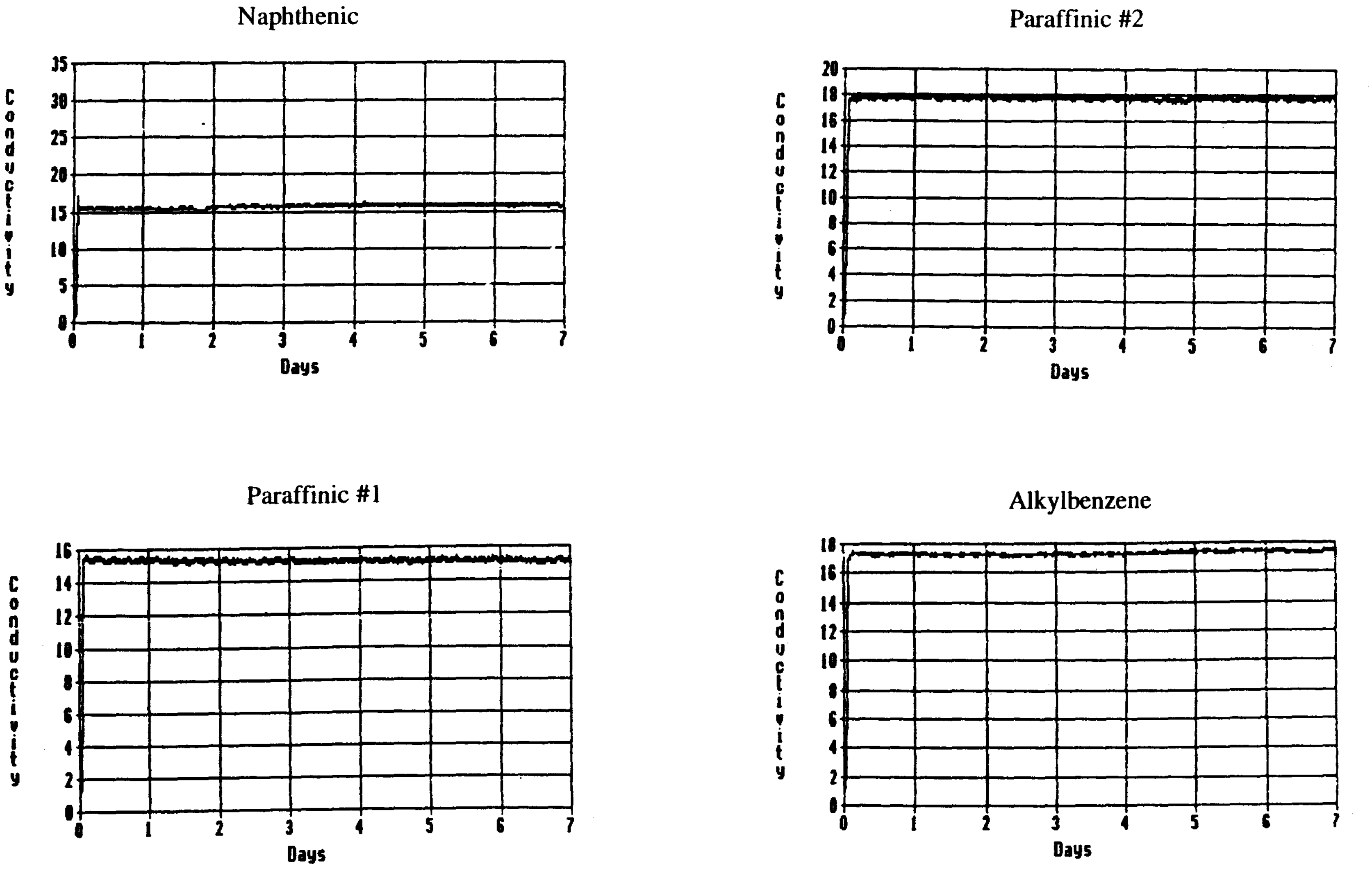


Figure B-22. *In Situ* Conductivity Versus Aging Time Plots of HFC-32 (30%)/HFC-134a (70%)/Mineral Oil Mixtures (Valve Steel Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

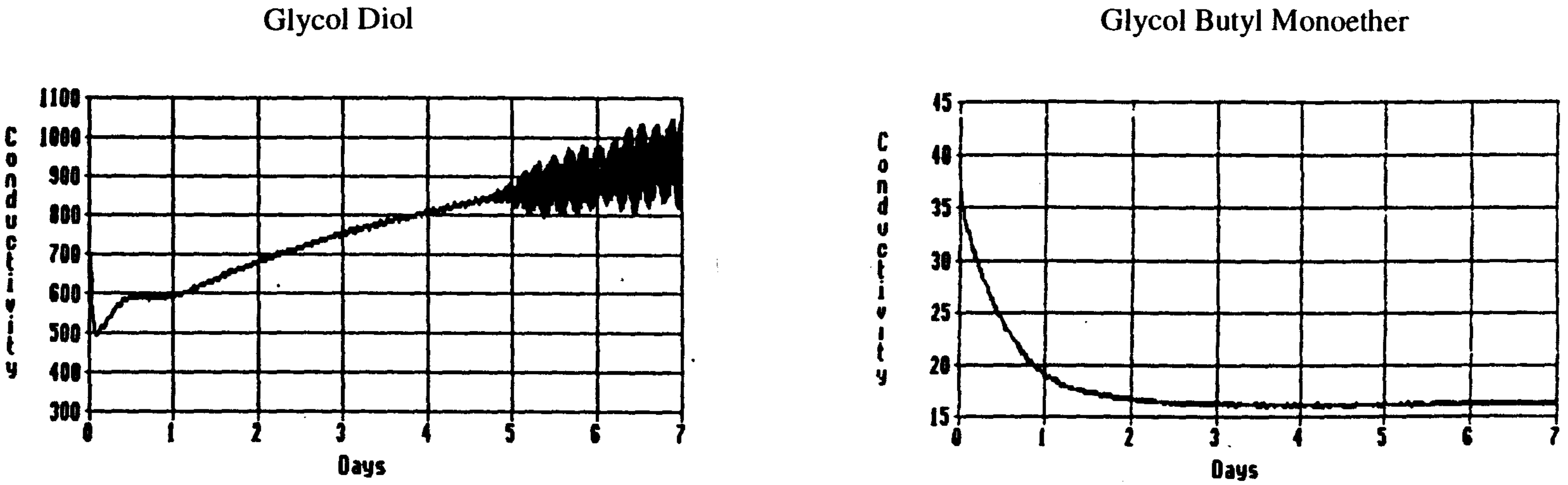
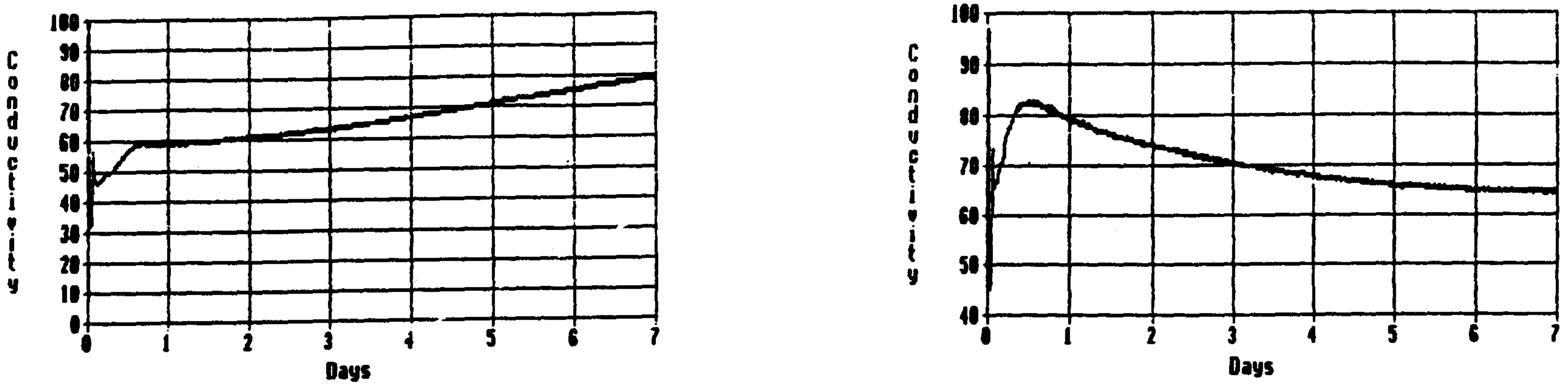


Figure B-23. *In Situ* Conductivity Versus Aging Time Plots of HFC-32 (30%)/HFC-134a (70%)/Polypropylene Glycol mixtures (Valve Steel Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

Mixed Acid #1

Branched Acid #2



Mixed Acid #2

Branched Acid #1

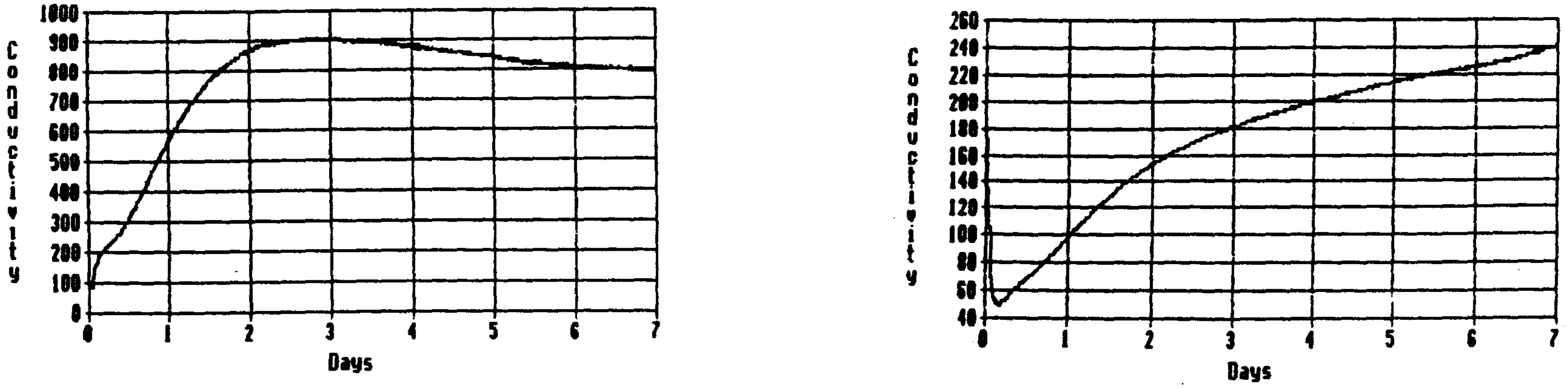


Figure B-24. *In Situ* Conductivity Versus Aging Time Plots of HFC-32 (30%)/HFC-134a (70%)/Polyolester Oil Mixtures (Valve Steel Catalyst) Aged at 175°C (347°F) in the Multichannel Aluminum Block Heater.

APPENDIX C

PERCENT VOLATILE DEGRADATION PRODUCT DETERMINATION

Instrument

The volatile degradation product contents of the aged refrigerants were measured by gas chromatography (GC) using the following instrumental parameters:

Column:	
Type:	Packed
Supplier:	Supelco, Inc. (Bellefonte, PA)
Coating:	5% Fluorcol
Support:	60/80 mesh Carbopack B
I.D. x Length:	0.125 inch x 10 ft
Carrier Flow Rate:	3-30 ml/min
Temperature Program:	
Initial Temperature:	-10°C (Hold 1 min)
Ramp Rate:	2°C/min
Final Temperature:	75°C (Hold 5 min)
Injection Temperature:	75°C
Detector Temperature:	100°C
Detector Type:	Flame Ionization

% Volatile Degradation Product Concentration Determination

To determine the % concentration of an identified degradation product (e.g., HCFC-22 in CFC-12) in an aged refrigerant, a gas sampling bulb was filled with fresh (unaged) refrigerant. A GC analysis of the fresh refrigerant (100 µm of gas) was performed to establish the GC response in the area of the identified degradation product (Appendix A, Figure A-1). Measured amounts of the identified degradation product were then injected into the gas sampling bulb filled with refrigerant. The gas combination was allowed to mix and a second GC analysis of the spiked refrigerant was performed to establish the GC response in the area of the added degradation product. Usually additional amounts of degradation product were added to the gas sampling bulb followed by GC analysis to establish the linearity of the GC response to the degradation product.

The concentrations of the degradation products in the stressed refrigerants were determined by breaking the aged glass tubes and allowing the refrigerant gas to expand into an evacuated gas sampling bulb. A typical calculation is described below for HCFC-22 in a stressed CFC-12 sample.

Sample	**GC Peak Area (counts)**	**Counts per 0.1% of HCFC-22 (-Blank)**
Blank (Fresh CFC-12)	501,053	----------
Blank		
+ 0.1% HCFC-22	1,243,084	742,031
+ 0.2% HCFC-22	1,891,681	695,314
		Average 718,672 (± 3%)
Stressed CFC-12	1,449,514	

$$\% \text{ Increase of HCFC-22 in stressed CFC-12} = \frac{1{,}449{,}514 - 501{,}053 \text{ counts}}{718{,}672 \text{ counts} / 0.1\% \text{ HCFC-22}}$$

$$= 0.13\%$$

Consequently, the % increase volatile degradation product determination is a % increase in volatile degradation product with respect to the entire refrigerant, not the degradation product in the unaged refrigerant, since the original concentration of degradation product is unknown.

APPENDIX D

PRIMARY CHEMICALS USED IN THIS STUDY

TABLE D-1
SUPPLIES OF CHEMICALS USED IN THIS STUDY

Oil Samples	**Manufacturers**
Naphthenic: Suniso 3GS	Witco, New York, New York
Paraffinic: Sontex 160LT (# 1)	Penreco, Dickinson, Texas
Sontex 20OLT (#2)	Penreco, Dickinson, Texas
Alkylbenzene: Zerol 150	Shrieve Chemical Products, Woodlands, Texas
Polypropylene Gylcols: P425 (Diol)	Dow Chemical, Midland, Michigan
Emkarox RL118D (Butyl Monoether)	ICI Americas, Wilmington, Delaware
Polyesters: Emkarate RL22H (Mixed Acid #I)	ICI Americas, Wilmington, Delaware
EAL 22A (Mixed Acid #2)	Mobil Chemical, Fairfax, Virginia
2928 (Branched Acid #2)	Henkel/Emery, Cincinnati, Ohio
Icematic SW32 (Branched Acid #1)	Castrol, Irvine, California

Refrigerant Samples

CFC-12, HCFC-22, HFC-23, and HFC-134a

TABLE D-2

ANALYTICAL RESULTS OF OIL USED IN THIS STUDY

Oil Samples	**Fe**	**Cu**	**Dried**	**As Received**	**mg of KOH/g of oil**		**Hydroperoxide** [a]	**Phosphorus** [b]
	ppm	**ppm**	**H_2O(ppm)**	**H_2O(ppm)**	**D974**	**D664**		**(ppm)**
Mineral Oils:								
Naphthenic	0.1	< 0.1	11	78	< 0.01	0.04	No	< 0.1
Paraffinic #1	< 0.1	< 0.1	14	33	< 0.01	0.04	No	< 0.1
Paraffinic #2	< 0.1	< 0.1	23	32	< 0.01	< 0.01	No	< 0.1
Alkylbenzene	< 0.1	< 0.1	29	85	< 0.01	< 0.01	No	< 0.1
Polypropylene Gylcols:								
Diol	0.1	< 0.1	42	637	0.04	0.22	Yes	< 0.1
Butyl Monoether	0.1	< 0.1	36	134	0.04	< 0.01	No	903
Polyolesters:								
Mixed Acid #1 (P)	0.5	< 0.1	33	50	0.02	0.04	No	< 0.1
Mixed Acid #2	0.1	< 0.1	26	95	0.03	0.04	No	407
Branched Acid #2	0.5	< 0.1	38	162	0.01	< 0.01	No	< 0.1
Branched Acid #1 (AA)	0.2	< 0.1	42	176	0.05	0.30	Yes[c]	< 0.1
REQUIREMENT	< 1.0	< 0.1	< 30[d], < 50[e]	--	<0.01[d],<0.05[e]	--	--	< 0.1

[a] Detection limit -0.5 mmoles of hydroperoxide / liter of oil

[b] Indicates oil contains antiwear additive

[c] After exposure to sunlight for 24 hours

[d] Mineral oils

[e] Polypropylene glycol and polyolester oils

[P] Indicates oil contains phenolic antioxidant

[AA] Indicates oil contains aromatic amine antioxidant