Air-Conditioning, Heating and Refrigeration Technology Institute

Final Report

AHRTI Report No. 09004-01

MATERIAL COMPATIBILITY & LUBRICANTS RESEARCH FOR LOW GWP REFRIGERANTS – PHASE I: THERMAL AND CHEMICAL STABILITY OF LOW GWP REFRIGERANTS WITH LUBRICANTS

Final Report

March 2012

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Funding for this project was provided by (listed alphabetically):
- Air-Conditioning, Heating and Refrigeration Institute (AHRI)
- Copper Development Association (CDA)
- Heating, Refrigeration and Air Conditioning Institute of Canada (HRAI)
- New York State Energy Research and Development Authority (NYSERDA)

EXECUTIVE SUMMARY

With the growing concern over global warming and the signing and ratification by many countries of the Kyoto Protocol, new refrigerants with low global warming potential (GWP) such as hydrofluoroolefins HFO-1234yf and HFO-1234ze with GWP under 10 have been proposed as replacements for hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC). The long-term reliability of air-conditioning and refrigeration systems of the past fifty years depends on the thermal stability of the refrigerant/lubricant working fluids and their compatibility with the materials of construction of the compressor. The objectives of this two-phase study are to determine the thermal and chemical stability of HFO-1234yf and HFO-1234ze with lubricants and their long-term material compatibility with motor materials commonly used in stationary air-conditioning and refrigeration systems. This research parallels an extensive study known as the Material Compatibility and Lubricant Research (Huttenlocher, 1992; Cavestri, 1993; 1997; Doerr and Kujak, 1993; Hamed, Seiple and Taikum, 1994; Field, 1995; Rohatgi, 1998) contracted by ARTI (Air-conditioning Research Technology Institute) in the 1990's during the phase-out of chlorofluorocarbon (CFC) refrigerants.

This research project dealt with Phase I and focused on testing the thermal and chemical stability of the refrigerant/lubricant working fluids. Refrigerants HFO-1234yf, HFO-1234ze and a mixture of HFO-1234yf blended with R-32 (50/50 by weight) were tested with two POE oils (a mixed acid and a branched acid POE), and one PVE oil. All three oils contained Butylated Hydroxy Toluene (BHT) antioxidant.

Using the fluoride ion concentrations after aging as indicators of refrigerant decomposition and Total Acid Numbers (TAN) as indicators of lubricant decomposition, the stabilities of the refrigerant/lubricant mixtures (when aged at 175^{o}C for 14 days in sealed tubes) were compared with the following general conclusions:

- With R-134a and R-410A, there was no refrigerant decomposition (no fluoride ion detected by IC).
- HFO-1234ze was more stable than HFO-1234yf and HFO-1234yf/R-32 mixture, with fluoride ion concentrations less than 150 ppm in all three lubricants tested.
- With HFO-1234yf and HFO-1234yf/R-32, refrigerant decompositions were small ($<$ 100 ppm fluoride ions) in ISO 32 mixed and branched acid lubricants when there was no air present. The presence of air contributed to higher refrigerant decomposition at low as well as high moisture levels.
- At 2000 ppm air, HFO-1234yf was more stable than HFO-1234yf/R-32 when tested with ISO 32 Mixed and Branched Acid lubricants, but relatively less stable when tested with PVE 32-A.
- The presence of air led to higher lubricant decomposition in all cases.
- When all five refrigerants were tested with PVE 32-A, the lubricant decompositions were very small (TAN$\leq$ 0.5 mg KOH/g) at all levels of moisture and air.
- The same conclusion applies to ISO 32 Branched Acid without air.
- The same conclusion applies to ISO 32 Mixed Acid lubricant without air and at low moisture.

- With 2000 ppm air, ISO 32 Branched Acid lubricant decomposition was very small in R-134a, R-410A and HFO-1234ze at both moisture levels. It is high (TAN > 1.0 mg KOH/g) in HFO-1234yf, and HFO-1234yf/R-32 at 517 ppm water.
- With 2000 ppm air and 495 ppm water, the decomposition of ISO 32 Mixed Acid was significant (TAN > 2.0 mg KOH/g) with all five refrigerants tested.
- HFO-1234ze showed a small amount of refrigerant decomposition when compared to the controls R-134a and R-410A in all cases; however, the TAN after aging, indicative of lubricant decomposition was comparable to the controls.
- With HFO-1234yf, refrigerant decomposition was small (< 100 ppm fluoride ions) and TAN after aging was comparable to the controls in ISO 32 mixed and branched acid lubricants when there was no air present. In PVE lubricant, without air refrigerant decomposition was higher (~200 to 300 ppm fluoride ions) and lubricant decomposition was slightly higher than the controls.
- With HFO-1234yf and 2000 ppm air, refrigerant decomposition was higher (up to 1000 ppm fluoride ions) but the TAN after aging was comparable to the controls, except in the case of HFO-1234yf/ISO 32 Branched Acid Lubricant at 517 ppm water when the TAN was significantly higher than the controls.
- With HFO-1234yf/R-32, without air present, refrigerant decomposition was small (< 120 ppm fluoride ions) and TAN after aging was comparable to the controls in all three lubricants tested.
- With HFO-1234yf/R-32 and 2000 ppm air, refrigerant decomposition was higher (up to 1200 ppm fluoride ions) and the TAN after aging was comparable to or slightly higher than the controls in all three lubricants tested.

The trends identified in this study may help in the design and formulation of new lubricants with greater thermal stability in HFO systems. However, compatibility and thermal stability are only two of the many lubricant properties (including lubricity, solubility, viscosity, miscibility) that require careful evaluation. Lubricant manufacturers should constantly be seeking to develop products that give performance enhancement with greater chemical stability.

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NOMENCLATURE

BHT	Butylated Hydroxy Toluene
CFC	Chloro-Fluoro-Carbon
CFD	Computational Fluid Dynamics
COP	Coefficient of Performance
FID	Flame Ionization Detector
GC	Gas Chromatography
GWP	Global Warming Potential
HCFC	Hydro-Chloro-Fluoro-Carbon
HFC	Hydro-Fluoro-Carbon
HFO	Hydro-Fluoro-Olefin
IC	Ion Chromatography
LCCP	Life Cycle Climate Performance
MCLR	Material Compatibility and Lubricant Research
PAG	Poly-Alkylene-Glycol
POE	Polyolester
TAN	Total Acid Number
TC	Thermal Conductivity
TFA	Tri-Fluoroacetic-Acid

1. INTRODUCTION

1.1. Background

With the growing concern over global warming and the signing and ratification by many countries of the Kyoto Protocol, new refrigerants with low global warming potential (GWP) such as hydrofluoroolefins HFO-1234yf and HFO-1234ze with GWP under 10 have been proposed as replacements for hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC). The long-term reliability of air-conditioning and refrigeration systems of the past fifty years depends on the thermal stability of the refrigerant/lubricant working fluids and their compatibility with the materials of construction of the compressor. The objectives of this two-phase study are to determine the thermal and chemical stability of HFO-1234yf and HFO-1234ze with lubricants and their long-term material compatibility with motor materials commonly used in stationary air-conditioning and refrigeration systems. This research parallels an extensive study known as the Material Compatibility and Lubricant Research (Huttenlocher, 1992; Cavestri, 1993; 1997; Doerr and Kujak, 1993; Hamed, Seiple and Taikum, 1994; Field, 1995; Rohatgi, 1998) contracted by ARTI (Air-conditioning Research Technology Institute) in the 1990's during the phase-out of chlorofluorocarbon (CFC) refrigerants.

1.2. Objectives

This research project dealt with Phase I and focused on testing the thermal and chemical stability of the refrigerant/lubricant working fluids. Refrigerants HFO-1234yf, HFO-1234ze and HFO-1234yf blended with R-32 (50/50 by weight) were tested with two POE oils (a mixed acid and a branched acid POE), and one PVE oil. All three oils contained Butylated Hydroxy Toluene (BHT) antioxidant.

1.3. Scope

The scope of the project involved literature search and review and data collection and analysis. In the literature search and review, data bases such as Engineering Index (ENGI), Science Abstracts (INSPEC), National Technical Information Service (NTIS), Applied Science and Technology Abstracts Citation, Academic Press Journals, IBM Patent server, Science Citation Index, and Ferret, were accessed. Key words such as refrigerant HFO, HFO-1234yf, HFO-1234ze, R-32, HFO/R-32 mixture, HFO mixture, lubricant POE, PVE, compatibility, chemical stability and thermal stability, were used to gather published data pertaining to the chemical and thermal stability of the alternative working fluids and their compatibility with system construction materials.

In the experimental data collection, the thermal and chemical stability tests were conducted according to the matrix shown in Table 1. Three refrigerants were tested including: HFO-1234yf, HFO-1234ze and HFO-1234yf/R-32 (50/50 weight %). Three lubricants were tested including: mixed acid POE; branched acid POE; and PVE oil. All three oils contained BHT. Three contaminants were tested including: air (2000 ppm based on refrigerant weight); water (at 500 ppm); both air and water. Control samples with refrigerants R-134a and R-410A were also included.

Triplicate sealed tubes were prepared according to ASHRAE standard 97-2007 (ASHRAE 2007), each containing one gram of refrigerant, one gram of lubricant and Cu/Al/Steel coupons.

The tubes were aged at 175^{o} C for 14 days. After aging the tube contents were visually examined for change in lubricant color, cloudiness in the lubricant, floc or particulate formation, film formation on tube walls, corrosion of metal coupons, and/or copper plating on the steel surface. Digital pictures of the tubes before and after aging were obtained for the record. The tube contents were also analyzed by gas chromatography (GC), for Total Acid Number (TAN) and by ion chromatography (IC) to measure chloride, fluoride and organic acid ion concentrations and to determine refrigerant and/or lubricant decomposition.

Table 1: Test Matrix

Refrigerant	Lubricant	Contaminant	Test conditions
HFO-1234yf	Mixed Acid POE	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
	Branched Acid POE	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
	PVE Oil	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
HFO-1234ze	Mixed Acid POE	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
	Branched Acid POE	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
	PVE Oil	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
R-32/HFO-1234yf (50/50 weight %)	Mixed Acid POE	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
	Branched Acid POE	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
	PVE Oil	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
Control R-134a	Mixed Acid POE	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
	Branched Acid POE	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
	PVE Oil	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
Control R-410A	Mixed Acid POE	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
	Branched Acid POE	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	
	PVE Oil	No contaminant	$175^{o}C$/14 days
		Air	
		Water	
		Both air and water	

2. LITERATURE SEARCH AND REVIEW

2.1. HFO REFRIGERANTS:

With the growing concern over global warming and the signing and ratification by many countries of the Kyoto Protocol, alternative refrigerants to HFC, such as HFO, have been proposed.

a. HFO-1234yf: This refrigerant has been developed and evaluated for use in mobile air-conditioning (Minor and Spatz, 2008; Xueliang, Qin and Kefeng, 2010; Filho, Mendoza and Coelho, 2010; Mathur, 2010a; Seeton and Wilson, 2010; Powell, 2011), chillers (Kontomaris and Leck, 2009), refrigeration applications (Leck, 2009; Lee, Han, Lee and Jeon 2011), and air-conditioning of large buildings (Kontomaris, Leck and Hughes, 2010). The thermodynamic properties of HFO-1234yf have been measured (Di Nicola, Di Nicola, Pacetti, Polonara and Santori, 2010; Di Nicola, Polonara and Santori, 2010; Tanaka and Higashi, 2010; Tanaka, Higashi and Akasaka, 2010; Dang et al., 2010). They have also been modeled (Neto and Barbosa, 2010; Skarmoutsos and Hunt, 2010; Akasaka, 2010a; Akasaka, Tanaka and Higashi 2010; Raabe and Maginn, 2010). Del Col, Torresin and Cavallini (2010) measured the heat transfer and pressure drop during condensation of HFO-1234yf in a mini-channel, while Mathur (2010b) studied its performance in parallel flow condenser, suction line heat exchanger (2011a) and laminate evaporator (2011b). Padilla and Revellin (2011) recently reported on the flow regimes and two-phase pressure gradient of HFO-1234yf in horizontal straight tubes. Its flammability characteristics have been reviewed (Monforte and Caretto, 2009; Minor and Herrmann, 2010) and Kontamaris and Leck (2009) concluded that HFO-1234yf is safe to use in automobile with ASHRAE "Class 2L" flammability rating.

b. HFO-1234ze: This refrigerant has a shorter history than HFO-1234yf. Its thermodynamic properties have been measured (Tanaka, Takahashi and Higashi, 2010a; Tanaka, Takahashi and Higashi, 2010b; Higashi and Tanaka, 2010; Kagawa, Matsuguchi and Watanabe 2011). They have also been modeled (Akasaka, 2010b; 2011).

2.2 HFO AND THE ENVIRONMENT:

Life Cycle Climate Performance (LCCP) studies indicated that replacing R-134a with HFO-1234yf in automotive air-conditioning is environmentally beneficial (Koban, 2009; Papasavva and Andersen, 2011). LCCP were also used to evaluate the effect of using HFO-1234yf in heat pump applications (Horie, Kamiaka, Dang and Hihara, 2010). Luecken et al. (2010) used a regional-scale three-dimensional atmospheric model to evaluate the effects of HFO-1234yf atmospheric degradation products such as Tri-Fluoroacetic-Acid (TFA) on air quality in North America and Papasavva, Luecken, Waterland, Taddonio and Andersen (2009) estimated the 2017 refrigerant emissions of HFC-1234yf in the United States resulting from automobile air-conditioning. To understand the impact of accidental releases of HFO-1234yf into a garage environment, Koban and Herrmann (2011) used computational fluid dynamics (CFD) modeling to simulate releases of the refrigerant under various air-conditioning line rupture scenarios, while Schuster, Bertermann, Rusch and Dekart (2010) reported on its toxicity.

2.3 HFO MIXTURES

a. HFO-1234yf mixtures**:** Fujikata, Shimizu, Sato and Kawabe (2010) studied the use of HFO-1234yf and HFO-1234yf/R-32 mixtures in room air-conditioners and concluded that the performance of R-32/HFO-1234yf improved as the R-32 concentration increased, and the coefficients of performance (COPs) of R-32/HFO-1234yf at 50/50 weight percent were 95% under cooling conditions and 94% under heating conditions when compared to R-410A. The thermophysical properties of HFO-1234yf/R-32 mixtures have been measured (Arakawa, Kim, Kamiaka, Dang and Hihara, 2010).

b. HFO-1234ze mixtures: Koyama, Takada, Matsuo, Yoshitake and Fukuda (2010) in investigating the possibility of using HFO-1234ze and its mixture with R-32 in heat pump/refrigeration systems concluded that HFO-1234ze could be used in turbo refrigeration system while its mixture with R-32 can replace R-410A in domestic heat pump systems. Koyama, Takada and Fukuda (2010) also described drop-in experiments using HFO-1234ze and its mixtures with R-32 in heat pumps. The thermal conductivity of HFO-1234-ze/R-32 mixture was measured (Miyara, Tsubaki and Sato, 2010) as well as the isochoric specific heat capacity of HFO-1234ze/CO_2 mixture (Yamaya, Matsuguchi, Kagawa and Koyama, 2011).

2.4 HFO and Lubricants

Polyolesters (POE) used in R-410A systems were shown to be miscible with HFO-1234yf in all proportions (Fujikata et al., 2010); however, mineral oil and alkyl benzene were not (Kontomaris and Leck, 2009). Talley (2010) noted that for automotive application, a poly-alkylene-glycol (PAG) oil would be used with HFO-1234yf, while Gordon, Eustice and Brooks (2011) reported on the study of oil migration in automotive air-conditioning system using refrigerant HFO-1234yf and PAG lubricant.

2.5 HFO Stability and Compatibility:

Leck (2009) reported that HFO-1234yf showed stability and compatibility with refrigeration system materials similar to R-134a and Stehouwer (2010) evaluated compressor durability and material compatibility in several different compressor types. Fujikata et al. (2010) showed that the acid numbers of POE lubricants were significantly greater after aging in HFO-1234yf containing air as compared to aging in R-410A; however, other materials used in R-410A room air-conditioner can be used with HFO-1234yf. The authors also investigated the reaction of HFO-1234yf with air and a small amount of moisture and identified oxidation products of the refrigerant such as alcohol, aldehyde, ketone, and ester. Ikegami, Iguchi, Aoki and Iijima tested HFO-1234yf with two PAG and two POE lubricants at two different aging temperatures (175^{o}C and 200^{o}C) and three different moisture levels (<10 ppm; 1000 ppm; and 10000 ppm); however, there was no air present. Seeton and Wilson (2010) presented thermal stability data of HFO-1234yf/PAG systems and concluded that air increases and water decreases the TAN and fluoride concentration after accelerated aging. They recommended development of improved lubricant additive packages to control the effects of air and water on the stability of the HFO-1234yf/PAG systems. The presence of HFO-1234ze as an impurity in HFO-1234yf (at a concentration of 0.1%) was also studied and determined to have no significant effect on the stability of the HFO-1234yf/PAG system.

3. EXPERIMENTAL METHODS

3.1 SEALED TUBE PREPARATION:

Triplicate sealed tubes were prepared according to ASHRAE Standard 97-2007, each tube containing one gram of refrigerant, one gram of lubricant and steel/aluminum/copper coupons. The test tubes were cleaned by rinsing first with deionized water, then by two rinses with methanol and one rinse with toluene. They were dried at 175^{o} C and kept dry in desiccators prior to use. The copper, aluminum, steel catalyst coupons (copper was CDA 110 or C11000; steel 1010; and aluminum 1100) were prepared by punching 3.3x19.3 mm coupons from thin sheets. The coupons were held together by aluminum wire such that the steel and copper were separated by the aluminum. These prepared coupons were thoroughly cleaned and kept dry prior to use. The metal coupons were placed in each tube, which was then necked down to a size through which a standard cannula could fit.

Prior to its addition into the sealed tube, the lubricant sample was tested for moisture by Karl Fischer coulometry. The moisture level was then adjusted to the desired value (~500 ppm) by vacuum or by absorption of moisture from ambient air or by addition of liquid deionized water. The final water content in the lubricant was measured by Karl Fischer. The lubricant was added accurately to each tube with a syringe and cannula. The tube was evacuated to 30 microns followed by accurate charging of refrigerant through condensation from a calibrated gas handling system while the tube was submerged in liquid nitrogen.

With the tube still submerged in liquid nitrogen, the gas handling system was evacuated and atmospheric air was introduced into the system to a pressure of ~0.28 atm, yielding a concentration in the tube of ~2000 ppm air based on refrigerant weight. Finally, the tube neck was sealed and annealed. The sealed tubes were placed in drilled holes in large aluminum blocks, which were heated in air circulating ovens.

The sealed tubes were aged at 175^{o}C for 14 days. After aging, the tube contents were visually examined for change in lubricant color, cloudiness in the lubricant, floc or particulate formation, film formation on tube walls, changes in appearance of the metal coupons, surface corrosion and/or copper plating on the steel surface. Digital pictures of the tubes before and after aging were taken for the record. The tube contents were also analyzed by gas chromatography, for Total Acid Number (TAN) and by Ion Chromatography to determine total halide, total organic and total inorganic anion concentrations.

3.2. ANALYSES OF TUBE CONTENTS AFTER AGING

Total Acid Number. The method for measuring TAN is based on ASTM D664 with the following modifications to accommodate small sample sizes:

- Calibration in solvent solution with oil, rather than water solution;
- KOH normality of 0.01, rather than 0.10;
- Use of 8 ml of solvent, rather than 125 ml; and
- Titration of the lubricant samples was to a pH of 11.

Ion Chromatography. In the determination of anion concentrations by ion chromatography (IC), the sealed tube was placed in liquid nitrogen to reduce internal pressure, cut open and inverted into a pre-weighed plastic cup containing 30 milliliters of deionized water. The water/lubricant mixture was stirred continuously for 24 hours to allow for extraction of halide ions and water-soluble anions from the lubricant. The water extract was then analyzed by ion chromatography.

The DX-100 integrated ion chromatography system consisted of a high pressure pump to push the sample through the system, a negative ion exchange column to separate the ions in the sample, and a conductivity detector to indicate how much of each ion was present in the sample. The solution flowing through the machine, also called the eluent, was a dilute solution of sodium hydroxide. The sample was injected in the eluent stream just before the column. In the column, negatively charged ions were separated by their individual affinity for the ion exchange column packing producing a predictable time and order of elution from the column. The smaller anions such as Fluoride and Formate eluted quickly, while larger anions such as Heptanoate and Sulfate eluted more slowly. The concentrations of halide ions, organic and inorganic anions were obtained by calibrating the ion chromatograph with standard solutions so that the peak area was proportional to the anion concentration.

Gas Chromatography (GC). In the GC analyses of samples, the gas phase from each sealed tube was carefully expanded into an evacuated one-liter Mylar gas-sampling bag. A 20 microliter sample was drawn from the bag using a 100 microliter gas-tight syringe and injected into the gas chromatograph. Gas chromatography was conducted using a Supelco Flurocol column 2-meter-long by 3 mm ID and flame ionization detector (FID). The carrier gas was Nitrogen at a flow rate of 20cc/min. This method allowed for the determination of organic gas species ignoring non-condensable gases such as air. The results were expressed as percent of FID carbon response. The refrigerant sample before aging was used as standard and reported as 100% FID carbon response. Any gaseous decomposition products were recognized as unknown peaks and reported as FID percent of the total (refrigerant response plus decomposition product response). The percent refrigerant decomposition was calculated from the difference between the FID carbon response of the standard before-aging refrigerant sample and the FID carbon response of the aged sample.

4. RESULTS AND DISCUSSIONS

4.1 R-134a AND LUBRICANTS

The results for R-134a and the three different lubricants are shown in Tables 2-10 and Figures 1-4. There was no refrigerant decomposition in any of the aged sealed tubes as indicated by GC and IC data. Lubricant decomposition (based on TAN and IC data) was most significant with ISO 32 Mixed Acid. As shown in Figures 5 and 6, both moisture and air concentrations affected lubricant decomposition with increasing moisture and air resulting in increasing TAN and total organic acid (TOA) ion concentration such as propanoate and hexanoate. Lubricant decomposition was small (TAN<0.5 mg KOH/g and TOA<1000 ppm) when this refrigerant was aged in ISO 32 Branched Acid and PVE 32-A lubricants.

4.2. R-410A AND LUBRICANTS

The results for R-410A and the three different lubricants are shown in Tables 11-19 and Figures 7-10. There was no refrigerant decomposition in any of the aged sealed tubes as indicated by GC and IC data. (The numbers shown in Tables 13, 16, and 19 as %-refrigerant decomposed actually reflected the presence and change in concentration of an unknown peak, probably impurity, also found in the standard unaged R-410A.) Lubricant decomposition (based on TAN and IC data) was most significant with ISO 32 Mixed Acid. As shown in Figures 11 and 12, both moisture and air concentrations affected lubricant decomposition with moisture having a greater effect than air. Lubricant decomposition was small (TAN<0.5 mg KOH/g and TOA<1000 ppm) when this refrigerant was aged in ISO 32 Branched Acid and PVE 32-A lubricants.

4.3. HFO-1234yf AND LUBRICANTS

The results for HFO-1234yf and the three different lubricants are shown in Tables 20-28 and Figures 13-16. Fluoride ions were detected in the aged sealed tubes indicative of refrigerant decomposition, especially when there was air present (Figure 17). In the presence of air and high moisture, the highest fluoride ion concentration was recorded when this refrigerant was aged in ISO 32 Branched Acid and the lowest when it was aged in ISO 32 Mixed Acid. In addition, increases in TAN and the presence of organic acid ion after aging showed lubricant decomposition. As shown in Figure 18, with this refrigerant the TAN of ISO 32 Mixed Acid after aging was significant (TAN $\geq$ 1.0 mg KOH/g) while the TAN of PVE 32-A was small (TAN <0.5 mg KOH/g). ISO 32 Branched Acid had small TAN values at low moisture and without air, but showed higher TAN at 517 ppm moisture and 2000 ppm air (TAN=1.44 Mg KOH/g). These results/conclusions were similar to those reported by Fujitaka, Shimizu, Sato and Kawabe (2010), when HFO-1234yf was tested with POE refrigeration oil from Nippon Oil Corporation: in the presence of air, TAN was 1.39 mg KOH/g at <10 ppm moisture and 2.13 mg KOH/g at 1000 ppm moisture.

4.4. HFO-1234ze AND LUBRICANTS

The results for HFO-1234ze and the three different lubricants are shown in Tables 29-37 and Figures 19-22. Fluoride ions were detected in the aged sealed tubes indicative of refrigerant decomposition, especially when there was air present (Figure 23). The fluoride ion concentration was small (less than 65 ppm) in all cases, except for the HFO-1234ze/ISO 32 Branched Acid mixture at 48 ppm moisture and 2000 ppm air when it was 142 ppm. In addition, increases in TAN and the presence of organic acid ion after aging showed lubricant decomposition. As shown in Figure 24, the TAN was small (TAN ≤ 0.5 mg KOH/g) when this refrigerant was aged in ISO 32 Mixed Acid without air present, but became significant (TAN =2.14 mg KOH/g) at 495 ppm water and 2000 ppm air. The TAN of ISO 32 Branched Acid and PVE 32-A lubricants were small when aged with this refrigerant at both air levels and both moisture levels.

4.5 HFO-1234yf/R-32 AND LUBRICANTS

The results for HFO-1234yf/R-32 and the three different lubricants are shown in Tables 38-46 and Figures 25-28. Fluoride ions were detected in the aged sealed tubes indicative of refrigerant decomposition, especially when there was air present (Figure 29). In the presence of air and both (high and low) moisture levels, the highest fluoride ion concentration was recorded when this refrigerant mixture was aged in ISO 32 Mixed Acid and the lowest when it was aged in PVE 32-A. In addition, increases in TAN and the presence of organic acid ion after aging showed lubricant decomposition. As shown in Figure 30, when aged in this refrigerant mixture, the TAN of ISO 32 Mixed Acid was significant (TAN ≥ 1.0 mg KOH/g) while that of PVE 32-A was small (TAN <0.5 mg KOH/g). For the ISO 32 Branched Acid, the TAN value was small at low moisture and without air, but became significant at 517 ppm moisture and 2000 ppm air (TAN=1.77 Mg KOH/g).

4.6. REFRIGERANT DECOMPOSITION BASED ON FLUORIDE ION COMPARED TO GC RESULTS

The fluoride ion concentrations and the gas chromatography results were both indicative of refrigerant decomposition; however, when decomposition products were not in the gas phase (such as when they were soluble in the lubricants or precipitated out), they could not be detected by GC. Furthermore the flame ionization detector might not pick up some chemicals. Thus, for the HFO-1234yf and HFO-1234yf/R-32 samples, although the fluoride ion concentrations were high indicative of significant refrigerant decomposition, the decomposition products detected by GC were small.

On the other hand, in some of the HFO-1234ze samples, the fluoride ion concentration was small, but the GC data showed 1.0-1.5% refrigerant decomposition. In these cases, the refrigerant decomposition was calculated based on the presence of unknown peaks (which were recognized as decomposition products). The unknown peak detected by GC had a retention time that was the same as that of HFO-1234yf, suggesting that the refrigerant did not decompose, but changed its chemical structure from HFO-1234ze to HFO-1234yf; however, the actual presence of HFO-1234yf needs to be confirmed by gas-chromatography/mass-spectrometry (GC/MS), which was outside the scope of the current project.

5. CONCLUSIONS

5.1 REFRIGERANT DECOMPOSITION

Using the fluoride ion concentrations after aging as indicators of refrigerant decomposition, the stabilities of the refrigerants (when aged at 175°C for 14 days in sealed tubes) were compared in Figures 31-36. The following general conclusions were drawn:

- With R-134a and R-410A, there was no refrigerant decomposition (no fluoride ion detected by IC).
- HFO-1234ze was more stable than HFO-1234yf and HFO-1234yf/R-32 mixture, with fluoride ion concentrations less than 150 ppm in all three lubricants tested.
- With HFO-1234yf and HFO-1234yf/R-32, refrigerant decompositions were small (< 100 ppm fluoride ions) in ISO 32 mixed and branched acid lubricants when there was no air present. The presence of air contributed to higher refrigerant decomposition at low as well as high moisture levels.
- At 2000 ppm air, HFO-1234yf was more stable than HFO-1234yf/R-32 when tested with ISO 32 Mixed and Branched Acid lubricants, but relatively less stable when tested with PVE 32-A.

5.2 LUBRICANT DECOMPOSITION:

Using TAN after aging as indicators of lubricant decomposition, the stabilities of the refrigerant/lubricant mixtures (when aged at 175°C for 14 days in sealed tubes) were compared in Figures 37-42. The following general conclusions were drawn:

- The presence of air led to higher lubricant decomposition in all cases.
- When all five refrigerants were tested with PVE 32-A, the lubricant decompositions were very small (TAN≤ 0.5 mg KOH/g) at all levels of moisture and air.
- The same conclusion applies to ISO 32 Branched Acid without air.
- The same conclusion applies to ISO 32 Mixed Acid lubricant without air and at low moisture.
- With 2000 ppm air, ISO 32 Branched Acid lubricant decomposition was very small in R-134a, R-410A and HFO-1234ze at both moisture levels. It is high (TAN > 1.0 mg KOH/g) in HFO-1234yf, and HFO-1234yf/R-32 at 517 ppm water.
- With 2000 ppm air and 495 ppm water, the decomposition of ISO 32 Mixed Acid was significant (TAN > 2.0 mg KOH/g) with all five refrigerants tested.

5.2 COMPARING HFO-1234yf, HFO-1234ze AND HFO-1234yf/R-32 WITH THE CONTROLS R-134a AND R-410A

- HFO-1234ze showed a small amount of refrigerant decomposition when compared to R-134a and R-410A in all cases; however, the TAN after aging, indicative of lubricant decomposition was comparable to the controls.
- With HFO-1234yf, refrigerant decomposition was small (< 100 ppm fluoride ions) and

TAN after aging was comparable to the controls in ISO 32 mixed and branched acid lubricants when there was no air present. In PVE lubricant, without air refrigerant decomposition was higher (~200 to 300 ppm fluoride ions) and lubricant decomposition was slightly higher than the controls.

- With HFO-1234yf and 2000 ppm air, refrigerant decomposition was higher (up to 1000 ppm fluoride ions) but the TAN after aging was comparable to the controls, except in the case of HFO-1234yf/ISO 32 Branched Acid Lubricant at 517 ppm water.
- With HFO-1234yf/R-32, without air present, refrigerant decomposition was small (< 120 ppm fluoride ions) and TAN after aging was comparable to the controls in all three lubricants tested.
- With HFO-1234yf/R-32 and 2000 ppm air, refrigerant decomposition was higher (up to 1200 ppm fluoride ions) and the TAN after aging was comparable to or slightly higher than the controls in all the three lubricants tested.

Table 2:Summary of Visual Observations of Aged Sealed Tubes (R-134a/ISO 32 Mixed Acid)

Visual Observations (R-134a/ISO 32 Mixed Acid)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
51	0	Faint cloudiness; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Medium brown color (color=4.5 versus 2.0 for unaged); no deposit	Unchanged	Heavy darkening	Unchanged
495	0	Light cloudiness; color unchanged (color=2.0); white ring on tube wall	Unchanged	Unchanged	Unchanged
	2000	Medium brown color (color=4.5 versus 2.0 for unaged); no deposit	Unchanged	Heavy darkening	Unchanged

Table 3: Summary of Analytical Results of Aged Sealed Tubes (R-134a/ ISO 32 Mixed Acid)

Analytical Results (R-134a/ ISO 32 Mixed Acid)							
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm			
				Fluoride	Propanoate	Hexanoate	Unknown
Unaged	N/A	N/A	0.04	0	0	0	0
Aged	51	0	0.25	0	0	885	0
		2000	1.14	0	46	2057	0
	495	0	1.46	0	5	3934	0
		2000	2.36	0	0	5085	0

Table 4: Summary of GC Results of Aged Sealed Tubes (R-134a/ ISO 32 Mixed Acid)

Gas Chromatography Results (R-134a/ ISO 32 Mixed Acid)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			R-134a %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	100	0	0
Aged	51	0	100	0	0
		2000	100	0	0
	495	0	100	0	0
		2000	100	0	0

Table 5: Summary of Visual Observations of Aged Sealed Tubes (R-134a/ISO 32 Branched Acid)

Visual Observations (R-134a/ISO 32 Branched Acid)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
48	0	Clear; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; darker color (color=3.0 versus 2.0 for unaged); no deposit	Unchanged	Light darkening	Unchanged
517	0	Faint cloudiness; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Medium brown color (color=4.5 versus 2.0 for unaged); Faint white deposit on tube wall	Top of coupon turned dull tan	Medium darkening	Unchanged

Table 6: Summary of Analytical Results of Aged Sealed Tubes (R-134a/ISO 32 Branched Acid)

Analytical Results (R-134a/ISO 32 Branched Acid)							
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm			
				Fluoride	Propanoate	Hexanoate	Unknown
Unaged	N/A	N/A	0	0	0	0	0
Aged	48	0	0.06	0	0	302	0
		2000	0.16	0	244	0	0
	517	0	0	0	0	526	0
		2000	0.26	0	330	0	0

Table 7: Summary of GC Results of Aged Sealed Tubes (R-134a/ ISO 32 Branched Acid)

Gas Chromatography Results (R-134a/ ISO 32 Branched Acid)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			R-134a %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	100	0	0
Aged	48	0	100	0	0
		2000	100	0	0
	517	0	100	0	0
		2000	100	0	0

Table 8: Summary of Visual Observations of Aged Sealed Tubes (R-134a/PVE 32-A)

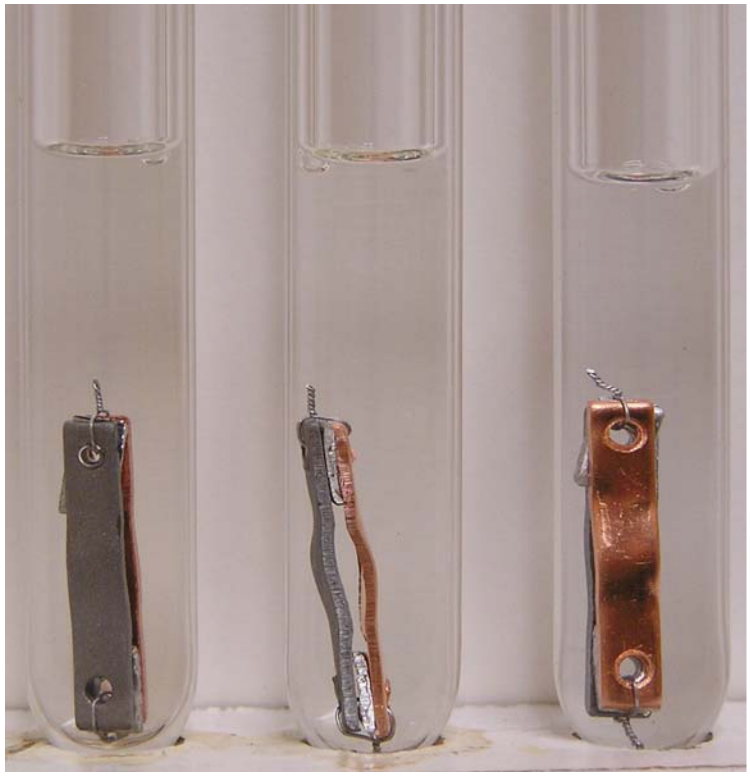
Visual Observations (R-134a/PVE 32-A)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
24	0	Clear; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color unchanged (color=2.0); Light brown stain in vapor space on tube wall	Unchanged	Unchanged	Unchanged
490	0	Faint cloudiness; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color unchanged (color=2.0); Light brown stain in vapor space on tube wall	Unchanged	Unchanged	Unchanged

Table 9: Summary of Analytical Results of Aged Sealed Tubes (R-134a/PVE 32-A)

Analytical Results (R-134a/PVE 32-A)							
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm			
				Fluoride	Propanoate	Hexanoate	Unknown
Unaged	N/A	N/A	0.01	0	0	0	0
Aged	24	0	0.05	0	68	0	0
		2000	0.16	0	703	0	0
	490	0	0.01	0	0	0	0
		2000	0.29	0	522	0	0

Table 10: Summary of GC Results of Aged Sealed Tubes (R-134a/ PVE 32-A)

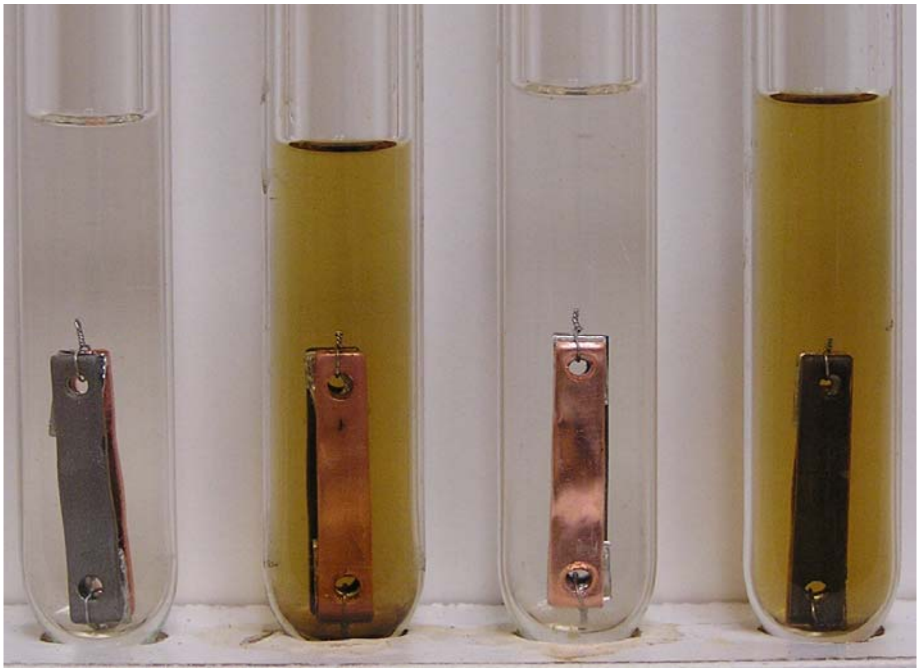
Gas Chromatography Results (R-134a/ PVE 32-A)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			R-134a %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	100	0	0
Aged	24	0	100	0	0
		2000	100	0	0
	490	0	100	0	0
		2000	100	0	0



a. White Background

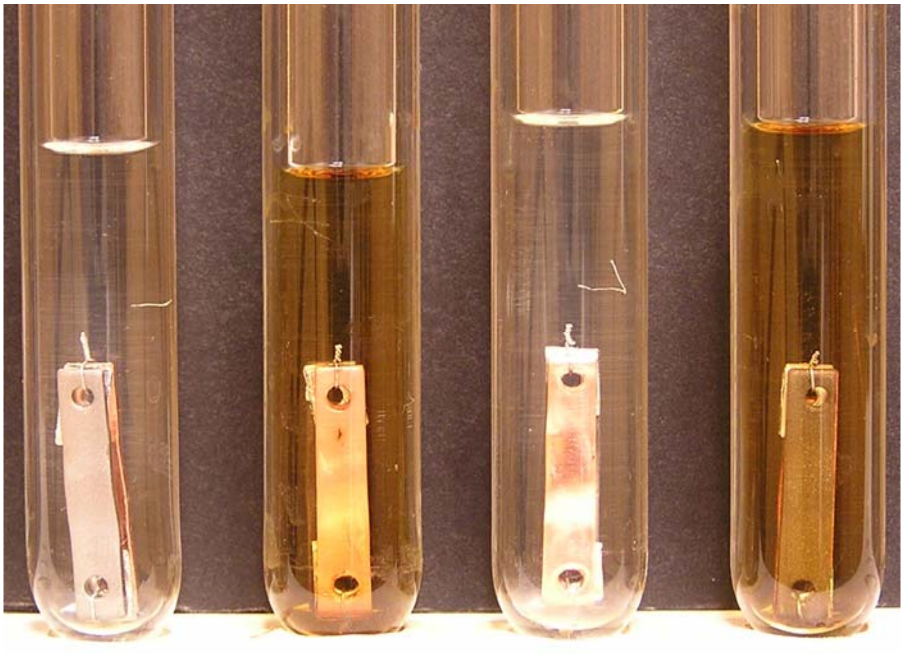
b. Black Background

Figure 1: Photographs of Sealed Tubes Containing R-134a/Lubricant Before Aging



Water	**51 ppm**	**51 ppm**	**495 ppm**	**495 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

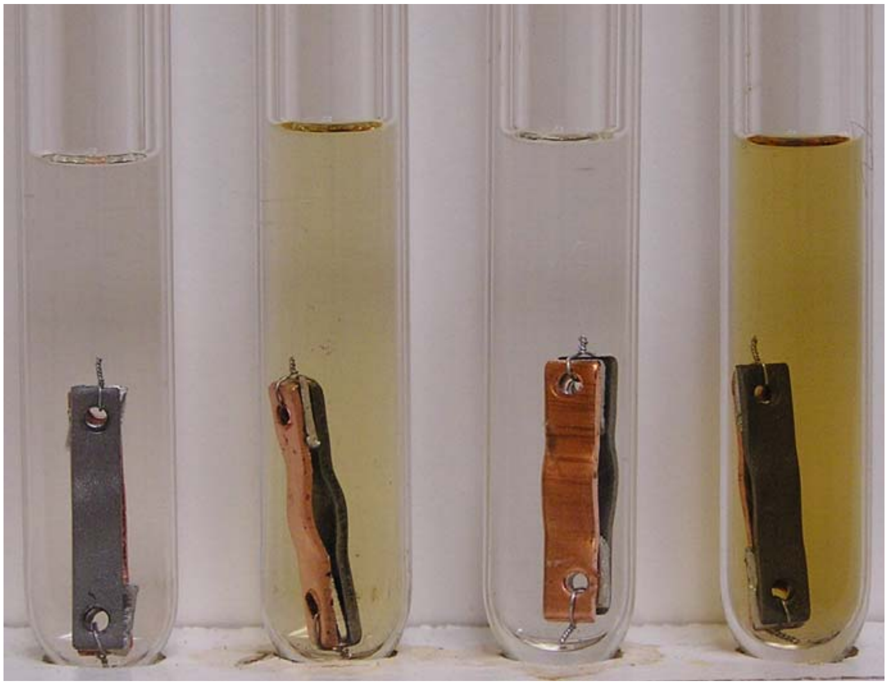
a. White Background



Water	**51 ppm**	**51 ppm**	**495 ppm**	**495 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

b. Black Background

Figure 2: Photographs of Sealed Tubes Containing R-134a/ISO 32 Mixed Acid After Aging



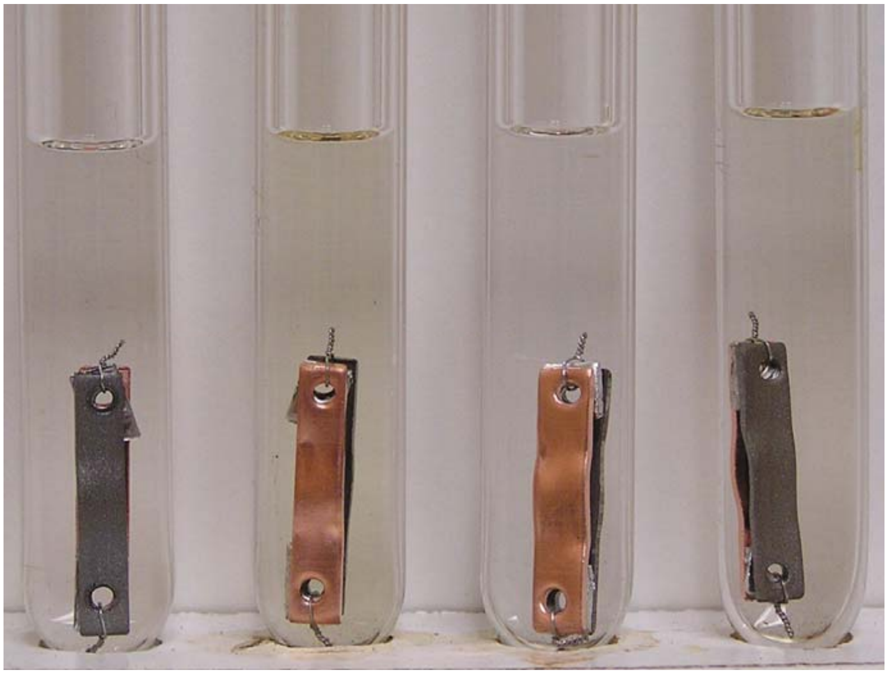
Water	48 ppm	48 ppm	517 ppm	517 ppm
Air	0 ppm	2000 ppm	0 ppm	2000 ppm

a. White Background

Water	48 ppm	48 ppm	517 ppm	517 ppm
Air	0 ppm	2000 ppm	0 ppm	2000 ppm

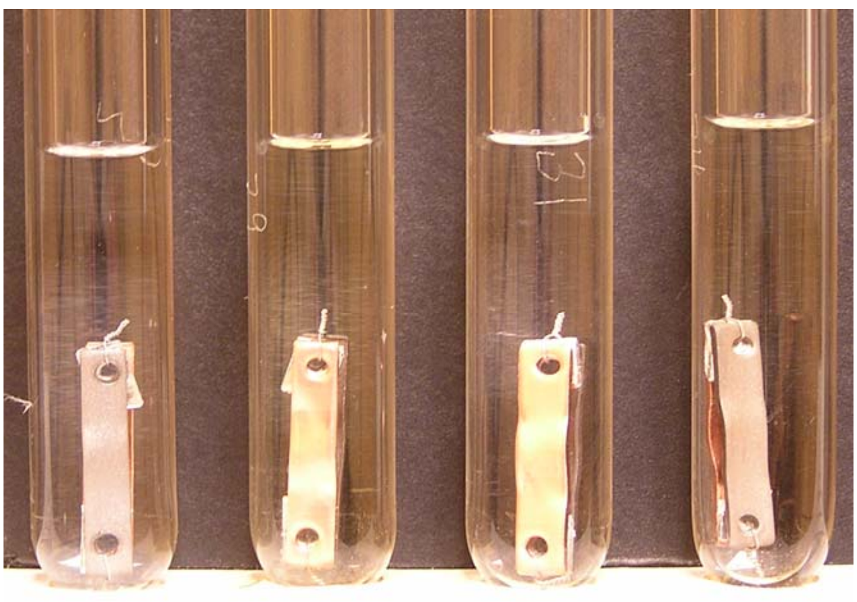
b. Black Background

Figure 3: Photographs of Sealed Tubes Containing R-134a/ISO 32 Branched Acid After Aging



Water	**24 ppm**	**24 ppm**	**490 ppm**	**490 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

a. White Background



Water	**24 ppm**	**24 ppm**	**490 ppm**	**490 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

b. Black Background

Figure 4: Photographs of Sealed Tubes Containing R-134a/PVE 32-A After Aging

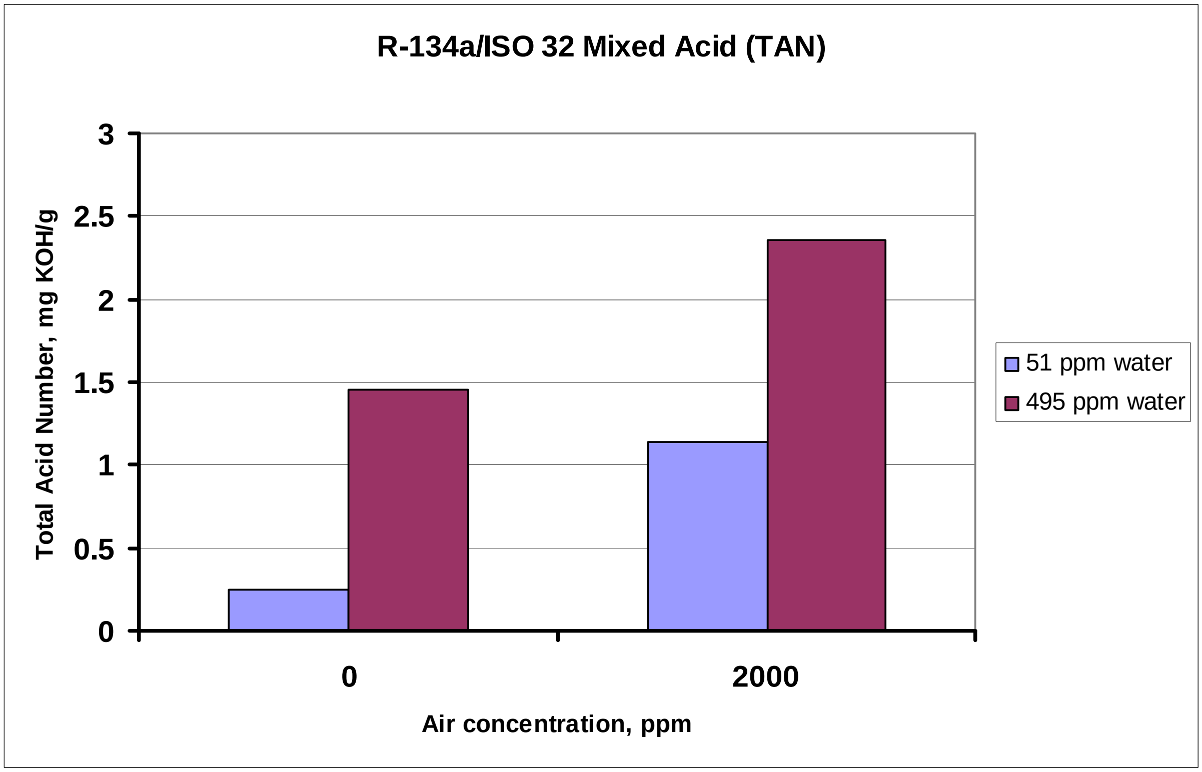


Figure 5: Total Acid Numbers of Sealed Tubes Containing R-134a and Mixed Acid

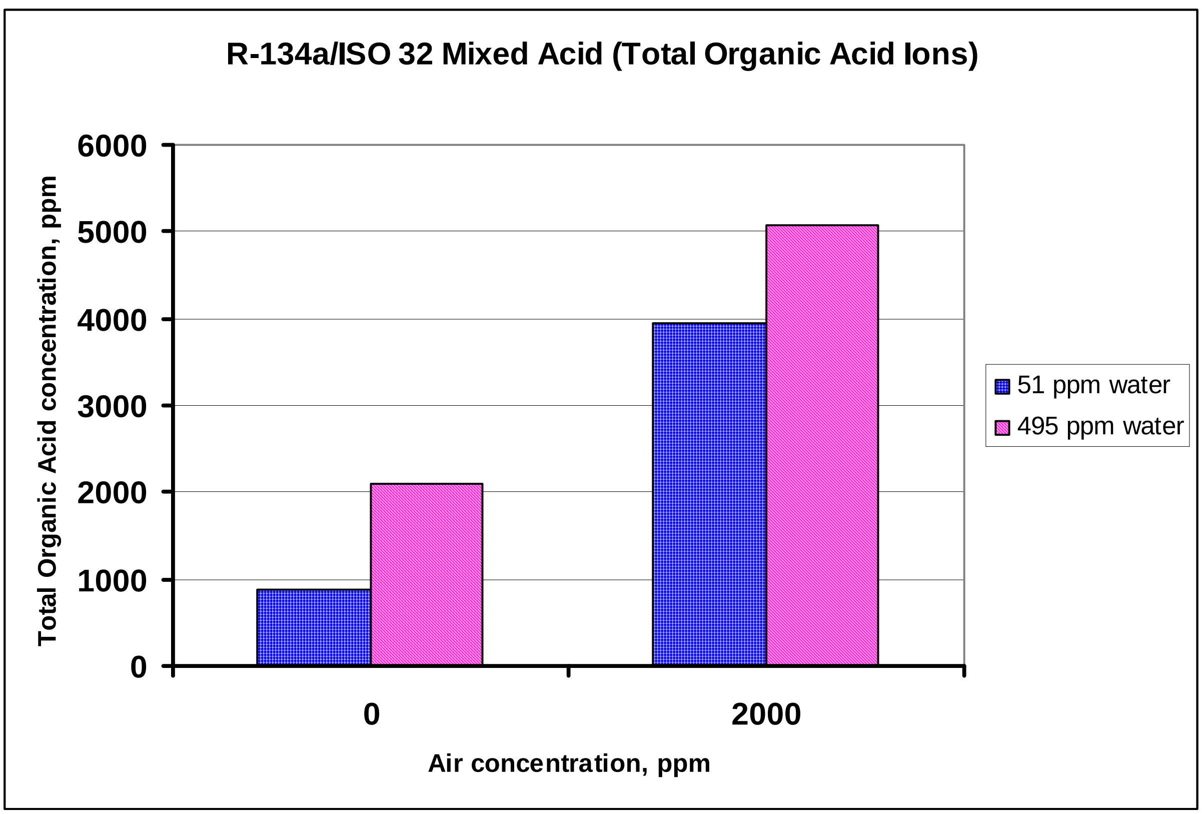


Figure 6: Total Organic Acid Concentrations of Sealed Tubes Containing R-134a and Mixed Acid

Table 11: Summary of Visual Observations of Aged Sealed Tubes (R-410A/ISO 32 Mixed Acid)

Visual Observations (R-410A/ISO 32 Mixed Acid)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
51	0	Light cloudiness; color slightly darker (color=2.5 versus 2.0 for unaged); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color darker (color=4.0 versus 2.0 for unaged); no deposit	Slight darkening at top of coupon	Medium darkening of coupon surface	Unchanged
495	0	Light cloudiness; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color darker (color=4.5 versus 2.0 for unaged); no deposit	Coupon became dull tan color	Medium darkening of coupon surface	Unchanged

Table 12: Summary of Analytical Results of Aged Sealed Tubes (R-410A/ISO 32 Mixed Acid)

Analytical Results (R-410A//ISO 32 Mixed Acid)							
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm			
				Fluoride	Propanoate	Hexanoate	Unknown
Unaged	N/A	N/A	0.04	0	0	0	0
Aged	51	0	0.28	0	425	0	0
		2000	0.66	0	296	1163	0
	495	0	1.31	0	189	5154	0
		2000	2.32	0	0	7741	0

Table 13: Summary of GC Results of Aged Sealed Tubes (R-410A/ISO 32 Mixed Acid)

Gas Chromatography Results (R-410A//ISO 32 Mixed Acid)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			R-410A %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	99.97	1	0
Aged	51	0	99.95	1	0.03 *
		2000	99.95	1	0.02 *
	495	0	---	---	---
		2000	99.94	1	0.03 *

* These numbers reflect the presence of an unknown peak (probably impurity) also found in the standard unaged R-410A

Table 14: Summary of Visual Observations of Aged Sealed Tubes (R-410A/ISO 32 Branched Acid)

Visual Observations (R-410A/ISO 32 Branched Acid)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
48	0	Faint cloudiness; color unchanged (color=2.0) ; no deposit	Unchanged	Unchanged	Unchanged
	2000	Faint cloudiness; color slightly darker (color=2.5 versus 2.0 for unaged); no deposit	Unchanged	Unchanged	Unchanged
517	0	Faint cloudiness; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Faint cloudiness; color slightly darker (color=2.5 versus 2.0 for unaged); no deposit	Unchanged	Unchanged	Unchanged

Table 15: Summary of Analytical Results of Aged Sealed Tubes (R-410A/ISO 32 Branched Acid)

Analytical Results (R-410A/ISO 32 Branched Acid)								
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm				
				Fluoride	Propanoate	Hexanoate	Heptanoate	Unknown
Unaged	N/A	N/A	0	0	0	0	0	0
Aged	48	0	0.08	0	0	0	0	0
		2000	0.15	0	506	0	0	0
	517	0	0.02	0	0	0	401	0
		2000	0.25	0	870	0	0	0

Table 16: Summary of GC Results of Aged Sealed Tubes (R-410A/ISO 32 Branched Acid)

Gas Chromatography Results (R-410A/ISO 32 Branched Acid)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			R-410A %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	99.97	1	0
Aged	48	0	99.94	1	0.03 *
		2000	99.94	1	0.03 *
	517	0	99.97	1	0
		2000	99.93	1	0.05 *

* These numbers reflect the presence of an unknown peak (probably impurity) also found in the standard unaged R-410A

Table 17: Summary of Visual Observations of Aged Sealed Tubes (R-410A/PVE 32-A)

Visual Observations (R-410A/PVE 32-A)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
24	0	Clear; color unchanged (color=2.0) ; no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color unchanged (color=2.0); Light brown stain in vapor space on tube wall	Unchanged	Unchanged	Unchanged
490	0	Clear; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color unchanged (color=2.0); Light brown stain in vapor space on tube wall	Unchanged	Unchanged	Unchanged

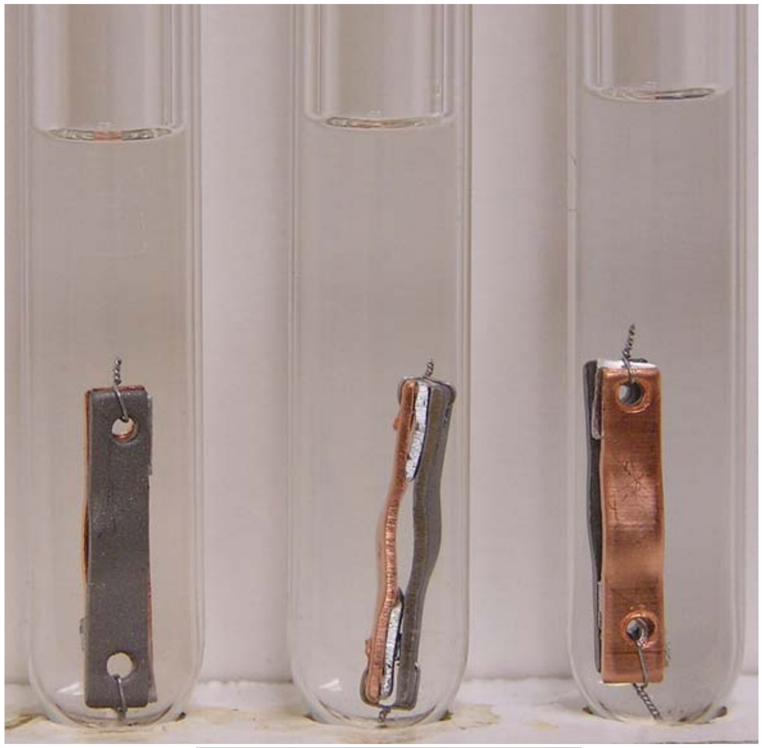
Table 18: Summary of Analytical Results of Aged Sealed Tubes (R-410A/PVE 32-A)

Analytical Results (R-410A/PVE 32-A)							
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm			
				Fluoride	Propanoate	Hexanoate	Unknown
Unaged	N/A	N/A	0.01	0	0	0	0
Aged	24	0	0.08	0	0	1075	0
		2000	0.19	0	861	0	0
	490	0	0.03	0	0	1044	0
		2000	0.20	0	891	0	0

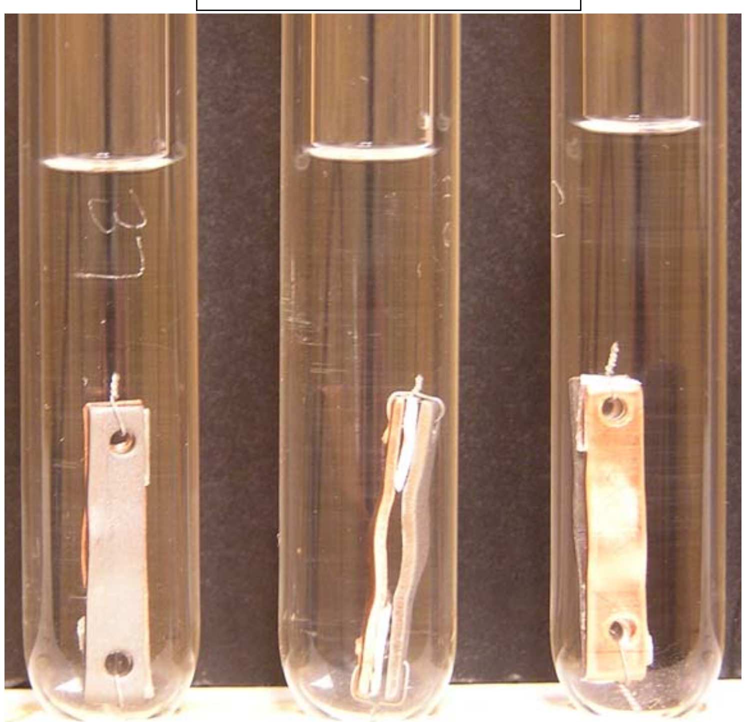
Table 19: Summary of GC Results of Aged Sealed Tubes (R-410A/PVE 32-A)

Gas Chromatography Results (R-410A/PVE 32-A)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			R-410A %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	99.97	1	0
Aged	24	0	99.95	1	0.02 *
		2000	99.95	1	0.02 *
	490	0	99.95	1	0.03 *
		2000	99.95	1	0.02 *

* These numbers reflect the presence of an unknown peak (probably impurity) also found in the standard unaged R-410A



a. White Background

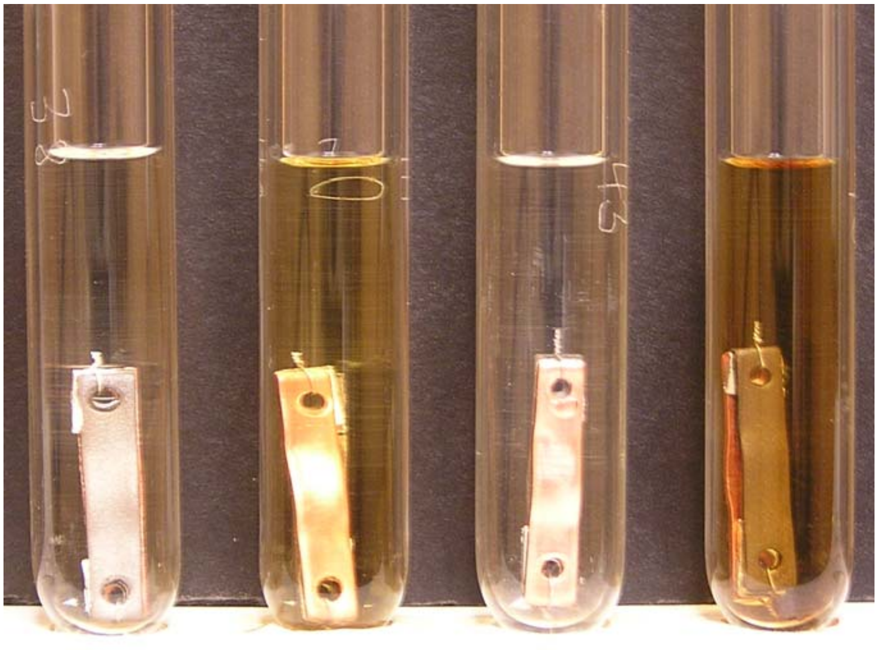


b. Black Background

Figure 7: Photographs of Sealed Tubes Containing R-410A/Lubricant Before Aging

Water	51 ppm	51 ppm	495 ppm	495 ppm
Air	0 ppm	2000 ppm	0 ppm	2000 ppm

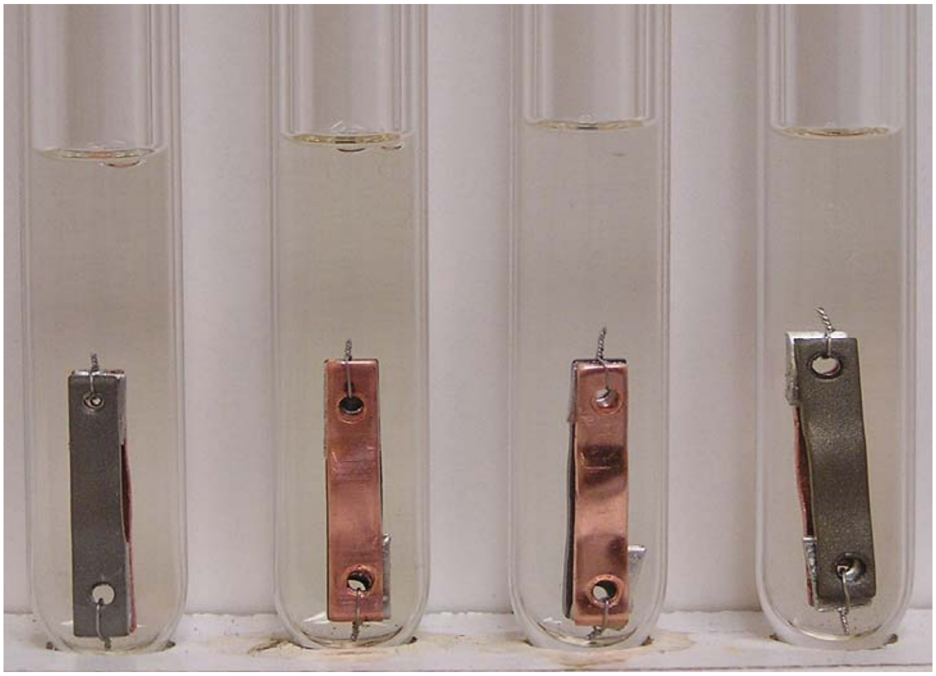
a. White Background



Water	51 ppm	51 ppm	495 ppm	495 ppm
Air	0 ppm	2000 ppm	0 ppm	2000 ppm

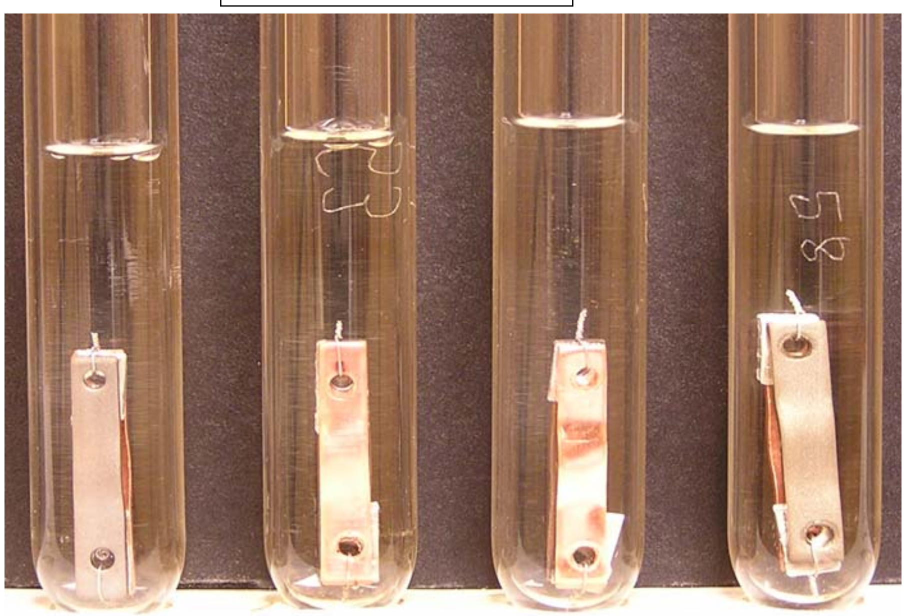
b. Black Background

Figure 8: Photographs of Sealed Tubes Containing R-410A/ISO 32 Mixed Acid After Aging



Water	**48 ppm**	**48 ppm**	**517 ppm**	**517 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

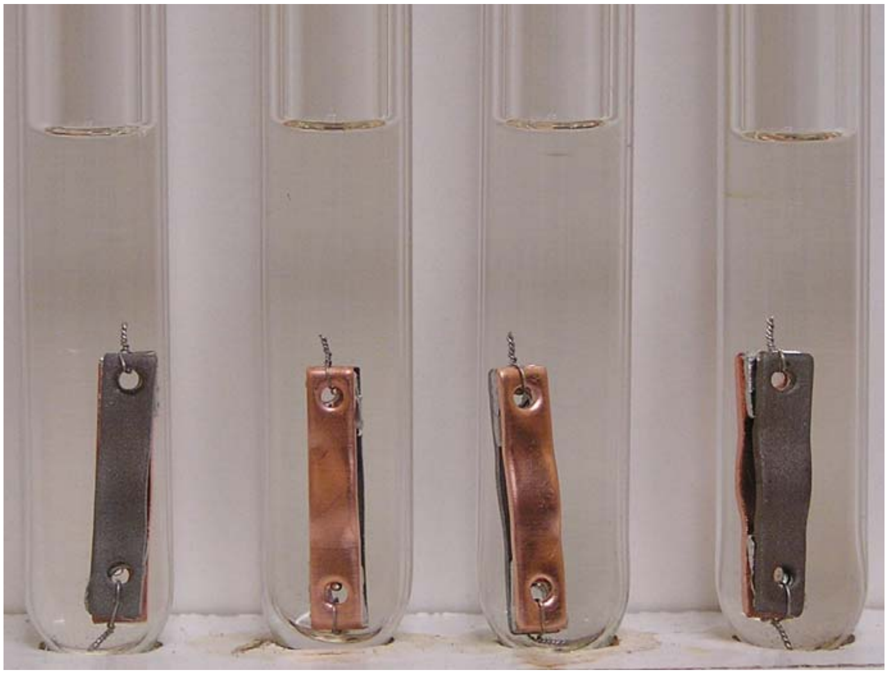
a. White Background



Water	**48 ppm**	**48 ppm**	**517 ppm**	**517 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

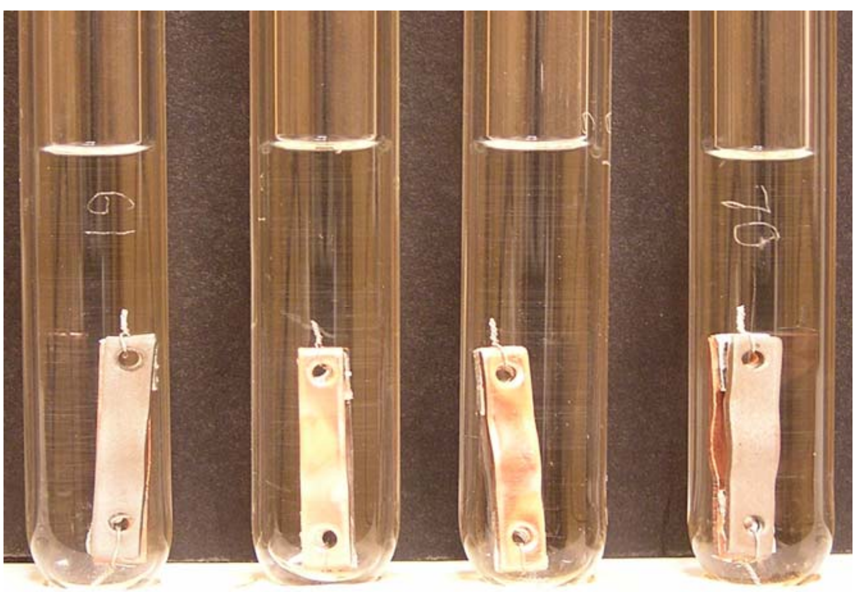
b. Black Background

Figure 9: Photographs of Sealed Tubes Containing R-410A/ISO 32 Branched Acid After Aging



Water	**24 ppm**	**24 ppm**	**490 ppm**	**490 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

a. White Background



Water	**24 ppm**	**24 ppm**	**490 ppm**	**490 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

b. Black Background

Figure 10: Photographs of Sealed Tubes Containing R-410A/PVE 32-A After Aging

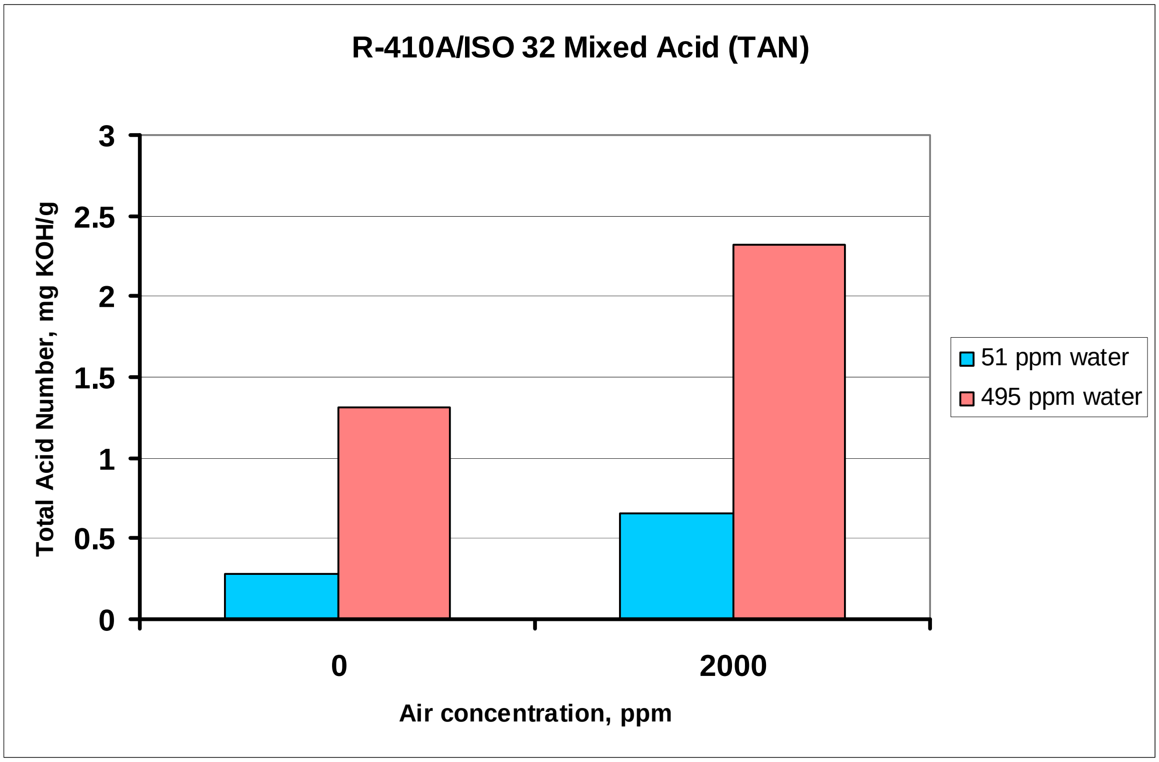


Figure 11: Total Acid Numbers of Sealed Tubes Containing R-410A and Mixed Acid

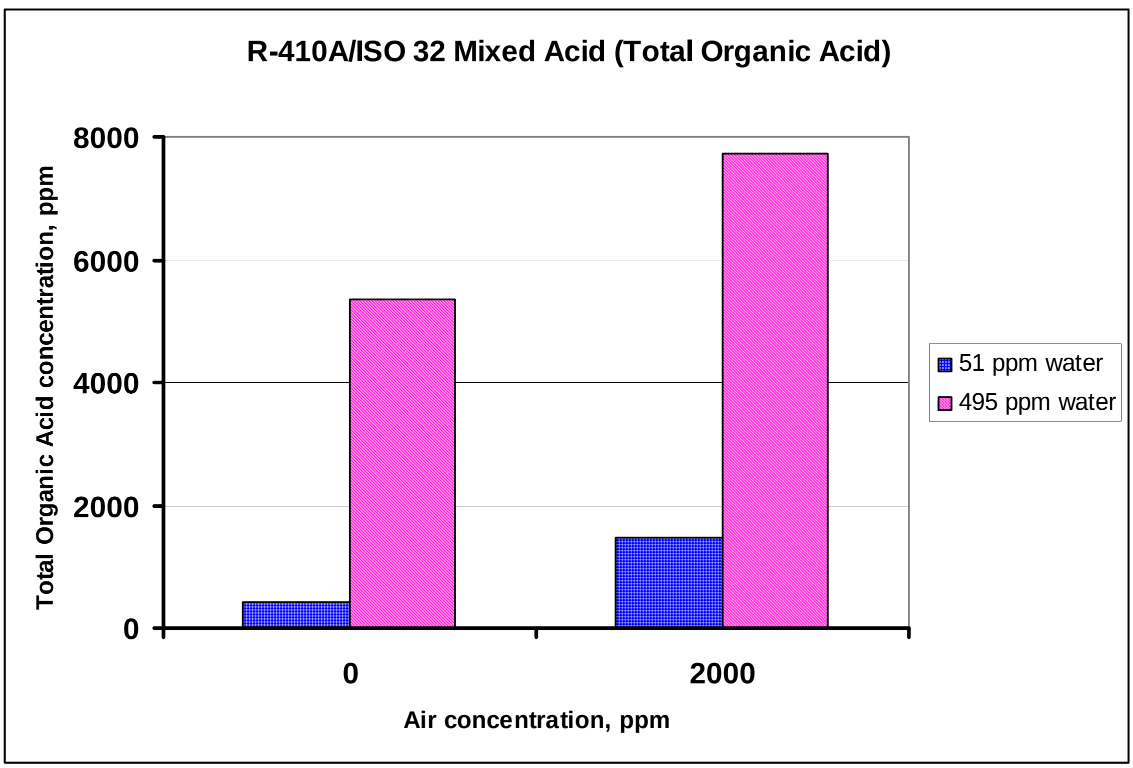


Figure 12: Total Organic Acid Concentrations of Sealed Tubes Containing R-410A and Mixed Acid

Table 20: Summary of Visual Observations of Aged Sealed Tubes (HFO-1234yf/ISO 32 Mixed Acid)

Visual Observations (HFO-1234yf/ISO 32 Mixed Acid)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
51	0	Very faint cloudiness; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color darker (color=3.5 versus 2.0 for unaged); no deposit	Unchanged	Unchanged	Unchanged
495	0	Medium cloudiness; color slightly darker (color=2.5 versus 2.0 for unaged); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color darker (color=3.5 versus 2.0 for unaged); no deposit	Unchanged	Slight darkening of coupon surface	Unchanged

Table 21: Summary of Analytical Results of Aged Sealed Tubes (HFO-1234yf/ISO 32 Mixed Acid)

Analytical Results (HFO-1234yf/ISO 32 Mixed Acid)								
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm				
				Fluoride	Propanoate	Pentanoate	Hexanoate	Unknown
Unaged	N/A	N/A	0.04	0	0	0	0	0
Aged	51	0	0.12	9	0	0	959	0
		2000	1.04	512; 399*	0	375; 299*	0	0
	495	0	1.58	31; 33*	0	635; 667*	0	0
		2000	2.33	117; 101*	0	846; 1186*	0	0

* Repeated measurements

Table 22: Summary of GC Results of Aged Sealed Tubes (HFO-1234yf/ISO 32 Mixed Acid)

Gas Chromatography Results (HFO-1234yf/ISO 32 Mixed Acid)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			HFO-1234yf %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	100	0	0
Aged	51	0	99.81	2	0.19
		2000	99.99	2	0.01
	495	0	99.80	2	0.20
		2000	100	1	0

Table 23: Summary of Visual Observations of Aged Sealed Tubes (HFO-1234yf/ ISO 32 Branched Acid)

Visual Observations (HFO-1234yf/ISO 32 Branched Acid)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
48	0	Clear; color unchanged (color=2.0) ; no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color darker (color=3.5 versus 2.0 for unaged); no deposit	Unchanged	Unchanged	Unchanged
517	0	Clear; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color darker (color=3.5 versus 2.0 for unaged); no deposit	Unchanged	Unchanged	Unchanged

Table 24: Summary of Analytical Results of Aged Sealed Tubes (HFO-1234yf/ISO 32 Branched Acid)

Analytical Results (HFO-1234yf/ISO 32 Branched Acid)								
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm				
				Fluoride	Propanoate	2-Ethyl Hexanoate	Heptanoate	Unknown
Unaged	N/A	N/A	0	0	0	0	0	0
Aged	48	0	0.02	10	0	0	647	0
		2000	0	196; 44*	0	0	0; 0*	0
	517	0	0.12	8	0	0	359	0
		2000	1.44	721; 969*	0	648	656; 614*	0

* Repeated measurements

Table 25: Summary of GC Results of Aged Sealed Tubes (HFO-1234yf/ISO 32 Branched Acid)

Gas Chromatography Results (HFO-1234yf/ISO 32 Branched Acid)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			HFO-1234yf %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	100	0	0
Aged	48	0	100	1	0
		2000	100	1	0
	517	0	99.99	1	0.01
		2000	99.99	1	0.01

Table 26: Summary of Visual Observations of Aged Sealed Tubes (HFO-1234yf/ PVE 32-A)

Visual Observations (HFO-1234yf/PVE 32-A)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
24	0	Clear; color unchanged (color=2.0) ; no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color slightly darker (color=2.75 versus 2.0 for unaged); Light brown stain in vapor space on tube wall	Unchanged	Unchanged	Unchanged
490	0	Clear; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color slightly darker (color=2.75 versus 2.0 for unaged); Light brown stain in vapor space on tube wall	Unchanged	Unchanged	Unchanged

Table 27: Summary of Analytical Results of Aged Sealed Tubes (HFO-1234yf/PVE 32-A)

Analytical Results (HFO-1234yf/PVE 32-A)								
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm				
				Fluoride	Propanoate	Pentanoate	Hexanoate	Unknown
Unaged	N/A	N/A	0.01	0	0	0	0	0
Aged	24	0	0.06	224; 296*	0	0	0	0
		2000	0.31	498; 412*	0	0	0	0
	490	0	0.06	267; 193*	0	0	0	0
		2000	0.33	514; 612*	0	0	0	0

* Repeated measurements

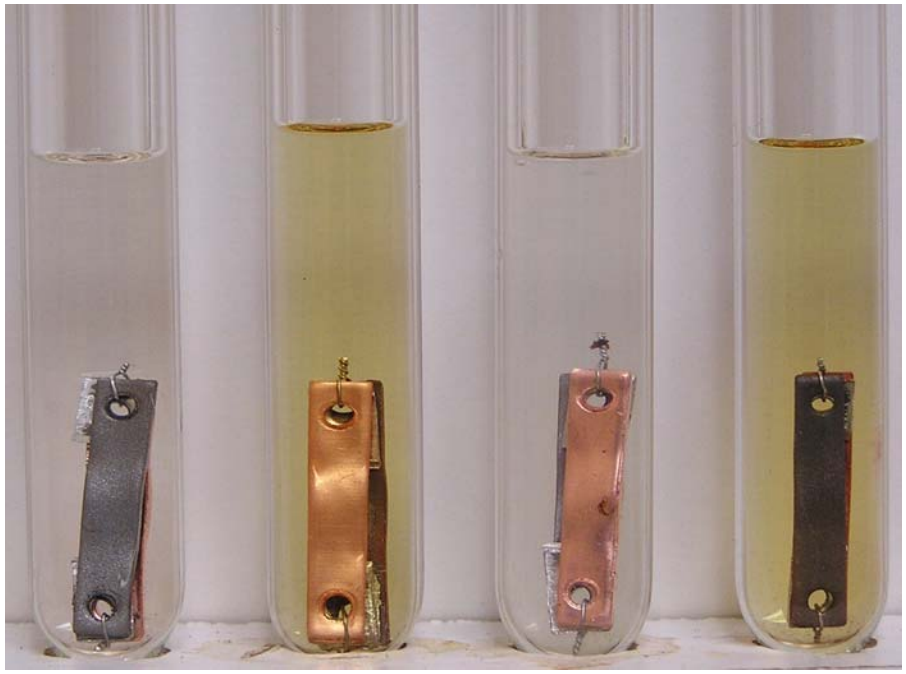
Table 28: Summary of GC Results of Aged Sealed Tubes (HFO-1234yf/PVE 32-A)

Gas Chromatography Results (HFO-1234yf/PVE 32-A)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			HFO-1234yf %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	100	0	0
Aged	24	0	100	1	0
		2000	99.99	1	0.01
	490	0	100	0	0
		2000	98.59	1	1.41

a. White Background

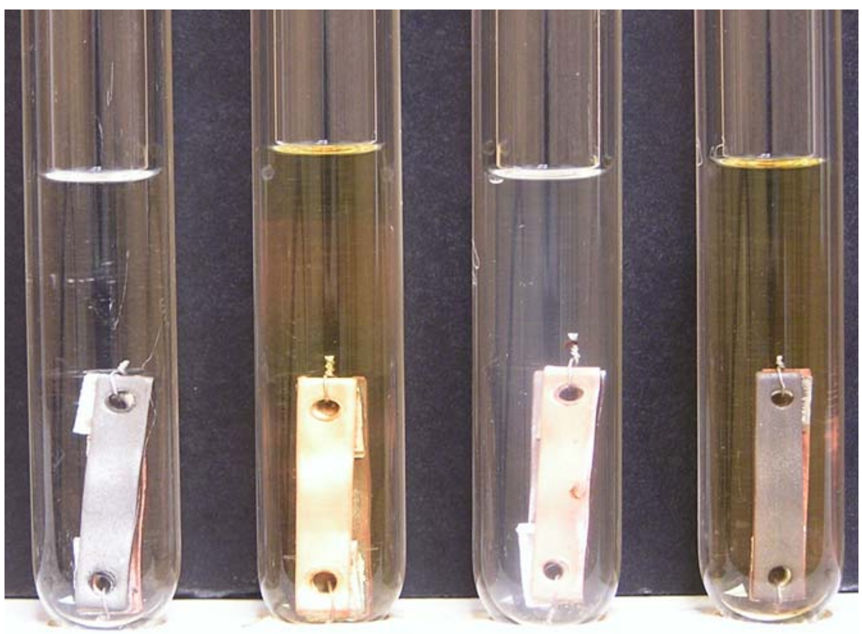
b. Black Background

Figure 13: Photographs of Sealed Tubes Containing HFO-1234yf/Lubricant Before Aging



Water	51 ppm	51 ppm	495 ppm	495 ppm
Air	0 ppm	2000 ppm	0 ppm	2000 ppm

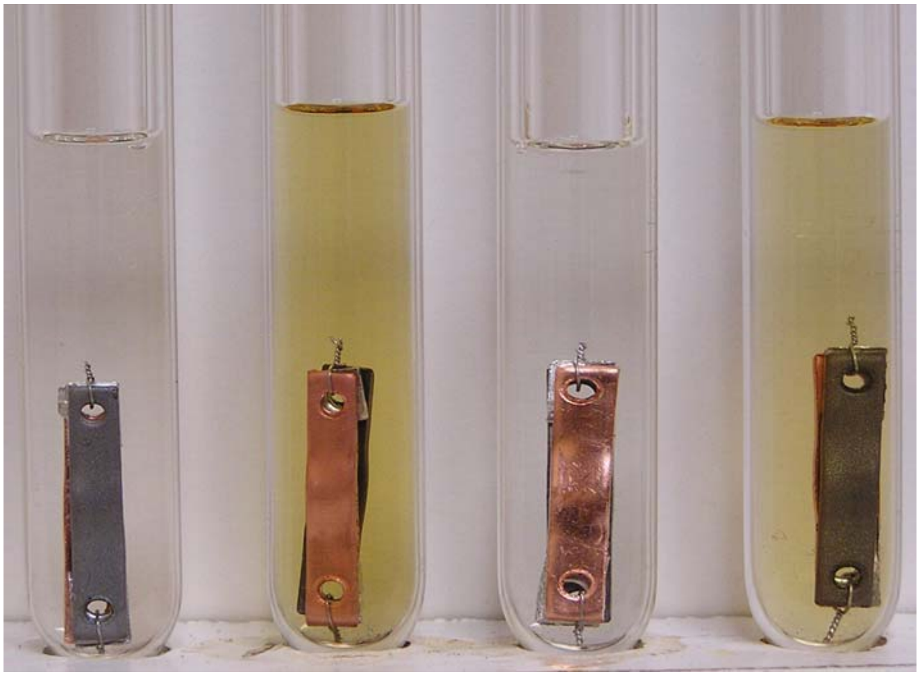
a. White Background



Water	51 ppm	51 ppm	495 ppm	495 ppm
Air	0 ppm	2000 ppm	0 ppm	2000 ppm

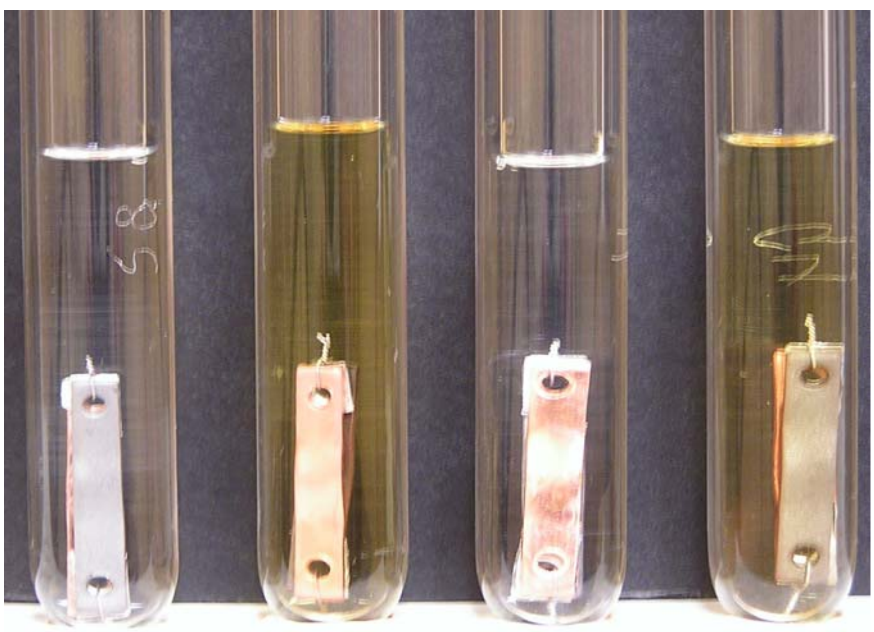
b. Black Background

Figure 14: Photographs of Sealed Tubes Containing HFO-1234yf/ISO 32 Mixed Acid After Aging



Water	**48 ppm**	**48 ppm**	**517 ppm**	**517 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

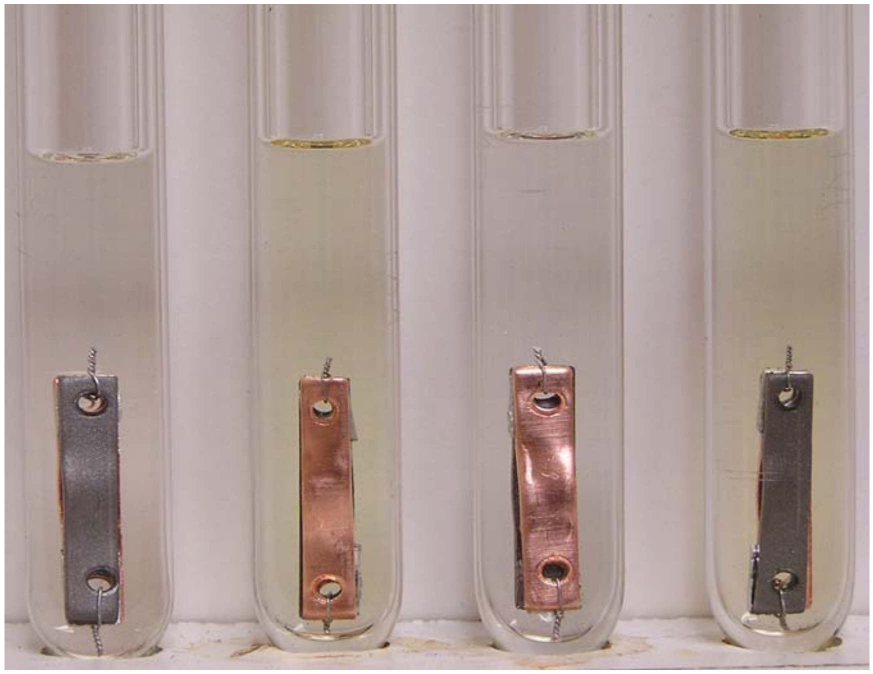
a. White Background



Water	**48 ppm**	**48 ppm**	**517 ppm**	**517 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

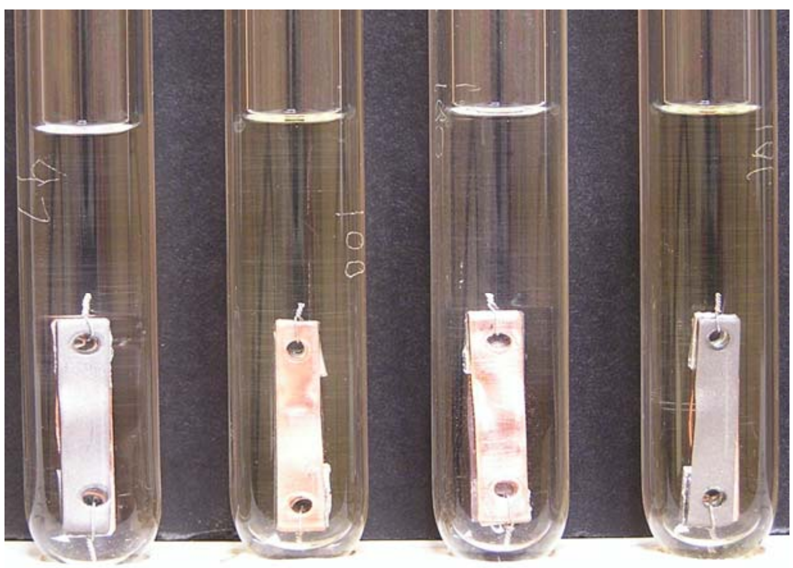
b. Black Background

Figure 15: Photographs of Sealed Tubes Containing HFO-1234yf/ISO 32 Branched Acid After Aging



Water	24 ppm	24 ppm	490 ppm	490 ppm
Air	0 ppm	2000 ppm	0 ppm	2000 ppm

a. White Background



Water	24 ppm	24 ppm	490 ppm	490 ppm
Air	0 ppm	2000 ppm	0 ppm	2000 ppm

b. Black Background

Figure 16: Photographs of Sealed Tubes Containing HFO-1234yf/PVE 32-A After Aging

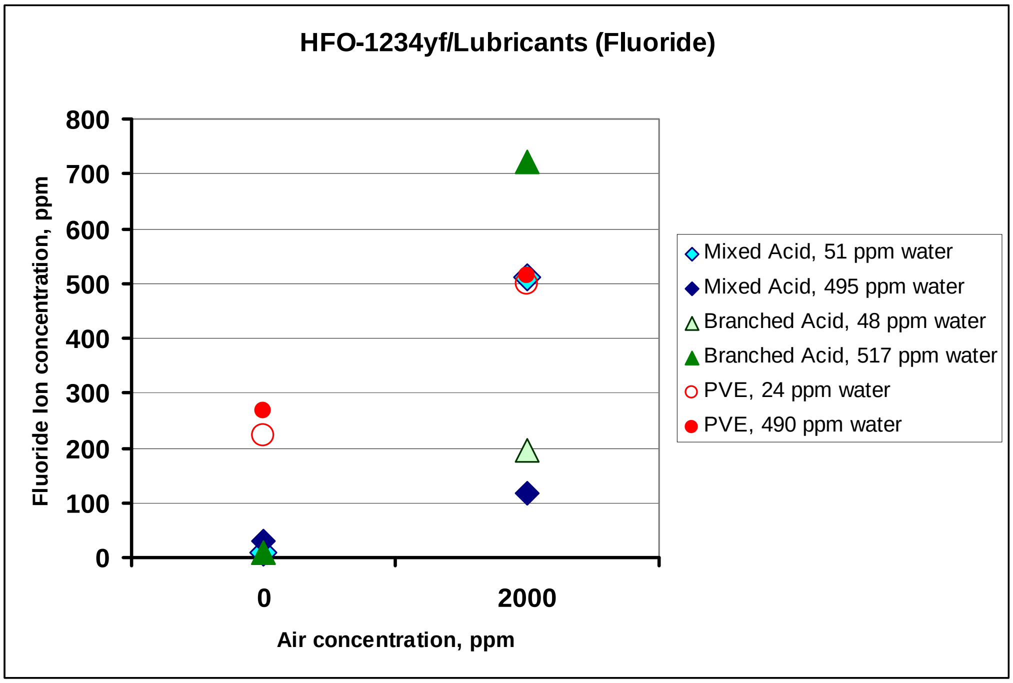


Figure 17: Fluoride Ion Concentrations in Sealed Tubes Containing HFO-1234yf and Lubricants

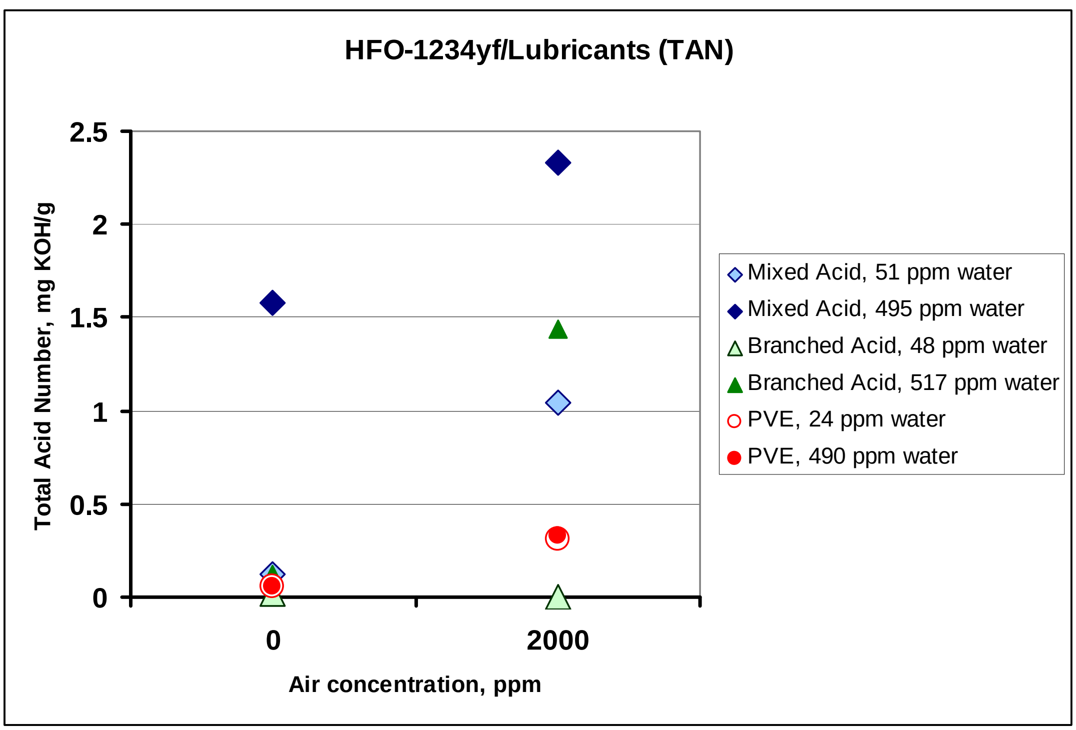


Figure 18: Total Acid Numbers of Sealed Tubes Containing HFO-1234yf and Lubricants

Table 29: Summary of Visual Observations of Aged Sealed Tubes (HFO-1234ze/ISO 32 Mixed Acid)

Visual Observations (HFO-1234ze/ISO 32 Mixed Acid)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
51	0	Very faint cloudiness; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color darker (color=3.75 versus 2.0 for unaged); no deposit	Darker amber color at top of coupon	Medium darkening	Unchanged
495	0	Very faint cloudiness; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color darker (color=4.0 versus 2.0 for unaged); no deposit	Darker amber color at top of coupon	Medium darkening	Unchanged

Table 30: Summary of Analytical Results of Aged Sealed Tubes (HFO-1234ze/ ISO 32 Mixed Acid)

Analytical Results (HFO-1234ze/ ISO 32 Mixed Acid)								
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm				
				Fluoride	Propanoate	Pentanoate	Heptanoate	Unknown
Unaged	N/A	N/A	0.04	0	0	0	0	0
Aged	51	0	0.08	57; 8*	0	0	0	0
		2000	0.67	51; 46*	0	181; 239*	0	0
	495	0	0.50	18; 15*	0	178; 155*	0	0
		2000	2.14	61	0	571	657	0

* Repeated measurements

Table 31: Summary of GC Results of Aged Sealed Tubes (HFO-1234ze/ ISO 32 Mixed Acid)

Gas Chromatography Results (HFO-1234ze/ ISO 32 Mixed Acid)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			HFO-1234ze %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	99.98	1	0
Aged	51	0	98.59	1	1.39
		2000	98.75	1	1.23
	495	0	99.89	1	0.09
		2000	99.96	1	0.02

Table 32: Summary of Visual Observations of Aged Sealed Tubes (HFO-1234ze/ISO 32 Branched Acid)

Visual Observations (HFO-1234ze/ISO 32 Branched Acid)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
48	0	Clear; color unchanged (color=2.0) ; no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color slightly darker (color=2.75 versus 2.0 for unaged); no deposit	Unchanged	Unchanged	Unchanged
517	0	Clear; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color slightly darker (color=2.75 versus 2.0 for unaged); no deposit	Unchanged	Slightly darker	Unchanged

Table 33: Summary of Analytical Results of Aged Sealed Tubes (HFO-1234ze/ISO 32 Branched Acid)

Analytical Results (HFO-1234ze/ISO 32 Branched Acid)								
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm				
				Fluoride	Propanoate	2-Ethyl Hexanoate	Heptanoate	Unknown
Unaged	N/A	N/A	0	0	0	0	0	0
Aged	48	0	0.02	0; 0*	0	0	0	0
		2000	0.16	142	0	0	0	0
	517	0	0.02	48	0	0	0	0
		2000	0.27	59	0	0	0	0

* Repeated measurements

Table 34: Summary of GC Results of Aged Sealed Tubes (HFO-1234ze/ISO 32 Branched Acid)

Gas Chromatography Results (HFO-1234ze/ISO 32 Branched Acid)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			HFO-1234ze %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	99.98	1	0
Aged	48	0	99.79	1	0.19
		2000	99.98	1	0
	517	0	99.98	1	0
		2000	99.97	1	0.01

Table 35: Summary of Visual Observations of Aged Sealed Tubes (HFO-1234ze/PVE 32-A)

Visual Observations (HFO-1234ze/PVE 32-A)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
24	0	Clear; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color slightly darker (color=2.75 versus 2.0 for unaged); Light brown stain in vapor space on tube wall	Unchanged	Unchanged	Unchanged
490	0	Clear; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color slightly darker (color=2.75 versus 2.0 for unaged); Light brown stain in vapor space on tube wall	Unchanged	Unchanged	Unchanged

Table 36: Summary of Analytical Results of Aged Sealed Tubes (HFO-1234ze/PVE 32-A)

Analytical Results (HFO-1234ze/PVE 32-A)								
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm				
				Fluoride	Formate	Pentanoate	Hexanoate	Unknown
Unaged	N/A	N/A	0.01	0	0	0	0	0
Aged	24	0	0.02	0	0	0	0	0
		2000	0.15	54	0	0	0	0
	490	0	0	9	0	0	0	0
		2000	0.17	59	44	0	0	0

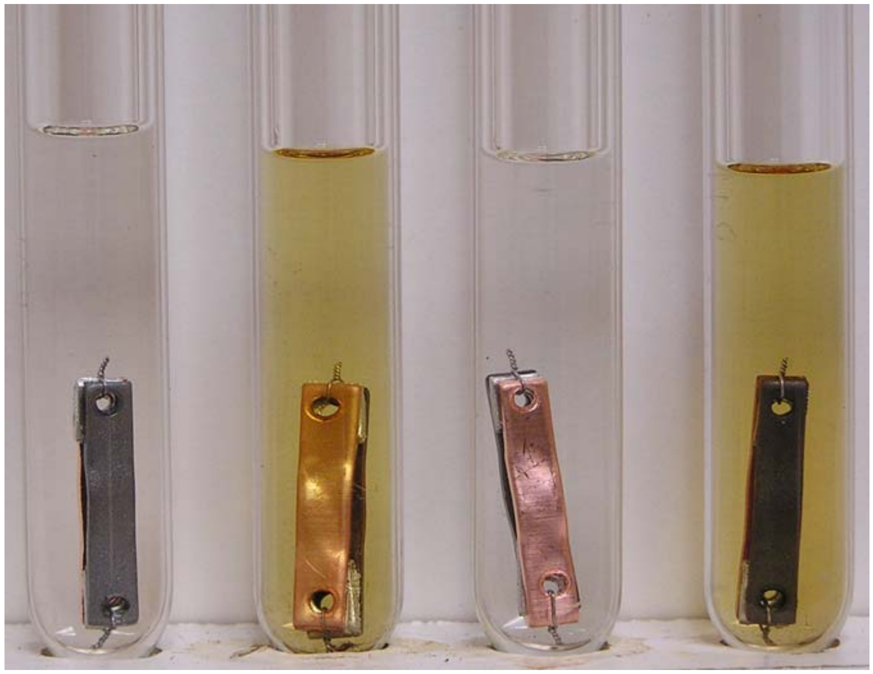
Table 37: Summary of GC Results of Aged Sealed Tubes (HFO-1234ze/PVE 32-A)

Gas Chromatography Results (HFO-1234ze/PVE 32-A)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			HFO-1234ze %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	99.98	1	0
Aged	24	0	99.98	1	0
		2000	100	1	0
	490	0	100	1	0
		2000	100	1	0

a. White Background

b. Black Background

Figure 19: Photographs of Sealed Tubes Containing HFO-1234ze/Lubricant Before Aging



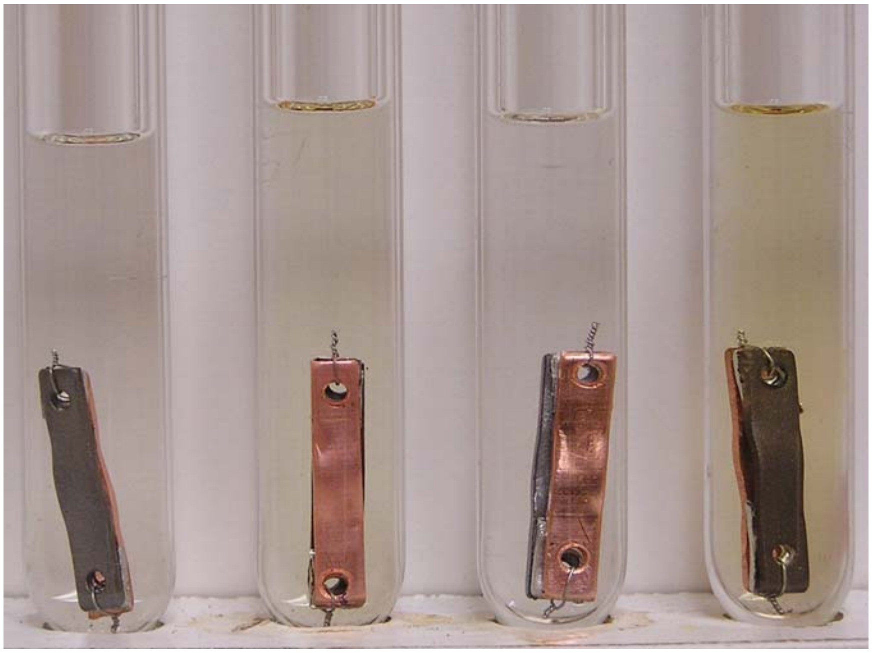
Water	**51 ppm**	**51 ppm**	**495 ppm**	**495 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

a. White Background

Water	**51 ppm**	**51 ppm**	**495 ppm**	**495 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

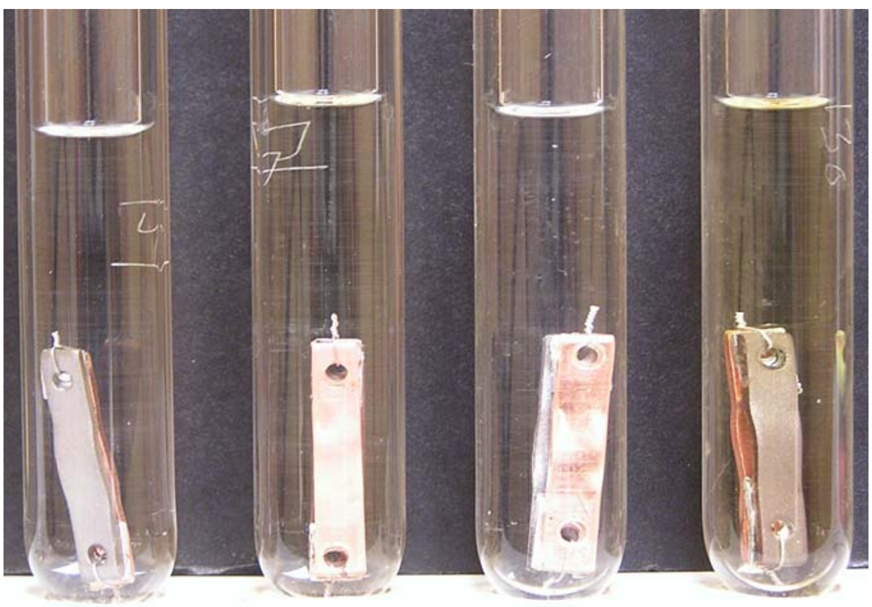
b. Black Background

Figure 20: Photographs of Sealed Tubes Containing HFO-1234ze/ISO 32 Mixed Acid After Aging



Water	**48 ppm**	**48 ppm**	**517 ppm**	**517 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

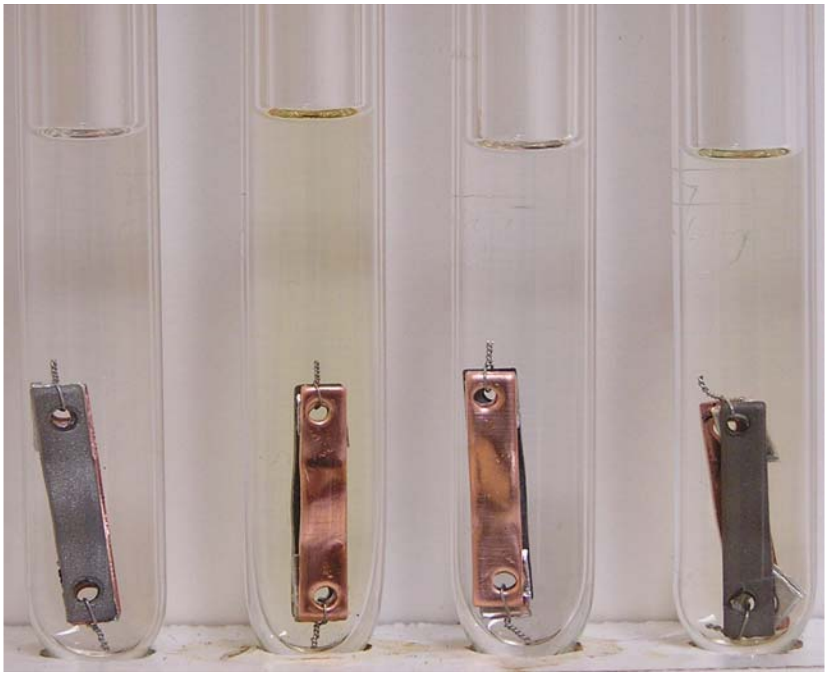
a. White Background



Water	**48 ppm**	**48 ppm**	**517 ppm**	**517 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

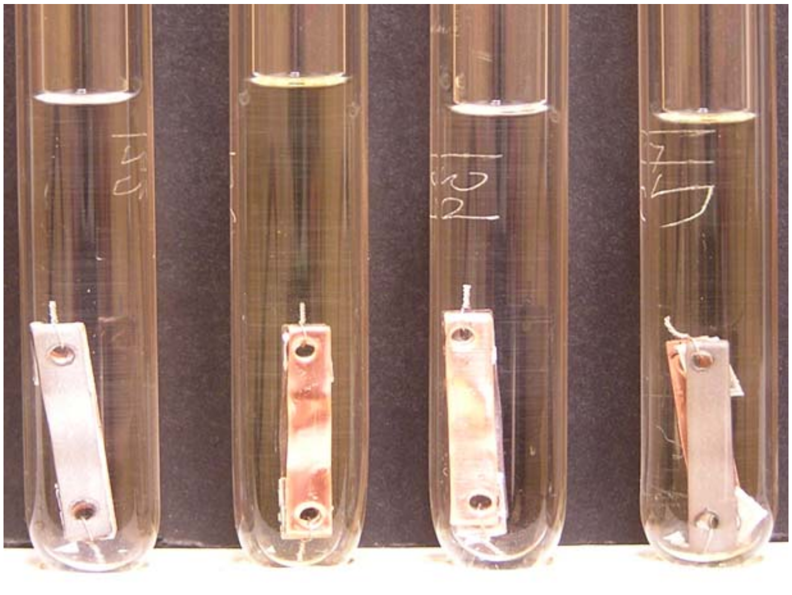
b. Black Background

Figure 21: Photographs of Sealed Tubes Containing HFO-1234ze/ISO 32 Branched Acid After Aging



Water	**24 ppm**	**24 ppm**	**490 ppm**	**490 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

a. White Background



Water	**24 ppm**	**24 ppm**	**490 ppm**	**490 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

b. Black Background

Figure 22: Photographs of Sealed Tubes Containing HFO-1234ze/PVE 32-A After Aging

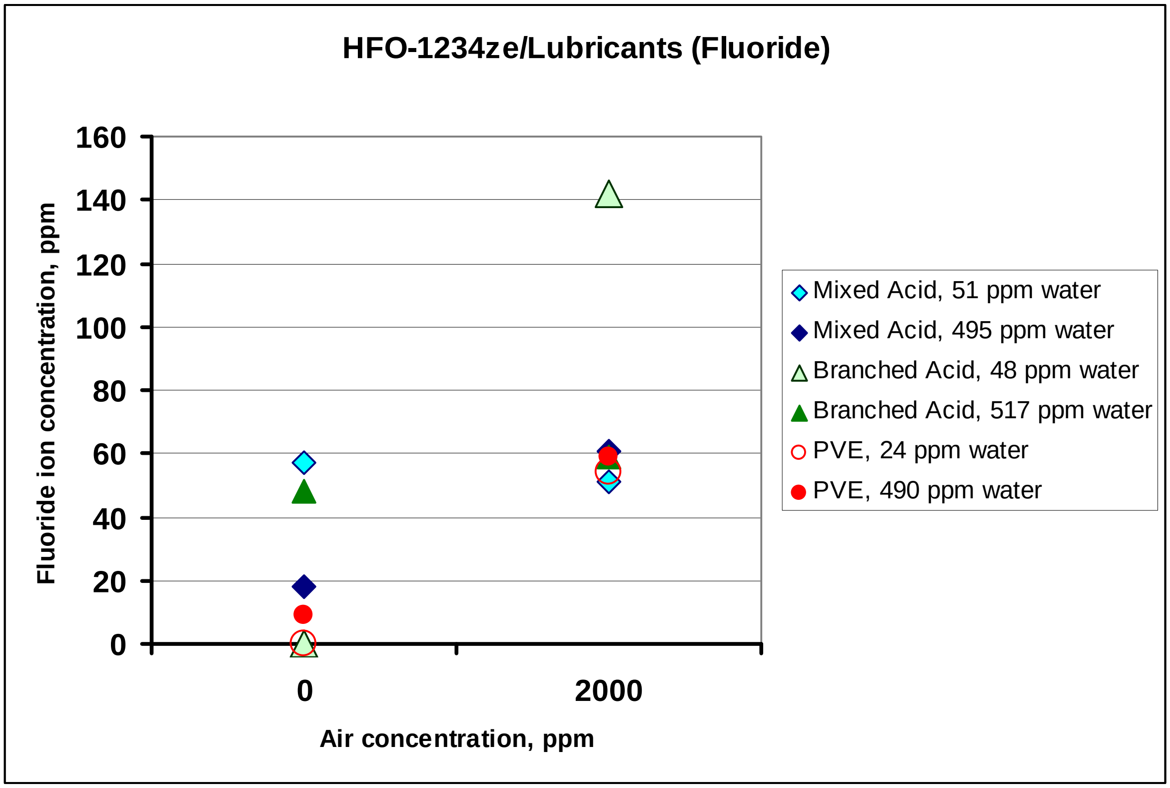


Figure 23: Fluoride Ion Concentrations in Sealed Tubes Containing HFO-1234ze and Lubricants

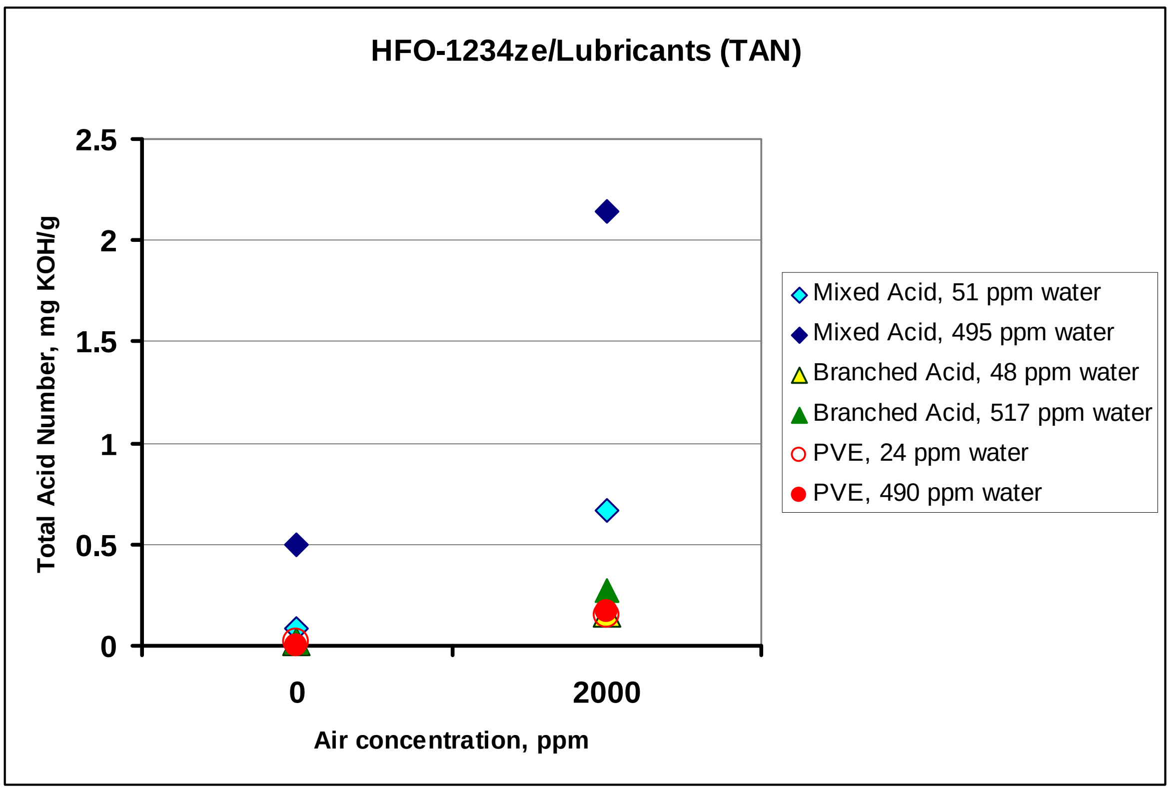


Figure 24: Total Acid Numbers of Sealed Tubes Containing HFO-1234ze and Lubricants

Table 38: Summary of Visual Observations of Aged Sealed Tubes (Refrigerant Mixture/ISO 32 Mixed Acid)

Visual Observations (Refrigerant Mixture/ISO 32 Mixed Acid)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
51	0	Very faint cloudiness; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color slightly darker (color=2.75 versus 2.0 for unaged); no deposit	Unchanged	Unchanged	Unchanged
495	0	Faint cloudiness; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color slightly darker (color=2.75 versus 2.0 for unaged); no deposit	Unchanged	Unchanged	Unchanged

Table 39: Summary of Analytical Results of Aged Sealed Tubes (Refrigerant Mixture/ ISO 32 Mixed Acid)

Analytical Results (Refrigerant Mixture/ ISO 32 Mixed Acid)								
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm				
				Fluoride	Propanoate	Pentanoate	Hexanoate	Unknown
Unaged	N/A	N/A	0.04	0	0	0	0	0
Aged	51	0	0.14	18	0	120	0	0
		2000	1.31	770; 417*	0	319; 161*	0	0
	495	0	0.88	64	0	461	0	0
		2000	2.79	1167; 671*	0	1428; 731*	0	1; 0*

* Repeated measurements

Table 40: Summary of GC Results of Aged Sealed Tubes (Refrigerant Mixture/ ISO 32 Mixed Acid)

Gas Chromatography Results (Refrigerant Mixture/ ISO 32 Mixed Acid)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			Refrigerant %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	100	0	0
Aged	51	0	98.05	1	1.95
		2000	100	1	0
	495	0	100	0	0
		2000	100	0	0

Table 41: Summary of Visual Observations of Aged Sealed Tubes (Refrigerant Mixture/ISO 32 Branched Acid)

Visual Observations (Refrigerant Mixture/ISO 32 Branched Acid)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
48	0	Clear; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color darker (color=3.0 versus 2.0 for unaged); no deposit	Unchanged	Unchanged	Unchanged
517	0	Clear; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color slightly darker (color=2.75 versus 2.0 for unaged); no deposit	Unchanged	Unchanged	Unchanged

Table 42: Summary of Analytical Results of Aged Sealed Tubes (Refrigerant Mixture/ISO 32 Branched Acid)

Analytical Results (Refrigerant Mixture/ISO 32 Branched Acid)								
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm				
				Fluoride	Propanoate	2-Ethyl Hexanoate	Heptanoate	Unknown
Unaged	N/A	N/A	0	0	0	0	0	0
Aged	48	0	0.04	54	0	0	0	0
		2000	0.84	908; 696*	0	0	0	0
	517	0	0.04	82	0	0	0	0
		2000	1.77	793	0	799	0	0

* Repeated measurements

Table 43: Summary of GC Results of Aged Sealed Tubes (Refrigerant Mixture/ISO 32 Branched Acid)

Gas Chromatography Results (Refrigerant Mixture/ISO 32 Branched Acid)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			Refrigerant %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	100	0	0
Aged	48	0	100	0	0
		2000	100	0	0
	517	0	100	0	0
		2000	100	0	0

Table 44: Summary of Visual Observations of Aged Sealed Tubes (Refrigerant Mixture/PVE 32-A)

Visual Observations (Refrigerant Mixture/PVE 32-A)					
Moisture ppm	Air ppm	Visual Observations			
		Liquid	Copper	Steel	Aluminum
24	0	Clear; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color slightly darker (color=2.75 versus 2.0 for unaged); light brown deposit in vapor space on tube wall	Unchanged	Unchanged	Unchanged
490	0	Clear; color unchanged (color=2.0); no deposit	Unchanged	Unchanged	Unchanged
	2000	Clear; color slightly darker (color=2.75 versus 2.0 for unaged); light brown deposit in vapor space on tube wall	Unchanged	Unchanged	Unchanged

Table 45: Summary of Analytical Results of Aged Sealed Tubes (Refrigerant Mixture/PVE 32-A)

Analytical Results (Refrigerant Mixture/PVE 32-A)								
Lubricant	Moisture ppm	Air ppm	Total Acid Number mg KOH/g	Ion Chromatography Results, ppm				
				Fluoride	Formate	Hexanoate	Heptanoate	Unknown
Unaged	N/A	N/A	0.01	0	0	0	0	0
Aged	24	0	0.04	95	0	0	0	0
		2000	0.22	205; 186*	37	0	0	0
	490	0	0.04	117	0	0	0	0
		2000	0.25	227	0	0	0	0

* Repeated measurements

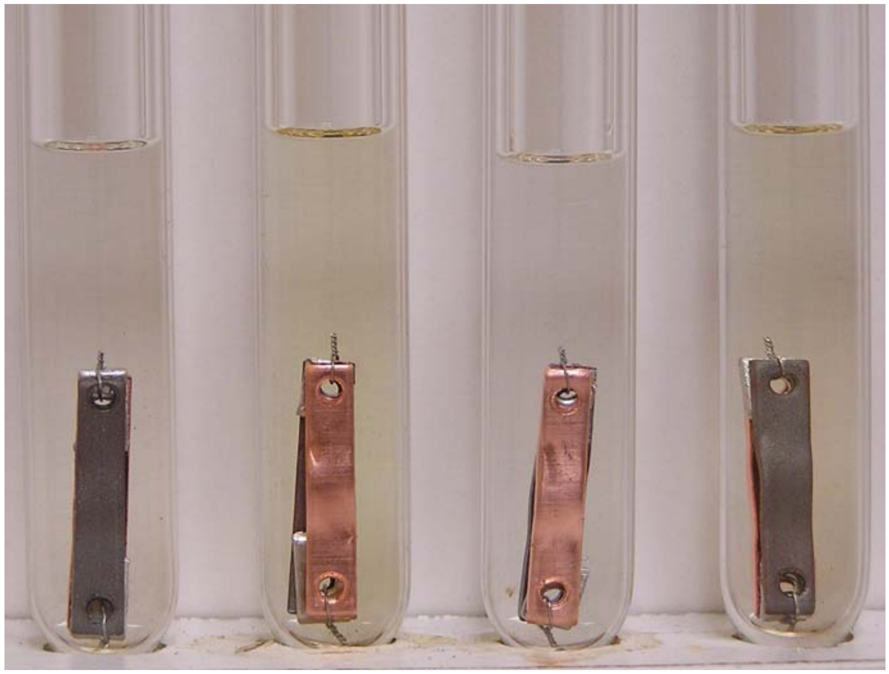
Table 46: Summary of GC Results of Aged Sealed Tubes (Refrigerant Mixture/PVE 32-A)

Gas Chromatography Results (Refrigerant Mixture/PVE 32-A)					
Refrigerant	Moisture ppm	Air ppm	Gas Chromatography Results		
			Refrigerant %	Number of unknown peaks	% refrigerant decomposed
Unaged	N/A	N/A	100	0	0
Aged	24	0	100	0	0
		2000	99.99	0	0.01
	490	0	100	0	0
		2000	100	0	0

a. White Background

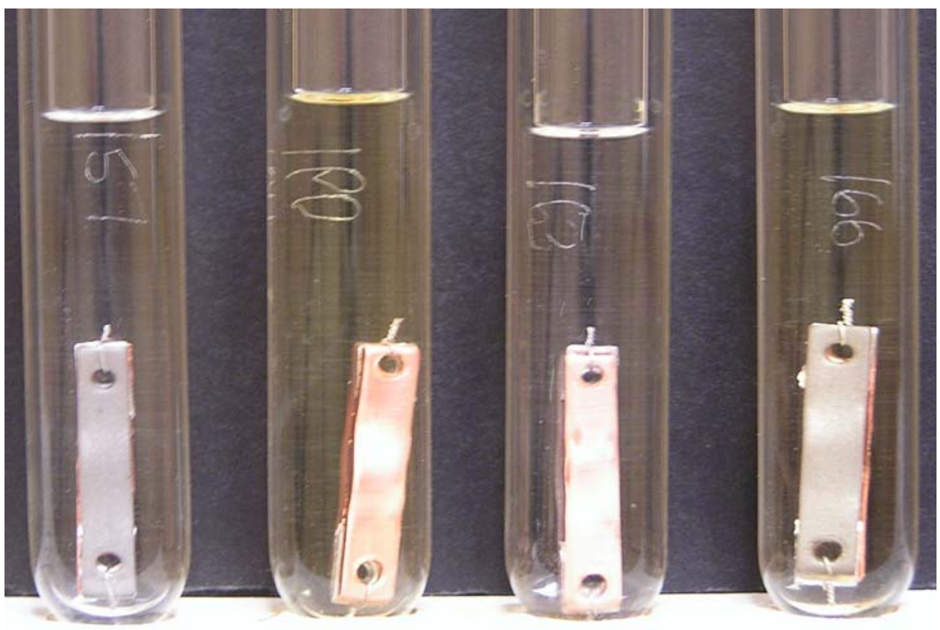
b. Black Background

Figure 25: Photographs of Sealed Tubes Containing Refrigerant Mixture/Lubricant Before Aging



Water	**51 ppm**	**51 ppm**	**495 ppm**	**495 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

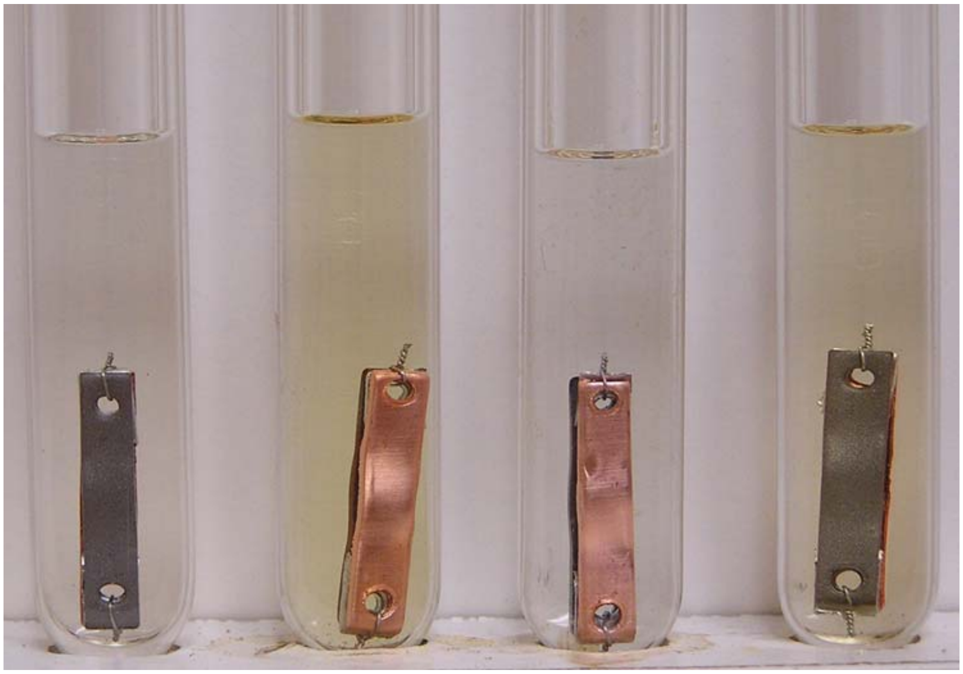
a. White Background



Water	**51 ppm**	**51 ppm**	**495 ppm**	**495 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

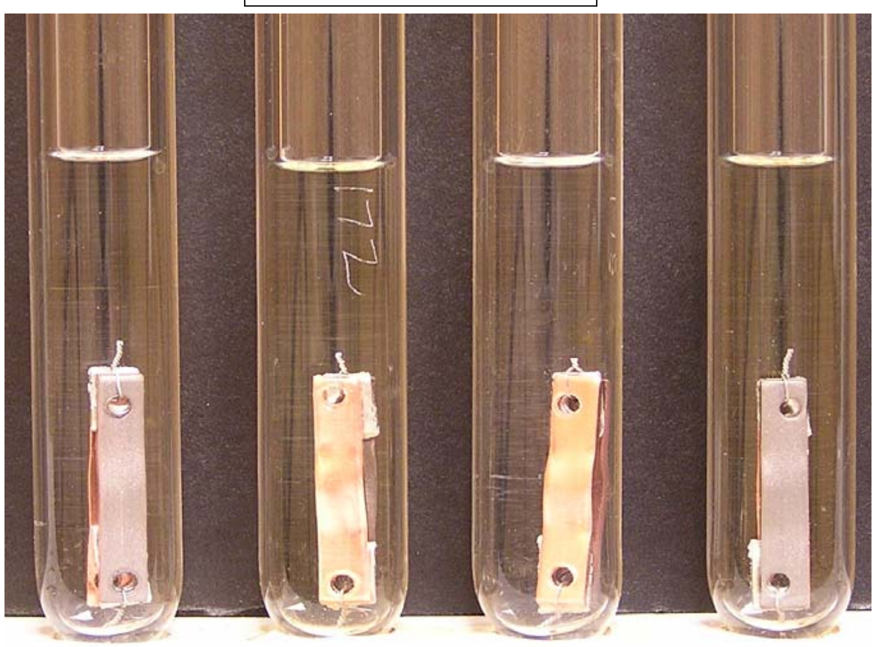
b. Black Background

Figure 26: Photographs of Sealed Tubes Containing Refrigerant Mixture/ISO 32 Mixed Acid After Aging



Water	**48 ppm**	**48 ppm**	**517 ppm**	**517 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

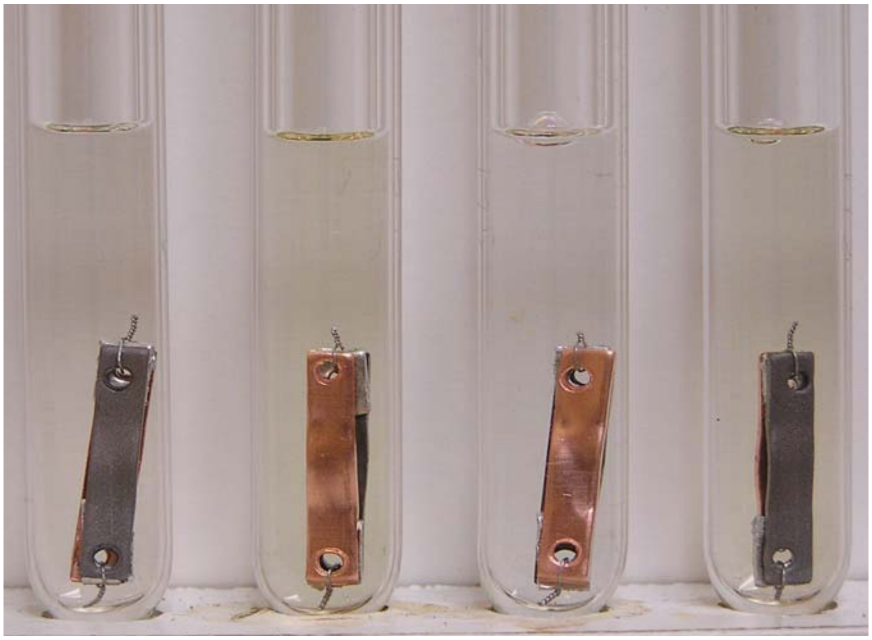
a. White Background



Water	**48 ppm**	**48 ppm**	**517 ppm**	**517 ppm**
Air	**0 ppm**	**2000 ppm**	**0 ppm**	**2000 ppm**

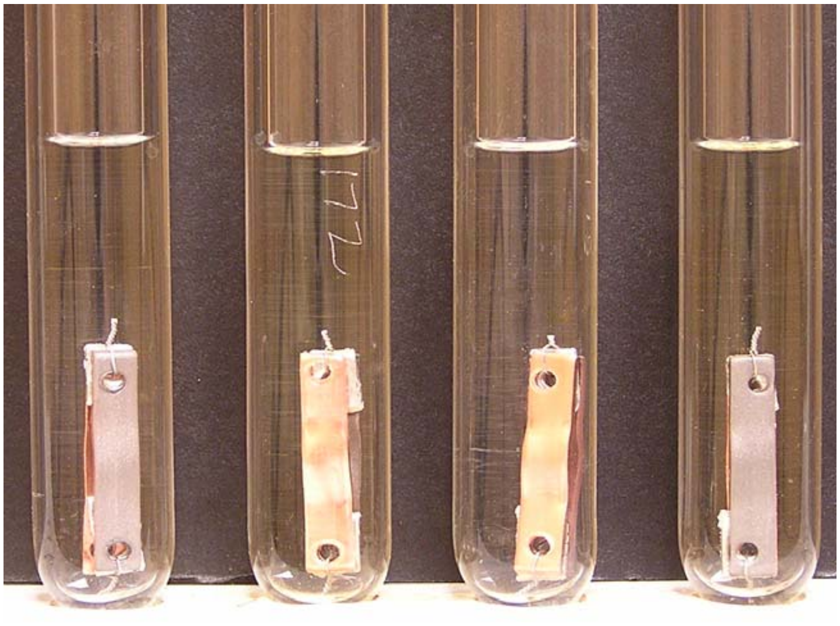
b. Black Background

Figure 27: Photographs of Sealed Tubes Containing Refrigerant Mixture/ISO 32 Branched Acid After Aging



Water	24 ppm	24 ppm	490 ppm	490 ppm
Air	0 ppm	2000 ppm	0 ppm	2000 ppm

a. White Background



Water	24 ppm	24 ppm	490 ppm	490 ppm
Air	0 ppm	2000 ppm	0 ppm	2000 ppm

b. Black Background

Figure 28: Photographs of Sealed Tubes Containing Refrigerant Mixture/PVE 32-A After Aging

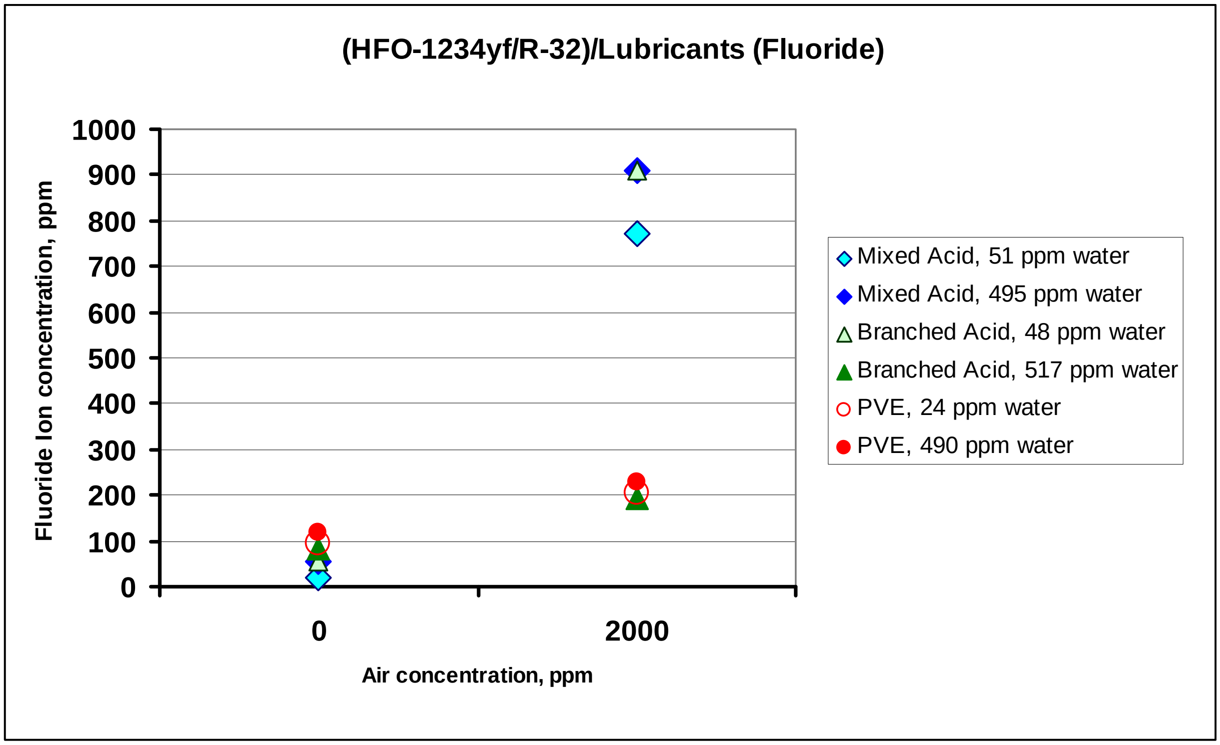


Figure 29: Fluoride Ion Concentrations in Sealed Tubes Containing HFO-1234yf/R-32 and Lubricants

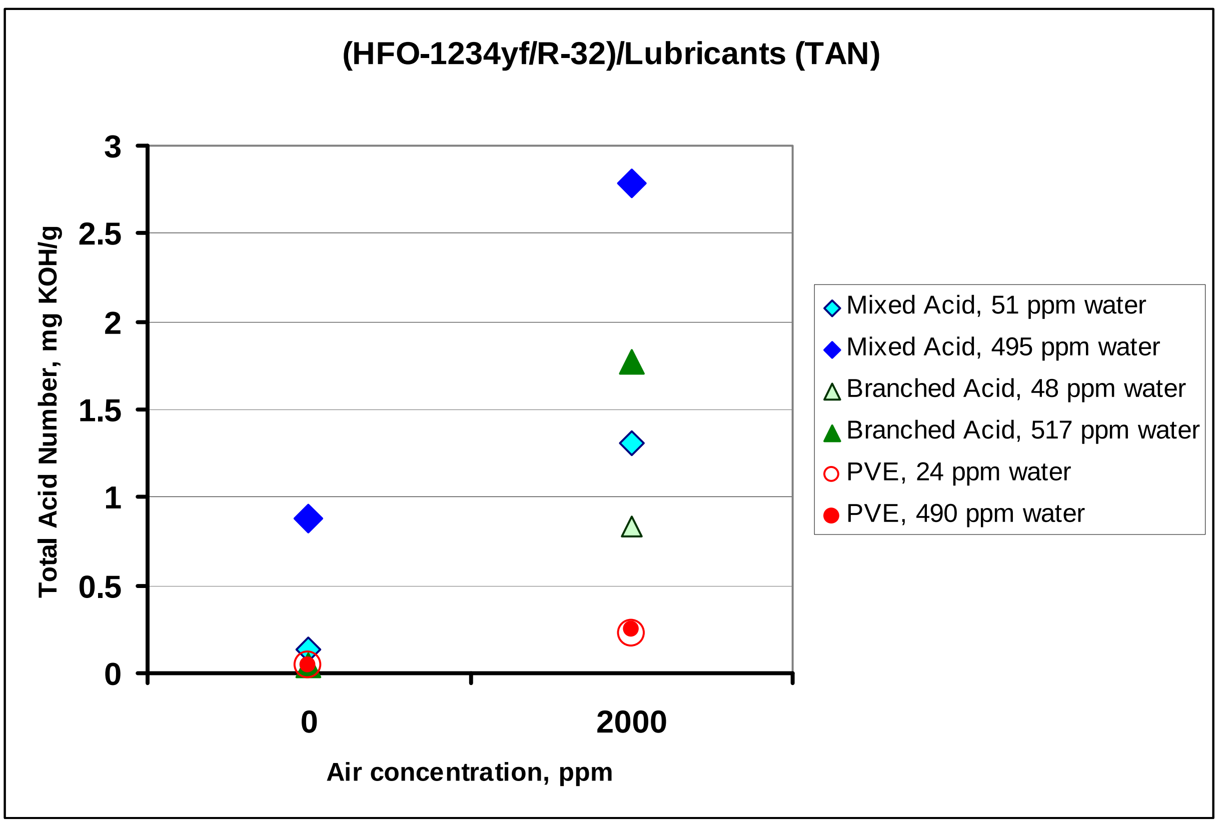


Figure 30: Total Acid Numbers of Sealed Tubes Containing HFO-1234yf/R-32 and Lubricants

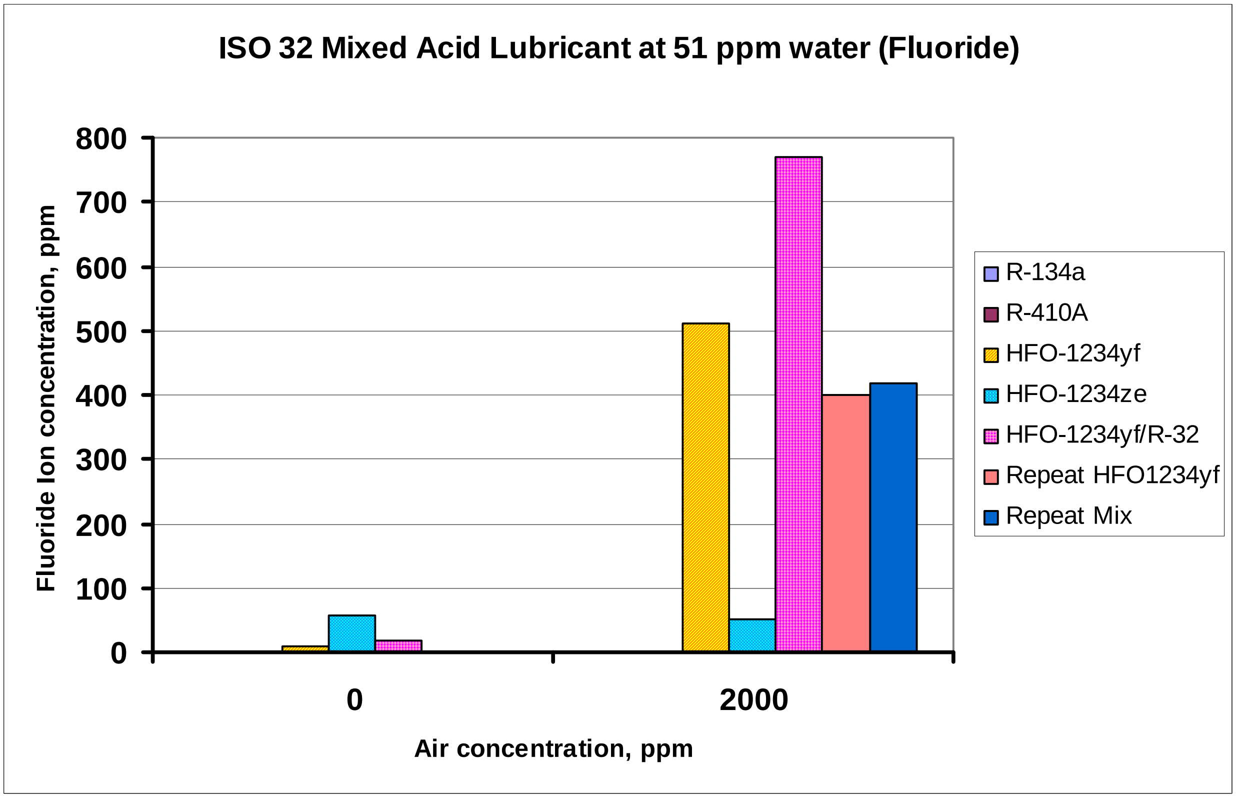


Figure 31: Comparison of Refrigerants Aged with Mixed Acid at Low Moisture (Fluoride Ion)

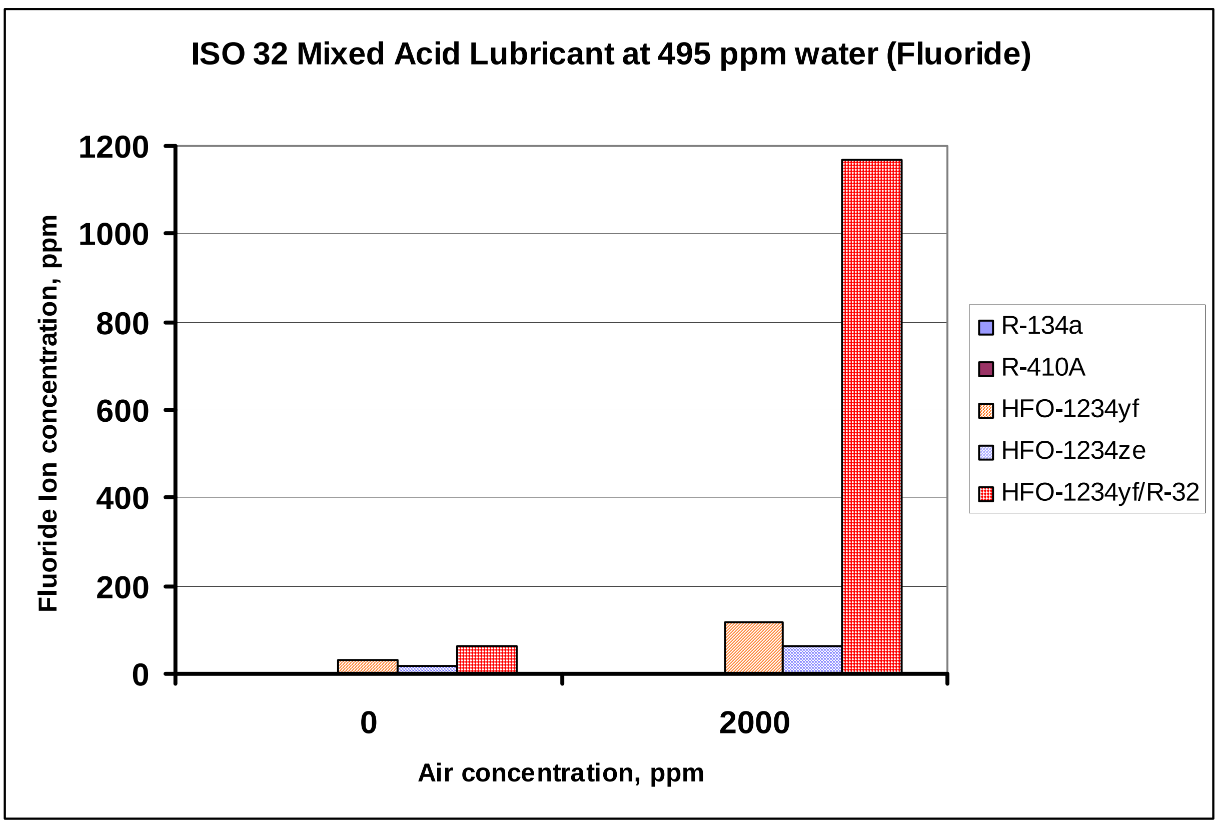


Figure 32: Comparison of Refrigerants Aged with Mixed Acid at High Moisture (Fluoride Ion)

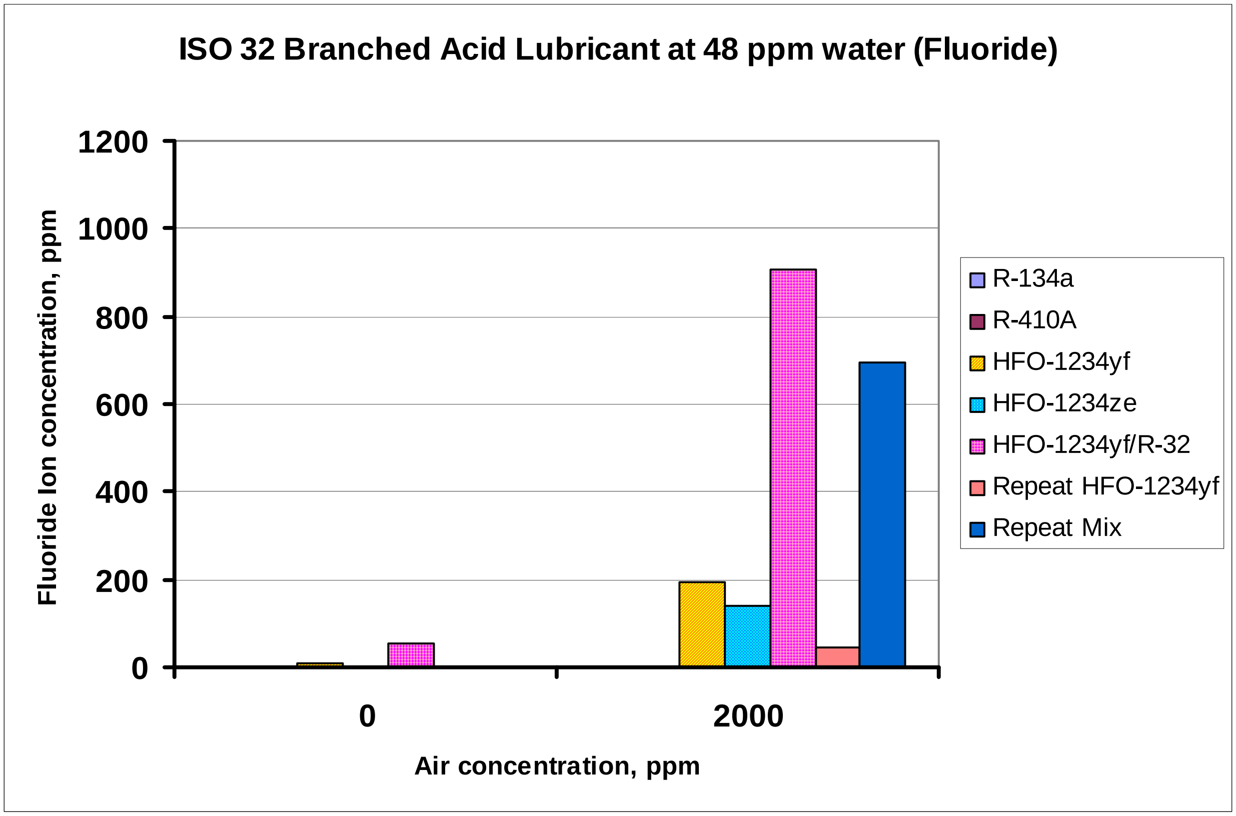


Figure 33: Comparison of Refrigerants Aged with Branched Acid at Low Moisture (Fluoride Ion)

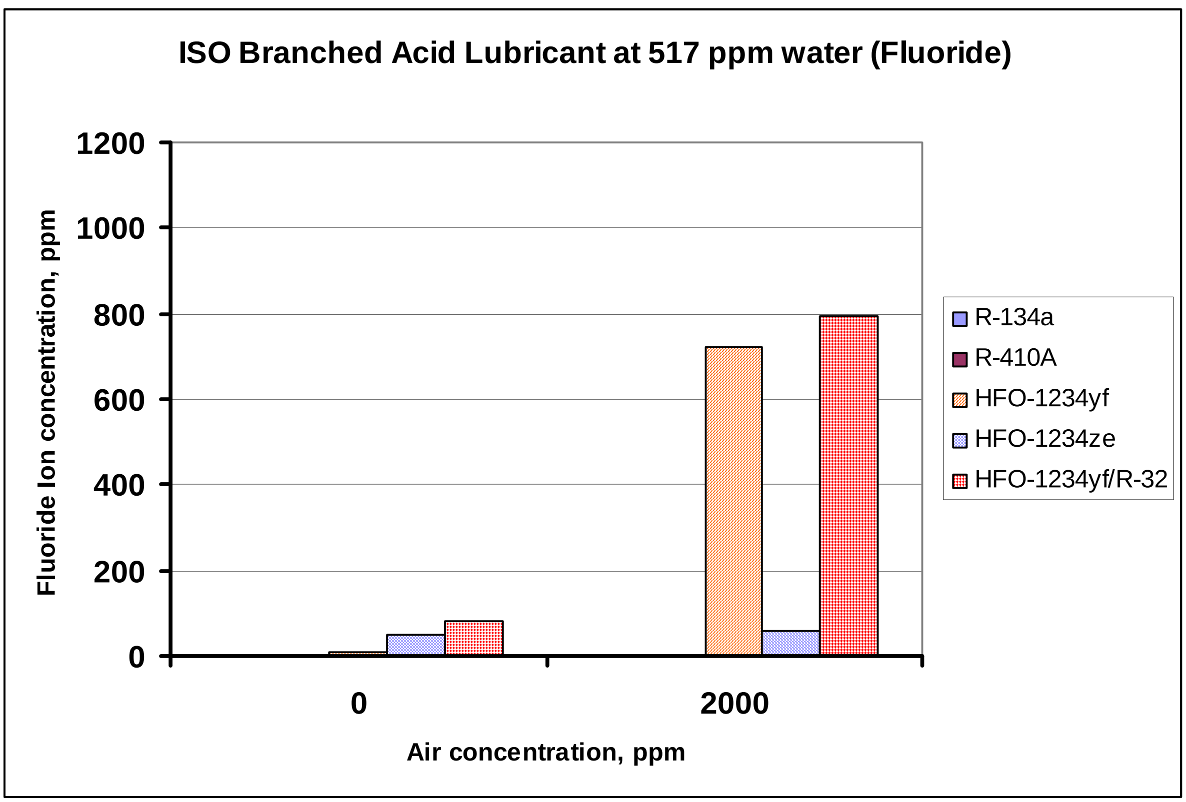


Figure 34: Comparison of Refrigerants Aged with Branched Acid at High Moisture (Fluoride Ion)

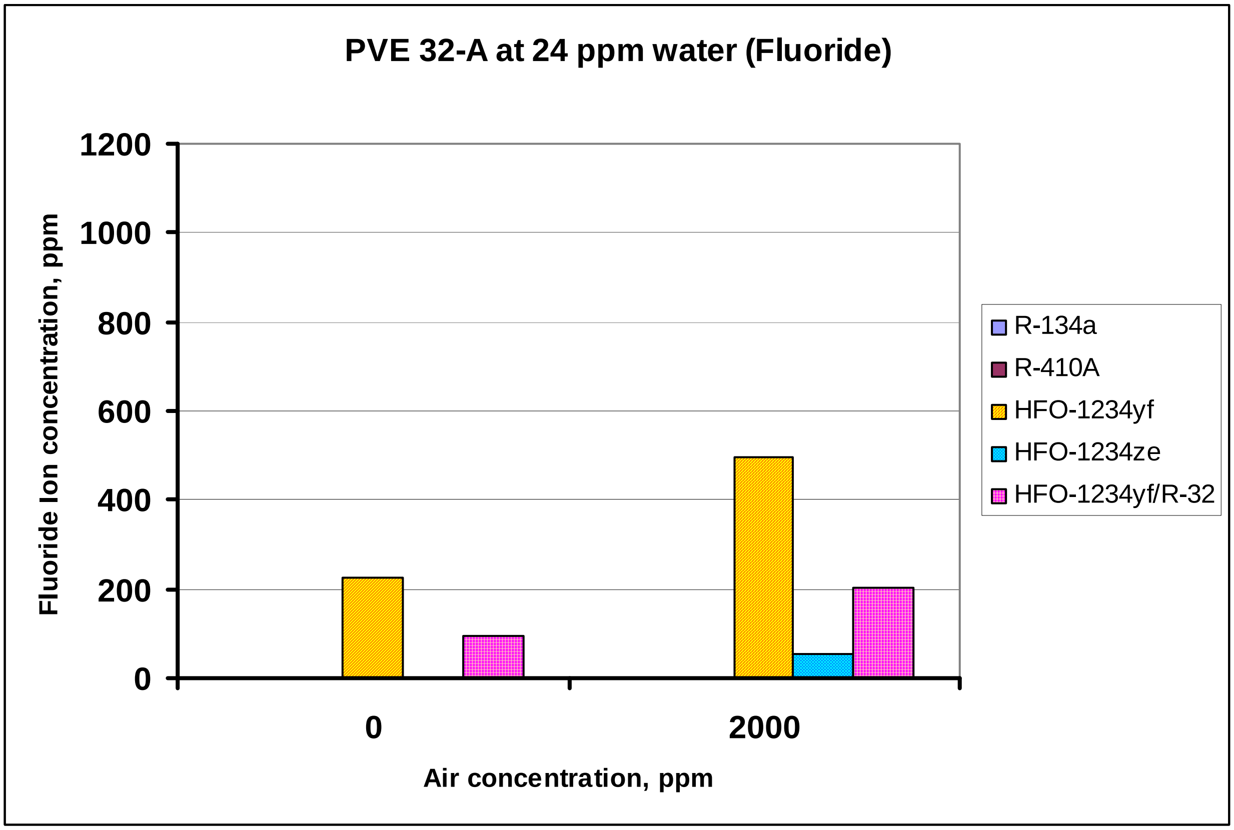


Figure 35: Comparison of Refrigerants Aged with PVE 32-A at Low Moisture (Fluoride Ion)

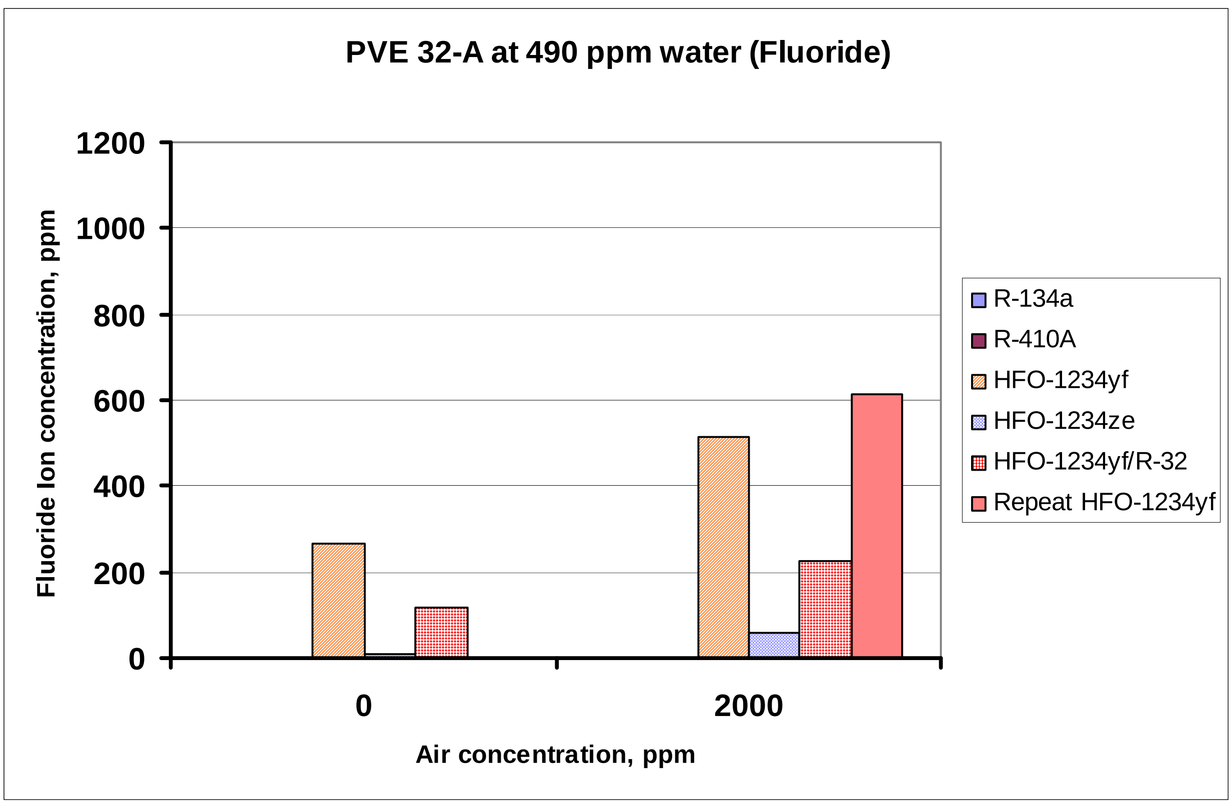


Figure 36: Comparison of Refrigerants Aged with PVE 32-A at High Moisture (Fluoride Ion)

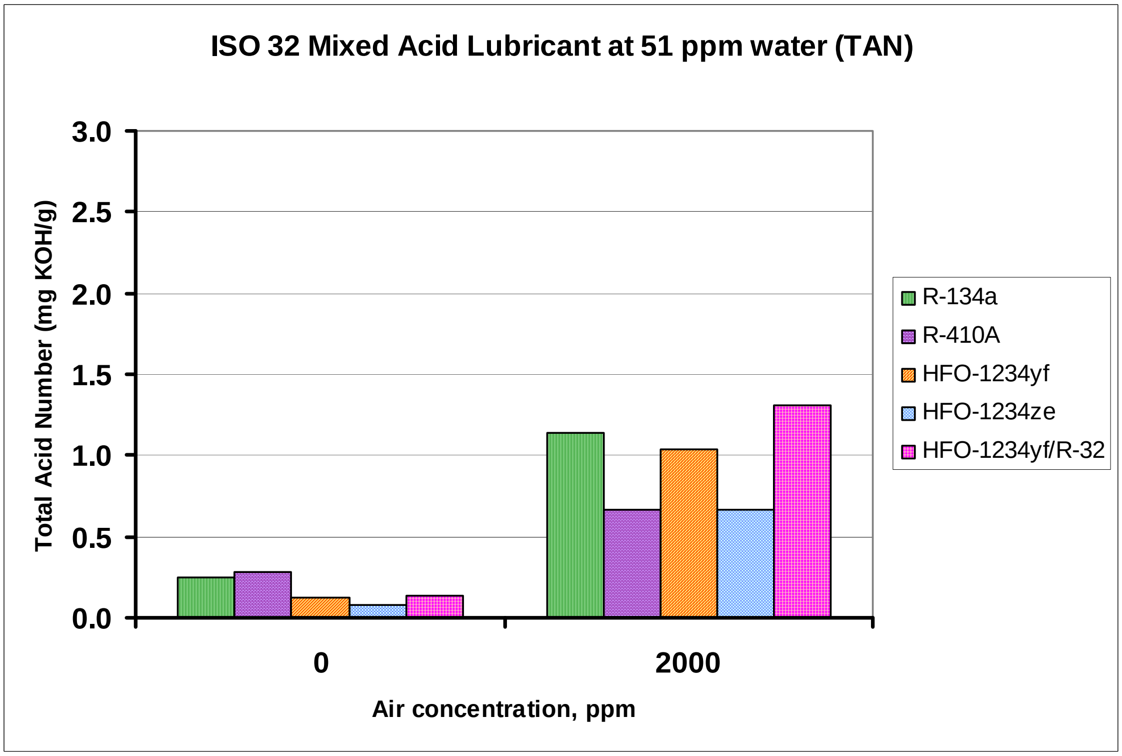


Figure 37: Comparison of Refrigerants Aged with Mixed Acid at Low Moisture (Total Acid Number)

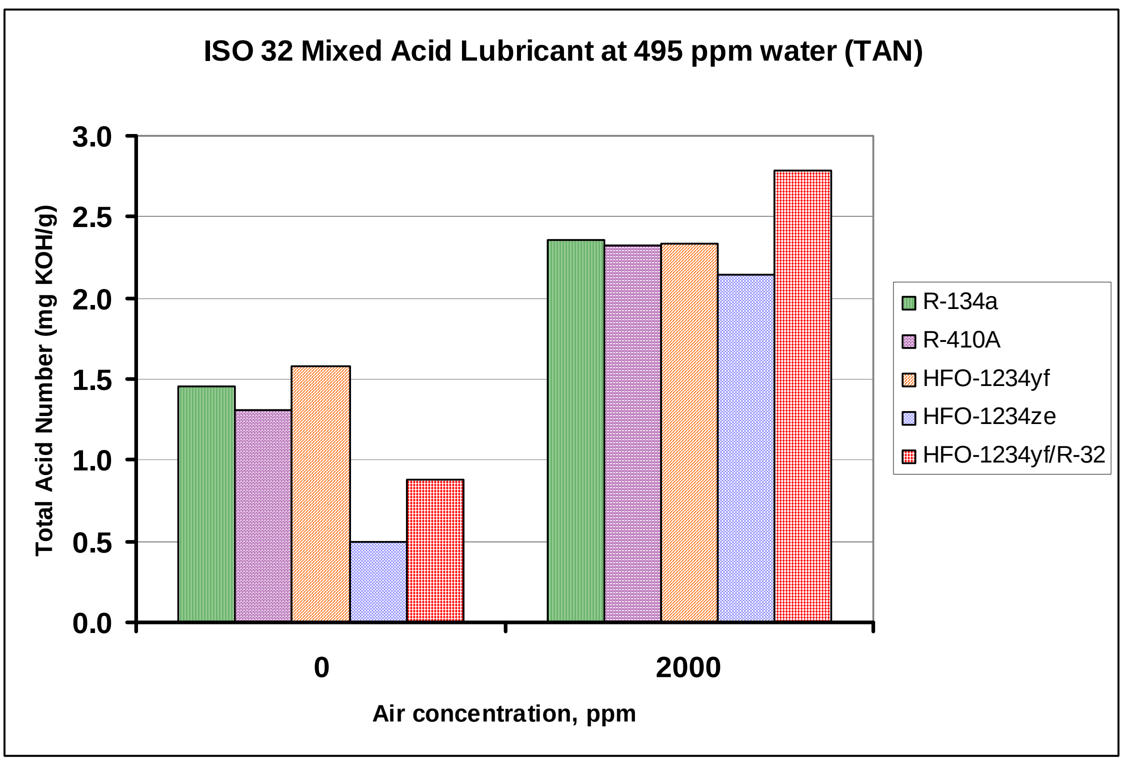


Figure 38: Comparison of Refrigerants Aged with Mixed Acid at High Moisture (Total Acid Number)

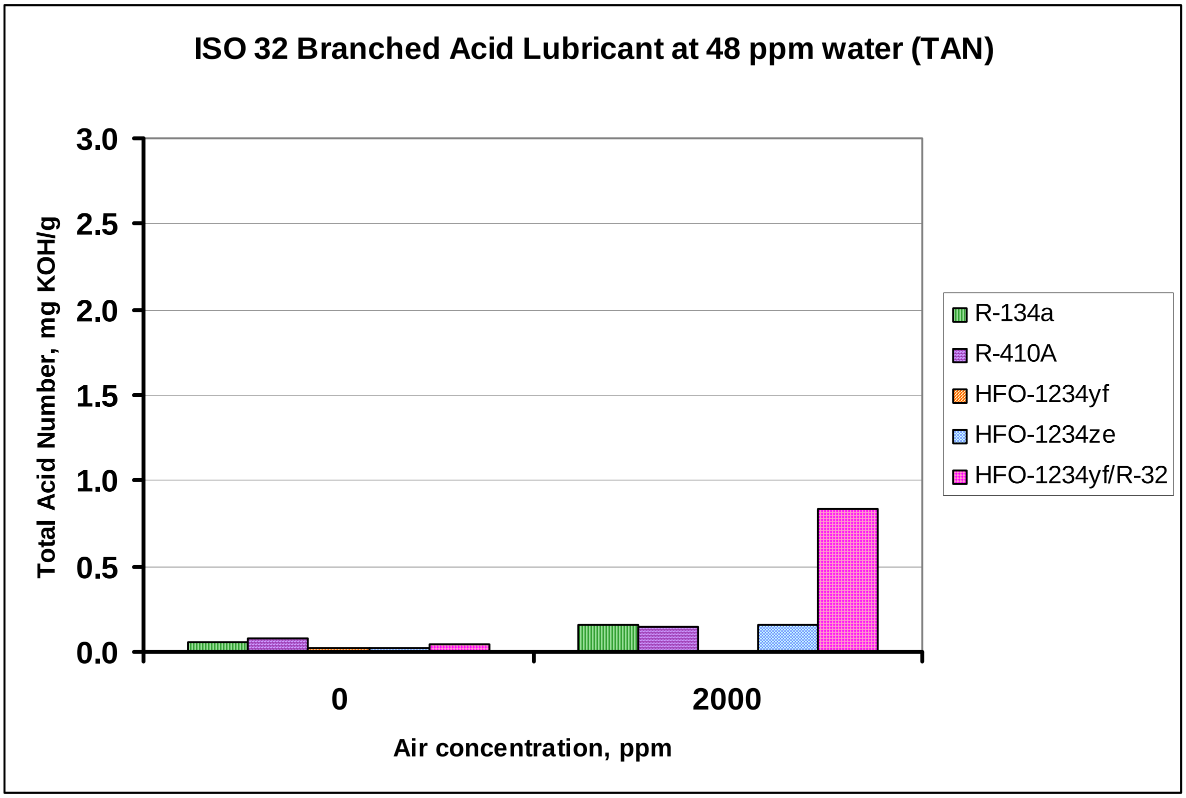


Figure 39: Comparison of Refrigerants Aged with Branched Acid at Low Moisture (Total Acid Number)

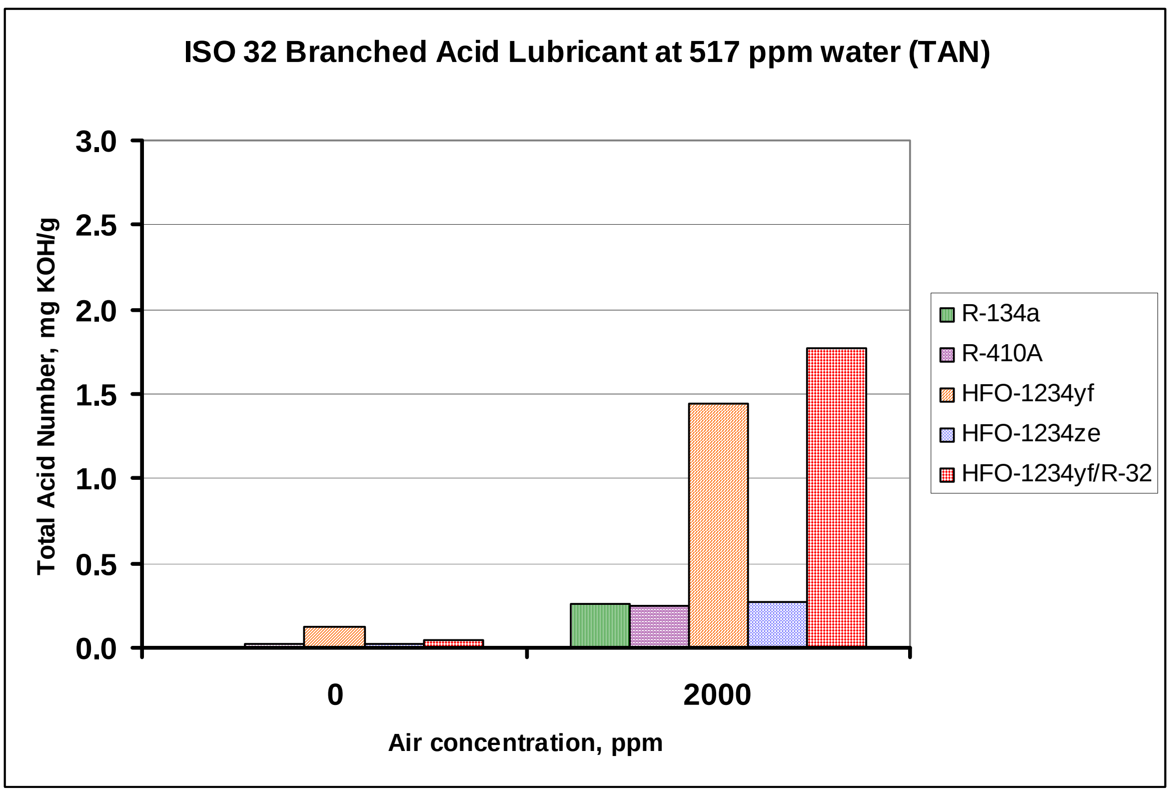


Figure 40: Comparison of Refrigerants Aged with Branched Acid at High Moisture (Total Acid Number)

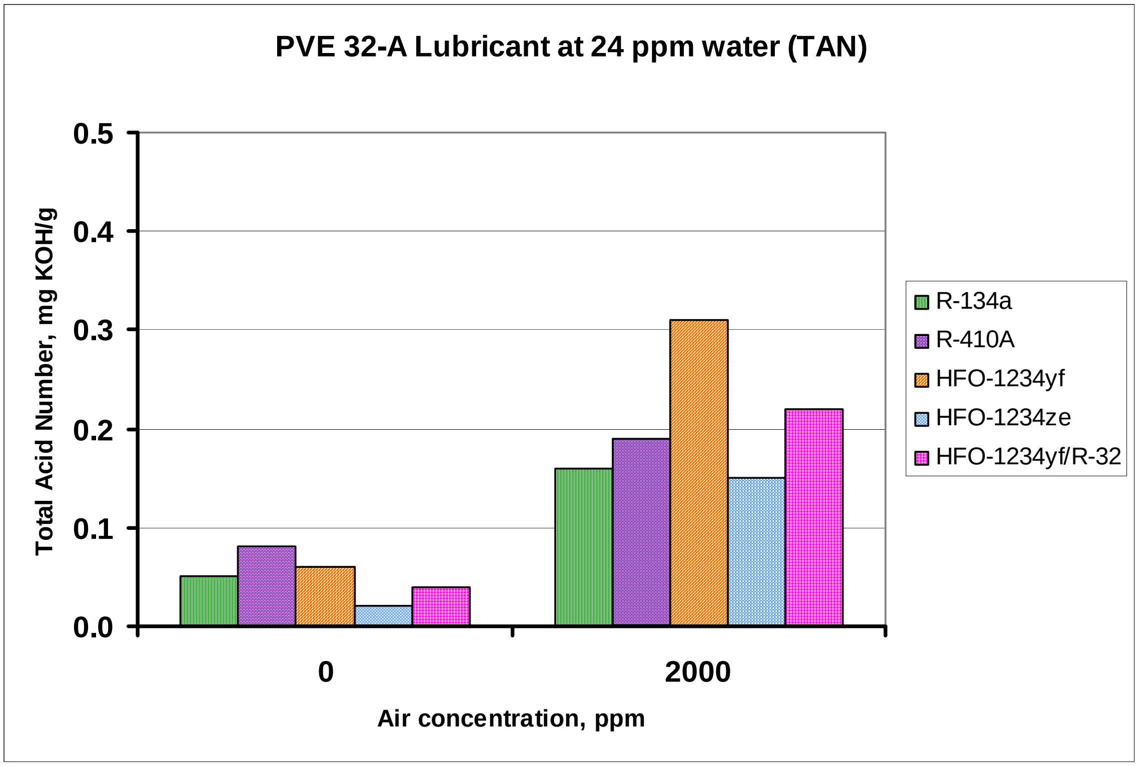


Figure 41: Comparison of Refrigerants Aged with PVE 32-A at Low Moisture (Total Acid Number)

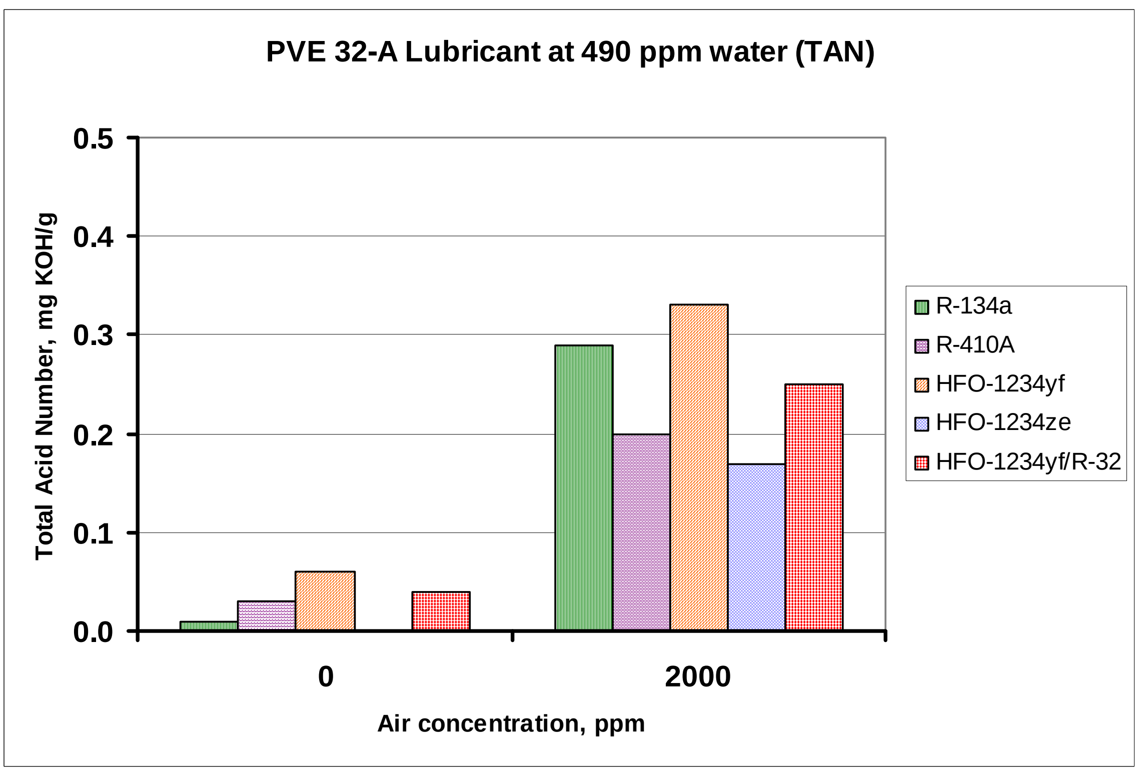


Figure 42: Comparison of Refrigerants Aged with PVE 32-A at High Moisture (Total Acid Number)

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