

AHRTI Project 9016-1 Final Report

# MATERIALS COMPATIBILITY AND LUBRICANTS RESEARCH FOR LOW GWP REFRIGERANTS: CHEMICAL STABILITY OF LOW GWP REFRIGERANTS WITH LUBRICANTS

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#### **EXECUTIVE SUMMARY**

AHRTI Material Compatibility and Lubricants Research (MCLR) for Low GWP Refrigerants Project 9016-1 was a 12-month research effort initiated at Trane Technologies on September 1, 2020. The information contained in this report is designed to assist the heating, ventilation, air-conditioning, and refrigeration (HVACR) industry in identification of potential chemical compatibility concerns that may result from interactions between new refrigerants, new refrigerant blends, and currently used HVACR system materials, including lubricants, system metals, and filter drier media. Refrigerants, lubricants, and materials of interest were selected by the project monitoring subcommittee to cover a broad range of system chemistries.

The evaluation program summarized in this report was divided into two phases of testing. The goal of the Phase I test program was to understand the thermal and chemical stability of low GWP refrigerants, in the presence or absence of compressor lubricants, with common system materials. The evaluation was performed on six low pressure refrigerants (R-1233zd(E), R-1224yd(Z), R-1336mzz(Z), R-1336mzz(E), R-514A, and R-123), six medium pressure refrigerants (R-1234ze(E), R-450A, R-515B, R-1234yf, R-513A, and R-516A), and four high pressure refrigerants (R-454C, R-455A, R-468A, and R-466A). Lubricants evaluated in Phase I included mineral oils, polyalkylene glycol (PAG), polyol ester (POE), and polyvinyl ether (PVE) lubricants with their compatible refrigerants. The PAG, POE, and PVE lubricants were studied without the presence of additive packages, except for antioxidants. The exposures focused on common system metal catalysts, based on aluminum, copper, iron, brass, and zinc. Following review of Phase I test results, Phase II testing was proposed and focused on five key areas of additional study: Phase IIA – The evaluation of PAG and PVE lubricants with additives with select refrigerants; Phase IIB – The evaluation of new blend components R-152a and R-227ea; Phase IIC – The evaluation of POE lubricant additives on R-466A stability; Phase IID – The expanded evaluation of R-32/R-1234yf blends; and Phase IIE – The evaluation of desiccant materials with select refrigerants and lubricants.

The decomposition of refrigerant was monitored by measuring inorganic anions (fluoride, chloride, and iodide) by High Pressure Liquid Chromatography (HPLC) as well as evaluating the headspace of the aged sealed glass tubes by Gas Chromatography Mass Spectrometry (GC-MS). Lubricant decomposition was monitored by Total Acid Number (TAN), organic acid analysis (for POE lubricants only), as well as by observation of key species by GC-MS. Further interactions between decomposition of the refrigerant or lubricant with the materials of interest (metals or desiccant materials), was monitored both visually as well as through evaluation of the lubricant phase by measurement of dissolved elements using Inductively Coupled Plasma Optical Emissions Spectroscopy (ICP-OES).

Overall, good chemical stability was observed across the many refrigerants evaluated in this testing program, only a few instances of reactivity were observed, as well as other subtleties in the interactions (physical and chemical) between the refrigerants, lubricants, and materials. Four refrigerants were noted to have potential for increased reactivity relative to other refrigerants. R-1311 (CF<sub>3</sub>I), contained in the R-466A blend, was found to have significant reactivity when evaluated at elevated temperatures with PAG, POE and PVE lubricants. Follow-on evaluation of a proprietary additized POE enabled significant improvements in overall stability, however challenges in compatibility were still observed with zinc-containing materials. Evaluation of R-152a, a blending component in R-516A, was found to have significant reactivity with zinc-containing materials, specifically the zinc-aluminum alloy used in this study. When used as a blend component of R-516A, the reactivity was very subtle, and is something to be mindful of when utilizing this fluid as a blending agent. R-1336mzz(Z) was determined to have potential for reactivity. Observations of increased fluoride generation, relative to R-1336mzz(E), were observed in multiple conditions, and the stereoisomerization reaction product, R-1336mzz(E), was measured in the aged fluid head space in concentrations up to 6% of the GCMS total peak area. Finally, R-468A, which contains the new HFO (hydrofluoroolefin) molecule R-1132a, was determined

to have instances of elevated fluoride generation as well, when compared to other R-1234yf containing blends that were evaluated in this study.

Lubricant chemistry was determined to have a role in breakdown observations of HFO refrigerants. Evaluation of HFO and HFO-HFC (hydrofluorocarbon) blends with unadditized PAG, POE and PVE lubricants found consistent results to indicate the generation of refrigerant breakdown, as measured by fluoride, in the unadditized PAG and PVE lubricants, while POEs did not exhibit this trend. PVE lubricants were determined to drive the creation of a unique breakdown product in the presence of each unique HFO chemistry. These breakdown products are suspected to be due to chemical reactions between the HFO refrigerant and PVE and were determined to be semi-volatile given their detection during GC-MS headspace analysis of the aged fluids. The addition of an additive package to the PVE lubricant reduced the generation of fluoride after aging, to below reportable levels in many instances. In addition, the unique HFO-PVE reaction products were still detected but with reduced peak areas. The addition of an additive package to the PAG lubricant was determined to have variability in its impact, with potential contribution to increases or decreases in measured fluoride relative to the unadditized conditions. For conditions which yielded measurable fluoride in the unadditized PAG conditions (typically R-1234yf containing fluids), the PAG additive package was determined to reduce generated fluoride in the mixed metal condition (Copper/Iron/Aluminum), while impact to fluoride reduction with brass and zinc-alloy had variability.

Zinc-containing materials were observed to accelerate reactivity in numerous conditions, both in driving refrigerant reactions as well as increased lubricant decomposition. As mentioned previously, R-13I1 and R-152a were found to be blend components that exhibited significant increases in reactivity when in the presence of zinc. Other refrigerants also had trace indicators of breakdown in the presence of zinc, for example R-1233zd(E) and R-1224yd(Z) which had unique breakdown products detected in the headspace of the aged tube. Breakdown of POE lubricant in the presence of zinc containing materials was another observation consistent across the refrigerants evaluated in this project with elevated TAN noted in numerous brass and zinc conditions and dissolved zinc present when evaluated by ICP-OES. Continued use of zinc-containing materials in HVACR systems should be studied further given potential system chemistry issues which could arise from its use.

Future work is recommended to better understand the interactions and risks associated with the observations in this study.

- Stereoisomer rearrangement or other chemical stability reactions (R-466A) should be more closely studied, especially in fluids where the cis (Z) isomer is present or when the fluid might be considered for high temperature applications. Work should focus on developing Arrhenius relationships with potential accelerants.
- Studies to date have been challenged in ability to fully detect generation of potential refrigerant breakdown products in R-1234yf, R-1234ze(E) and R-1132a, despite presence of fluoride. Improved assessment of semi or non-volatile breakdown products in the lubricant phase of the aged fluids should be pursued, given that this is a missing piece of HFO studies to date.
- Understand the nature and impact of the unique HFO-PVE interactions that were observed in the GC-MS analysis.
- Further evaluation of individual materials of construction or processing should be considered, given unique chemical reactions observed in this study, e.g. with brass, zinc, PVEs.
- New HFO chemistries continue to emerge and should be considered for initial assessment, e.g, R-1123, R-1132(E).
- Evaluation of lubricant additives and/or refrigerant stabilizers should be studied to further understand their impacts.

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Companies	Contact	<b>Refrigerants/Lubricant</b>			
		R-1233zd(E)			
		R-1234ze(E)			
		R-450A			
Heneywell	Samuel Yana Motta	R-515B			
Honeyweii	Ankit Sethi	R-455A			
		R-466A			
		R-227ea			
		Additized POE			
		R-1336mzz(E)			
Charren	lien Cun Dienka	R-513A			
Chemours	Jian Sun Bianks	R-454C			
		R-152a			
Arkema	Sarah Kim	R-516A			
Koura	Robert Low	R-468A			
AGC	Jim Scott	R-1224yd(Z)			
	Dred Degrees	POE			
Emerson	Brad Boggess	PVE			
Christen		PAG			
Shrieve	Joe Karnaz	Additized PAG			
Idemitsu	Ryan Stanton	Additized PVE			

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#### INTRODUCTION

A whole new class of refrigerant chemistry has been developed as a reaction to new regulatory actions to restrict and lower the direct global warming potential (GWP) impact of many hydrofluorocarbons (HFC) or fluorocarbon (F-gas) refrigerants. These new refrigerants can be referred to as alkenes, or unsaturated hydrocarbons, which means they contain two or more carbon atoms linked by a double bond. Today it is generally common for these fluorinated refrigerants to be referred to as hydrofluoroolefins (HFOs), olefins, or unsaturated HFCs. A number of these olefins contain a combination of fluorine and chlorine as well and the nomenclature can be further refined to hydrochlorofluoroolefins (HCFOs) and hydrochloroolefins (HCOs). The new HFO chemistries are designed to facilitate refrigerant degradation in the atmosphere in days rather than years, and this presents the possibility that these refrigerants could be unstable with traditional construction materials and contaminants in heating, ventilation, air conditioning, and refrigeration (HVACR) systems. Chemical and material compatibility of refrigerants are important parameters given the expectation that HVACR products will have design lives of 10 to 20+ years.

AHRTI-9016 provides a comprehensive look at the chemical stability of 16 olefin-based or olefin blended refrigerants in combination with appropriate lubricants and select materials of construction (metals and desiccants). Included in the study are 8 ultra-low GWP olefin-based refrigerants (R-1130(E), R-1336mzz(Z), R-1233zd(E), R-1224yd(Z), R-1336mzz(E), R-1234ze(E), R-1234yf, and R-1132a) in pure form or blended with other refrigerants. Ultra-low GWP refrigerant trifluoroiodomethane (CF<sub>3</sub>I) is also included in this study. The evaluation was performed on six low pressure refrigerants (R-1233zd(E), R-1224yd(Z), R-1336mzz(Z), R-1336mzz(Z), R-1336mzz(E), R-514A, and R-123), six medium pressure refrigerants (R-1234ze(E), R-450A, R-515B, R-1234yf, R-513A, and R-516A), and four high pressure refrigerants (R-454C, R-455A, R-468A, and R-466A). Lubricants evaluated were mineral oil, polyalkylene glycol (PAG), polyol ester (POE), and polyvinyl ether (PVE) chemistries. The study also included evaluation of new HFC blending components to the HVACR industry, R-152a and R-227ea.

Good refrigerant chemical stability in HVACR systems is defined as the ability to perform over a wide range of temperatures, in the presence of materials (necessary for the system operation), with limited deterioration. New refrigerants must have an inherent level of thermal stability before being considered for use in HVACR systems. Once the general thermal stability of the refrigerant alone is established, it is then subjected to a wide range of construction materials and potential system containments, like residual air, water, and processing chemicals. The refrigerant must not be adversely affected by these materials. Various known and possible refrigerant reaction pathways will be discussed in the following sections.

Olefin refrigerants introduce a more complicated chemistry with the addition of the double bond and an increase in the number of carbon atoms over the refrigerant they are targeted to replace. For example, R-11 (a 1-carbon molecule) was replaced by R-123 (a 2-carbon molecule) and R-123 is being replaced by a combination of molecules and mixtures, including R-1233zd(E) (a 3-carbon molecule) and R-514A which is a blend of R-1336mzz(Z) (a 4-carbon molecule) and R-1130(E) (a 2-carbon molecule). R-12 (a 1-carbon molecule) was replaced by R-134a (a 2-carbon molecule) and R-134a is being replaced by combination of R-1234ze(E) (a 3-carbon molecule) and R-1234yf (a 3-carbon molecule) or blends of R-1234ze(E) and R-1234yf with other HFCs.

#### **Reduction and Disproportion Reactions with Olefin Refrigerants**

Two types of chemical reactions are common with CFCs, HCFCs, and, to a lesser extent, HFCs: reduction of the refrigerant by lubricant species and disproportionation of refrigerant. However, possible disproportionation reactions will not be addressed as part of this discussion. The primary refrigerant breakdown mechanism for CFCs and HCFCs are reduction reactions which involve a direct interchange of chlorine and hydrogen atoms between the refrigerant and the oil (Spauschus and Doderer, 1961). Measurement of the breakdown products formed in the reaction of the refrigerant with the lubricant has become the industry standard method of determining if a material in a system is acceptable for use. The reduction reaction does not always chlorinate the lubricant and aggressive chlorine-based species, such as hydrochloric acid, can be produced.

Reduction: R-22 + lubricant +catalyst $ ightarrow$ R-32 + other species	(1)
Disproportionation: R-22 + catalyst $\rightarrow$ R-23 + chloride + other species	(2)

The reduction reaction exchanges a hydrogen atom from a lubricant molecule for the chlorine atom in R-22, for the example in Equation 1. The proton transfer process can be thought of as a simple kind of nucleophilic substitution reaction, which is later discussed, where the halogen is exchanged for a hydrogen. Each molecule of R-32 represents the decomposition of one molecule of R-22. When the chlorine is released, it can then form aggressive chlorine-based species, such as hydrochloric acid, and attack metals and other construction materials. Typically, a lubricant sample can be analyzed for total acid number to determine how much refrigerant breakdown has occurred in systems, while the refrigerant can be analyzed by gas chromatography to evaluate the formation of reduction products.

Unlike the saturated halogenated refrigerants, olefin-based refrigerants have been studied and few refrigerant reduction reactions with the lubricant have been observed in sealed glass tube studies (Majurin et al., 2014, Rohatgi et al., 2012, Fuji-taka, 2010). The reduction products of the various olefins would require the elimination of fluorine or chlorine from the molecule and substitution by hydrogen atom. Table 1 gives summary of potential reduction products if they were to occur with various olefin refrigerants. R-1336mzz(Z) does not possess a fluorine on the double bond so a reduction reaction and elimination of a halogen would not occur.

Table 1: Summary of Possible Ole	fin Refrigerant Reduction Products
Refrigerant	Breakdown Product
R-1130(E)	R-1140
R-1336mzz(Z)	Not Applicable
R-1233zd(E)	R-1243zf
R-1224yd(Z)	R-1234yf or R-1233zd
R-1336mzz(E)	Not Applicable
R-1234ze(E)	R-1243zf
R-1234yf	R-1243zf
R-1132a	R-1141

#### Stereoisomer Rearrangement Reactions with Olefin Refrigerants

Unlike the saturated halogen refrigerants which are free to rotate into different orientations in three-dimensional space, olefin refrigerants contain a carbon double bond that does not allow the molecule to rotate freely. This double bond can lead to the formation of stereoisomers with different properties yet the same chemical formulation. Refrigerant nomenclature specifies when there are different stereoisomers by using a designation of "E" (trans, E: Entgegen (German) meaning opposite) or "Z" (cis, Z: Zusammen (German) meaning together), in the formula. Figure 1 gives an example of the two stereoisomers for R-1234ze. The "Z" isomer has the hydrogen atoms on the same side of the double bond while the "E" isomer has the hydrogen atoms on the opposite side. In general, the "Z" suffix is added to the name if the priority substituents are on the same side of the double bond. Interestingly, this small change in stereochemistry results in a rather large boiling point difference of  $\Delta 28.7$ °C ( $\Delta 51.7$ °F); R-1234ze(E) has a boiling point of -19°C (-2.2°F) and R-1234ze(Z) has a boiling point of 9.7°C (49.5°F). Typically, trans-alkenes are less polar, more symmetrical and have lower boiling points than cis-alkenes.



Figure 1: Chemical Model Depictions of R-1234ze Stereoisomers

All olefins in this study are susceptible to stereoisomer rearrangement except for R-1234yf which does not have an associated stereoisomer. Stereoisomer rearrangement processes have been well studied and documented in literature, but limited information is published with the new olefin refrigerants which have the potential for stereoisomer rearrangement. R-1233zd(E), R-514A and R-1234ze(E) are used in chillers today with no reported stereoisomer rearrangement issues. Kujak and Sorenson (2018b) published the stereoisomer rearrangement data for R-1233zd(E), R-1234ze(E) and R-514A which compares these values to published reduction reaction studies for R-11, R-12, R-123, R-22, R-32, R-134a, and R-125. As shown in Figure 2 below, stereoisomer rearrangement reaction rates are very low and not a significant concern, with reactions rates being on the order of R-22 reduction reaction stability, and well below R-11, R-12 and R-123 reduction reactions. This study was very limited in catalysts and temperature, so further work would be recommended to better understand the reaction rates for stereoisomers rearrangement reactions. Generally, trans-alkenes are more stable, meaning less susceptible to stereoisomer rearrangement than cis-alkenes, due to the increased unfavorable steric substituents in the cis-isomer. There are exceptions to this generality with fluorinated alkenes. Cis-1,2-difluoroethylene, R-1132(Z), is more stable than the trans, (E), isomer.



Figure 2: Comparison of Various Refrigerants Chemical Stability in the Presence of Lubricant Versus Temperature (Kujak, et al., 2018b and Huttenlocher, 1992)

#### **Oligomerization or Polymerization Reactions with Olefin Refrigerants**

The presence of a double bond can lead to the potential for oligomerization (small number of monomers joined together) or polymerization (large numbers of monomers joined together) of the olefin refrigerant, as shown in Figure 3. Secton (2018) reported occurrences of R-1234yf polymerization in automotive applications, but it was attributed to having uncured elastomers with residual crosslinking chemistries present that lead to the oligomerization/polymerization. Review of sealed glass tube

studies under typical HVACR system chemistry conditions have not documented the potential for these types of reactions, but detection of small amounts of oligomers/polymers would be unlikely given the typical sample preparation and analytical methods used in these studies.



Figure 3: Example of Oligomerization and Polymerization Reaction

#### **Nucleophilic Substitution Reactions with Olefin Refrigerants**

In organic chemistry, nucleophilic substitution is a fundamental class of reactions in which an electron rich nucleophile selectively attacks the positive or partially positive charge of an atom or group of atoms to replace a leaving group (Figure 4). Alkyl halide bonds have electronegativities significantly greater than carbon except for iodine. This reactivity is based on the covalent bond strength of the carbon bonding and the bonded species ability to become a leaving group. The strongest of the carbon-halogen covalent bonds is that to fluorine. It is roughly 30 kcal/mole stronger than a carbon-carbon bond and about 15 kcal/mole stronger than a carbon-hydrogen bond. As a result, alkyl fluorides and fluorocarbons are generally quite chemically and thermodynamically stable, and do not share any of the reactivity patterns shown by the other alkyl halides. Nucleophilic substitution across a halogenated double bond is possible, but hydrogen, fluorine, and chlorine atoms along with trifluoromethyl (-CF<sub>3</sub>) groups attached to the double bond are not favorable leaving groups, whereas bromine and iodine are able to act as favorable leaving groups depending on their bonding characteristics. In addition, the formation of hydrofluoric or hydrochloric acid as the result of limited reduction reactions with olefins is possible, but unlikely to occur because these acids are quickly neutralized by system materials or the filter drier component before they can reach significant concentrations to initiate the reaction.



Figure 4: Examples of a Nucleophilic Substitution Reactions

Table 2 shows possible nucleophilic substitution reactions that could occur with the three chlorinated olefins evaluated in this study, R-1130(E), R-1233zd(E), and R-1224yd(Z) where hydrogen and chlorine were substituted across the double bond.

Refrigerant	Breakdown Product
R-1130(E)	R-140
R-1233zd(E)	R-243dn & R-243fo
R-1224yd(Z)	R-234bo & R-234en

#### SUMMARY OF PREVIOUS CHEMICAL STABILITY STUDIES

Several studies have been published regarding the potential risks associated with using the new olefin refrigerants in HVACR systems over the past 10+ years. These studies have been mostly focused on R-1234yf since it was introduced first as a replacement for R-134a in automotive applications. The background discussion here will focus on multiple olefin refrigerants, R-1311, as well as the new HFCs, R-152a and R-227ea, which have not been commonly used in HVACR products. The AHRTI funded literature review conducted by Spauschus provides the various references and background for this discussion (Rohatgi, 2020).

#### R-1336mzz(E) and R-1336mzz(Z) Chemical Stability (1,1,1,4,4,4-hexafluoro-2-butenes)

Few chemical stability studies exist in literature that describe the chemical stability of R-1336mzz(E) and R-1336mzz(Z) and identify potential refrigerant breakdown products. Juhasz (2017) and Hughes and Juhasz (2019) used sealed tube tests to determine the thermal stability of R-1336mzz(E) with POE lubricant and carbon steel, copper, and aluminum coupons at 175°C (347°F) for 14 days. Tests were also conducted with R-1336mzz(E) without lubricant, but with brass, zinc, and nickel at 175°C (347°F) for 14 days and with steel, copper, and aluminum at 250°C (482°F) for seven days. Results showed that R-1336mzz(E) was stable under all test conditions.

Kontomaris (2014) indicated R-1336mzz(Z) was very stable at high temperatures. Fluoride formation in sealed glass tube tests was negligible even after exposure to 250°C (482°F) for 14 days in the presence of carbon steel, copper, and aluminum. Lubricants were not considered in this study. Further work by Kontomaris showed that at 7.6 mm Hg air pressure and moisture at 200 ppm there was little impact on the stability of R-1336mzz(Z) after exposure to 250°C (482°F) for seven days.

Saito and Sundaresan (2017) investigated the effects of air and water at high temperature on the stability of the R-1336mzz(Z)/POE VG220 combination. TAN of the exposed lubricant went from 0.07 mg KOH/g at 200°C (392°F) with <0.1 ppm air and <100 ppm water to 0.49 mg KOH/g oil at 200°C (392°F) with 100 ppm air and 500 ppm water. TAN increased to 18.43 mg KOH/g oil at 250°C (482°F) with <0.1 ppm air and <100 ppm water. Temperature was seen to have a greater effect on the TAN than the concentrations of air and water.

Huo et al. (2019) studied the decomposition of R-1336mzz(Z) in a high temperature, high pressure vessel. The experimental results showed that the pressure had a great effect on the dissociation of R-1336mzz(Z) and the decomposition products. Breakdown products as measured by a Fourier Transform Infrared Spectrometer (FTIR) included HF, CF<sub>4</sub>, CHF<sub>3</sub>, C<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>2</sub>HF<sub>5</sub>, and C<sub>3</sub>F<sub>8</sub>. This study was a highly accelerated condition and not typical of HVACR equipment operation.

## R-514A (75.7% R-1336mzz(Z)/24.3% R-1130(E)) Chemical Stability

The first reported use of R-1130(E), trans 1,2 dichloroethylene, was in 1922. Willis Carrier introduced the first centrifugal chiller application using the refrigerant called dielene which is a blend of R-1130(E) and R-1130(Z), before being displaced with the invention of the nonflammable CFC alternatives in the 1930s. Since that time, there are no reported uses of R-1130(E) specifically in HVACR products as the primary refrigerant or as a blend in a refrigerant prior to the introduction of R-514A. R-1130(E) has been widely used for 70+ years as a cleaning agent and can be left behind as a contaminant in HVACR products. Rohatgi (2016) conducted a research project aimed at determining the effects of halogenated unsaturated contaminants present in refrigerants on the stability of refrigerant/lubricant system. R-1130(E) was studied as a contaminant in R-134a and was recommended the maximum contamination concentration be kept below 1000 ppm.

Only one chemical stability study of R-514A was identified in literature. Majurin, et al. (2017) investigated the chemical stability of R-514A with a POE based lubricant at three temperatures and a variety of system materials and contaminants in sealed glass tubes and in a chiller. The primary decomposition reaction reported was the stereoisomer rearrangement of both the R-1336mzz(Z) and R-1130(E) to the corresponding R-1336mzz(E) and R-1130(Z) at very low levels. Good chemical stability was noted for R-514A versus the R-123 by a greater than 4 to 1 ratio.

#### R-1233zd(E) Chemical Stability

R-1233zd(E), trans-1-chloro-3,3,3-trifluoro-1-propene, was introduced in HVACR products around 2015 and few chemical stability studies have been published since that time. Kujak et al. (2015b) reported on a study to determine the stability of R-1233zd(E) with and without the presence of mineral oil (MO). Sealed glass tube test results indicated that R-1233zd(E) was approximately 10 times more stable than R-123 and approximately 100 times more stable than R-11. One of the primary degradation products was the stereoisomer rearrangement reaction to form R-1233zd(Z). It was formed only under extreme conditions, a 14 day exposure at 200°C, at less than 1% in concentration.

Majurin et al. (2017) evaluated the chemical stability of R-1233zd(E) with white mineral oil and three metal catalysts representing the system materials of construction – cast aluminum, carbon steel, and copper. Exposures were conducted at three different temperatures 135°C (275°F), 145°C (293°F), and 155°C (311°F) for seven days. Test results showed that the R-1233zd(E)/MO system was stable with TAN values less than 0.1 mg KOH/g oil, along with observations of dissolved aluminum, copper, and iron concentrations less than 10 ppm. The degradation product was the R-1233zd(Z) stereoisomer rearrangement product.

Rached, et al. (2018) reported on the chemical stability of R-1233zd(E) in energy recovery applications. While under extreme accelerated life testing, R-1233zd(E) was found to undergo fairly low stereoisomer rearrangement, about 1.6%, at 180°C (356°F) for 14 days, and significant stereoisomer rearrangement, about 9%, at 220°C (428°F) for 14 days. They also demonstrated the use of a stabilizer significantly reduced the formation of the R-1233zd(Z) isomer at the higher temperatures. The formation of acidity or TAN in the lubricant evaluations were reported as low, even though significant discoloration was seen with some of the POEs evaluated in the study.

#### R-1224yd(Z) Chemical Stability

Only a few chemical stability studies of R-1224yd(Z), cis-1-chloro-2,3,3,3-tetrafluoro-1-propene, have been reported in literature, and specific refrigerant breakdown species were not reported by the investigators. Saito and Sundaresan (2017) reported that naphthenic mineral oil VG56 had good compatibility with R-1224yd(Z) when tested in sealed tubes at 175°C (347°F) for 14 days. TAN after exposure was 0.03 mg KOH/g oil. In addition, tests of R-1224yd(Z) with naphthenic mineral oil VG100 and an additive at 200°C (392°F) for 14 days also showed good compatibility with TAN value of 0.05 mg KOH/g oil without air and water, and TAN value of 0.01 mg KOH/g oil with 100 ppm air and 100 ppm water.

Kaika, Fukushima and lizuka (2019) reported on the chemical stability of R-1224yd(Z) with a PAG oil in the presence of metals by sealed tube testing, with comparison to R-245fa. Each tube was prepared with 60 grams refrigerant and 60 grams oil and included the three metal catalysts representing the system materials of construction: steel, copper and aluminum. Each tube was aged in a heated oven at 150°C (302°F) for 14 days. Although the acid number and the color of the PAG oil with R-1224yd(Z) was slightly higher compared to values with R-245fa, there were no other significant differences observed between the stability R-1224yd(Z) and R-245fa.

#### R-13I1 and R-466A Chemical Stability

R-13I1, trifluoroiodomethane, was considered in the CFC/HCFC to HFC transition period but was abandoned because of chemical stability concerns driven by the iodine atom in the molecule. Halogenated refrigerant chemical stability generally follows the rule that fluorine substitutions are most stable, followed by chlorine, bromine, and finally iodine. The chemical stability of R-13I1 (CF<sub>3</sub>I) was first studied in the 1990's because of a need to replace R-13B1 as a flame suppressor for aircraft applications. R-466A is a Class A1 blend of R-13I1 with R-32 and R-125 proposed as a replacement for R-410A.

Kujak and Sorenson (2021) reported results of sealed glass tube evaluations of both R-13I1 and R-466A as well as chemical stability studies in accelerated equipment operation. Sealed glass tube studies were performed with and without lubricants at varying times and temperatures to develop an understanding of reaction kinetics and Arrhenius behavior. Conditions ranged

from 80°C (176°F) to 150°C (302°F), at times ranging from 238 to 14 days. Copper, aluminum and iron catalysts were tested together in lubricant-free conditions as well as with unadditized and additized POE lubricants. Post exposure testing determined the primary breakdown product to be the traditional CFC/HCFC reduction product, R-23, which is a result of the loss of iodine. Evaluation of R-23 generation allowed determination of first order rate kinetics within the time range studied. Elevated reactivity was determined with R-466A in the presence of unadditized POE when tested at 150°C (302°F) for 14 days, with R-23 generation rates possibly as high as 20% in the condition tested with a zinc-aluminum coupon. Follow on work using a more chemically stable POE with a proprietary additive package determined significant reduction o R-23 production with all metal coupons tested (copper, aluminum, iron, brass and zinc-aluminum alloy). Equipment accelerated life tests (ALT) were conducted with the optimization of materials and additives to verify the results of the sealed tube tests performed at 150°C (302°F) for 14 days. The optimized units with additives and heat exchanger materials experienced low R-23 generation rates that remained stable over the course of the testing.

As part of the evaluation above and in prior publications by the authors (Kujak and Sorenson, 2018a), the approach to accelerated studies of reactive chemistries, based on reaction kinetics, Arrhenius theory, and equipment operation was detailed. Through assessment of reaction rates across the temperature ranges of modeled HVAC systems, the authors proposed that use of HALT conditions of 150°C (302°F) for 14 days is more than sufficient, as opposed to employing the traditional HALT condition of 175°C (347°F) for 14 days. Kujak and Sorenson (2018a) used a new interpretative numerical methodology they developed for extrapolating small scale highly accelerated laboratory results to real life HVACR operational conditions using a simple thermodynamic model, equipment operational conditions, and climate zone data. Using the Arrhenius theory, 175°C (347°F) was determined to accelerate chemical reactivity rates ~32,000 times greater than the rates observed at average system temperatures which are characterized using condenser, evaporator, compressor, and compressor discharge temperatures. This acceleration is equivalent to 1227 years of equipment operation which may be an unreasonable acceleration factor for unitary equipment and 150°C (302°F) is sufficiently vigorous to accelerate chemical stability for air conditioning and heat pump systems.

#### R-1234yf and R-1234ze(E) Chemical Stability

The chemical stability of R-1234yf, 2,3,3,3-tetrafluoro-1-propene, and R-1234ze(E), trans-1,3,3,3,-tetrafluoro-1-propene, will be discussed together since many chemical stability studies and refrigerant blends contain both HFOs. Fujitaka, Shimizu, Sato and Kawabe (2010) studied the chemical stability of R-1234yf with POE lubricant in the presence of air and water contaminants. The studies were conducted with copper, aluminum, and steel coupons in stainless steel containers with the refrigerant, lubricant, and contaminant(s) exposed for 14 days at 175°C (347°F). Test results indicated minor instability of R-1234yf when contaminants were not present. However, significant R-1234yf instability was observed in the presence of air, and it appeared to be accelerated even more in the presence of both air and moisture. It is important to note that the POE lubricant in the study was formulated with additives including an acid catcher and an antioxidant, which were measured after the exposures. Analyses of the lubricants from the R-410A baseline samples exposed to both air and moisture indicated that the acid catcher and antioxidant were nearly depleted (approximately 90%) as well. In the case of the corresponding R-1234yf exposures, the acid catcher was completely depleted, but the antioxidant was still present at significant concentrations. These results suggested that R-1234yf was preferentially reactive with air and that significant acids were formed, resulting in depletion of the acid catcher additive.

A more recent study was facilitated by AHRTI (Rohatgi, Clark, and Hurst, 2012) in which the stabilities of R-1234yf, R-1234ze(E), and mixtures of R-1234yf blended with R-32 (50% of each by weight), were evaluated with two POE lubricants and one PVE lubricant. R-134a and R-410A were evaluated as baseline controls for comparison with the HFOs and HFO/HFC blend refrigerants. This study constituted Phase I of the Material Compatibility and Lubricant Research (MCLR) for Low GWP Refrigerants program and involved preparation of samples in sealed glass tubes in accordance with ASHRAE standard 97-2007 with copper, aluminum, and steel catalysts. Prepared samples were aged for 14 days at 175°C (347°F) and the impacts of three contaminant conditions — air, water, and air with water—were evaluated. This study revealed evidence of refrigerant breakdown under specific scenarios

and reinforced that additional work was required to understand the refrigerant system chemistry implications of using HFOs in HVACR systems.

A follow up Phase II study was conducted by AHRTI to expand upon the initial chemical stability work conducted in Phase I (Majurin et al., 2014). Chemical compatibility experiments were conducted in sealed glass tubes with a three-refrigerant composite blend of R-1234yf, R-1234ze(E), and R-32 (33.3% by weight of each) in combination with one POE and one PVE lubricant and 41 different materials of construction. Control baseline samples with the same materials and lubricants were prepared with R-134a for comparison. Overall, results of the chemical compatibility portion of this study suggest that the chemical stability of the three-refrigerant blend and the implied chemical stability of the individual components is similar to R-134a when in contact with many of today's common HVACR materials, but some chemical interactions were noted. An interaction was noted between the three-refrigerant blend and the PVE lubricant that resulted in the detection of volatile compounds that were not observed in the corresponding R-134a control samples exposed with PVE lubricants. These compounds were detected at very low concentrations, and the relevance of this observation was not determined. Similar interactions with olefins in the PVEs were observed and are discussed in this project's report. Also, eight materials (Nomex<sup>®</sup> 410 and mica glass cloth motor phase insulations, nylon 6,6 polymer, Loctite 640, Garlock® 3300 gasket material, and epichlorohydrin, butyl rubber, and nitrile-based NBR elastomers) were determined to contribute to significant fluoride concentrations (>500 ppm) in at least one of the three-refrigerant blend sample test conditions in this study. However, it was not confirmed in this study that the observed fluoride was due to refrigerant degradation or that these fluoride concentrations were greater than what would be generated from material exposures with today's HFC refrigerants.

Matsumoto et al. (2017) described the development of PVE lubricants for use with HFO refrigerants (R-1234yf and R-1234ze(E)) and HFO/HFC blended refrigerants (R-448A, R-449A, R-452A, R-452B, and R-454B). Lubricants evaluated were PVE32A and PVE68A, which contained additives such as an antioxidant and an acid catcher. Additionally, an HFO refrigerant stabilizer was used when tested with HFOs. There were two water levels (less than 50 ppm and 500 ppm) and two air levels (<0.7 kPa and 13 kPa) tested and exposures were carried out at 175°C (347°F) for 14 days. After exposure, the acid number did not increase with the baseline R-404A and R-410A and PVE (with and without stabilizer) in low air/low water and high air/high water. However, TAN increased with HFO refrigerants in PVE (without stabilizer) in high air/high water tests. The TAN was reduced with the addition of the HFO stabilizer to a level similar to the R-404A/POE and R-410A/POE systems. In addition, there was no sludge visible after the tests, when using the stabilizer.

Kujak et al. (2015a) reported on the compatibility testing of nine different process chemicals (including six rust preventives, two detergents and one cutting fluid) in sealed glass tubes with a three-refrigerant blend of R-1234yf, R-1234ze(E), and R-32 (33.3% by weight of each) and POE lubricant at 175°C (347°F) for 14 days. Control samples were prepared with R-407C, using the same materials and lubricant. Post-exposure assessments included evaluation of the fluoride content of the exposed fluids as an indicator of refrigerant decomposition. Test results showed that with process chemicals refrigerant decomposition was measured in the refrigerant blend samples but was not detected in the R-407C/POE control samples. The fluoride concentration after exposure in the presence of the rust preventatives was as high as 200 ppm, with detergents it was up to 65 ppm, and with cutting fluid it was 50 ppm.

Rohatgi (2019) determined the effects of 25 process chemicals on the chemical stability of a low-GWP refrigerant blend of R-1234yf, R-1234ze(E), and R-32 (33.3% by weight of each) and a non-additized ISO22 POE lubricant, using sealed tube tests at 175°C (347°F) for 14 days. Test results were compared to previous results with R-134a/POE. It was concluded that many of the chemicals found in process fluids would react with the R-134a/POE and HFO-Blend/POE systems. Chemical reactions resulted in changes in a number of properties, such as darker lubricant color, cloudiness, deposit, film formation, darker metal color, dullness, corrosion, increased TAN, increased total organic acids (TOA), presence of metals in solution, and presence of reaction products (such as fluoride ions in the HFO-blend/POE system). The extent of reaction depended on the chemical and its concentration, the aging temperature, and the aging time.

#### **R-1132a Chemical Stability**

R-1132a (1,1-difluoroethylene), also known as vinylidene fluoride, is primarily used in the production of fluoropolymers, but recently has been introduced for use as a blending agent with HFCs and HFOs to create potential low-GWP refrigerant alternatives. In this work, R-1132a was evaluated as a blending agent in R-468A (R-1132a/32/1234yf, 3.5%/21.5%/75%). Limited literature references exist that evaluate the chemical stability of R-1132a.

Low (2018) presented the evaluation of potential uses of R-1132a as a refrigerant blend component and presented some limited chemical stability data. R-1132a was subjected to a series of extended duration autoclave tests at temperatures of 90°C (194°F), 100°C (212°F) and 120°C (248°F) and approximately 40 bar autogenous pressure. No evidence of degradation of material or pressure rise was observed during these tests. The length of exposure time was not reported.

#### **R-152a Chemical Stability**

The chemical stability of R-152a, 1,1-difluoroethane, has been studied infrequently over the last 30 years. Since it was not introduced as a refrigerant in HVACR products, there was limited need to study it in its pure form or as a blending agent. It is now being proposed for use as a blending agent since R-152a has a GWP of <150 (AR4). In this study, R-516A contains R-152a.

Bier et al. (1990) studied R-152a, which showed traces of HF at 180°C (356°F) after five days in a steel container. Bier et al. suggested that vinyl fluoride forms during thermal decomposition of R-152a and can then react with water to form acetaldehyde. Hansen and Finsen (1992) conducted lifetime tests on small hermetic compressors with a ternary mixture of R-22/152a/124 and an alkyl benzene lubricant. In agreement with Bier et al., they found that vinyl fluoride and acetaldehyde formed in the compressor and decomposition also increased with time. Aluminum, copper, brass, and solder joints lower the temperature at which decomposition begins.

Huttenlocher (1992) presented the results of a sealed tube stability study with R-152a with various lubricants. Each test mixture was aged at three temperatures: 150°C (300°F), 175°C (347°F), and 200°C (392°F). There was no observable refrigerant or lubricant decomposition reported with R-152a and alkylbenzene lubricant.

## **R-227ea Chemical Stability**

The chemical stability of R-227ea, 1,1,1,2,3,3,3-heptafluoropropane, has not been studied for use in HVACR products. R-227ea is used as a flame suppression gas in data processing and telecommunication facilities. Since it was not introduced as a refrigerant in HVACR products, there was limited need to study it in its pure form or as a blending agent. In this study, R-515B contains R-227ea.

There is only one study reported in the literature. Angelino and Invernizzi (2003) studied the thermal stability of R-227ea in a stainless-steel pressure vessel and showed that even at 425°C (797°F) there was no detectable sign of degradation after 50 hours, which denoted the remarkable thermal stability of R-227ea. At 450°C (842°F) a first indication of a decomposition onset was observed after 46 hours.

# **1. MATERIALS**

#### Table 1.1: Refrigerant and Lubricant Information

Fluid	Details					
Refrigerants						
R-123	Chemours, LOT:130000024258, CAS 306-83-2 (1,1-Di-chloro-2,2,2-trifluoroethane)					
R-32	National Refrigerants, Inc, LOT: P19112511, CAS 75-10-5 (Difluoromethane)					
R-152a	Arkema Inc, LOT: 588930, CAS 75-37-6 (1,1-Difluoroethane)					
R-227ea	Airgas, LOT: 2B12717, CAS 431-89-0 (Heptafluoropropane)					
R-1233zd(F)	Honeywell I OT: 1108-2714 CAS 102687-65-0 (trans-1-chloro-3 3 3-trifluoropropene)					
B-1224vd(Z)	AGC LOT: 700618 CAS 111512-60-8 (/7)-1-Chloro-2 3 3 3-Tetrafluoropropene)					
N=122490(2)	AGC, ECT. 200013, CAS 111512-00-8 ((2)-1-Chloro-2,3,3,5-16t and orbitopene)					
R-1336mzz(Z)	Chemours, LOT: 13000132649, CAS 692-49-4 ((2)-1,1,1,4,4,4-Hexanuoro-2-butene)					
R-1336mzz(E)	Chemours, LOT: 130000144116, CAS 66711-86-2 ((E)-1,1,1,4,4,4-Hexafluoro-2-butene)					
R-1234yf	Chemours, LOT: 130000043292, CAS 754-12-1 (2,3,3,3-Tetrafluoropropene)					
R-1234ze(E)	Honeywell, LOT: L108-2714, CAS 29118-24-9 (trans-1,3,3,3-Tetrafluoroprop-1-ene)					
R-450A	Honeywell, LOT: BE097-10-12, R-134a/R-1234ze(E), 42.0/58.0, CAS 811-97-2/29118-24-9, (1,1,1,2- Tetrafluoroethane/ trans-1,3,3,3-Tetrafluoroprop-1-ene)					
R-454B	Chemours, LOT: CPO-10086623-1, R-32/R-1234yf, 68.9/31.1, CAS 75-10-5/754-12-1,					
	(Difluoromethane/2,3,3,3-Tetrafluoropropene)					
R-454C	Chemours, LOT: 1354857-00036, R-32/R-1234yf, 21.5/78.5, CAS 75-10-57754-12-1, (Difluoromethane/					
	Honeywell   OT:   108-2725 R-744/R-32/R-1234vf 3 0/21 5/75 5 CAS 124-38-9/75-10-5/754-12-1					
R-455A	(Carbon dioxide/Difluoromethane/2,3,3,3-Tetrafluoroprop-1-ene)					
B-466A	Honeywell, LOT: L108-2726, R-32/R-125/R-13I1, 49.0/11.5/39.5, CAS 75-10-5/354-33-6/2314-98-8,					
N-400A	(Difluoromethane/Pentafluoroethane/Trifluoroiodomethane)					
R-468A	Koura, LOT: UN3161, R-1132a/R-32/R-1234yf, 3.5/21.5/75.0, CAS 75-38-7/75-10-5/754-12-1, (1,1-					
	Difluoroethylene/Difluoromethane/2,3,3,3-Tetrafluoropropene)					
R-513A	Tetrafluoroethane/2333-Tetrafluoronronene)					
	Chemours, LOT: 130000143454, R-1130(F)/R-1336mzz(7), 25.3/74.7, CAS 156-60-5/691-49-9, (Trans-					
R-514A	1,2-Dichloroethylene/(Z)-1,1,1,4,4,4-Hexafluoro-2-butene)					
D E1ED	Honeywell, LOT: BR20153R, R-227ea/R-1234ze(E), 8.9/91.1, CAS 431-89-0/29118-24-9, (1,1,1,2,3,3,3-					
K-515B	Heptafluoropropane/ trans-1,3,3,3-Tetrafluoroprop-1-ene)					
R-516A	Arkema, LOT: 04075#4, R-1234yf/R-134a/R-152a, 77.5/8.5/14.0, CAS 754-12-1/811-97-2/75-37-6,					
	(2,3,3,3-tetrafluoro-1-Propene/1,1,1,2-tetrafluoro-ethane/1,1-difluoro-ethane)					
Lubricants						
Polyol ester (POE)	CPI Fluid Engineering, RL32-3MAF, 32 cSt, mixed acid with only antioxidant					
Polyvinyl ether (PVE)	PVE 68 cSt, with only antioxidant					
Polyalkylene Glycol (PAG)	Shrieve, PAG 46, 46 cSt, dimethylcapped propylene oxide with only antioxidant					
Mineral Oil (MO)	Trane, Oil00022, 58 cSt, Naphthenic White Mineral Oil					
	Honeywell, 32 cSt mixed acid POE with stability additive package (free radical stabilizer, acid-catcher					
Additized polyol ester (POE)	and antioxidant) (2% TCP, 2% alkylated naphthalene, 1.5% 2-ethylhexyl glycidyl ether was added to the standard POE oil)					
Additized polyvinyl ether (PVE)	Idemistu, FVC68D, 56cSt, PVE with proprietary additive package (anti-wear, antioxidant and acid- catcher)					
Additized polyalkylene glycol	Shrieve, PAG 46, 46 cSt, dimethylcapped propylene oxide with proprietary additive package					
(PAG)	(antioxidant and acid-catcher)					

#### Table 1.2: Metal Coupon Information

Material Name	Details	
Aluminum (Al)	UNS AL3800, Cut from Casting Material to 0.125"x1.25"x 0.05"	
Iron (Fe)	1095 Spring Steel, McMaster-Carr, Part Number 9014K913, 6"x 25"x 0.05",	
	Cut to 0.125"x 1.25"x0.05	
Connor (Cu)	110 Copper ½ Hard Temper, McMaster-Carr, Part Number 8963K133, 2"x36"x0.05",	
copper (cu)	Cut to 0.125"x1.25"x0.05"	
Zinc	Zinc-Aluminum Alloy, Zamak ZA 8 Ingot, RotoMetals, Received as Cast Bars,	
ZINC	Cut to 0.125"x 1.25"x 0.05"	
Brass	260 Brass, McMaster-Carr, Part Number 8956K127, 2"x 36"x 0.05",	
	Cut to 0.125" x 1.25" 0.05"	

#### Table 1.3: Desiccant Materials Information

Material Name	Details
3A Molecular Sieve	Grace, type 594 3A molecular sieve
4A Molecular Sieve	Grace, type 594 4A molecular sieve
Activated Alumina (AA)	UOP, type D-201 activated Alumina

#### **1.1 CHARACTERIZATION OF MATERIALS**

Key baseline measurements are recorded in Tables 1.1.1 and 1.1.2, for refrigerants and lubricants used in this study.

Refrigerant	Moisture	Fluoride	Chloride	Iodide
nemgerunt	(ppm)	(ppm)	(ppm)	(ppm)
R-123	18	<10	<10	
R-32	17	<10	<10	
R-152a	24	<10	<10	
R-227ea	<5	<10	<10	
R-1233zd(E)	11	<10	<10	
R-1224yd(Z)	<5	<10	<10	
R-1336mzz(Z)	31	<10	<10	
R-1336mzz(E)	10	<10	<10	
R-1234yf	10	<10	<10	
R-1234ze(E)	8	<10	<10	
R-450A	9	<10	<10	
R-454B	37	<10	<10	
R-454C	63	<10	<10	
R-455A	8	<10	<10	
R-466A	9	<10	<10	<100
R-468A	6	<10	<10	
R-513A	14	<10	<10	
R-514A	48	<10	<10	
R-515B	13	<10	<10	
R-516A	43	<10	<10	

#### Table 1.1.1: Moisture Concentrations and Anions in As-Received Refrigerants

Lubricant	Fluoride	Chloride	TAN	Diss	Dissolved Elements in Lubricants by ICP (ppm)					
	(ppm)	(ppm)	mg KOH/g oil	Al	Cu	Fe	Zn	Si		
Mineral Oil	<10	<10	<0.05	<3	<1	<1	<1	<3		
PAG	<10	<10	<0.05	<3	<1	<1	<1	<3		
POE	<10	<10	<0.05	<3	<1	<1	<1	<3		
PVE	<10	<10	<0.05	<3	<1	<1	<1	<3		
Additized PAG	<10	<10	<0.05	<3	<1	<1	<1	<3		
Additized POE	<10	<10	<0.05	<3	<1	<1	<1	<3		
Additized PVE	<10	<10	<0.05	<3	<1	<1	<1	3		

Table 1.1.2: Anions, TAN and Dissolved Elements in As-Received Lubricants

#### 2. EXPERIMENTAL METHODS

The chemical and thermal stability of refrigerant and lubricants was evaluated by preparing material and fluid samples in sealed glass tubes, accelerating their aging through use of elevated temperatures, followed by detailed inspection of the materials and aged fluids. The evaluation program was divided into two phases of testing. The goal of the Phase I test program was to understand the thermal and chemical stability of low GWP refrigerants, in the presence or absence of compressor lubricants, with common system materials. The evaluation was performed on six low pressure refrigerants (R-1233zd(E), R-1224yd(Z), R-1336mzz(Z), R-1336mzz(E), R-514A, and R-123), six medium pressure refrigerants (R-1234ze(E), R-450A, R-515B, R-1234yf, R-513A, and R-516A), and four high pressure refrigerants (R-454C, R-455A, R-468A, and R-466A). Following review of Phase I test results, Phase II testing was proposed, and focused on five key areas of additional study: Phase IIA – The evaluation of PAG and PVE lubricant additives with select refrigerants; Phase IIB – The evaluation of new blend components R-152a and R-227ea; Phase IIC – The evaluation of POE lubricant additives on R-466A stability; Phase IID – The expanded evaluation of R-32/R-1234yf blends; and Phase IIE – The evaluation of desiccant materials with select refrigerants and lubricants. Detailed information on the fluids and materials studied is contained in Tables 1.1-1.3, with details to exposure conditions outlined in Tables 4.1-4.13.

#### **2.1 SAMPLE PREPARATION AND EXPOSURES**

Evaluations conducted in this test program utilized 20 refrigerants between Phase I and II. Lubricants evaluated included mineral oils, polyol ester (POE), polyvinyl ether (PVE), polyalkylene glycol (PAG) lubricants, or lubricant-free test conditions. The selection of testing temperature was based on refrigerant applications and thermal stability considerations. The selection of lubricant and refrigerant combinations was based on refrigerant miscibility and solubility in the lubricant. The materials evaluated included the metal coupons detailed in Table 1.2 and filter drier materials detailed in Table 1.3.

Sealed tubes for this study were prepared in accordance with the general procedure outlined in ASHRAE Standard 97-2007 (Sealed Glass Tube Method to Test the Chemical Stability of Materials for Use within Refrigerant Systems). The glass tubes utilized in this study were larger than those described in the standard to facilitate sufficient volumes of fluid for analytical methodologies. Duplicate sealed tubes were prepared for each test condition, and contained 20% by weight refrigerant with the lubricants of interest, as well as at 100% refrigerant where appropriate. Preparation of duplicate tubes was performed for each test condition for analytical purposes. One tube was consumed for the evaluation of inorganic anions by HPLC, and the second tube was first used for evaluation by GC-MS, followed by TAN, ICP-OES, and GC-FID evaluations. Tubes were prepared with fluid volumes that prevented over pressurization during the thermal aging process and provided optimal volumes for analytical testing. For low pressure refrigerants, 1.5 grams of refrigerant and 6 grams of lubricant were used, while for medium and high pressure refrigerants, 1.25 grams of refrigerant and 5 grams of lubricant were used. For 100% refrigerant conditions, the mass of refrigerant was kept consistent to the mass of refrigerant in the refrigerant-lubricant mixture conditions, utilizing 1.5 or 1.25 grams according to fluid pressures. Metal coupons were prepared by cutting from thin sheets or machining from castings, as detailed in Table 1.2. The prepared coupons were thoroughly polished, cleaned and kept dry prior to use. Desiccant materials were dried for at least 4 hours at 300°C (572°F) prior to addition to the tubes. The materials or coupons were added to the tube prior to addition of refrigerant and lubricant. For conditions with multiple coupons present, the coupons were individually inserted into the pre-necked tubes, without intentional placement order or separation.

The material under investigation was added to the tube first, followed by the lubricant. Prior to addition of the lubricant to the tube, the lubricant was tested for moisture by Karl Fischer coulometry and Total Acid Number (TAN) by titration. Lubricant moisture concentration requirements were  $\leq$ 50 ppm for Mineral Oil and POE, and  $\leq$ 100 ppm for PVE and PAG lubricants. TAN requirements were  $\leq$ 0.05 mg KOH/gram of oil for all lubricants. The TAN requirements were met in all instances throughout the duration of this project. When the lubricant moisture result exceeded the requirement, the lubricant was dried and degassed

prior to use. Lubricant was added accurately to each tube with a syringe and cannula. Subsequently, the tube was evacuated to <26.7 Pa (<200 mTorr) prior to introduction of the refrigerant.

Refrigerant samples were assessed for purity by gas chromatography and moisture by Karl Fischer coulometry prior to charging the tubes. Refrigerant moisture concentration requirements were ≤10 ppm for all refrigerants in this test program. When the refrigerant moisture results exceeded the requirement, the lubricant moisture requirement was lowered, resulting in consistent moisture limits applied to total tube contents, with the exception of conditions tested with 100% refrigerant. For medium and high-pressure refrigerants, accurate charging of refrigerant was conducted through liquid addition with a tube charging apparatus while the tube was cooled with liquid nitrogen. For low pressure refrigerants, accurate charge was performed via introduction of liquid to the glass tube with a gas tight syringe. After addition of the refrigerant to the tube, the tube was submerged in liquid nitrogen while attached to the gas handling system, and the tube neck was sealed and annealed. Batches of sealed tube samples were placed in Parr pressure vessels for aging.

Exposures were conducted in air circulating ovens. Low pressure refrigerants, excluding R-1336mzz(Z) and R-1336mzz(E), were aged for 14 days at 127°C (261°F). Medium and high-pressure refrigerants, as well as R-1336mzz(Z) and R-1336mzz(E), were aged for 14 days at 175°C (347°F). R-466A was evaluated for 14 days at 150°C (302°F). Aging temperatures were selected based on application considerations and established time and temperature considerations for accelerated aging, published in prior works (Kujak, 2015; Kujak, et.al., 2018a; Kujak, et.al., 2021). The evaluation of desiccant materials, in Phase IIE, were aged for 28 days at 100°C (212°F) to enable consistency to previous work, which demonstrated instability of refrigerants and lubricants with these materials at elevated temperatures (Field, 1995; Rohatgi, 1998; Majurin, et.al., 2014).

Aging studies were conducted in air circulating ovens, at temperatures selected based on refrigerant applications, chemical stability considerations, as well as established industry practices (Huttenlocher, 1992; Kujak, 2015; Kujak, et.al., 2018a; Kujak, et.al., 2021). It is recognized that standard industry practices often elect to use accelerated testing at HALT conditions of 175°C (347°F) for 2 weeks. While this is a standard approach to screen and assess chemical stability, there is no data to support its correlation to equipment operation or life. Additionally, these test conditions are often considered overly accelerated for certain scenarios, such as in the evaluation of low-pressure applications (such as water-cooled chillers) and less stable chemistries (R-123, R1311). To enable a broad screening of chemical stability in this project, accelerated aging for Phase I testing was performed at 175°C (347°F) for 2 weeks for refrigerants used in medium and high-pressure applications as well as low pressure refrigerants used in heat pump cycles. Refrigerants R-123, R-1233zd(E), R-1224yd(Z), and R-514A, are proposed for use in low pressure applications, were tested at 127°C (261°F) for 14 days. R-466A, a refrigerant with known stability challenges with unadditized lubricants (Kujak, 2018a), was chosen for study at 150°C (302°F) for 14 days. To enable consistency in the assessment of chemical stability between Phases, the established times and temperatures outlined in Phase I were also applied in Phase IIA-IID of this study. In Phase IIE, desiccant materials were aged for 28 days at 100°C (212°F) to enable consistency to previous work, which demonstrated instability of refrigerants and lubricants with these materials at elevated temperatures (Field, 1995; Rohatgi, 1998; Majurin, et.al., 2014).

#### **2.2 SAMPLE ANALYSIS**

Sealed tubes were imaged in a photo booth and inspections were performed before and after aging to document visual changes of the fluids and materials, particulate formation, and film formation on the tube walls. After visual analysis was completed, the tube contents were analyzed by multiple analytical methods. High performance liquid chromatography (HPLC) was utilized to quantify inorganic anion concentrations. Gas chromatography-mass spectrometry (GC-MS) was employed to identify and semi-quantify volatile components. Lubricant acidity (Total Acid Number, or TAN) was measured through titration. Dissolved element contents in lubricants were quantified through Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Lastly, gas

chromatography (GC) with flame ionization detection (FID) was applied to quantify specific organic acids in the POE lubricant samples.

Organic acid quantification was only conducted on the POE lubricant samples. POE lubricants have an ester backbone that generate organic acids as byproducts of reactions with water (i.e. hydrolysis reactions). Increases in TAN can be observed as POE degradation occurs and the concentration of organic acids increases in the lubricant as consequence of hydrolysis. Polyvinyl ether (PVE) and polyalkylene glycol (PAG) lubricants have different chemical structures and follow different degradation pathways than POE lubricants. PVEs and PAGs likely decompose to small chained alcohols but there is not established method within the industry for monitoring PVE and PAG lubricant breakdown products. More review on PVE and PAG chemistries and a review of any relevant testing technologies would be needed to identify appropriate testing strategies.

#### 2.3 DETAILED SAMPLE ANALYSIS PROCEDURES

#### 2.3.1 INORGANIC ANIONS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

HPLC analysis was conducted to determine the inorganic anion concentrations of fluoride and chloride in all test conditions. In analysis of the R-466A test conditions, the concentration of iodide was also determined, because iodine is present in the trifluoroiodomethane refrigerant used within the blend. The entire contents of the sealed tube were transferred into a high-density polyethylene bottle containing a known mass of deionized water and the mixture was stirred continuously for 16 hours at room temperature to promote the extraction of water-soluble anions. The water extract was then separated for analysis.

The HPLC system utilizes a high-pressure pump to deliver sample to a reverse phase column that drives separation of the ions in the sample, after separation, a conductivity detector is used to quantify the ions present in the sample.

Two separate mobile phases were used in this investigation depending on the target anion. For chloride and fluoride analysis, the mobile phase was a dilute solution of p-hydroxybenzoic acid mixed with 2.5% methanol. For chloride, fluoride, and iodide analysis, the mobile phase was a dilute solution of potassium acid phthalate. The concentrations of anions were determined by calibrating the chromatograph with anion standard solutions so that the peak area was proportional to the anion concentration. Results are reported in ppm based on the mass of refrigerant used, not the total mass of tube contents. The quantitation limit for both methods was determined to be  $\leq 10$  ppm fluoride,  $\leq 10$  ppm chloride, and  $\leq 100$  ppm iodide in the refrigerant.

#### 2.3.2 VOLATILE COMPOUND ANALYSIS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS)

After aging and recording the appearance changes, the tube was frozen with liquid nitrogen, opened, fitted with a valve, and briefly evacuated to remove residual air before being allowed to warm to room temperature for analysis. The gas phase was analyzed by connecting the valve on the tube to an evacuated gas-sampling loop to fill for injection on the gas chromatograph. For samples below atmospheric pressure, the gas-sampling loop was equalized with the pressure in the tube and injected under vacuum. For samples above atmospheric pressure, the gas sampling loop was equalized with the pressure in the glass tube up 15 psi, vented to atmospheric pressure, and injected. While this approach provides the ability to rapidly detect and identify the production of volatile or semi-volatile species that result from chemical reactions, it is challenged in its ability to be quantitative across a range of refrigerants and lubricants, without use of calibration for each condition. GC-MS data in this report is therefore considered semi-quantitative, with components reported in peak area percentages. Future work should seek to utilize qualitative insights from this project to identify calibrations needed to improve the understanding of key reaction products.

Gas chromatography separation was conducted using a capillary column with a 6% cyanopropylphenyl/94% dimethyl polysiloxane stationary phase and helium carrier gas. A column temperature program with sub-ambient cooling was necessary to separate the components on the analytical column. Upon elution from the column, each chemical was ionized by electron ionization at 70 eV and ions between 22 and 500 m/z (mass/charge) units were detected. For each sample, the total ion chromatogram was integrated and the results of key species are expressed as percent or ppm area of the total MS response.

Components of interest were given proposed identifications based on interpretation of mass spectra using NIST and internal libraries, as well as fragmentation knowledge. This method allowed for semi-quantitation of organic volatile species with a molecular mass of at least 22 g/mol. This methodology has sufficient sensitivity to detect low concentrations of volatile components present in the range of 0.001% total peak area, and results are reported for peaks determined to be >0.01% total peak area.

After the completion of GC-MS analysis, the residual refrigerant was removed from the lubricant via evaporation at slightly elevated temperatures (35°C (95°F)). The lubricant samples were then analyzed for acidity, dissolved elements, and organic acids, where applicable.

## 2.3.3 LUBRICANT ACIDITY BY TOTAL ACID NUMBER (TAN) TITRATION

ASTM D665 (Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration) provided the basis for the method used to measure TAN. The quantitation limit for this method is 0.05 mg KOH/g of oil.

#### 2.3.4 DISSOLVED ELEMENTS BY INDUCTIVELY COUPLED PLASMA-OPTICAL EMISSION SPECTROSCOPY (ICP-OES)

ICP-OES was used to quantify dissolved elements in lubricants. Lubricant samples were diluted in kerosene and an internal standard was used to account for potential interferences in the matrix of the exposed samples. A stock multi-element, oil-based standard was used to create external calibration curves. The sample responses at select wavelengths could then be compared to the response of the standards prepared at known concentrations, and the concentration of each dissolved element in the lubricant sample could be determined. The following elements were evaluated: silver (Ag), aluminum (Al), boron (B), barium (Ba), calcium (Ca), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), phosphorus (P), lead (Pb), silicon (Si), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn). The quantitation limit of this method was determined to be  $\leq 1$  ppm for elements listed above, with exception of barium ( $\leq 2$  ppm), sodium ( $\leq 2$  ppm), aluminum ( $\leq 3$  ppm), silicon ( $\leq 3$  ppm), potassium ( $\leq 5$  ppm), and phosphorus ( $\leq 5$  ppm). Results are reported for key elements that were observed above the reporting limit of the method and specific metals used in the test program.

#### 2.3.5 ORGANIC ACIDS BY GAS CHROMATOGRAPHY WITH FLAME IONIZATION DETECTION (GC-FID)

The lubricant samples from the POE-containing conditions were analyzed via GC-FID for quantitation of organic acids generated during the hydrolysis of the POE molecule. Gas chromatography was conducted using a capillary column with an acid-modified polar stationary phase and helium carrier gas with a FID detector with a hydrogen-air flame. Using external calibration curves prepared for isobutyric, isovaleric, valeric, hexanoic, heptanoic, branched nonanoic, and linear nonanoic acids, the concentration of each organic acid in the lubricant was determined by comparing the measured peak area in the sample to the calibration curve for each organic acid. The quantitation limits were determined experimentally for each of the acids as concentration in the lubricant prior to dilution. The quantitation limit of this method was determined to be 200 ppm for all acids of interest.

#### **3. RESULTS AND DISCUSSION**

#### **3.1 CHLORINATED REFRIGERANTS**

#### 3.1.1 R-123 WITH MINERAL OIL

The results for R-123 in the absence and presence of mineral oil are shown in Tables 5.1, 5.2, 5.59, and 5.68. R-123 was evaluated to establish baseline data on refrigerant and lubricant stability given lack of historic data at the time and temperature used in this aging study. In the presence of lubricant, breakdown of R-123 was indicated by the presence of chloride at elevated concentrations (>100 ppm). In the absence of lubricant, R-123 was determined to have limited refrigerant breakdown by evaluation of fluoride and chloride. The GC-MS evaluation of the headspace of the aged R-123 conditions with mineral oil indicated an increase in the concentration of R-133a which is the expected decomposition product of R-123 produced via dechlorination of R-123. In addition, R-1132a was detected, indicating further breakdown of the R-133a. No lubricant decomposition was noted in the evaluation of TAN, and limited interaction with metal coupons were observed, with no reportable dissolved metals by ICP-OES.

R-123 tested without lubricant was observed to have a 5 to 10 times reduction in observed decomposition products compared to lubricated test conditions. New decomposition products were also observed, with proposed identification as R-1122 and R-1122a. R-1122 and R-1122a are olefin products which indicate the elimination of HCl from the R-123 rather than the reduction chloride from R-123 in the presence of lubricant. Both of these reaction mechanisms are well understood and not new to the researchers. The presence of lubricant typically drives greater instability with chlorinated saturated fluorocarbons.

#### 3.1.2 R-1233zd(E) WITH MINERAL OIL

The results of R-1233zd(E) in the absence and presence of mineral oil are shown in Tables 5.3, 5.4, 5.59, and 5.69. Limited refrigerant decomposition was indicated by anion and GC-MS analysis. No stereoisomer rearrangement is believed to have occurred as a result of the aging process, however low levels of the stereoisomer R-1233zd(Z) were detected in the baseline refrigerant and all test conditions. There was one exposure that indicated some thermal instability with an increase in chloride concentration. The condition containing mixed metals (Cu, Fe, Al) and mineral oil showed 60 ppm in chlorides. No lubricant decomposition was noted in the evaluation of TAN, and limited interaction with metal coupons were observed, with no reportable dissolved metals by ICP-OES.

#### 3.1.3 R-1224yd(Z) WITH MINERAL OIL

The results of R-1224yd(Z) in the absence and presence of mineral oil are shown in Tables 5.5, 5.6, 5.59, and 5.70. There was no refrigerant decomposition indicated by anion analysis. For the evaluation of R-1224yd(Z), the GC-MS analytical method was challenged in its ability to measure changes in concentrations of the stereoisomer reaction product, R-1224yd(E), due to its elevated concentration in the baseline refrigerant and variability in peak area response with the headspace methodology. Therefore, no conclusions could be drawn on stereoisomerization reactions of this refrigerant in this study. The GC-MS analysis was able to determine the presence of two new species in the headspace at trace to low concentrations, with proposed identities as 3,3,3-trifluoro-1-propyne and 3,3,3-trifluoropropene (R-1243zf), both of which indicate the elimination and/or/both reduction of chlorine. In the case of the formation of the propyne, HF was eliminated from the R-1224yd(Z) and the formation of R-1243zf indicates the possible reduction of HF from the R-1224yd(Z). No lubricant decomposition was noted in the evaluation of TAN, and limited interaction with metal coupons were observed, with no reportable dissolved metals by ICP-OES.

#### **3.2 LOW PRESSURE REFRIGERANTS**

#### 3.2.1 R-514A WITH UNADDITIZED LUBRICANTS

The results for the evaluation of R-514A in the absence and presence of unadditized lubricants are shown in Tables 5.7, 5.8, 5.60, and 5.71. Fluoride and chloride ions were detected in several of the aged fluids, indicating refrigerant decomposition. These

observations occurred more prevalently in conditions tested without lubricant and in the presence of PAG and PVE lubricants. GC-MS analysis produced limited insights to refrigerant decomposition or stereoisomerization products, and the only observation of potential fluid degradation was observed as a late eluting unknown in the GC-MS analysis of all conditions tested with PVE (Figure 3.6.1). The authors propose that this is a possible chemical interaction between the R-1336mzz(Z) and the PVE lubricant breakdown products. All HFOs evaluated formed a unique HFO-PVE breakdown product with either additized or unadditized PVE. Identification of this and the other HFO-PVE unknown compounds has not been determined at this time. Various PMS members and their companies are helping with the proposed identifications. Additional breakdown products attributed to PAG breakdown were observed but were not an interaction with the HFOs. No lubricant decomposition was measured in the evaluation of TAN, and only subtle interactions were visually observed with metal coupons. Evaluation of the lubricant for dissolved metals in lubricant determined small amounts ( $\leq$ 10 ppm) of zinc in conditions containing brass and the zinc alloy tested with PAG, POE, and PVE.

#### 3.2.2 R-1336mzz(Z) WITH UNADDITIZED AND ADDITIZED LUBRICANTS

The results for the evaluation of R-1336mzz(Z) in the absence or presence of unadditized and additized lubricants are shown in Tables 5.9-5.12, 5.60, and 5.72. Fluoride ions were measured in several of the aged fluids with PAG (unadditized and additized) and PVE (unadditized and additized), indicating refrigerant decomposition. The presence of the additive package in the PVE was noted to reduce observed fluoride levels, while the additive package in the PAG had comparable or increased levels of measured fluoride in the aged fluids. GC-MS analysis produced further insights to refrigerant decomposition and stereoisomerization. Two components were detected in the headspace of the aged tubes, at varying composition, indicating reactivity of the refrigerant due to accelerated aging. R-1336mzz(E), the stereoisomer of R-1336mzz(Z), was measured in elevated concentrations in conditions tested without lubricants, as well as with POE lubricants. In the instances without lubricant present, this stereoisomer was measured in peak area concentrations up to 6% after aging. Given the differences in boiling points between the (E) and (Z) stereoisomers (Δ7.5°C (Δ45.5°F) and Δ33.4°C (Δ92.1°F) respectively) of R-1336mzz, the impact of partial pressures on component response can contribute to challenges in use of GC peak response as means of comparing stereoisomerization across conditions. Analytical calibration of GC response would be necessary to properly quantify the extent of this observed reactivity. 1,1,1,4,4,4hexafluorobutane, the saturated version of R-1336mzz, was also detected in varying concentrations, with elevated concentrations in both the additized and unadditized PVE conditions. A late eluting peak of interest as described previously as a possible HFO-PVE interaction, was detected in all conditions tested with PVE (Figure 3.6.1). This late eluting component was found at potentially elevated concentrations, with peak area percentages from 1-3%, however the effect of the high boiling point refrigerant (R-1336mzz(Z)) on contaminant peak response remains an open question. Additional impurities were present in the GC-MS chromatograms and were attributed to be PAG or PVE breakdown and the presence of additives yielded limited impact on reduction of these observed peaks. Increases in TAN and the presence of organic acids after aging showed POE lubricant decomposition. Elevated TAN was most significant when in the presence of POE with the zinc alloy, however results were consistent ( $\leq 0.3$  mg KOH/g oil) when compared to other refrigerants with the same test condition. The presence of elevated concentrations of dissolved zinc complemented the elevated TAN, and other conditions yielded minimal reportable levels of dissolved metals by ICP-OES with the exception of silicon which was detected in all unadditized and additized PVE conditions at low concentrations (<15 ppm). The presence of elevated silicon is noted to potentially originate from reactions with the glass in the sealed tubes, but a corresponding presence of boron was not at reportable levels in the analysis.

#### 3.2.3 R-1336mzz(E) WITH UNADDITIZED AND ADDITIZED LUBRICANTS

The results for the evaluation of R-1336mzz(E) in the absence and presence of unadditized and additized lubricants are shown in Tables 5.13-5.16, 5.60, and 5.72. Fluoride ions were measured just above reporting limits in several of the aged fluids with PAG (unadditized and additized) and PVE (unadditized), indicating refrigerant decomposition. The presence of the additive package in the PVE was noted to reduce observed fluoride levels, while the impact of the additive package in the PAG was challenging to discern due to low levels reported. GC-MS analysis produced further insights to refrigerant decomposition and stereoisomerization. The presence of R-1336mzz(Z), was detected in all fluids tested, as well as in the baseline material, however

no conclusion to its increase or decrease in concentration could be made. 1,1,1,4,4,4-hexafluorobutane was monitored closely given its formation in the above R-1336mzz(Z) evaluations. Its presence, while trace, was observed to vary across tests, with presence most commonly observed in aged fluids containing the additized and unadditized PVE lubricants. This observation is consistent with results from R-1336mzz(Z) evaluations in which this component was found to have the greatest concentration in the PVE test conditions (unadditized and additized). A continued observation of a late eluting peak due to the interaction between breakdown products of R-1336mzz and PVE lubricant, was detected in all conditions tested with PVE (Figure 3.6.1). Additional impurities were present in the GC-MS chromatograms and were attributed to be PAG or PVE breakdown. The presence of additives yielded limited impact on reduction of these observed compounds. Increases in TAN and the presence of organic acids after aging showed POE lubricant decomposition. Elevated TAN was most significant when in the presence of POE with the zinc alloy, however results were consistent ( $\leq 0.3 \text{ mg KOH/g}$  oil) when compared to other refrigerants with the same test condition. The presence of dissolved zinc complemented the elevated TAN, and other conditions yielded minimal reportable levels of dissolved metals by ICP-OES with the exception of silicon which was detected in several conditions at low concentrations (<15 ppm). The presence of boron was not at reportable levels in the analysis.

#### 3.3 R-1234ze(E) AND ITS BLENDS

#### 3.3.1 EVALUATION OF R-1234ze(E) AND ITS BLEND WITH R-134a (R-450A) WITH UNADDITIZED AND ADDITIZED LUBRICANTS

The results for the evaluation of R-1234ze(E) and R-450A in the absence and presence of unadditized and additized lubricants are shown in Tables 5.17-5.22, 5.61, and 5.73. With the exception of small amounts of reported fluoride in one test condition (R-1234ze(E), additized PAG, brass), no fluoride ions were measured in any other test conditions. Two key species were monitored during GC-MS testing to understand refrigerant breakdown and stereoisomerization of the R-1234ze(E). Review of chromatograms for the presence of R-1234ze(Z) and 3,3,3-trifluoropropene (R-1243zf), did not yield insights to any production of these molecules after aging. A late eluting peak of interest was detected, spectra and proposed chemistry of this unknown are captured in Figure 3.6.2. This component was present in all conditions tested with unadditized and additized PVE lubricants. Additional species were present in the GC-MS chromatograms and were attributed to be PAG or PVE breakdown. The presence of lubricant additives yielded some impact to the quantity of breakdown detected, however did not fully reduce the observed breakdown. Increases in TAN and the presence of organic acids after aging indicated POE lubricant decomposition. Elevated TAN was most significant when in the presence of POE with the zinc alloy, however results were consistent (<0.3 mg KOH/g oil) when compared to other refrigerants with the same test condition. The presence of dissolved zinc complemented the elevated TAN, and other conditions at low concentrations (<15 ppm). The presence of elevated silicon is noted to potentially originate from reactions with the glass in the sealed tubes, but a corresponding presence of boron was not at reportable levels in the analysis.

#### 3.3.2 EVALUATION OF R-515B AND R-227ea WITH UNADDITIZED LUBRICANTS

The results for the evaluation of R-515B in the absence and presence of unadditized lubricants are shown in Tables 5.23, 5.24, 5.61, 5.73. During initial study, fluoride was observed in 3 test conditions, indicating potential refrigerant decomposition, and follow-on study confirmed the elevated fluoride determined in the condition tested with POE and zinc. Two key species were monitored during GC-MS testing to understand refrigerant breakdown and stereoisomerization of the R-1234ze(E) component. Review of chromatograms for the presence of R-1234ze(Z) and 3,3,3-trifluoropropene (R-1243zf), did not yield insights to any production of these molecules after aging, in alignment to results determined with testing of pure R-1234ze(E) and R-450A. In further consistency to other HFOs, a late eluting peak of interest was detected, with spectra and proposed chemistry of this unknown are captured in Figure 3.6.2. This peak was present in all conditions tested with PVE. Additional species were present in the GC-MS chromatograms and were attributed to be PAG or PVE breakdown. Increases in TAN and the presence of organic acids after aging indicated POE lubricant decomposition. Elevated TAN was most significant when in the presence of POE with the zinc alloy, however results were consistent ( $\leq 0.3 \text{ mg KOH/g oil}$ ) when compared to other refrigerants with the same test

condition. The presence of dissolved zinc complemented the elevated TAN, and other conditions yielded no reportable levels of dissolved metals by ICP-OES with the exception of silicon which was detected in several conditions at low concentrations ( $\leq$ 10 ppm), with only one reported value >10 ppm in the instance of R-227ea with PVE and zinc. The presence of elevated silicon is noted to potentially originate from reactions with the glass in the sealed tubes, but a corresponding presence of boron was not at reportable levels in the analysis.

Given initial observations of reportable fluoride levels that indicated differences in reactivity of R-515B compared to R-1234ze(E) and R-450A results, further review of the new blending agent, R-227ea, was pursued in its pure form. The results for the evaluation of R-227ea in lubricant free and unadditized lubricant conditions are shown in Tables 5.57, 5.58, 5.67, and 5.81. There was no refrigerant decomposition indicated by anion data or in the GC-MS evaluation. GC-MS testing did identify several additional species in the chromatograms which were attributed to PAG and PVE breakdown. Increases in TAN and the presence of organic acids after aging indicated POE lubricant decomposition. Elevated TAN was most significant when in the presence of POE with the zinc alloy, however results were consistent ( $\leq$ 0.3 mg KOH/g oil) when compared to other refrigerants with the same test condition. The presence of dissolved zinc complemented the elevated TAN, and other conditions at very low concentrations ( $\leq$ 10 ppm). The presence of elevated silicon is noted to potentially originate from reactions with the glass in the sealed tubes, but a corresponding presence of boron was not at reportable levels in the analysis. These evaluations with pure R-227ea indicate that the R-515B may have some chemical instability and will generate fluoride, however further study would be needed to improve understanding of the potential breakdown products.

#### 3.4 R-1234yf AND ITS BLENDS

#### 3.4.1 EVALUATION OF R-1234yf AND ITS BLEND WITH R-134a (R-513A) WITH UNADDITIZED AND ADDITIZED LUBRICANTS

The results for the evaluation of R-1234yf and R-513A in the absence or presence of unadditized and additized lubricants are shown in Tables 5.25-5.32, 5.62, and 5.74. Fluoride ions were measured in several of the aged fluids with PAG (unadditized and additized) and PVE (unadditized), indicating refrigerant decomposition. The presence of the additive package in the PVE was determined to reduce fluoride levels below reporting limits, while the impact of the additive package in the PAG was determined to have most effectiveness in the reduction of fluoride in conditions tested with mixed metals (Cu/Fe/Al). Review of GC-MS chromatograms for the presence of 3,3,3-trifluoropropene (R-1243zf), did not yield insights to production of this molecule after aging. A continued observation of a late eluting peak of interest was detected and is referenced as "R-1234yf-PVE Unknown", with mass spectra noted in Figure 3.6.3. Review of the mass spectra suggests a potential empirical formula of  $C_5H_7F_3$  (MW 124). The potential source is proposed to be defluorination of R-1234yf combined with a -CH<sub>2</sub>CH<sub>3</sub> fragment (m/z 29) from the breakdown of the PVE lubricant. This component was present in all conditions tested with unadditized and additized PVE lubricants. Additional species were present in the GC-MS chromatograms and were attributed to be PAG or PVE breakdown. The presence of additives in the PAG lubricant did not appear to reduce the presence of observed breakdown products in the GC-MS chromatograms, while the presence of additives in the PVE did appear to reduce the presence of PVE breakdown products, as well as the presence of the unknown peak. Increases in TAN and the presence of organic acids after aging indicated POE lubricant decomposition. TAN was most significant when in the presence of POE with the zinc containing materials (brass and zinc alloy), however results were consistent ( $\leq$ 0.3 mg KOH/g oil) when compared to other refrigerants with the same test conditions. ICP-OES further support the interaction with zinc-containing materials, as zinc dissolution was observed in the aged fluids evaluated with brass and zinc alloys. Silicon was also detected in several conditions at low concentrations (≤10 ppm), with only two reported values >10 ppm in instances with PVE lubricants and R-1234yf. The presence of elevated silicon is noted to potentially originate from reactions with the glass in the sealed tubes; however, boron was only measured at or below reportable limits in the analysis. The pure R-1234yf evaluations indicate that the R-1234yf has some chemical instability and will generate fluoride, however full understanding of the refrigerant decomposition product(s) are unknown at this time much like they are with R-1234ze(E).

#### 3.4.2 EVALUATION OF R-516A AND R-152a WITH UNADDITIZED LUBRICANTS

The results for the evaluation of R-516A in the absence or presence of unadditized and additized lubricants are shown in Tables 5.33, 5.34, 5.63, and 5.75. Fluoride ions were measured in several of the aged fluids with PAG and PVE, indicating refrigerant decomposition. Review of chromatograms for the presence of 3,3,3-trifluoropropene (R-1243zf), did not yield insights to any production of this molecule after aging due to potential co-elution on the GC column with R-152a in the blend. A new component was detected in the zinc-containing conditions after aging, at low peak area concentrations, with a proposed identification of vinyl fluoride (R-1141). Consistent with R-1234yf-PVE breakdown noted previously, a late eluting peak of interest was detected in all PVE containing conditions and is referenced as "R-1234yf-PVE Unknown", with mass spectra noted in Figure 3.6.3. Additional species were present in the GC-MS chromatograms and were attributed to be PAG or PVE breakdown. Increases in TAN and the presence of organic acids after aging indicated POE lubricant decomposition. Elevated TAN was most significant when in the presence of POE with the zinc alloy, however results were consistent ( $\leq 0.3$  mg KOH/g oil) when compared to other refrigerants with the same test condition. Elevated TANs were additionally measured in POE conditions with Al/Cu/Fe. The presence of dissolved zinc complemented the elevated TAN, and other conditions yielded no significant reportable levels of dissolved metals by ICP-OES. Silicon was also detected at low levels ( $\leq 16$  ppm) in several conditions, particularly all conditions containing PVE, which could be indicative of reactivity with the glass tubes as well, but a corresponding presence of boron was not at reportable levels in the analysis.

Further review of R-152a was pursued given observations of a vinyl fluoride (R-1141) refrigerant decomposition product in the GC-MS evaluation of R-516A. The results for the evaluation of R-152a in the absence or presence of unadditized lubricants are shown in Tables 5.53-5.56, 5.67, and 5.80. Initial observations after tube aging indicated severe reactivity as there were challenges with tube breakage while under test, specifically in conditions containing zinc. If vinyl fluoride formation is significant, then tube overpressure would be expected since vinyl fluoride has a boiling point -72°C (-98°F). Tubes were prepared a second time and aging was performed with an increased countercharge of refrigerant in the pressure vessel to enable an improved opportunity to maintain tube integrity while aging at elevated temperatures. Visual observations after aging supported catalytic reactivity with zinc, as variability in visual results was significant, with several conditions showing indication of significant reactions via color change and impact to catalysts (Table 5.55 and 5.56). Fluoride ions were measured in several of the aged fluids, with the majority of observations aligning to the presence of zinc. Review of GC-MS chromatograms further indicated reactivity with zinc, given elevated levels of vinyl fluoride produced, consistent with GC-MS findings for R-516A. Additional species were present in the GC-MS chromatograms and were attributed to be PAG or PVE breakdown. Increases in TAN and the presence of organic acids after aging indicated POE lubricant decomposition. As with other refrigerants, the increase in TAN was most significant in the presence of zinc, however measured TAN was 5 to 6 times higher than the TAN levels typically observed with other refrigerants and this lubricant/metal combination. Finally, review of dissolved metals also yielded some uniqueness in results. Despite elevated TAN in the presence of POE and zinc, the dissolved zinc was not significantly elevated, and instead, untypical for POEs, an increase in silicon and boron was detected, signifying likely reactivity with the glass tube. Silicon was also detected at low levels (≤10 ppm) in conditions containing PVE, which could be indicative of reactivity with the glass tubes as well.

These results are consistent with work performed by Bier et al. (1990). Bier et al. suggested that vinyl fluoride forms during thermal decomposition of R-152a and can then react with water to form acetaldehyde. Hansen and Finsen (1992) conducted lifetime tests on small hermetic compressors with a ternary mixture of R-22/152a/124 and an alkyl benzene lubricant. In agreement with Bier et al., they found that vinyl fluoride and acetaldehyde formed in the compressor and decomposition also increased with time.

#### 3.4.3 EVALUATION OF BLENDS OF R-1234yf AND R-32 WITH UNADDITIZED AND ADDITIZED LUBRICANTS

Two blends of R-1234yf and R-32 were investigated to improve the understanding of potential impact of R-1234yf concentrations on the stability of the blends. Results for R-454B (31.1% R-1234yf) and R-454C (78.5% R-1234yf) in the absence or presence of unadditized lubricants are shown in Tables 5.35-5.40, 5.64, and 5.76. This data was evaluated against data for each pure

component, R-1234yf, discussed in 3.4.1, and R-32 whose results with unadditized lubricants are detailed in Tables 5.51, 5.52, 5.67, and 5.79. Fluoride ions were measured in conditions for all 4 fluids studied, R-32, R-454B, R-454C, and R-1234yf. Even though fluoride was noted in most exposures that contained R-1234yf, the amount of fluoride was not correlated to the amount of R-1234yf present.

For R-32, fluoride was not detected in the majority of exposures, with the exception of the evaluation of R-32 with unadditized PVE and zinc metal. The presence of silicon was observed in the 100% R-32 evaluations with unadditized PVEs at low levels. The presence of elevated silicon is noted to potentially originate from reactions with the glass in the sealed tubes; however, boron was detected at levels near the reporting limit (1 ppm).

For the evaluation of R-1234yf-containing fluids with PAGs, a slight correlation is observed between elevated R-1234yf concentrations and fluoride generation. In general, the least amount of fluoride was measured with R-454B and unadditized PAG, followed by R-454C, and R-1234yf test conditions.

No correlation was determined in the case of fluoride generation with these fluids when exposed to PVEs, as all R-1234yf containing refrigerants appeared to have similar levels of fluoride generation when tested with the unadditized PVE as well as similar reductions in measured fluoride when tested with the additized PVE. Review of GC-MS chromatograms across these varying blends of R-1234yf with R-32 did not yield any new insights on reactivity. In general, GC-MS observations were consistent across the different blend compositions with the exception of R-32 which yielded no observation of the late eluting unknown component attributed to interaction between the PVE and R-1234yf molecules.

Increases in TAN and the presence of organic acids after aging indicated POE lubricant decomposition in several conditions, in alignment with prior discussion on increased POE interactions with zinc-containing materials (brass and zinc). No increases in TAN appeared to correlate with variations in the concentration of R-1234yf. ICP-OES results further supported the observation of interaction with zinc-containing materials, as zinc dissolution was observed in the aged fluids evaluated with brass and zinc alloys. Silicon was also detected in several conditions up to ~30 ppm. Its presence in the aged fluid did not appear to correlate to the concentration of R-1234yf in the refrigerant blend and was more typically observed in tests with additized and unadditized PVE and PAG lubricants. The presence of elevated silicon is noted to potentially originate from reactions with the glass in the sealed tubes; however, boron was only detected at levels near the reporting limit (1 to 3 ppm).

#### 3.4.4 EVALUATION OF R-32/R-1234yf BLEND CONTAINING R-774 (R-455A) WITH UNADDITIZED LUBRICANTS

The results for the evaluation of R-455A in the presence of unadditized lubricants are shown in Tables 5.41, 5.42, 5.64, and 5.76. Generally, the addition of R-744 (CO<sub>2</sub>) did not increase the reactivity of R-32 and R-1234yf chemistries. GC-MS analysis gave no indication of any unique breakdown or interactions due to the presence of R-744 (CO<sub>2</sub>). Review of the GC-MS chromatograms indicated typical breakdown products of PAG and PVE lubricants, as well as the presence of the decomposition peak attributed to the interaction of R-1234yf and PVE. The peaks area percentages of these components appeared to be reduced when compared to data from other blends containing R-1234yf.

Fluoride ions were measured in several of the aged fluids with PAG and PVE, indicating refrigerant decomposition. Increases in TAN and the presence of organic acids after aging indicated POE lubricant decomposition. Elevated TAN was most significant when in the presence of POE with the brass and zinc alloy, however results were consistent ( $\leq 0.3 \text{ mg KOH/g oil}$ ) when compared to other refrigerants with the same test condition. The presence of dissolved zinc was also found to be present in these same conditions. The other evaluated lubricants had limited dissolved metals present, with only small amounts of reported zinc in several instances in test conditions with PAG. The presence of elevated silicon is noted to potentially originate from reactions with the glass in the sealed tubes, but a corresponding presence of boron was not at reportable levels in the analysis.

#### 3.4.5 EVALUATION OF R-1234yf BLENDED WITH R-1132a (R-468A) WITH UNADDITIZED AND ADDITIZED LUBRICANTS

The results for the evaluation of R-468A with unadditized and additized lubricants are shown in Tables 5.43-5.46, 5.65, and 5.77. GC-MS analysis gave no indication of any unique breakdown or interactions due to the presence of R-1132a, but the addition of R-1132a showed increased reactivity than that of just an R-32 and R-1234yf blend.

Fluoride ions were measured at elevated concentrations in several of the aged fluids with PAG and PVE, as well as one condition with POE, indicating refrigerant decomposition. The presence of the additive packages in the PVE and PAG lubricants were determined to reduce fluoride levels compared to the unadditized conditions. For additized PVE, fluoride was reduced to below reporting limits, while for additized PAG, the fluoride levels were significantly reduced, but still measured. Reportable TANs were found in all POE test conditions, as well as in the exposure with additized PVE and zinc. The elevated TAN observed with PVE was not typical to other evaluations with zinc and could be indications of increased reactivity. Elevated TANs in the presence of POE with the brass and zinc alloy were consistent ( $\leq$ 0.3 mg KOH/g oil) when compared to other refrigerants with the same test condition. ICP-OES further supported the interaction with zinc-containing materials and POEs, as zinc dissolution was observed in the aged fluids evaluated with brass and zinc alloys. Silicon was also detected in several conditions at varying concentrations up to ~30 ppm. The presence of elevated silicon is noted to potentially originate from reactions with the glass in the sealed tubes. In addition, the presence of boron was at low reportable levels (2-5 ppm) in the analysis, further confirming an interaction with the glass.

#### 3.5 IODINATED REFRIGERANTS, CF3I BLEND (R-466A)

The results for the evaluation of R-466A in the absence and presence of unadditized lubricants is shown in Tables 5.47-5.50, 5.66, and 5.78. R-466A was the only high pressure refrigerant evaluated in a lubricant free conditions since it is known that lubricants can cause instability of the R-1311. Significant amounts of fluoride and iodide were generated in exposures containing unadditized PAG, POE, and PVE lubricants, while no reportable anions were measured with the lubricant-free test conditions. Given significant levels of refrigerant breakdown observed during anion analysis, only conditions with <500ppm fluoride were evaluated in subsequent testing. Review of the GC-MS chromatograms indicated the presence of several decomposition products in the headspace of the aged tubes. Trifluoromethane (R-23) was observed in all test conditions evaluated, ranging from 0.4-6.7% peak area, with more significant levels (~6% peak area R-23) observed in tubes containing lubricant versus tubes that were lubricant-free (<1.5% peak area R-23). In addition to R-23 generation, small amounts of other iodine-containing breakdown products were observed in all test conditions, as well as the presence of fluoroethane in the PVE test condition.

Review of the GC-MS chromatogram for the common peaks associated with PVE lubricant breakdown (isobutane, acetaldehyde, ethane, and ethanol) yielded limited peak presence, with only ethanol detected in measurable quantities; any production of ethane would potentially co-elute with R-23. It is possible the reduced temperature used in aging the R-466A had a role in the decreased presence of lubricant decomposition when measured by GC-MS. Elevated TANs were observed in the limited conditions that were available for evaluation. For PVE and POE conditions evaluated with brass, significant increases in TAN were observed, compared to observations in other refrigerant-lubricant systems tested with brass. For POE, TAN levels were 3 times greater than typically observed ( $\leq 0.25$  mg KOH/g oil) with brass, while TAN levels with mixed metals (Cu/Al/Fe) were elevated at 0.09 mg KOH/g oil. For PVE test conditions with brass, the TAN was elevated at 0.47 mg KOH/g oil, which is significantly higher than all other unadditized PVE data points with brass material, which typically had TAN values not exceeding 0.08 mg KOH/g oil. Both conditions that were evaluated with brass were found to contain elevated levels of dissolved zinc, low concentrations of boron ( $\leq 6$  ppm), and increased silicon levels in all three aged fluids. The presence of silicon and boron are noted to potentially originate from reactions with the glass in the sealed tubes.

Follow-on work in Phase IIC was conducted to determine the impact of a proprietary POE additive package<sup>1</sup> on the stability of R-466A. Evaluations were expanded to review standard system metals (Cu/Al/Fe, brass, and zinc) along with individual copper, aluminum, and iron coupons. Results of the aging study are shown in Tables 5.49 and 5.50 and indicate limited refrigerant reactivity. Fluoride was reportable in only one test condition, in the presence of copper. No other reportable fluoride or iodide was measured. Review of the GC-MS chromatograms further indicated limited reactivity of the refrigerant or lubricant. While trifluoromethane (R-23) was observed in all test conditions, its presence was significantly reduced, with peak area percentage ranging from 150-310 ppm. As typical with POEs, no lubricant breakdown products were detected in the GC-MS headspace analysis of the aged tubes, and increased TAN levels were only observed in the condition with zinc, indicating continued compatibility challenges with this metal. Evaluation of organic acids had no detectable species across the metals evaluated, despite the elevated TAN observed with zinc. It is likely other acidic degradation species could be present in this additized lubricant, driving an increased TAN after aging with zinc. In addition to no detectable organic acids, the evaluation of the lubricant phase by ICP-OES found there to be very limited dissolved elements in the aged fluids after test.

#### 3.6 SUMMARY OF INTERACTIONS BETWEEN HFO REFRIGERANTS AND LUBRICANT

Evaluation of the headspace of the sealed glass tubes by GC-MS gave insights beyond the typical monitoring of refrigerant breakdown products. In addition to monitoring key refrigerant species after aging tests, GC-MS allowed further insights to lubricant breakdown as well as the potential interactions between lubricant and refrigerant chemistries. Of the lubricants studied in this program, PAG and PVE lubricants had breakdown products that were able to be observed due to their semi-volatility. For test conditions with PAG lubricants, GC-MS analysis frequently detected peaks with the proposed identities of propanal, acetaldehyde, and acetone, all being components which were not observed in the headspace of the new lubricant. Aged test fluids with PVE lubricants were found to have several proposed breakdown products detected by GC-MS as well, with identities proposed as ethane, acetaldehyde, ethanol, and isobutane. In addition to these low molecular weight species, PVEs were also discovered to form unique breakdown products with R-1336mzz(E/Z), R-1234ze(E), and R-1234yf. While R-1132a and R-1130(E) are two additional olefin chemistry that were studied, neither was determined to create a unique breakdown product when aged with PVE. This observation could be due to the concentrations in the blend studied, or from lack of reactivity with the PVE lubricant. Further work is needed to understand if R-1132a or R-1130(E) can react with PVE.

This observation of HFO interactions with PVE lubricants was previously observed in AHRI 8007, when GC-MS analysis was performed on aged tubes with a blend of R-1234ze(E), R-1234yf, and R-32. This AHRTI 9016 study separated the various HFO chemistries, except for R-514A and R-468A, and it was quickly determined from the GC-MS chromatograms that unique decomposition HFO-PVE products are formed at various levels. With the isolation of contributing chemistries, further mass spectra interpretation was performed, and is discussed in Figures 3.6.1-3.6.3.

<sup>&</sup>lt;sup>1</sup> 2% TCP, 2% alkylated naphthalene, 1.5% 2-ethylhexyl glycidyl ether was added to the standard POE oil



Figure 3.6.1: GC-MS spectra of late eluting unknown compound present in R-1336mzz(E), R-1336mzz(Z), and R-514A exposures with PVE lubricants, noted as "R-1336mzz-PVE Unknown" in GC-MS tables. Current mass spectra interpretation suggests a potential empirical formula of C<sub>9</sub>H<sub>8</sub>F<sub>4</sub>, with likely unsaturation and fluorination. Potential source is a proposed reaction with R-1336mzz breakdown combined with PVE breakdown. [Credit: Rob Yost, National Refrigerants]



Figure 3.6.2: GC-MS spectra of late eluting unknown present in R-1234ze(E) exposures with PVE lubricants, noted as "R-1234ze(E)-PVE Unknown" in GC-MS tables. This unknown compound had spectral similarities to 2-fluoro-2-methylpropane, and is likely a higher molecular weight compound consisting of a CH<sub>3</sub>CFCH<sub>3</sub>- ion or other ion fragment with a mass/charge ratio of 61.



Figure 3.6.3: GC-MS spectra of late eluting unknown present in R-1234yf exposures with PVE lubricants, noted as "R-1234yf-PVE Unknown" in GC-MS tables. Current mass spectra interpretation suggests a potential empirical formula of C<sub>5</sub>H<sub>7</sub>F<sub>3</sub>. Potential source is a proposed defluorination of R-1234yf and the addition of an ethane group from PVE breakdown.

#### **3.7 CHEMICAL COMPATIBILITY WITH FILTER DRIER MATERIALS**

The results for the evaluation of twelve refrigerants (R-1233zd(E), R-1224yd(Z), R-514A, R-1336mzz(Z), R-1336mzz(E), R-1234ze(E), R-515B, R-1234yf, R-516A, R-455A, R-468A, and R-466A) with 3 filter drier materials in the absence and presence lubricant are shown in Tables 5.82-5.118. Overall, limited reactivity was seen, likely because of the lower temperature test conditions. There was no refrigerant decomposition indicated in the anion data, and only two test conditions yielded any indication of refrigerant reactivity by GC-MS. Trace amounts of 3,3,3-trifluoro-1-propyne were detected in lubricant-free conditions tested with R-1233zd(E), and trace amounts of vinyl fluoride were observed in R-516A testing, most typically in the presence of activated alumina. The presence of PAG and PVE decomposition species, previously detected by GC-MS in this study, were not observed in significance during evaluation of the filter drier materials. GC-MS indicated only trace refrigerant breakdown product in a few cases and few lubricant breakdown products in the headspace of the sealed glass tube.

Review of low pressure refrigerants, R-1233zd(E) and R-1224yd(Z), tested with mineral oils had limited observations to indicate lubricant reactivity. In the evaluation of R-1233zd(E) with mineral oil, there were observations of increased TAN in all conditions tested with mineral oil, with no reportable dissolved elements. For R-1224yd(Z), resulting TAN and dissolved elements both had no reportable observations.

Review of the remaining medium and high pressure refrigerants, tested with POE, additized PAG and PVE lubricants indicated limited lubricant reactivity, with some subtle observations consistent across lubricants. For additized PAGs and PVEs, slight increases in TAN ( $\leq 0.08$  mg KOH/g oil) were observed in only a few instances. In testing with POEs, slight increases in TAN ( $\leq 0.10$  mg KOH/ g oil) were observed in some instance with 3A and 4A molecular sieve materials, and testing with activated alumina produced consistent increases in TAN (0.16-0.66 mg KOH/g oil) and organic acids measured with all refrigerants tested. Evaluations with all three lubricants yielded no detectable dissolved elements by ICP-OES with the exception of silicon. Silicon was detected in many conditions, with slight increases in instances with tested PAG and POE lubricants ( $\leq 10$  ppm), while PVE lubricants were noted to have consistent measurements of elevated silicon (6-46 ppm Si). The presence of elevated silicon is noted to potentially originate from reactions with the glass in the sealed tubes, or potentially due to interactions with materials

and binders of the desiccant materials. Boron concentrations were only observed at reportable limits in a few instances, at low concentration (1-2 ppm), likely indicating interaction with the desiccant materials as opposed to the glass of the tubes.

An observation across all test conditions with filter drier materials was the frequent visual observation of faint amounts of fine particles in the tubes. Inspection of tubes before and after aging determined a presence of these faint particles, with a slight increase in their presence after aging in many conditions. Further evaluations were pursed to understand the origination and nature of the particles found in the testing. To better understand particle origination, additional tubes were prepared by adding the activated desiccant (3A, 4A, and AA) materials to the glass tubes, and evaluating the impact of the addition of R-1234ze(E) as well as an HFC (R-134a) for reference. Materials were subject to liquid only exposure, as well as the liquid immersion with the liquid nitrogen freeze-thaw cycle that is typical of sealed glass tube preparation. Results from this evaluation indicated that particles could originate from the desiccant materials before any exposure to refrigerants, and that exposure to refrigerants, especially when paired with a freeze-thaw cycle, increased the amount of particles present similarly in both refrigerants (Image 3.7.1). Further review of the particles liberated during these non-aged experiments, with particles obtained from aged sealed tubes, indicated the chemical composition to be consistent with the make-up of the desiccant beads, with a slight shift in elemental composition to indicate that the shed particles were richer in silicon than the elemental composition of the unused desiccant beads.



Image 3.7.1: Particles present after exposure of desiccant beads with liquid refrigerant, prior to any accelerated aging. (Left to right, 3A Molecular Sieve, 4A Molecular Sieve, and Activated Aluminum)

# 4. TEST PLANS

Refrigerant	Lubricant	%	Metal	Temp	Duration	Visual	GC-MS	TAN	Organic	Anions	ICP
- 0		Lubricant			•	Inspection	Analysis		Acids		
	No Oil	0	Al/Cu/Fe	127°C	14 days	Х	х			Х	
	No Oil	0	Brass	127°C	14 days	Х	Х			Х	
D 122	No Oil	0	Zinc	127°C	14 days	Х	Х			Х	
R-125	Mineral Oil	80	Al/Cu/Fe	127°C	14 days	Х	Х	Х		Х	Х
	Mineral Oil	80	Brass	127°C	14 days	Х	Х	Х		Х	Х
	Mineral Oil	80	Zinc	127°C	14 days	Х	Х	Х		Х	Х
	No Oil	0	Al/Cu/Fe	127°C	14 days	Х	Х			Х	
	No Oil	0	Brass	127°C	14 days	Х	Х			Х	
P 1222-d/E)	No Oil	0	Zinc	127°C	14 days	Х	Х			Х	
K-125520(E)	Mineral Oil	80	Al/Cu/Fe	127°C	14 days	Х	Х	Х		Х	Х
	Mineral Oil	80	Brass	127°C	14 days	Х	Х	Х		Х	Х
	Mineral Oil	80	Zinc	127°C	14 days	Х	Х	Х		Х	Х
	No Oil	0	Al/Cu/Fe	127°C	14 days	Х	Х			Х	
	No Oil	0	Brass	127°C	14 days	Х	Х			Х	
R-1224yd(Z)	No Oil	0	Zinc	127°C	14 days	Х	Х			Х	
	Mineral Oil	80	Al/Cu/Fe	127°C	14 days	Х	Х	Х		Х	Х
	Mineral Oil	80	Brass	127°C	14 days	Х	Х	Х		Х	Х
	Mineral Oil	80	Zinc	127°C	14 days	Х	Х	Х		Х	Х

#### Table 4.1: Phase I Test Plan – Low Pressure Refrigerants

Refrigerant	Lubricant	% Lubricant	Metal	Temp.	Duration	Visual Inspection	GC-MS Analysis	TAN	Organic Acids	Anions	ICP
<b>R-514A</b> 25.3% R-1130(E) 74.7% R-1336mzz(Z)	No Oil	0	Al/Cu/Fe	127°C	14 days	x	X			Х	
	No Oil	0	Brass	127°C	14 days	Х	Х			Х	
	No Oil	0	Zinc	127°C	14 days	Х	Х			Х	
	PAG	80	Al/Cu/Fe	127°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Brass	127°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Zinc	127°C	14 days	Х	Х	Х		Х	Х
	POE	80	Al/Cu/Fe	127°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Brass	127°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Zinc	127°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	127°C	14 days	Х	х	Х		Х	Х
	PVE	80	Brass	127°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	127°C	14 days	Х	Х	Х		Х	Х
	No Oil	0	Al/Cu/Fe	175°C	14 days	Х	Х			Х	
R-1336mzz(Z)	No Oil	0	Brass	175°C	14 days	Х	Х			Х	
	No Oil	0	Zinc	175°C	14 days	Х	Х			Х	
	PAG	80	Al/Cu/Fe	175°C	14 days	Х	х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
R-1336mzz(E)	No Oil	0	Al/Cu/Fe	175°C	14 days	Х	Х			Х	
	No Oil	0	Brass	175°C	14 days	Х	х			Х	
	No Oil	0	Zinc	175°C	14 days	Х	Х			Х	
	PAG	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Zinc	175°C	14 days	Х	х	Х		Х	Х
	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	х	Х	Х		Х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	х	Х	Х		Х	Х

#### Table 4.2: Phase I Test Plan – Low Pressure Refrigerants

Table 4.3: Phase	I Test Plan -	- Medium	Pressure	Refrigerants
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Refrigerant	Lubricant	% Lubricant	Metal	Temp.	Duration	Visual Inspection	GC-MS Analysis	TAN	Organic Acids	Anions	ICP
R-1234ze(E)	No Oil	0	Al/Cu/Fe	175°C	14 days	Х	Х			Х	
	No Oil	0	Brass	175°C	14 days	Х	Х			Х	
	No Oil	0	Zinc	175°C	14 days	Х	Х			Х	
	PAG	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
	No Oil	0	Al/Cu/Fe	175°C	14 days	Х	Х			Х	
	No Oil	0	Brass	175°C	14 days	Х	Х			Х	
	No Oil	0	Zinc	175°C	14 days	Х	Х			Х	
	PAG	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
R-450A	PAG	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
42.0% R-134a 58.0% R-1234ze(E)	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
<b>R-515B</b> 8.9% R-227ea 91.1% R-1234ze(E)	No Oil	0	Al/Cu/Fe	175°C	14 days	Х	Х			Х	
	No Oil	0	Brass	175°C	14 days	Х	Х			Х	
	No Oil	0	Zinc	175°C	14 days	Х	Х			Х	
	PAG	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Zinc	175°C	14 days	X	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	х	Х	Х		Х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	х	Х	Х		Х	х
Refrigerant	Lubricant	%	Metal	Temp.	Duration	Visual	GC-MS	TAN	Organic	Anions	ICP
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		Lubricant				Inspection	Analysis		Acids		
	No Oil	0	Al/Cu/Fe	175°C	14 days	Х	Х			Х	
	No Oil	0	Brass	175°C	14 days	Х	Х			Х	
	No Oil	0	Zinc	175°C	14 days	Х	Х			Х	
	PAG	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
P 1224vf	PAG	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
K-1234yi	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
	No Oil	0	Al/Cu/Fe	175°C	14 days	Х	Х			Х	
	No Oil	0	Brass	175°C	14 days	Х	Х			Х	
	No Oil	0	Zinc	175°C	14 days	Х	Х			Х	
	PAG	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
R-513A	PAG	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
44.0% R-134a	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
50.0% K-1234yj	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
	No Oil	0	Al/Cu/Fe	175°C	14 days	Х	Х			Х	
	No Oil	0	Brass	175°C	14 days	Х	Х			Х	
	No Oil	0	Zinc	175°C	14 days	Х	Х			Х	
	PAG	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
D 5164	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
<b>R-310A</b> 77 5% R-1234vf	PAG	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
8.5% R-134a	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
14.0% R-152a	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Zinc	175°C	14 days	х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	х	х	х		х	Х
	PVE	80	Brass	175°C	14 days	х	Х	х		Х	Х
	PVE	80	Zinc	175°C	14 days	х	Х	Х		Х	Х

#### Table 4.4: Phase I Test Plan – Medium Pressure Refrigerants

Refrigerant	Lubricant	% Lubricant	Metal	Temp.	Duration	Visual Inspection	GC-MS Analysis	TAN	Organic Acids	Anions	ICP
	PAG	80	Al/Cu/Fe	175°C	14 days	х	Х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
R-454C	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
21.5% R-32	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
78.5% R-1234yf	POE	80	Zinc	175°C	14 days	х	Х	х	х	х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	х	Х	х		х	Х
	PVE	80	Brass	175°C	14 days	х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	х	Х	х		х	Х
	PAG	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	х	Х	х		х	Х
	PAG	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
R-455A	POE	80	Al/Cu/Fe	175°C	14 days	х	Х	Х	Х	Х	Х
3.0% R-744	POE	80	Brass	175°C	14 days	х	Х	х	х	х	Х
75.5% R-1234yf	POE	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	х	Х	х		х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	х	Х	Х		Х	Х
	PAG	80	Al/Cu/Fe	175°C	14 days	х	Х	х		х	Х
	PAG	80	Brass	175°C	14 days	х	Х	Х		Х	Х
	PAG	80	Zinc	175°C	14 days	х	Х	х		х	Х
R-468A	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
3.5% R-1132a	POE	80	Brass	175°C	14 days	х	Х	Х	Х	Х	Х
75.0% R-1234yf	POE	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х

## Table 4.5: Phase I Test Plan – High Pressure Refrigerants

Refrigerant	Lubricant	% Lubricant	Metal	Temp.	Duration	Visual Inspection	GC-MS Analysis	TAN	Organic Acids	Anions	ICP
	No Oil	0	Al/Cu/Fe	150°C	14 days	Х	X		710100	х	
	No Oil	0	Brass	150°C	14 days	х	Х			Х	
	No Oil	0	Zinc	150°C	14 days	х	Х			Х	
	PAG	80	Al/Cu/Fe	150°C	14 days	х	Х	Х		Х	Х
P 466A	PAG	80	Brass	150°C	14 days	х	х	Х		Х	х
49.0% R-32	PAG	80	Zinc	150°C	14 days	х	Х	Х		Х	Х
11.5% R-125	POE	80	Al/Cu/Fe	150°C	14 days	х	Х	Х	Х	Х	Х
39.5% R-13I1	POE	80	Brass	150°C	14 days	х	х	Х	Х	Х	Х
	POE	80	Zinc	150°C	14 days	х	Х	Х	Х	Х	х
	PVE	80	Al/Cu/Fe	150°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Brass	150°C	14 days	х	х	х		Х	Х
	PVE	80	Zinc	150°C	14 days	Х	Х	Х		Х	Х

## Table 4.6: Phase I Test Plan – High Pressure Refrigerants

Defrigerant	Lubricont	%	Motol	Tomp	Duration	Visual	GC-MS	TAN	Anions	
Keingerant	Lubricant	Lubricant	Ivietai	remp.	Duration	Inspection	Analysis	IAN	AIIIUIIS	ICP
	PAG-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х
	PAG-Additives	80	Brass	175°C	14 days	Х	Х	х	Х	Х
P 1226m77(7)	PAG-Additives	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х
K-15501122(2)	PVE-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х
	PVE-Additives	80	Brass	175°C	14 days	Х	Х	Х	Х	Х
	PVE-Additives	80	Zinc	175°C	14 days	Х	Х	х	Х	Х
	PAG-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х
	PAG-Additives	80	Brass	175°C	14 days	Х	Х	Х	Х	Х
P 1226m77(E)	PAG-Additives	80	Zinc	175°C	14 days	Х	Х	х	Х	Х
K-1330m22(E)	PVE-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х
	PVE-Additives	80	Brass	175°C	14 days	Х	Х	Х	Х	Х
	PVE-Additives	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х
	PAG-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х
	PAG-Additives	80	Brass	175°C	14 days	Х	Х	Х	Х	Х
P 122470(E)	PAG-Additives	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х
K-123428(E)	PVE-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х
	PVE-Additives	80	Brass	175°C	14 days	Х	Х	Х	Х	Х
	PVE-Additives	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х
	PAG-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х
	PAG-Additives	80	Brass	175°C	14 days	Х	Х	Х	Х	Х
D 1224.f	PAG-Additives	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х
R-1234yt	PVE-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х
	PVE-Additives	80	Brass	175°C	14 days	Х	Х	Х	Х	Х
	PVE-Additives	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х
	PAG-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х
	PAG-Additives	80	Brass	175°C	14 days	Х	Х	Х	Х	Х
R-513A	PAG-Additives	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х
44.0% R-134a 56.0% R-1234vf	PVE-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х
50.070 11 12 5 4 4 5	PVE-Additives	80	Brass	175°C	14 days	Х	Х	Х	Х	Х
	PVE-Additives	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х
	PAG-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х
	PAG-Additives	80	Brass	175°C	14 days	Х	Х	Х	Х	Х
R-454C	PAG-Additives	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х
21.5% R-32 78 5% R-1234vf	PVE-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х
70.570 11 12 5 4 4 5	PVE-Additives	80	Brass	175°C	14 days	Х	х	Х	Х	Х
	PVE-Additives	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х
	PAG-Additives	80	Al/Cu/Fe	175°C	14 days	Х	х	Х	Х	Х
5 4694	PAG-Additives	80	Brass	175°C	14 days	Х	Х	Х	Х	Х
R-468A	PAG-Additives	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х
21.5% R-32	PVE-Additives	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	x
75.0% R-1234yf	PVE-Additives	80	Brass	175°C	14 days	Х	Х	Х	Х	х
	PVE-Additives	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х

# Table 4.7: Phase IIA Test Plan – Evaluation of PAG and PVE Lubricant Additives with Select Refrigerants

Refrigerant	Lubricant	% Lubricant	Metal	Temp.	Duration	Visual Inspection	GC-MS Analysis	TAN	Organic Acids	Anions	ICP
	No Oil	0	Al/Cu/Fe	175°C	14 days	Х	Х			Х	
	No Oil	0	Brass	175°C	14 days	Х	Х			Х	
	No Oil	0	Zinc	175°C	14 days	Х	Х			Х	
	PAG	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
D 1520	PAG	80	Zinc	175°C	14 days	х	Х	Х		Х	х
K-152a	POE	80	Al/Cu/Fe	175°C	14 days	х	Х	Х	Х	Х	Х
	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
	No Oil	0	Al/Cu/Fe	175°C	14 days	Х	Х			Х	
	No Oil	0	Brass	175°C	14 days	х	х			Х	
	No Oil	0	Zinc	175°C	14 days	х	Х			Х	
	PAG	80	Al/Cu/Fe	175°C	14 days	х	Х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	х
D 22700	PAG	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
R-227ea	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	х	Х	Х		Х	Х

#### Table 4.8: Phase IIB Test Plan – Evaluation of New Blend Components.

## Table 4.9: Phase IIC Test Plan – Evaluation of R-466A with Additized POE

Refrigerant	Lubricant	% Lubricant	Metal	Temp.	Duration	Visual Inspection	GC-MS Analysis	TAN	Organic Acids	Anions	ICP
	POE-Additives	80	Al/Cu/Fe	150°C	14 days	Х	Х	Х	Х	Х	Х
B-466A	POE-Additives	80	Brass	150°C	14 days	Х	Х	Х	Х	Х	Х
49.0% R-32	POE-Additives	80	Zinc	150°C	14 days	Х	Х	Х	Х	Х	Х
11.5% R-125	POE-Additives	80	Aluminum	150°C	14 days	Х	Х	Х	Х	Х	Х
39.5% R-13I1	POE-Additives	80	Copper	150°C	14 days	Х	Х	Х	Х	Х	Х
	POE-Additives	80	Iron	150°C	14 days	х	Х	Х	Х	Х	Х

Pofrigorant	Lubricant	%	Motal	Tomp	Duration	Visual	GC-MS	TAN	Organic	Anions	
Kenngerant	Lubricant	Lubricant	wietai	remp.	Duration	Inspection	Analysis	TAN	Acids	Anions	ICP
	PAG	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
R-454B	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
68.9% R-32	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
31.1% R-1234yf	POE	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PAG	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х
	POE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х	Х	Х	Х
R-32	POE	80	Brass	175°C	14 days	Х	Х	Х	Х	Х	Х
	POE	80	Zinc	175°C	14 days	Х	Х	Х	Х	Х	Х
	PVE	80	Al/Cu/Fe	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Brass	175°C	14 days	Х	Х	Х		Х	Х
	PVE	80	Zinc	175°C	14 days	Х	Х	Х		Х	Х

## Table 4.10: Phase IID Test Plan – Expanded Evaluation of R-32 and R-1234yf Blends

Refrigerant	Lubricant	% Lubricant	Material	Temp.	Duration	Visual	GC-MS Analysis	TAN	Organic Acids	Anions	ІСР
	No Oil	0	3A	100°C	28 days	Х	X			Х	
	No Oil	0	4A	100°C	28 days	Х	Х			Х	
D (000 1/5)	No Oil	0	AA	100°C	28 days	Х	Х			Х	
R-1233zd(E)	Mineral Oil	80	3A	100°C	28 days	Х	Х	Х		Х	Х
	Mineral Oil	80	4A	100°C	28 days	Х	Х	Х		Х	Х
	Mineral Oil	80	AA	100°C	28 days	Х	Х	Х		Х	Х
	No Oil	0	3A	100°C	28 days	Х	Х			Х	
	No Oil	0	4A	100°C	28 days	Х	Х			Х	
D 4004 (7)	No Oil	0	AA	100°C	28 days	Х	Х			Х	
R-1224yd(2)	Mineral Oil	80	3A	100°C	28 days	Х	Х	Х		Х	Х
	Mineral Oil	80	4A	100°C	28 days	Х	Х	Х		Х	Х
	Mineral Oil	80	AA	100°C	28 days	Х	Х	Х		Х	Х
	No Oil	0	3A	100°C	28 days	Х	Х			Х	
	No Oil	0	4A	100°C	28 days	Х	Х			Х	
	No Oil	0	AA	100°C	28 days	Х	Х			Х	
	PAG-Additives	80	3A	100°C	28 days	Х	Х	Х		Х	Х
	PAG-Additives	80	4A	100°C	28 days	Х	Х	х		Х	Х
R-514A	PAG-Additives	80	AA	100°C	28 days	Х	Х	Х		Х	Х
25.3% R-1130(E) 74 7% R-1336mzz(7)	POE	80	3A	100°C	28 days	Х	Х	Х	Х	Х	Х
74.776 N 15561122(2)	POE	80	4A	100°C	28 days	Х	Х	Х	Х	Х	Х
	POE	80	AA	100°C	28 days	Х	Х	Х	Х	Х	Х
	PVE-Additives	80	3A	100°C	28 days	Х	Х	Х		Х	Х
	PVE-Additives	80	4A	100°C	28 days	Х	Х	Х		Х	Х
	PVE-Additives	80	AA	100°C	28 days	Х	Х	Х		Х	Х
	No Oil	0	3A	100°C	28 days	Х	Х			Х	
	No Oil	0	4A	100°C	28 days	Х	Х			Х	
	No Oil	0	AA	100°C	28 days	Х	Х			Х	
	PAG-Additives	80	3A	100°C	28 days	Х	Х	х		Х	Х
	PAG-Additives	80	4A	100°C	28 days	Х	Х	х		Х	Х
B 1226mzz(7)	PAG-Additives	80	AA	100°C	28 days	Х	Х	х		Х	Х
K-15501122(2)	POE	80	3A	100°C	28 days	Х	Х	х	Х	Х	Х
	POE	80	4A	100°C	28 days	х	Х	х	Х	Х	Х
	POE	80	AA	100°C	28 days	Х	Х	Х	Х	Х	Х
	PVE-Additives	80	3A	100°C	28 days	Х	Х	Х		Х	Х
	<b>PVE-Additives</b>	80	4A	100°C	28 days	Х	Х	х		Х	Х
	<b>PVE-Additives</b>	80	AA	100°C	28 days	Х	Х	х		Х	Х
	No Oil	0	3A	100°C	28 days	Х	Х			Х	
	No Oil	0	4A	100°C	28 days	Х	Х			Х	
	No Oil	0	AA	100°C	28 days	Х	Х			Х	
	PAG-Additives	80	3A	100°C	28 days	Х	Х	Х		Х	Х
	PAG-Additives	80	4A	100°C	28 days	х	Х	Х		х	Х
D 1226	PAG-Additives	80	AA	100°C	28 days	Х	Х	Х		Х	Х
R-1330MZZ(E)	POE	80	3A	100°C	28 days	Х	Х	Х	Х	Х	Х
	POE	80	4A	100°C	28 days	Х	Х	Х	Х	Х	Х
	POE	80	AA	100°C	28 days	Х	Х	Х	Х	Х	Х
	<b>PVE-Additives</b>	80	3A	100°C	28 days	Х	Х	Х		Х	Х
	PVE-Additives	80	4A	100°C	28 days	Х	Х	Х		Х	Х
	<b>PVE-Additives</b>	80	AA	100°C	28 days	х	х	Х		Х	Х

# Table 4.11: Phase IIE Test Plan – Evaluation of Desiccant Materials with Select Refrigerants and Lubricants

Refrigerant	Lubricant	% Lubricant	Material	Temp.	Duration	Visual	GC-MS Analysis	TAN	Organic Acids	Anions	ICP
	No Oil	0	3A	100°C	28 days	Х	Х			Х	
	No Oil	0	4A	100°C	28 days	Х	Х			Х	
	No Oil	0	AA	100°C	28 days	Х	Х			Х	
	PAG-Additives	80	3A	100°C	28 days	Х	Х	Х		Х	Х
	PAG-Additives	80	4A	100°C	28 days	Х	Х	Х		Х	Х
D (224 (5)	PAG-Additives	80	AA	100°C	28 days	Х	Х	Х		Х	Х
K-1234Ze(E)	POE	80	3A	100°C	28 days	Х	Х	Х	Х	Х	Х
	POE	80	4A	100°C	28 days	х	х	Х	Х	Х	Х
	POE	80	AA	100°C	28 days	Х	Х	Х	Х	Х	Х
	PVE-Additives	80	3A	100°C	28 days	х	Х	Х		Х	Х
	PVE-Additives	80	4A	100°C	28 days	Х	Х	Х		Х	Х
	<b>PVE-Additives</b>	80	AA	100°C	28 days	Х	Х	Х		Х	Х
	No Oil	80	3A	100°C	28 days	х	Х			Х	
	No Oil	80	4A	100°C	28 days	Х	Х			Х	
	No Oil	80	AA	100°C	28 days	Х	Х			Х	
	PAG-Additives	80	3A	100°C	28 days	х	Х	Х		Х	Х
	PAG-Additives	80	4A	100°C	28 days	х	х	Х		Х	х
R-515B	PAG-Additives	80	AA	100°C	, 28 days	х	х	х		х	х
8.9% R-227ea	POE	80	3A	100°C	, 28 davs	х	х	х	х	х	х
91.1% R-1234Ze(E)	POF	80	4A	100°C	28 days	X	X	X	X	X	X
	POF	80	AA	100°C	28 days	X	X	X	X	X	X
	PVF-Additives	80	34	100°C	28 days	x	x	x	~	X	x
	PVF-Additives	80	44	100°C	28 days	x	x	x		x	x
	PVE-Additives	80	47	100°C	20 days 28 days	X	X	X		X	X
	No Oil	0	34	100°C	20 days	× ×	× ×	~		x	~
	No Oil	0	3A 4A	100 C	20 uays	×	× ×			×	
	No Oil	0	4A	100 C	20 udys	^ V	^ V			^ V	-
		0		100 C	28 udys	X	X	v		X	V
	PAG-Additives	80	3A	100 C	28 days	X	X	X		X	X
	PAG-Additives	80	4A	100°C	28 days	X	X	X		X	X
R-1234yf	PAG-Additives	80	AA	100°C	28 days	X	X	X		X	X
-	POE	80	3A	100°C	28 days	X	Х	X	Х	Х	X
	POE	80	4A	100°C	28 days	Х	Х	Х	Х	Х	Х
	POE	80	AA	100°C	28 days	Х	Х	Х	Х	Х	Х
	PVE-Additives	80	3A	100°C	28 days	Х	Х	Х		Х	Х
	PVE-Additives	80	4A	100°C	28 days	Х	Х	Х		Х	Х
	PVE-Additives	80	AA	100°C	28 days	Х	Х	Х		Х	Х
	No Oil	80	3A	100°C	28 days	Х	Х			Х	
	No Oil	80	4A	100°C	28 days	X	X			X	
	NO UII	80	AA	100°C	28 days	X	X	v		X	v
	PAG-Additives	80	3A 4 A	100°C	28 days	X	X	X		X	X
R-516A	PAG-Additives	80	4A AA	100°C	28 days	x	X	× ×		X	X
77.5% R-1234yf	POE	80	3A	100°C	28 days	x	X	X	x	X	X
8.5% R-134a 14.0% R-152a	POE	80	4A	100°C	28 davs	x	x	X	X	X	X
	POF	80	ΔΔ	100°C	28 days	x	x	x	x	x	x
	PVF-Additives	80	34	100°C	28 days	x	x	x	~	x	x
	PVF-Additives	80	<u> </u>	100°C	20 days	x	x x	x		X	x x
		00		100°C	20 days	v v	v	v		v	v
	FVL-Additives	80	AA	100 C	zo udys	^	^	^		^	^

# Table 4.12: Phase IIE Test Plan – Evaluation of Desiccant Materials with Select Refrigerants and Lubricants

Refrigerant	Lubricant	%	Material	Temp.	Duration	Visual	GC-MS	TAN	Organic	Anions	ICP
- 0		Lubricant				Inspection	Analysis		Acids		
	PAG-Additives	80	3A	100°C	28 days	Х	Х	Х		Х	Х
	PAG-Additives	80	4A	100°C	28 days	х	Х	Х		Х	Х
	PAG-Additives	80	AA	100°C	28 days	х	Х	Х		Х	Х
R-455A	POE	80	3A	100°C	28 days	х	Х	х	Х	Х	Х
3.0% R-744	POE	80	4A	100°C	28 days	х	Х	Х	Х	Х	Х
75.5% R-1234yf	POE	80	AA	100°C	28 days	Х	Х	Х	Х	Х	Х
	<b>PVE-Additives</b>	80	3A	100°C	28 days	Х	Х	Х		Х	Х
	PVE-Additives	80	4A	100°C	28 days	Х	Х	Х		Х	Х
	PVE-Additives	80	AA	100°C	28 days	Х	Х	Х		Х	Х
	PAG-Additives	80	3A	100°C	28 days	х	Х	Х		Х	Х
	PAG-Additives	80	4A	100°C	28 days	Х	Х	Х		Х	Х
	PAG-Additives	80	AA	100°C	28 days	Х	Х	Х		Х	Х
R-468A	POE	80	3A	100°C	28 days	Х	Х	Х	Х	Х	Х
3.5% R-1132a	POE	80	4A	100°C	28 days	Х	Х	Х	Х	Х	Х
75.0% R-1234yf	POE	80	AA	100°C	28 days	Х	Х	Х	Х	Х	Х
	<b>PVE-Additives</b>	80	3A	100°C	28 days	Х	Х	Х		Х	Х
	PVE-Additives	80	4A	100°C	28 days	Х	Х	Х		Х	Х
	PVE-Additives	80	AA	100°C	28 days	Х	Х	Х		Х	Х
R-466A	POE-Additives	80	3A	100°C	28 days	Х	Х	Х	Х	Х	Х
49.0% R-32	POE-Additives	80	4A	100°C	28 days	Х	Х	Х	Х	Х	Х
11.3% K-125 39 5% R-1311	POE-Additives	80	AA	100°C	28 days	Х	Х	Х	Х	Х	Х

# Table 4.13: Phase IIE Test Plan – Evaluation of Desiccant Materials with Select Refrigerants and Lubricants

# **5. CHEMICAL STABILITY RESULTS**

Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	lron G1095	Aluminum AA380	Brass C260	Zinc ZA8
	Al/Cu/Fe	No Oil	-	-	Tarnished (silver and red discoloration	-	-		
		Mineral Oil	-	-	-	Slight copper plating	-		
R-123	Brass	No Oil	-	Brown ring at liquid line				Copper coloration above liquid line	
		Mineral Oil	-	Faint residue				Dulled/copper coloration	
	7:00	No Oil	-	-					-
	ZINC	Mineral Oil	-	-					-

#### Table 5.1: Appearance Changes for R-123 Phase I Evaluations

'-' indicates no detected change

#### Table 5.2: Pre and Post Exposure Photographs for R-123 Phase I Evaluations

Al/Cu/Fe	Conditions	Brass Co	onditions	Zinc Cor	nditions
100% Refrigerant (left)	, Refrigerant-Oil (right)	100% Refrigerant (left)	, Refrigerant-Oil (right)	100% Refrigerant (left)	, Refrigerant-Oil (right)
Pre-Exposure	Post-Exposure	Pre-Exposure	Post-Exposure	Pre-Exposure	Post-Exposure
VV					

Table 5.3: Appearance	Changes for F	R-1233zd(E) Pha	ase I Evaluations

Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		No Oil	-	-	Slight Darkening	-	-		
	Al/Cu/Fe					Tarnished,			
		Mineral Oil	-	-	-	slight copper	-		
			ļ			plating			1
R-1233zd(E)		No Oil	-	-				-	
	Brass	Mineral Oil	_	_				Dulled/Copper	
_		Winter at Off						coloration	
	Zinc	No Oil	-	-					-
		Mineral Oil	-	-					-

# Table 5.4: Pre and Post Exposure Photographs for R-1233zd(E) Phase I Evaluations



Table 5.5: Appearance	Changes for	R-1224yd(Z)	Phase I	Evaluations
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	lron G1095	Aluminum AA380	Brass C260	Zinc ZA8
R-1224yd(Z)	Al/Cu/Fe	No Oil	-	-	Tarnished (Silver and Red Discoloration)	-	-		
		Mineral Oil	-	-	-	-	-		
	Brass	No Oil	-	-				Slight copper coloration	
		Mineral Oil	-	-				Slight copper coloration	
	7	No Oil	-	-					-
	Zinc	Mineral Oil	-	-					-

# Table 5.6: Pre and Post Exposure Photographs for R-1224yd(Z) Phase I Evaluations



Table 5.7: Appearance Change	for R-514A Phase I Evaluations
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		No Oil	-	Slight dark ring	Slight darkening above liquid line	Slight darkening	-		
	Al/Cu/Fe	PAG	-	-	Slight darkening	Slight darkening	-		
		POE	-	-	Slight yellowing	-	-		
		PVE	-	-	-	-	-		
	Brass	No Oil	-	-				Copper colored below liquid line	
R-514A		PAG	-	-				-	
25.3% R-1130(E) 74.7% R-1336mzz(Z)		POE	-	-				Slight copper coloration	
		PVE	-	-				Slight copper coloration	
		No Oil	-	-					-
	<b>_</b> .	PAG	-	-					Slight darkening
	Zinc	POE	-	-	]				-
		PVE	-	-					Slight darkening

# Table 5.8: Pre and Post Exposure Photographs for R-514A Phase I Evaluations



Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		No Oil	-	-	-	Slight darkening	-		
		PAG	-	-	-	-	-		
	Al/Cu/Fe	POE	Slight yellowing	-	Brassy coloration	Dark tarnish and copper plating	-		
		PVE	-	-	-	-	-		
	Brass	No Oil	-	-				-	
R-1336mzz(Z)		PAG	-	-				Slight copper coloration	
		POE	Slight yellowing	-				Slight copper coloration	
		PVE	-	-				-	
		No Oil	-	-					-
		PAG	-	-					Slight darkening
	Zinc	POE	Slight yellowing	-					Slight darkening
		PVE	-	-					Slight darkening

## Table 5.9: Appearance Changes for R-1336mzz(Z) Phase I Evaluations

'-' indicates no detected change

## Table 5.10: Pre and Post Exposure Photographs for R-1336mzz(Z) Phase I Evaluations



Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	lron G1095	Aluminum AA380	Brass C260	Zinc ZA8
R-1336mzz(Z)		Additized PAG	-	-	-	-	-		
	AI/Cu/Fe	Additized PVE	-	-	-	-	-		
	Brass	Additized PAG	-	-				Dull and darkened	
		Additized PVE	-	-				Dull and darkened	
	Zine	Additized PAG	-	-					-
	Zinc	Additized PVE	-	-					-

Table 5.11: Appearance Changes for R-1336mzz(Z) Phase IIA Evaluations

## Table 5.12: Pre and Post Exposure Photographs for R-1336mzz(Z) Phase IIA Evaluations



Table 5.13: Appearance Changes for R-1336mzz(E) Phase I Evaluations	

Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		No Oil	-	-	-	Slight tarnish	-		
		PAG	-	-	-	-	-		
	AI/Cu/Fe	POE	-	-	-	Slight tarnish	-		
		PVE	-	-	-	-	-		
	5	No Oil	-	-				-	
P 1226m77(E)		PAG	-	-				Slight copper coloration	
K-13301122(E)	DIGSS	POE	Slight yellow	-				Slight copper coloration	
		PVE	-	-				-	
		No Oil	-	-					-
	Zine	PAG	-	-					-
	ZINC	POE	-	-					-
		PVE	-	-					-

# Table 5.14: Pre and Post Exposure Photographs for R-1336mzz(E) Phase I Evaluations

	AI/Cu/Fe Conditions	Brass Conditions	Zinc Conditions			
	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)			
Pre-Exposure						
Post-Exposure						

Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
R-1336mzz(E)		Additized PAG	-	-	-	-	-		
	AI/Cu/Fe	Additized PVE	-	-	-	-	-		
	Brass	Additized PAG	-	-				Dull and Darkened	
		Additized PVE	-	-				Darkened	
	Zinc	Additized PAG	-	-					Slight Darkening
		Additized PVE	-	-					-

Table 5.15: Appearance Changes for R-1336mzz(E) Phase IIA Evaluations

#### Table 5.16: Pre and Post Exposure Photographs for R-1336mzz(E) Phase IIA Evaluations

	Additized PAG Conditions	Additized PVE Conditions
	Al/Cu/Fe, Brass, Zinc (Left to Right)	Al/Cu/Fe, Brass, Zinc (Left to Right)
Pre-Exposure		
Post-Exposure		

Table 5.17: Appearance	Changes for R-1234ze(E)	Phase I Evaluations
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		No Oil	-	-	-	-	-		
	AL/C/E.a	PAG	-	-	-	-	-		
	AI/Cu/Fe	POE	-	-	-	-	-		
		PVE	-	-	-	-	-		
	_	No Oil	-	-				-	]
D 1224-0/F)		PAG	-	-				-	
K-12342e(E)	Brass	POE	-	-				-	
		PVE	-	-				-	
		No Oil	-	-					-
	7:00	PAG	-	-					-
	ZINC	POE	-	-					-
		PVE	-	-					-

# Table 5.18: Pre and Post Exposure Photographs for R-1234ze(E) Phase I Evaluations

	Al/Cu/Fe Conditions	Brass Conditions	Zinc Conditions		
	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)		
Pre-Exposure					
Post-Exposure					

Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		Additized PAG	-	-	-	-	-		
	AI/Cu/Fe	Additized PVE	-	Faint particles	-	-	-		_
D 1324-0/F)	Duese	Additized PAG	-	-				Dull and darkened	
K-12342e(E)	DIdSS	Additized PVE	-	-				-	
		Additized PAG	-	-					-
	ZINC	Additized PVE	-	-					-

## Table 5.19: Visual Observations for R-1234ze(E) Phase IIA Evaluations

'-' indicates no detected change

### Table 5.20: Pre and Post Exposure Photographs for R-1234ze(E) Phase IIA Evaluations



## Table 5.21: Appearance Changes for R-450A Phase I Evaluations

Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	lron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		No Oil	-	-	-	-	-		
		PAG	-	-	-	-	-		
	AI/Cu/Fe	POE	-	-	-	-	-		
		PVE	-	-	-	-	-		_
	Brass	No Oil	-	-				-	
R-450A		PAG	-	-				-	
42.0% R-134a		POE	-	-				-	
58.0% R-1234ze(E)		PVE	-	-				-	
		No Oil	-	-					-
		PAG	-	-					-
	Zinc	POE	Slight Yellowing	-					-
		PVE	-	-					-

'-' indicates no detected change

#### Table 5.22: Pre and Post Exposure Photographs for R-450A Phase I Evaluations

	Al/Cu/Fe Conditions	Brass Conditions	Zinc Conditions
	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)
Pre-Exposure			
Post-Exposure			

## Table 5.23: Appearance Changes for R-515B Phase I Evaluations

Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	lron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		No Oil	-	-	-	-	-		
		PAG	-	-	-	-	-		
	AI/Cu/Fe	POE	-	-	-	-	-		
		PVE	-	-	-	-	-		_
	Brass	No Oil	-	-				-	
R-515B		PAG	-	-				Slightly dulled	
8.9% R-227ea 91.1% R-1234ze(E)		POE	-	-				Slight copper coloration	
		PVE	-	-				-	
		No Oil	-	-					-
		PAG	-	-					-
	ZINC	POE	-	-					-
		PVE	-	-					Slightly dulled

'-' indicates no detected change

## Table 5.24: Pre and Post Exposure Photographs for R-515B Phase I Evaluations

	Al/Cu/Fe Conditions	Brass Conditions	Zinc Conditions
	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)
Pre-Exposure			
Post-Exposure			

Table 5.25: Appearance Changes for R-1234yf Phase I Evaluations	
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	lron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		No Oil	-	-	-	Darkened	-		
		PAG	-	-	-	-	-		
	AI/Cu/Fe	POE	-	-	-	-	-		
		PVE	-	-	-	-	-		
	Brass	No Oil	-	-				-	
		PAG	-	-				Dulled	
R-1234vf		POE	-	-				-	
N-1234y1		PVE	-	-				Slightly dulled	
		No Oil	-	-					-
		PAG	-	-					Slightly darkened/etched
	Zinc	POE	-	-					-
		PVE	-	-					Darkened/ etched

# Table 5.26: Pre and Post Exposure Photographs for R-1234yf Phase I Evaluations

	Al/Cu/Fe Conditions	Brass Conditions	Zinc Conditions
	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)
Pre-Exposure			
Post-Exposure			

Table 5.27:	Appearance	Changes fo	r R-1234yf	Phase	<b>IIA Evaluations</b>
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		Additized PAG	-	-	-	-	-		
	AI/CU/Fe	Additized PVE	-	-	-	-	-		
P 1324.4	Brass	Additized PAG	-	-				Dull and darkened	
K-1254yi		Additized PVE	-	Faint particles				-	
		Additized PAG	-	-					-
	Zinc	Additized PVE	-	-					Slight Darkening

#### Table 5.28: Pre and Post Exposure Photographs for R-1234yf Phase IIA Evaluations

	Additized PAG Conditions	Additized PVE Conditions
	Al/Cu/Fe, Brass, Zinc (Left to Right)	Al/Cu/Fe, Brass, Zinc (Left to Right)
sure		
Pre-Expo		
osure		
Post-Expc		

## Table 5.29: Appearance Changes for R-513A Phase I Evaluations

Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		No Oil	-	-	-	-	-		
		PAG	-	-	-	-	-		
	AI/CU/Fe	POE	-	-	-	-	-		
		PVE	-	-	-	-	-		
	Brass	No Oil	-	-				-	
R-513A		PAG	-	Faint particles				Dulled	
44.0% R-134a		DOE		-				Dulled, copper	
56.0% R-1234yf		FUL	-					coloration	
		PVE	-	-				Slightly dulled	
		No Oil	-	-					-
	7:	PAG	-	-					-
	ZINC	POE	-	-					-
		PVE	-	-					Slightly dulled

'-' indicates no detected change

## Table 5.30: Pre and Post Exposure Photographs for R-513A Phase I Evaluations

	AI/Cu/Fe Conditions	Brass Conditions	Zinc Conditions
	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)
sure			
Pre-Expo	IVII	LLL	ILL
osure			
Post-Expo	YYY		Labora .

	Table 5.31:	Appearance	Changes	for R-513A	Phase IIA	Evaluations
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		Additized PAG	-	-	-	-	-		
	AI/Cu/Fe	Additized PVE	-	-	-	-	-		_
R-513A	Brass	Additized PAG	-	-				Dull and darkened	
44.0% R-134a 56.0% R-1234yf		Additized PVE	-	-				Darkened regions	
	Zinc	Additized PAG	-	-					-
		Additized PVE	-	-					Slight darkening

# Table 5.32: Pre and Post Exposure Photographs for R-513A Phase IIA Evaluations

	Additized PAG Conditions	Additized PVE Conditions
	Al/Cu/Fe, Brass, Zinc (Left to Right)	Al/Cu/Fe, Brass, Zinc (Left to Right)
Pre-Exposure		
Post-Exposure		

Table 5.33:	Appearance	Changes	for R-516/	A Phase I	Evaluations
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	lron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		No Oil	-	-	-	-	-		
	AL/C. /E.	PAG	-	-	-	-	-		
	AI/Cu/Fe	POE	-	-	-	-	-		
		PVE	-	-	-	-	-		
	Brass	No Oil	-	-				-	
R-516A		PAG	-	-				Slightly dulled	
77.5% R-1234yf 8.5% R-134a 14.0% R-152a		POE	-	-				Slight copper coloration	
		PVE	-	-				-	
		No Oil	-	-					-
	7:00	PAG	-	-				Į	-
	ZINC	POE	-	-					-
		PVE	-	-				Ī	-

# Table 5.34: Pre and Post Exposure Photographs for R-516A Phase I Evaluations

	AI/Cu/Fe Conditions	Brass Conditions	Zinc Conditions
	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)
Pre-Exposure			
Post-Exposure			

Table 5.35: Appearance	Changes for R	-454B Phase IID	<b>Evaluations</b>
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		PAG	-	-	-	-	-		
	Al/Cu/Fe	POE	-	-	-	-	-		
		PVE	-	-	-	-	-		
	Brass	PAG	-	-				Dulled and darkened	
R-454B		POE	-	-				Darker yellow	
68.9% R-32 31.1% R-1234yf		PVE	-	-				Dulled and darkened	
		PAG	-	-					-
	Zinc	POE	-	-					-
		PVE	-	-					Dull and darkened

#### Table 5.36: Pre and Post Exposure Photographs for R-454B Phase IID Evaluations

	Al/Cu/Fe Conditions	Brass Conditions	Zinc Conditions		
	PAG, POE, PVE (Left to Right)	PAG, POE, PVE (Left to Right)	PAG, POE, PVE (Left to Right)		
Pre-Exposure					
Post-Exposure					

Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		PAG	-	-	-	-	-		
	Al/Cu/Fe	POE	-	-	-	Slightly darkened	-		
		PVE	-	-	-	-	-		
	Brass	PAG	-	-				-	
R-454C		POE	-	-				-	
21.5% R-32		PVE	-	-				-	
78.5% R-1234yf	Zinc	PAG	-	-					Slight darkening
		POE	-	-					Slight darkening
		PVE	-	-					Slight darkening

# Table 5.38: Pre and Post Exposure Photographs for R-454C Phase I Evaluations

	AI/Cu/Fe Conditions	Brass Conditions	Zinc Conditions
	PAG, POE, PVE (Left to Right)	PAG, POE, PVE (Left to Right)	PAG, POE, PVE (Left to Right)
Pre-Exposure			
Post-Exposure			

Table 5.39: Appearance	<b>Changes</b> for	R-454C Phase	<b>IIA Evaluations</b>
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		Additized PAG	-	-	-	-	-		
	AI/Cu/Fe	Additized PVE	-	-	-	-	-		_
R-454C	Brass	Additized PAG	-	-				Dull and darkened	
21.5% R-32 78.5% R-1234vf		Additized PVE	-	-				-	
	Zinc	Additized PAG	-	-					Slight darkening
		Additized PVE	-	-					-

# Table 5.40: Pre and Post Exposure Photographs for R-454C Phase IIA Evaluations

	Additized PAG Conditions	Additized PVE Conditions
	Al/Cu/Fe, Brass, Zinc (Left to Right)	Al/Cu/Fe, Brass, Zinc (Left to Right)
Pre-Exposure		
Post-Exposure		

Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		PAG	-	-	-	-	-		
	Al/Cu/Fe	POE	-	-	-	-	-		
		PVE	-	-	-	-	-		
P-455A		PAG	-	-				Slight copper coloration	
3.0% R-744	Brass	POE	-	-				Slightly dulled	
21.5% R-32 75.5% R-1234yf		PVE	-	-				Slight copper coloration	
	Zinc	PAG	-	-					-
		POE	-	-				Ĭ	Slight darkening
		PVE	-	-					-

# Table 5.42: Pre and Post Exposure Photographs for R-455A Phase I Evaluations

	Al/Cu/Fe Conditions	Brass Conditions	Zinc Conditions		
	PAG, POE, PVE (Left to Right)	PAG, POE, PVE (Left to Right)	PAG, POE, PVE (Left to Right)		
Pre-Exposure					
Post-Exposure					

Table 5.43: Appearance	<b>Changes</b>	for R-468A	Phase I	Evaluations
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	lron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		PAG	Faint pale yellow	-	-	-	-		
	Al/Cu/Fe	POE	Faint pale yellow	-	-	-	-		
		PVE	Faint pale yellow	-	-	-	-		_
R-468A	Brass	PAG	Faint pale yellow	Faint particles				Dulled	
3.5% R-1132a		POE	Faint pale yellow	-				-	
21.5% R-32		PVE	Faint pale yellow	-				Slightly dulled	
75.0% R-1234yj		PAG	Faint pale yellow	Faint particles					Slightly pitted
	Zinc	POE	Faint pale yellow	-					-
	ZINC	PVE	Faint pale yellow	-					Slightly darkened

# Table 5.44: Pre and Post Exposure Photographs for R-468A Phase I Evaluations



Table 5.4	5: Appearance	<b>Changes</b>	for R-468A	Phase IIA	Evaluations
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	lron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		Additized PAG	-	-	-	-	-		
<b>R-468A</b> 3.5% R-1132a 21.5% R-32 75.0% R-1234yf	AI/Cu/re	Additized PVE	-	Light particles	-	-	-		
	Brass	Additized PAG	-	-				Dull and darkened	
		Additized PVE	-	Light particles				Darkened	
	Zinc	Additized PAG	-	-					-
		Additized PVE	-	Light particles					-

## Table 5.46: Pre and Post Exposure Photographs for R-468A Phase IIA Evaluations



Table 5.47: Appearan	ce Changes for R-	466A Phase I Evaluations
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	lron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		No Oil	-	-	Dulled	-	-		
		PAG	Black, thicken	ed oil, film coati	ng all surfaces	s. Unable to a	assess metals.		
	Al/Cu/Fe	POE	Pale Color	Faint particulates	Chalky, dulled	-	-		
		PVE	Black, thicken	ed oil, film coati	ng all surfaces	s. Unable to a	assess metals.		
	Brass	No Oil	-	-				Dulled, copper coloration	
<b>R-466A</b> 49.0% R-32		PAG	Dark Orange	-				Significantly dulled	
11.5% R-125 39.5% R-1311		POE	Pale Color	Faint particulates				Chalky, dulled, copper coloration	
		PVE	Light Orange	-				Chalky, dulled	
		No Oil	-	-					-
		PAG	Brown	Opaque					Dulled
	Zinc	POE	Pale Color	-					Slightly darkened
		PVE	Light Orange	-					Dulled

# Table 5.48: Pre and Post Exposure Photographs for R-466A Phase I Evaluations



Table 5.49: Appearance	Changes for	R-466A Phase	<b>IIC Evaluations</b>
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Refrigerant	Lubricant	Material	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		Al/Cu/Fe	-	-	Dulled/Hazy	-			
		Brass	-	-				-	
<b>R-466A</b> 49.0% R-32	Additized	Zinc	-	-					-
11.5% R-125	POE	Aluminum	-	-			-	-	
59.5% N-1511		Copper	-	Faint particles	Dulled/Hazy			-	
		Iron	-	-		-			

#### Table 5.50: Pre and Post Exposure Photographs for R-466A Phase IIC Evaluations



Table 5.51:	Appearance	Changes fo	or R-32	Phase	IID	Evaluations
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper Coupon	Iron Coupon	Aluminum Coupon	Brass Coupon	Zinc Coupon
		PAG	-	Faint particles	-	-	-		
	Al/Cu/Fe	POE	-	-	-	-	-		
		PVE	-	-	-	-	-		
	Brass	PAG	-	Faint particles				-	
R-32		POE	-	-				Slight copper coloration	
		PVE	-	-				-	
	Zinc	PAG	-	-					Faint spots
		POE	-	-					Fain spots
		PVE	-	-					Faint darkening

# Table 5.52: Pre and Post Exposure Photographs for R-32 Phase IID Evaluations



Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260
		No Oil	-	-	-	-	-	
	Al/Cu/Fe	PAG	-	Faint dark particles	-	-	-	
	Brass	POE	Pale yellow	-	-	-	-	
		PVE	-	-	-	-	-	
R-152a		No Oil	-	-				Slight copper coloration
		PAG	-	Faint dark particles				-
		POE	Pale yellow	-				Slight copper coloration
		PVE	-	-				-

# Table 5.54: Pre and Post Exposure Photographs for R-152a Phase IIB Evaluations


Table 5.55: Appearance	Changes fo	r R-152a Pha	se IIB Evaluations
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Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Zinc ZA8
		No Oil	Variation – Clear to Brown	-	Variation – Dark Spotting – light heavy amounts
D 152-	Zinc	PAG	-	Small Amount of Grey Particles	Heavy amount of Dark Spotting
K-152a		POE	Variation – Pale to Brown	Variation – Light to heavy particles	Variation – Heavy Dark Spotting to loss of material
		PVE	Variation – No Change to Yellow	Light Particles	Variation – Dark Spotting – light and heavy amounts

#### Table 5.56: Pre and Post Exposure Photographs for R-152a Phase IIB Evaluations



Table 5.57: Appearance Changes for R-227ea Phase IIB Evaluations

Refrigerant	Metal	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Copper CDA 110	Iron G1095	Aluminum AA380	Brass C260	Zinc ZA8
		No Oil	-	-	-	-	-		
		PAG	-	-	-	-	-		
	AI/Cu/Fe	POE	-	Faint film	-	-	-		
		PVE	-	-	-	-	-		
		No Oil	-	-				Slightly dulled	
	Brass	PAG	-	-				-	
R-227ea		POE	-	-				Coppered and hazy	
		PVE	-	-				-	
		No Oil	-	-					-
	7	PAG	-	Faint particles				Ĭ	-
	ZINC	POE	-	-				ĺ	-
		PVE	-	-				Ì	-
'-'indicates no d	detected cha	ange							

## Table 5.58: Pre and Post Exposure Photographs for R-227ea Phase IIB Evaluations

	AI/Cu/Fe Conditions	Brass Conditions	Zinc Conditions
	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)
Pre-Exposure			
Post-Exposure			

Refrigerant	Lubricant	Metal	Inorgani (ppm in re	c Anions efrigerant)	TAN mg	Lubricant Organic (ppm, ug/g		c Acids ;)	Dissolved Elements in Lubricant (ppm)							
			Fluoride	Chloride	KOH/ g oil	Valeric	Heptanoic	Branched Nonanoic	AI	Cu	Fe	Zn	Si			
		Al/Cu/Fe	<10	<10												
R-123	No Oil	Brass	<10	<10												
N 125		Zinc	<10	<10												
127°C		Al/Cu/Fe	<10	114	<0.05				<3	<1	<1	<1	<3			
14 days	Mineral Oil	Brass	<10	258	<0.05				<3	<1	<1	<1	<3			
		Zinc	<10	242	<0.05				<3	<1	<1	<1	<3			
		Al/Cu/Fe	<10	<10												
R-1233zd(F)	No Oil	Brass	<10	<10												
		Zinc	<10	<10												
127°C		Al/Cu/Fe	<10	60	<0.05				<3	<1	<1	<1	<3			
14 days	Mineral Oil	Brass	<10	<10	<0.05				<3	<1	<1	<1	<3			
		Zinc	<10	<10	<0.05				<3	<1	<1	<1	4			
		Al/Cu/Fe	<10	<10												
R-1224vd(7)	No Oil	Brass	<10	<10												
		Zinc	<10	<10												
127°C		Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	<3			
14 days	Mineral Oil	Brass	<10	<10	<0.05				<3	<1	<1	<1	<3			
		Zinc	<10	<10	<0.05				<3	<1	<1	<1	<3			

## Table 5.59: Summary of Analytical Results of Aged Sealed Tubes, R-123, R-1233zd(E), R-1224yd(Z)

Inorganic Anions TAN Lubricant Organic Acids							<b>Dissolved Elements in</b>						
Refrigerant	Lubricant	Metal	(ppm in re	efrigerant)	mg		(ppm, ug	/g)		Lubri	icant (	ppm)	
			Fluoride	Chloride	KOH/ g oil	Valeric	Heptanoic	Branched Nonanoic	AI	Cu	Fe	Zn	Si
		Al/Cu/Fe	<10	15									
	No Oil	Brass	<10	<10									
		Zinc	<10	<10									
		Al/Cu/Fe	<10	11	<0.05				<3	<1	<1	<1	<3
R-514A	PAG	Brass	<10	12	<0.05				<3	<1	<1	1	<3
25.3% R-1130(E) 74 7% R-1336mzz(7)		Zinc	<10	<10	<0.05				<3	<1	<1	1	<3
,,		Al/Cu/Fe	<10	10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
127°C	POE	Brass	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	1	<3
14 days		Zinc	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	2	<3
		Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	6
	PVE	Brass	13	45	<0.05				<3	<1	<1	10	<3
		Zinc	<10	13	<0.05				<3	<1	<1	1	3
		Al/Cu/Fe	<10	<10									
	No Oil	Brass	<10	<10									
		Zinc	<10	<10									
		Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	<3
	PAG	Brass	11	<10	0.05				<3	<1	<1	<1	<3
		Zinc	<10	<10	<0.05				<3	<1	<1	2	<3
	م ما ما نه : – م ما	Al/Cu/Fe	11	<10	<0.05				<3	<1	<1	<1	<3
R-1336mzz(Z)	Additized	Brass	32	<10	<0.05				<3	<1	<1	<1	<3
	PAG	Zinc	13	<10	<0.05				<3	<1	<1	<1	3
175°C		Al/Cu/Fe	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
14 days	POE	Brass	<10	<10	0.06	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
		Zinc	<10	<10	0.20	<200 <sup>ND</sup>	240	<200 (~80 <sup>A</sup> )	<3	<1	<1	49	<3
	PVE	Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	12
		Brass	17	<10	<0.05				<3	<1	<1	<1	12
		Zinc	27	<10	0.05				<3	<1	<1	<1	8
	Additized	Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	11
	Additized	Brass	12	<10	<0.05				<3	<1	<1	<1	9
	FVL	Zinc	<10	<10	<0.05				<3	<1	<1	<1	6
		Al/Cu/Fe	<10	<10									
	No Oil	Brass	<10	<10									
		Zinc	<10	<10									
		Al/Cu/Fe	11	<10	<0.05				<3	<1	<1	<1	<3
	PAG	Brass	10	<10	<0.05				<3	<1	<1	<1	<3
		Zinc	<10	<10	<0.05				<3	<1	<1	<1	<3
	Additized	Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	<3
	PAG	Brass	13	<10	<0.05				<3	<1	<1	<1	<3
R-1336mzz(E)	17.6	Zinc	<10	<10	<0.05			п	<3	<1	<1	<1	<3
175°C		Al/Cu/Fe	<10	<10	0.08	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
14 days	POF	Brass	<10	<10	0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
		Zinc	<10	<10	0.22	<200 <sup>ND</sup>	<200 (~170 <sup>A</sup> )	<200 <sup>ND</sup>	<3	<1	<1	30	4
		Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	<3
	PVE	Brass	18	<10	<0.05	1			<3	<1	<1	<1	14
		Zinc	<10	<10	<0.05	1			<3	<1	<1	<1	3
	A 1 100 - 2	Al/Cu/Fe	<10	<10	<0.05	1			<3	<1	<1	<1	6
	Additized	Brass	<10	<10	<0.05	1			<3	<1	<1	<1	7
	PVE	Zinc	<10	<10	<0.05	1			<3	<1	<1	<1	8

## Table 5.60: Summary of Analytical Results of Aged Sealed Tubes, R-514A, R-1336mzz(Z), R-1336mzz(E)

			Inorgani	c Anions	TAN	Lubr	ricant Organic	Acids	[	Dissolv	ed Eler	nents i	n
Refrigerant	Lubricant	Metal	(ppm in re	efrigerant)	mg		(ppm, ug/g)			Lubr	icant (	ppm)	
nemgerunt	Lubricant	meta	Fluoride	Chloride	KOH/ g oil	Valeric	Heptanoic	Branched Nonanoic	AI	Cu	Fe	Zn	Si
		Al/Cu/Fe	<10	<10									
	No Oil	Brass	<10	<10									
Refrigerant         R-1234ze(E)         175°C         14 days         R-450A         42.0% R-1340         58.0% R-1234ze(E)         175°C         14 days         R-515B         8.9% R-227ea         91.1% R-1234ze(E)         175°C         14 days		Zinc	<10	<10									
		Al/Cu/Fe	<10	<10	< 0.05				<3	<1	<1	<1	<3
	PAG	Brass	<10	<10	< 0.05				<3	<1	<1	<1	<3
		Zinc	<10	<10	< 0.05				<3	<1	<1	<1	4
		Al/Cu/Fe	<10	<10	< 0.05				<3	<1	<1	<1	<3
R-123470(F)	Additized	Brass	12	<10	< 0.05				<3	<1	<1	<1	<3
N-12342C(L)	PAG	Zinc	<10	<10	< 0.05				<3	<1	<1	<1	<3
175°C		Al/Cu/Fe	<10	<10	< 0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	3
14 days	505	Brass	<10	<10	< 0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	4
	POE	Zinc	10	<10	0.20	<200 <sup>ND</sup>	<200 (~140 <sup>A</sup> )	<200 <sup>ND</sup>	<3	<1	<1	74	<3
		Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	8
	PVE	Brass	<10	<10	< 0.05				<3	<1	<1	<1	7
		Zinc	<10	<10	< 0.05				<3	<1	<1	<1	<3
		Al/Cu/Fe	<10	<10	< 0.05				<3	<1	<1	<1	11
	Additized	Brass	<10	<10	< 0.05				<3	<1	<1	<1	12
	PVE	Zinc	<10	<10	< 0.05				<3	<1	<1	<1	9
		Al/Cu/Fe	<10	<10					1				
	No Oil	Brass	<10	<10									
		Zinc	<10	<10									
	PAG	Al/Cu/Fe	<10	<10	0.06	]			<3	<1	<1	<1	<3
R-450A		Brass	<10	<10	< 0.05	-			<3	<1	<1	<1	<3
<b>R-450A</b> 42.0% R-134a		Zinc	<10	<10	<0.05				<3	<1	<1	<1	<3
58.0% R-1234ze(E)		Al/Cu/Fe	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	3
175°C		Brass	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
14 days	POE	Zinc	<10	<10	0.21	<200 <sup>ND</sup>	<200 (~130 <sup>A</sup> )	<200 <sup>ND</sup>	<3	<1	<1	48	<3
		Al/Cu/Fe	<10	<10	0.07				<3	<1	<1	<1	7
	PVE	Brass	<10	<10	0.07	1			<3	<1	<1	<1	5
		Zinc	<10	<10	< 0.05				<3	<1	<1	<1	12
		Al/Cu/Fe	<10	<10									
	No Oil	Brass	<10	<10									
		Zinc	<10	<10									
	DAG	Al/Cu/Fe	13 (<10 <sup>B</sup> )	<10	<0.05				<3	<1	<1	<1	4
R-515B	PAG	Brass	<10	<10	<0.05				<3	<1	<1	<1	<3
8.9% R-227ea		Zinc	<10	<10	<0.05				<3	<1	<1	1	<3
91.1% R-1234ze(E)		Al/Cu/Fe	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	3
175°C	POF	Brass	<10	<10	0.10	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	8	4
175°C 14 days		Zinc	58 (25 <sup>в</sup> )	<10	0.17	<200 <sup>ND</sup>	<200 (~90 <sup>A</sup> )	<200 <sup>ND</sup>	<3	<1	<1	17	5
	DVE	Al/Cu/Fe	23 (<10 <sup>B</sup> )	<10	<0.05				<3	<1	<1	<1	7
	"VE	Brass	<10	<10	<0.05				<3	<1	<1	<1	5
		Zinc	<10	<10	<0.05				<3	<1	<1	<1	<3

## Table 5.61: Summary of Analytical Results of Aged Sealed Tubes, R-1234ze(E), R-450A, R-515B

<sup>A</sup>Organic acids were detected at concentrations lower than the verified quantitation limit. Results are reported for informational purposes.

<sup>B</sup>Repeated measurements

NDNot Detected

Defrigerent	Lubricont	Matal	Inorgani (ppm in re	c Anions efrigerant)	TAN	Lub	ricant Organic / (ppm. ug/g)	Acids	Dissolved Elements in Lubricant (ppm)					
Kenngerant	Lubricant	weta	Fluoride	Chloride	KOH/ g oil	Valeric	Heptanoic	Branched Nonanoic	AI	Cu	Fe	Zn	Si	
		Al/Cu/Fe	<10	<10	-							.1		
	No Oil	Brass	<10	<10										
		Zinc	<10	<10										
		Al/Cu/Fe	78	<10	<0.05	]			<3	<1	<1	<1	7	
	PAG	Brass	34	<10	0.06				<3	<1	<1	<1	3	
		Zinc	33	<10	<0.05				<3	<1	<1	1	6	
	A -1 -1:4:	Al/Cu/Fe	28	<10	<0.05				<3	<1	<1	<1	4	
R-1234vf	Additized	Brass	44	<10	<0.05				<3	<1	<1	<1	5	
N-1234y1	PAG	Zinc	36	<10	<0.05				<3	<1	<1	<1	<3	
175°C		Al/Cu/Fe	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3	
14 days	POE	Brass	<10	<10	0.07	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	12	<3	
		Zinc	<10	<10	0.10	<200 <sup>ND</sup>	<200 (~80 <sup>A</sup> )	<200 <sup>ND</sup>	<3	<1	<1	37	<3	
		Al/Cu/Fe	60	<10	0.07				<3	<1	<1	<1	14	
	PVE	Brass	49	<10	0.06				<3	<1	<1	<1	4	
		Zinc	44	<10	0.06				<3	<1	<1	<1	7	
	Additized	Al/Cu/Fe	<10	<10	0.10				<3	<1	<1	<1	6	
		Brass	<10	<10	<0.05				<3	<1	<1	<1	31	
	r V L	Zinc	<10	<10	0.07				<3	<1	<1	<1	4	
	No Oil	Al/Cu/Fe	<10	<10										
		Brass	<10	<10										
		Zinc	<10	<10		_								
		Al/Cu/Fe	89	12	0.06				<3	<1	<1	1	7	
	PAG	Brass	51	<10	0.06				<3	<1	<1	1	5	
		Zinc	11	<10	0.07				<3	<1	<1	3	5	
	Additized	Al/Cu/Fe	16	<10	<0.05				<3	<1	<1	<1	<3	
D F124	PAG	Brass	32	<10	<0.05				<3	<1	<1	<1	<3	
<b>R-513A</b> 44.0% R-134a	17.0	Zinc	18	<10	<0.05				<3	<1	<1	<1	<3	
56.0% R-1234yf		Al/Cu/Fe	<10	<10	0.06	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	1	<1	<1	5	
175°C 14 days	POE	Brass	<10	<10	0.16	<200 <sup>ND</sup>	<200 (~110 <sup>A</sup> )	<200 <sup>ND</sup>	<3	<1	<1	53	<3	
1.00,0		Zinc	<10	<10	0.22	<200 <sup>ND</sup>	<200 (~120 <sup>A</sup> )	<200 (~80 <sup>A</sup> )	4	<1	<1	65	<3	
		Al/Cu/Fe	51	<10	<0.05		· ·		<3	<1	<1	<1	7	
	PVE	Brass	13	<10	<0.05	1			<3	<1	<1	<1	4	
		Zinc	<10	<10	0.05	1			<3	<1	<1	<1	<3	
		Al/Cu/Fe	<10	<10	<0.05	1			<3	<1	<1	<1	5	
	Additized	Brass	<10	<10	<0.05	1			<3	<1	<1	<1	4	
	PVE -	Zinc	<10	<10	0.05				<3	<1	<1	<1	5	

## Table 5.62: Summary of Analytical Results of Aged Sealed Tubes, R-1234yf, R-513A

Refrigerant	Lubricant	Metal	Inorgani (ppm in re	c Anions efrigerant)	TAN mg	Lub	cids	Dissolved Elements in Lubricant (ppm)						
henigerant	Lubricant	meta	Fluoride	Chloride	KOH/ g oil	Valeric	Heptanoic	Branched Nonanoic	AI	Cu	Fe	Zn	Si	
		Al/Cu/Fe	<10	<10										
	No Oil	Brass	<10	<10										
		Zinc	<10	<10		_								
R-516A		Al/Cu/Fe	22	<10	<0.05				<3	<1	<1	<1	<3	
<b>R-516A</b> 77.5% R-1234yf 8.5% R-134a	PAG	Brass	11	<10	<0.05				<3	<1	<1	<1	<3	
8.5% R-134a		Zinc	<10	<10	0.05				<3	<1	<1	1	3	
14.0% R-152a		Al/Cu/Fe	<10	<10	0.10	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3	
175°C	POE	Brass	<10	<10	0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	1	4	
14 days		Zinc	<10	<10	0.15	<200 <sup>ND</sup>	<200 (~150 <sup>A</sup> )	<200 <sup>ND</sup>	<3	<1	<1	50	<3	
		Al/Cu/Fe	14	<10	<0.05				<3	<1	<1	<1	6	
	PVE	Brass	13	<10	<0.05				<3	<1	<1	<1	16	
		Zinc	50	<10	0.05				<3	<1	<1	<1	11	

				Inorganic Anions		Lul	cids	Dissolved Elements in					
Refrigerant	Lubricant	Metal	(ppm in re	efrigerant)	mg KOH/ g		(ppm, ug/g)	Branched		Lubr	icant	(ppm)	
			Fluoride	Chloride	oil	Valeric	Heptanoic	Nonanoic	AI	Cu	Fe	Zn	Si
Refrigerant         R-454B         68.9% R-32         31.1% R-1234yf         175°C         14 days		Al/Cu/Fe	35	<10	0.06	-			<3	<1	<1	<1	6
	PAG	Brass	27	<10	<0.05	-			<3	<1	<1	<1	5
		Zinc	<10	<10	<0.05		Γ	[	<3	<1	<1	1	3
<b>K-454B</b> 68.9% R-32		Al/Cu/Fe	<10	<10	0.08	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
31.1% R-1234yf	POE	Brass	<10	<10	0.16	<200 <sup>ND</sup>	<200 (~90 <sup>A</sup> )	<200 <sup>ND</sup>	<3	<1	<1	10	<3
175°C 14 days		Zinc	<10	<10	0.28	<200 (~80 <sup>A</sup> )	<200 (~160 <sup>A</sup> )	<200 (~100 <sup>A</sup> )	<3	<1	<1	46	<3
		Al/Cu/Fe	29	<10	0.05	_			<3	<1	<1	<1	6
	PVE	Brass	19	<10	<0.05	_			<3	<1	<1	<1	11
		Zinc	39	<10	<0.05				<3	<1	<1	<1	28
		Al/Cu/Fe	104	<10	0.06	_			<3	<1	<1	<1	12
	PAG	Brass	17	<10	0.06				<3	<1	<1	<1	12
		Zinc	57	<10	0.05				<3	<1	<1	2	8
	A 1 1999 1	Al/Cu/Fe	22	<10	0.08				<3	<1	<1	<1	<3
	Additized	Brass	33	<10	0.07				<3	<1	<1	<1	<3
	FAU	Zinc	28	<10	0.07				<3	<1	<1	<1	<3
R-454C	POF	Al/Cu/Fe	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
<b>R-454C</b> 21.5% R-32 78.5% R-1234yf		Brass	<10	<10	0.22	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	27	<3
175°C 14 days	102	Zinc	<10	<10	0.27	<200 (~100 <sup>A</sup> )	<200 (~170 <sup>A</sup> )	<200 (~120 <sup>A</sup> )	13	<1	<1	206	3
		Al/Cu/Fe	15	<10	<0.05				<3	<1	<1	<1	17
	PVE	Brass	39	<10	<0.05				<3	<1	<1	<1	17
		Zinc	48	<10	<0.05				<3	<1	<1	<1	6
		Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	24
	Additized	Brass	<10	<10	<0.05				<3	<1	<1	<1	7
	PVE	Zinc	<10	<10	0.05				<3	<1	<1	<1	5
		Al/Cu/Fe	17	<10	<0.05				<3	<1	<1	2	3
	PAG	Brass	20	<10	<0.05				<3	<1	<1	3	3
R-455A		Zinc	<10	<10	<0.05				<3	<1	<1	1	<3
3.0% R-744		Al/Cu/Fe	<10	<10	0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	6
21.5% К-32 75.5% R-1234yf	POE	Brass	<10	<10	0.13	<200 <sup>ND</sup>	<200 (~80 <sup>A</sup> )	<200 <sup>ND</sup>	<3	<1	<1	28	<3
175°C		Zinc	<10	<10	0.13	<200 <sup>ND</sup>	<200 (~110 <sup>A</sup> )	<200 <sup>ND</sup>	<3	<1	<1	54	9
14 days		Al/Cu/Fe	17	<10	<0.05				<3	<1	<1	<1	<3
	PVE	Brass	25	<10	<0.05				<3	<1	<1	<1	12
		Zinc	19	<10	<0.05	1			<3	<1	<1	<1	<3

Table 5.64: Summary of Analytical Results of Aged Sealed Tubes, R-454B, R-454C, R-455A

			Inorgani	c Anions	TAN	Lub	oricant Organ	ic Acids	Dissolved Elements in					
Refrigerant	Lubricant	Metal	(ppm in re	efrigerant)	mg		g)	Lubricant (ppm)						
			Fluoride	Chloride	KOH/ g oil	Valeric	Heptanoic	Branched Nonanoic	AI	Cu	Fe	Zn	Si	
		Al/Cu/Fe	179	<10	<0.05				<3	<1	<1	<1	12	
	PAG	Brass	143	<10	<0.05				<3	<1	<1	<1	19	
		Zinc	197	<10	0.05				<3	<1	<1	3	31	
		Al/Cu/Fe	40	<10	<0.05				<3	<1	<1	<1	4	
	Additized PAG	Brass	52	<10	<0.05				<3	<1	<1	<1	6	
R-468A	170	Zinc	37	<10	<0.05				<3	<1	<1	<1	7	
<b>R-468A</b> 3.5% R-1132a	POE	Al/Cu/Fe	<10	<10	0.10	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3	
21.5% R-32 75.0% R-1234vf		Brass	<10	<10	0.08	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	4	3	
175°C		Zinc	169	<10	0.27	<200 <sup>ND</sup>	<200 (~170 <sup>A</sup> )	<200 (~110 <sup>A</sup> )	<3	<1	<1	59	10	
14 days		Al/Cu/Fe	84	<10	<0.05				<3	<1	<1	<1	7	
	PVE	Brass	54	<10	<0.05				<3	<1	<1	<1	9	
		Zinc	111	<10	<0.05				<3	<1	<1	<1	11	
-	4 dd:t:= = = d	Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	11	
	PVF	Brass	<10	<10	<0.05				<3	<1	<1	<1	8	
	PVE	Zinc	<10	<10	0.17				<3	<1	<1	<1	10	

## Table 5.65: Summary of Analytical Results of Aged Sealed Tubes, R-468A

<b>R-466A</b> 49.0% R-32 11.5% R-125 39.5% R-1311 150°C	Lubricant	Metal	Inorganic Anions (ppm in refrigerant)			TAN mg	TAN Lubricant Organic Acid mg (ppm, ug/g)				Dissolved Elements in Lubricant (ppm)					
nenigerant	Labricant	inclu	Fluoride	Chloride	Iodide	KOH/ g oil	Valeric	Heptanoic	Branched Nonanoic	AI	Cu	Fe	Zn	Si		
		Al/Cu/Fe	<10	<10	<100											
	No Oil	Brass	<10	<10	<100											
		Zinc	<10	<10	<100											
		Al/Cu/Fe	598	<10	2070											
	PAG	Brass	937	<10	10174			٦	lot Tested	A						
		Zinc	1531	<10	14063											
		Al/Cu/Fe	61	<10	165	0.09	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	7		
<b>R-466A</b>	POE	Brass	212	<10	366	0.89	270	590	400	<3	<1	<1	104	9		
11.5% R-125		Zinc	2210	<10	13246			١	lot Tested	A						
39.5% R-13/1		Aluminum	<10	<10	<100	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3		
150°C 14 days		Copper	14	<10	<100	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3		
	Additized	Iron	<10	<10	<100	0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3		
	POE	Al/Cu/Fe	<10	<10	<100	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3		
		Brass	<10	<10	<100	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3		
		Zinc	<10	<10	<100	0.70	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	1	3		
		Al/Cu/Fe					Not	Tested <sup>A</sup>								
	PVE	Brass	411	<10	414	0.47				<3	<1	<1	125	48		
		Zinc	734	<10	2261			٦	lot Tested	A						

#### Table 5.66: Summary of Analytical Results of Aged Sealed Tubes, R-466A

<sup>A</sup>Several conditions were not tested, either based on reaction severity indicated in visual observations, or significant reactivity determined from Anion evaluation that was used as a screening step.

<sup>ND</sup>Not Detected

			Inorgani	c Anions	TAN	Lubr	icant Organic	Acids	0	Dissolv	ed Eler	nents	in
Refrigerant	Lubricant	Metal	(ppm in r	efrigerant)	mg KOH/g		(ppm, ug/g)	Branched		Lubr	icant (	ppm)	
			Fluoride	Chloride	oil	Valeric	Heptanoic	Nonanoic	Al	Cu	Fe	Zn	Si
		Al/Cu/Fe	<10	<10	<0.05	-			<3	<1	<1	<1	<3
	PAG	Brass	<10	<10	<0.05	-			<3	<1	<1	<1	3
		Zinc	<10	<10	<0.05				<3	<1	<1	<1	<3
R-32		Al/Cu/Fe	<10	<10	0.12	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
175°C	POE	Brass	<10	<10	0.15	<200 <sup>ND</sup>	<200 (~100 <sup>A</sup> )	<200 (~80 <sup>A</sup> )	<3	<1	<1	22	<3
14 days		Zinc	<10	<10	0.24	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	3	<1	<1	67	<3
		Al/Cu/Fe	<10	<10	<0.05	_			<3	<1	<1	<1	4
	PVE	Brass	<10	<10	<0.05	_			<3	<1	<1	<1	14
		Zinc	25 (29 <sup>B</sup> )	<10	<0.05				<3	<1	<1	<1	7
		Al/Cu/Fe	<10	<10	_								
	No Oil	Brass	<10	<10	_								
		Zinc	1128	<10									
		Al/Cu/Fe	35	<10	<0.05	_			<3	<1	<1	<1	<3
	PAG	Brass	<10	<10	<0.05				<3	<1	<1	<1	<3
R-152a		Zinc	73	<10	<0.05				<3	<1	<1	5	<3
175°C		Al/Cu/Fe	<10	<10	0.11	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
14 days	POE	Brass	<10	<10	0.20	<200 <sup>ND</sup>	<200 (~90 <sup>A</sup> )	<200 <sup>ND</sup>	<3	<1	<1	42	<3
		Zinc	Not T	ested <sup>C</sup>	1.64	260	1190	910	<3	<1	<1	4	39
		Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	4
	PVE	Brass	<10	<10	0.08				<3	<1	<1	<1	<3
		Zinc	1689	<10	0.07				<3	<1	<1	<1	8
		Al/Cu/Fe	<10	<10									
	No Oil	Brass	<10	<10									
		Zinc	<10	<10		_							
		Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	<3
	PAG	Brass	<10	<10	<0.05		Not Analyzed	ł	<3	<1	<1	4	<3
R-227ea		Zinc	<10	<10	<0.05				<3	<1	<1	<1	3
		Al/Cu/Fe	<10	<10	0.07	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
175 C 14 days	POE	Brass	<10	<10	0.17	<200 <sup>ND</sup>	<200 (~90 <sup>A</sup> )	<200 <sup>ND</sup>	<3	<1	<1	29	<3
		Zinc	<10	<10	0.20	<200 <sup>ND</sup>	<200 (~120 <sup>A</sup> )	<200 (~110 <sup>A</sup> )	4	<1	<1	77	<3
		Al/Cu/Fe	<10	<10	<0.05				<3	<1	<1	<1	7
	PVE	Brass	<10	<10	<0.05		Not Analyzed	ł	<3	<1	<1	<1	6
		Zinc	<10	<10	<0.05				<3	<1	<1	<1	14

Table 5.67: Summary of Analytical Results of Aged Sealed Tubes, R-32, R-152a, R-227ea

<sup>A</sup>Organic acids were detected at concentrations lower than the verified quantitation limit. Results are reported for informational purposes. <sup>B</sup>Repeated measurement

<sup>c</sup>Not tested due to observed variability in duplicate tubes, and severe reactivity.

NDNot Detected

	Prop	osed Identification	R-133a	R-1132a	R-1122	R-1112a
	R-123, as rec'd		0.62%	-	-	-
		Al/Cu/Fe	0.29%	<100	100	130
R-123	No Oil	Brass	0.24%	290	3480	120
127°C		Zinc	0.23%	<100	560	620
127 C		Al/Cu/Fe	1.20%	220	-	-
	Mineral Oil	Brass	1.97%	2630	-	-
		Zinc	1.72%	2880	-	-

Table 5.68: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

'-' indicates not detected.

#### Table 5.69: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

	Proposed	Identification	R-1233zd(Z)	3,3,3-trifluoro-1-propyne	3,3,3-trifluoropropene
	R-1233zd(E), a	as rec'd	220	-	-
		Al/Cu/Fe	100	-	-
R-1233zd(E)	No Oil	Brass	130	-	-
		Zinc	150	-	390
127°C 14 days		Al/Cu/Fe	220	-	-
1.00,0	Mineral Oil	Brass	300	-	-
		Zinc	170	-	120

'-' indicates not detected.

#### Table 5.70: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

	Proposed	Identification	R-1224yd(E)	3,3,3-trifluoro-1-propyne	3,3,3-trifluoropropene
	R-1224yd(Z), a	s rec'd		-	-
		Al/Cu/Fe		470	-
R-1224yd(Z)	No Oil	Brass	lineble te detect	<100	-
4270		Zinc	changes	190	110
127 C		Al/Cu/Fe	changes	160	-
14 days	Mineral Oil	Brass		-	-
		Zinc		<100	<100

'-' indicates not detected.

#### Table 5.71: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

		Proposed Identification	R-1336mzz(Z)	R-1336mzz(E)	1,1,1,4,4,4- Hexafluoro- butane	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol	R-1336mzz-PVE Unknown
	R-514A,	as rec'd		4150	610	-	-	-	-	-	-	-
		Al/Cu/Fe		5170	450	-	-	-	-	-	-	-
	No Oil	Brass		7870	660	-	-	-	-	-	-	-
		Zinc		6550	570	-	-	-	-	-	-	-
R-514A		Al/Cu/Fe		950	200	210	<100	-	-	-	-	-
25.3% R-1130(E)	PAG	Brass		472	-	730	<100	-	-	-	-	-
74.7% R-1336mzz(Z)		Zinc		700	160	420	<100	-	-	-	-	-
127°C		Al/Cu/Fe		860	170	-	-	-	-	-	-	-
14 days	POE	Brass		420	100	-	-	-	-	-	-	-
		Zinc		630	120	-	-	-	-	-	-	-
		Al/Cu/Fe		1410	210	-	-	-	-	-	-	320
	PVE	Brass		520	160	-	-	-	-	-	-	430
		Zinc		830	150	-	-	-	-	-	-	710

	lc	Proposed dentification	R-1336mzz(Z)	R-1336mzz(E)	1,1,1,4,4- Hexafluorobutane	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol	R-1336mzz-PVE Unknown
	R-1336mz	z(Z), as rec'd		4400	270	-	-	-	-	-	-	-
		Al/Cu/Fe		43700	290	-	-	-	-	-	-	-
	No Oil	Brass		66600	540	-	-	-	-	-	-	-
		Zinc		66700	300	-	-	-	-	-	-	-
		Al/Cu/Fe		5400	270	1430	460	-	-	-	-	-
	PAG	Brass		5600	200	2110	120	-	-	-	-	-
		Zinc		5300	410	3020	250	-	-	-	-	-
	Additized	Al/Cu/Fe		6000	770	4930	660	-	180	-	-	-
R-1336mzz(Z)	Additized	Brass		7400	640	3260	610	-	100	-	-	-
175°C	PAG	Zinc		5500	870	2170	560	-	220	-	-	-
14 days		Al/Cu/Fe		33200	<100	-	-	-	-	-	-	-
,	POE	Brass		14600	<100	-	-	-	-	-	-	-
		Zinc		12000	<100	-	-	-	-	-	-	-
		Al/Cu/Fe		1600	1340	-	-	-	140	170	140	14700
	PVE	Brass		2800	2040	-	-	-	200	260	760	22500
		Zinc		2000	1650	-	-	-	180	200	1760	18500
	Additized	Al/Cu/Fe		3300	2330	-	-	-	140	190	<100	11100
	DVF	Brass		6700	3030	-	-	-	170	240	110	13400
	F VL	Zinc		4600	3080	-	-	-	180	270	<100	13200
	R-1336mz	z(E), as rec'd	1362	_	-	-	-	-	-	-	-	-
		Al/Cu/Fe	130		-	-	-	-	-	-	-	-
	No Oil	Brass	210		-	-	-	-	-	-	-	-
		Zinc	160	_	-	-	-	-	-	-	-	-
		Al/Cu/Fe	130	-	<100	580	100	-	-	-	-	-
	PAG	Brass	90	-	<100	410	<100	-	-	-	-	-
		Zinc	80	-	<100	220	<100	-	-	-	-	-
D ( D C ( T )	Additized	Al/Cu/Fe	70	-	-	450	220	-	120	-	-	-
R-1336mzz(E)	PAG	Brass	80	-	100	240	110	-	120	-	-	-
175°C	1710	Zinc	50	-	-	270	160	-	<100	-	-	-
14 days		Al/Cu/Fe	290	-	-	-	-	-	-	-	-	-
	POE	Brass	170	-	-	-	-	-	-	-	-	-
		Zinc	120	-	-	-	-	-	-	-	-	-
		Al/Cu/Fe	130	-	100	-	-	<100	<100	130	<100	5200
	PVE	Brass	100	-	<100	-	-	<100	<100	<100	<100	2750
		Zinc	100	-	120	-	-	<100	<100	190	230	7450
	Additized	Al/Cu/Fe	50	-	400	-	-	<100	<100	130	-	2590
	PVE	Brass	40	-	330	-	-	<100	<100	<100	-	2010
		Zinc	50		540	-	-	<100	120	200	-	3790

Table 5.72: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

		Proposed Identification	R-1234ze(Z)	3,3,3- trifluoropropene	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol	R-1234ze –PVE Unknown
	R-1234ze(	E), as rec'd			-	-	-	-	-	-	-
		Al/Cu/Fe			-	-	-	-	-	-	-
	No Oil	Brass			-	-	-	-	-	-	-
		Zinc	i	പ	-	-	-	-	-	-	-
		Al/Cu/Fe	0 U	u o	680	<100	-	-	-	-	-
	PAG	Brass	in o	in o	980	<100	-	-	-	-	-
		Zinc	9 8 9	8e	690	<100	-	-	-	-	-
	Additized	Al/Cu/Fe	Jan	Jan	260	150	-	310	<100	-	-
R-1234ze(E)	PAG	Brass	d cl	d cl	<100	120	-	380	<100	-	-
175°C	170	Zinc	cte	cte	260	220	-	400	<100	-	-
14 days		Al/Cu/Fe	ete	ete	-	-	-	-	-	-	-
	POE	Brass	o o	o Q	-	-	-	-	-	-	-
		Zinc	ب ب	Ĺ, D	-	-	-	-	-	-	-
		Al/Cu/Fe	sent	sent	-	-	100	290	600	-	2200
	PVE	Brass	res	res	-	-	<100	160	360	<100	1510
		Zinc		<u> </u>	-	-	<100	140	440	<100	1370
	Additized	Al/Cu/Fe			-	-	<100	<100	230	-	270
	PVF	Brass			-	-	<100	<100	160	-	300
		Zinc			-	-	<100	<100	260	-	300
	R-450A, as	rec'd	ن	പ	-	-	-	-	-	-	-
		Al/Cu/Fe	log	log	-	-	-	-	-	-	-
	No Oil	Brass	Ľ	in o	-	-	-	-	-	-	-
		Zinc	ge	ge	-	-	-	-	-	-	-
R-450A		Al/Cu/Fe	har	har	310	<100	-	-	-	-	-
42.0% R-134a	PAG	Brass	с q	с q	280	<100	-	-	-	-	-
58.0% K-1234ZE(E)		Zinc	cte	cte	150	<100	-	-	-	-	-
175°C		Al/Cu/Fe	ete	ete	-	-	-	-	-	-	-
14 days	POE	Brass	p o	p o	-	-	-	-	-	-	-
		Zinc	t, n	t, n	-	-	-	-	-	-	-
		Al/Cu/Fe	sen	sen	-	-	110	150	640	-	960
	PVE	Brass	j.	j.	-	-	<100	<100	280	-	650
		Zinc			-	-	<100	<100	210	-	280
	R-515B, as	rec'd	ي ي	2	-	-	-	-	-	-	-
		Al/Cu/Fe	co	Co	-	-	-	-	-	-	-
	No Oil	Brass	.⊆	<u> </u>	-	-	-	-	-	-	-
		Zinc	Jge	Jge	-	-	-	-	-	-	-
R-515B		Al/Cu/Fe	har	har	670	270	-	170	-	-	-
8.9% R-227ea	PAG	Brass	o p	o p	600	190	-	130	-	-	-
э1.170 К-1234ZE(E)		Zinc	cte	cte	650	370	-	350	-	-	-
175°C		Al/Cu/Fe	ete	ete	-	-	-	-	-	-	-
14 days	POE	Brass	p o	p o	-	-	-	-	-	-	-
		Zinc	t, n	t, n	-	-	-	-	-	-	-
		Al/Cu/Fe	sen	sen	-	-	270	780	1720	310	4020
	PVE	Brass	res	res	-	-	130	340	960	300	1970
		Zinc	<u>ц</u>	<u> </u>	-	-	130	250	1370	340	1340

Table 5.73: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

		Proposed Identification	3,3,3- trifluoropropene	Vinyl Fluoride	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol	R-1234yf-PVE Unknown
	R-1234yf, a	is rec'd		-	-	-	-	-	-	-	-
		Al/Cu/Fe		-	-	-	-	-	-	-	-
	No Oil	Brass		-	-	-	-	-	-	-	-
		Zinc	.:	-	-	-	-	-	-	-	-
		Al/Cu/Fe	onc	-	220	<100	-	-	-	-	-
	PAG	Brass	ū L	-	220	<100	-	-	-	-	-
		Zinc	ge i	-	330	<100	-	-	-	-	-
	المعاملة المعالم	Al/Cu/Fe	Jan	-	340	<100	-	<100	-	-	-
R-1234yf	Additized	Brass	1	-	800	<100	-	<100	-	-	-
	PAG	Zinc	tec	-	820	100	-	<100	-	-	-
175 C 14 days		Al/Cu/Fe	etec	-	-	-	-	-	-	-	-
14 00 95	POE	Brass	bde	-	-	-	-	-	-	-	-
		Zinc	Ĕ,	-	-	-	-	-	-	-	-
		Al/Cu/Fe	ent	-	-	-	-	230	290	120	720
	PVE	Brass	res	-	-	-	-	280	290	110	850
		Zinc	۵.	-	-	-	-	280	1510	470	780
	Additized	Al/Cu/Fe		-	-	-	-	<100	<100	-	<100
	Additized	Brass		-	-	-	-	<100	<100	-	<100
	FVL	Zinc		-	-	-	-	<100	<100	-	110
	R-513A, as	rec'd		-	-	-	-	-	-	-	-
		Al/Cu/Fe		-	-	-	-	-	-	-	-
	No Oil	Brass		-	-	-	-	-	-	-	-
		Zinc	G	-	-	-	-	-	-	-	-
		Al/Cu/Fe	0 D	-	180	<100	-	-	-	-	-
	PAG	Brass	i,	-	120	<100	-	-	-	-	-
		Zinc	g	-	150	<100	-	-	-	-	-
R-513A	Additized	Al/Cu/Fe	Jan	-	600	<100	-	<100	<100	-	-
44.0% R-134a	PAG	Brass	d ct	-	570	1220	-	<100	-	-	-
56.0% R-1234yf	FAG	Zinc	cteo	-	160	<100	-	<100	<100	-	-
175°C		Al/Cu/Fe	ete	-	-	-	-	-	-	-	-
14 days	POE	Brass	p o	-	-	-	-	-	-	-	-
		Zinc	Ĕ	-	-	-	-	-	-	-	-
		Al/Cu/Fe	ent	-	-	-	<100	230	360	<100	800
	PVE	Brass	res	-	-	-	<100	170	250	130	640
		Zinc	ட	-	-	-	<100	110	370	140	520
	Additized	Al/Cu/Fe		-	-	-	-	<100	<100	-	110
	PVF	Brass		-	-	-	-	<100	<100	-	150
	FVL	Zinc		-	-	-	-	<100	<100	-	100

Table 5.74: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

Table 5.75: Qualitative Summary of Key Species Identified in GC-INS Headspace Analysis of Aged Sealed Tubes, in Peak Area (	(ppm)
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		Proposed Identification	3,3,3- trifluoropropene	Vinyl Fluoride	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol	R-1234yf-PVE Unknown												
	R-516A, as	rec'd		-	-	-	-	-	-	-	-												
		Al/Cu/Fe		-	-	-	-	-	-	-	-												
	No Oil	Brass		-	-	-	-	-	-	-	-												
		Zinc	528	180	-	-	-	-	-	-	-												
R-516A		Al/Cu/Fe	R-1	-	<100	-	-	-	-	-	-												
77.5% R-1234yf 8 5% R-134a	PAG	Brass	th	-	<100	-	-	-	-	-	-												
14.0% R-152a		Zinc	Ň	170	<100	-	-	-	-	-	-												
		Al/Cu/Fe	tion	<100	-	-	-	-	-	-	-												
175 C 14 days	POE	Brass	elut	-	-	-	-	-	-	-	-												
1. 00,5		Zinc	Ö	620	-	-	-	-	-	-	-												
		Al/Cu/Fe	0			-	-	-	-	<100	<100	-	230										
	PVE	Brass				-		1 1	1		1					-	-	-	-	-	-	-	<100
		Zinc		220	-	-	-	110	130	-	310												

		Proposed Identification	3,3,3- trifluoropropene	Vinyl Fluoride	2-methyl-1- propene	Propanal	Acetone	lsobutane	Acetaldehyde	Ethane	Ethanol	R-1234yf-PVE Unknown
	R-454B, as	rec'd		-	-	-	-	-	-	-	-	-
		Al/Cu/Fe	5	-	<100	230	<100	-	-	-	-	-
	PAG	Brass	cteo C.	-	<100	270	<100	-	-	-	-	-
R-454B		Zinc	ete	-	<100	220	<100	-	-	-	-	-
68.9% R-32 31.1% R-1234yf		Al/Cu/Fe	o de in c	-	-	-	-	-	-	-	-	-
	POE	Brass	ge	-	-	-	-	-	-	-	-	-
175°C		Zinc	ent	-	-	-	-	-	-	-	-	-
14 Udys		Al/Cu/Fe	res	-	-	-	-	-	<100	350	-	420
	PVE	Brass	<u>م</u>	-	<100	-	-	-	120	570	<100	600
		Zinc		-	<100	-	-	-	<100	710	<100	490
	R-454C, as	rec'd		-	-	-	-	-	-	-	-	-
		Al/Cu/Fe		-	-	290	<100	-	-	-	-	-
	PAG	Brass	лс.	-	-	250	<100	-	-	-	-	-
		Zinc	Ō	-	-	460	180	-	-	-	-	-
	Additized	Al/Cu/Fe	u.	-	-	140	-	-	-	-	-	-
5 4546	Additized	Brass	nge	-	-	190	250	-	-	-	-	-
R-454C	PAG	Zinc	cha	-	-	320	<100	-	-	-	-	-
21.5% R-32 78.5% R-1234yf		Al/Cu/Fe	eq	-	-	-	-	-	-	-	-	-
	POE	Brass	ecti	-	-	-	-	-	-	-	-	-
175°C		Zinc	det	-	-	-	-	-	-	-	-	-
14 Udys		Al/Cu/Fe	οc	-	-	-	-	-	150	380	-	560
	PVE	Brass	ıt, ı	-	-	-	-	-	250	390	-	910
		Zinc	ser	-	-	-	-	-	240	120	-	170
		Al/Cu/Fe	Pre	-	-	-	-	-	<100	<100	-	<100
	Additized	Brass		-	-	-	-	-	<100	<100	-	130
	PVE	Zinc		-	-	-	-	-	<100	<100	-	<100
	R-455A, as	rec'd		-	-	-	-	-	-	-	-	-
		Al/Cu/Fe	-	-	-	140	-	-	-	-	-	-
R-455A	PAG	Brass	C cteo	-	-	<100	-	-	-	-	-	-
3.0% R-744		Zinc	etec	-	-	140	-	-	-	-	-	-
21.5% R-32		Al/Cu/Fe	o d∈ in c	-	-	-	-	-	-	-	-	-
75.5% R-1234yf	POE	Brass	, nc ge j	-	-	-	-	-	-	-	-	-
175°C		Zinc	ent	-	-	-	-	-	-	-	-	-
14 days		Al/Cu/Fe	res ch	-	-	-	-	-	-	<100	-	170
	PVE	Brass	<u>م</u>	-	-	-	-	-	-	<100	<100	<100
		Zinc	1	-	-	-	-	-	-	<100	<100	170

Table 5.76: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

		Proposed Identification	3,3,3- trifluoropropene	Vinyl Fluoride	2-methyl-1- propene	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol	R-1234yf-PVE Unknown
	R-468A, as	rec'd		-	-	-	-	-	-		-	-
		Al/Cu/Fe		-	100	250	<100	-	-		-	-
	PAG	Brass	change in conc.	-	<100	120	<100	-	-		-	-
		Zinc		-	<100	140	<100	-	-		-	-
	Additized	Al/Cu/Fe		-	<100	<100	<100	-	<100	2a	-	-
R-468A	Additized	Brass		-	<100	<100	<100	-	<100	113	-	-
3.5% R-1132a	FAG	Zinc		-	<100	<100	<100	-	-	Ľ.	-	-
21.5% R-32		Al/Cu/Fe	pe o	-	<100	-	-	-	-	ith	-	-
75.0% R-1234yf	POE	Brass	ecte	-	<100	-	-	-	-	2 2	-	-
175°C		Zinc	dete	-	<100	-	-	-	-	tio	-	-
14 days		Al/Cu/Fe	0 QL	-	<100	-	-	<100	170	ėlu	<100	620
	PVE	Brass	it, i	-	<100	-	-	<100	290	Ś	170	750
		Zinc	ser	-	<100	-	-	<100	170		230	660
	A	Al/Cu/Fe	Pre	-	<100	-	-	-	<100		-	<100
	Additized	Brass	<u> </u>	-	<100	-	-	-	-		-	<100
	PVE	Zinc		-	<100	-	-	-	<100		-	<100

Table 5.77: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

	I	Proposed dentification	Trifluor omethane (R-23)	<b>Fluor oethane</b>	Difluoroiodomethane	Pentafluoroethyliodide	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol	lodoethane
	R-466A, as	rec'd	-	-	-	-	-	-	-	-		-	-
		Al/Cu/Fe	4300	-	110	-	-	-	-	-		-	-
-	No Oil	Brass	14900	-	1550	100	-	-	-	-		-	-
		Zinc	7300	-	810	<100	-	-	-	-		-	-
		Al/Cu/Fe	_										
	PAG	Brass			١	lot Tested	A						
		Zinc									23		
R-466A		Al/Cu/Fe	60800	-	<100	-	-	-	-	-	Ľ.	-	-
49.0% R-32 11.5% R-125	POE	Brass	61800	-	<100	-	-	-	-	-	vith	-	-
39.5% R-13/1		Zinc			١	ot Tested	A				2		
150°C		Aluminum	150	-	-	-	-	-	-	-	rtic	-	-
150 C 14 davs		Copper	190	-	-	-	-	-	-	-	-el	-	-
,.	Additized	Iron	190	-	-	-	-	I	-	-	ပိ	-	-
	POE	Al/Cu/Fe	210	-	-	-	-	-	-	-		-	-
		Brass	160	-	-	-	-	-	-	-		-	-
		Zinc	310	-	-	-	-	-	-	-		-	-
		Al/Cu/Fe			١	ot Tested	A						
	PVE	Brass	66700	320	-	-	-	-	-	-		1220	3040
		Zinc			Ν	lot Tested	A						

Table 5.78: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

<sup>A</sup>Several conditions were not tested, either based on reaction severity indicated in visual observations, or significant reactivity determined from anion evaluation that was used as a screening step.

Table 5.79: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

		Proposed Identification	Trifluoromethane (R-23)	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol
	R-32, as re	ec'd	140	-	-	-	-	-	-
		Al/Cu/Fe	170	-	-	-	-	-	-
	PAG	Brass	120	-	-	-	-	-	-
R-32		Zinc	160	250	-	-	-	-	-
		Al/Cu/Fe	130	-	-	-	-	-	-
175°C	175°C POE	Brass	170	-	-	-	-	-	-
14 days		Zinc	100	-	-	-	-	-	-
		Al/Cu/Fe	150	-	-	170	210	2040	-
	PVE	Brass	160	-	-	240	310	2570	-
		Zinc	110	-	-	190	260	2940	-

'-' indicates not detected.

#### Table 5.80: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

		Proposed Identification	Vinyl Fluoride	Propene	2-methyl-1- propene	Propanal	Acetone	lsobutane	Acetaldehyde	Ethane	Ethanol
	R-152a, a	s rec'd	-	-	-	-	-	-	-	-	-
		Al/Cu/Fe	180	-	-	-	-	-	-	-	-
	No Oil	Brass	-	-	-	-	-	-	-	-	-
		Zinc	15700	-	-	-	-	-	380	1120	-
		Al/Cu/Fe	-	260	120	120	-	-	120	-	-
R-152a	PAG	Brass	-	210	170	-	160	-	-	-	-
		Zinc	34200	1140	180	500	<100	-	340	3160	-
175°C 14 days		Al/Cu/Fe	110	-	-	-	-	-	-	-	-
14 0893	POE	Brass	-	-	<100	-	-	-	-	-	-
		Zinc	29600	-	750	-	-	-	<100	880	-
		Al/Cu/Fe	<100	-	<100	-	390	280	510	3080	-
	PVE	Brass	-	-	<100	-	830	300	780	2900	-
		Zinc	260	-	<100	-	-	<100	190	620	-

		Proposed Identification	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol
	R-227ea, as	s rec'd	-	-	-	-	-	-
		Al/Cu/Fe	-	-	-	-	-	-
No C	No Oil	No Oil Brass		-	-	-	-	-
		Zinc	-	-	-	-	-	-
		Al/Cu/Fe	280	<100	-	-	-	-
R-227ea	PAG	Brass	900	220	-	-	-	-
		Zinc	320	140	-	-	-	-
1/5 C 14 days		Al/Cu/Fe	-	<100	-	-	-	-
110075	POE	Brass	-	-	-	-	-	-
		Zinc	-	-	-	-	-	-
		Al/Cu/Fe	-	-	230	740	3420	-
	PVE	Brass	-	-	290	880	3280	<100
		Zinc	-	130	190	440	2670	<100

Table 5.81: Qualitative Summary of Key Species Identified in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

Refrigerant	Material	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Material Appearance
	24 Malagular Sigua	No Oil	-	Faint particles <sup>1</sup>	-
	SA MORECULAR SIEVE	Mineral Oil	-	-	-
D 1222-4/5)		No Oil	-	Faint particles <sup>1</sup>	-
K-123320(E)	4A Molecular Sleve	Mineral Oil	-	-	-
		No Oil	-	-	-
	Activated Alumina	Mineral Oil	-	-	Some yellowing

Table 5.82: Appearance Changes for R-1233zd(E) Phase IIE Evaluations

<sup>1</sup>Faint particles observed pre and post exposure.

## Table 5.83: Pre and Post Exposure Photographs for R-1233zd(E) Phase IIE Evaluations

3A Molecular S	ieve Conditions	4A Molecular S	ieve Conditions	Activated Alumina Conditions		
100% Refrigerant (left)	, Refrigerant-Oil (right)	100% Refrigerant (left)	, Refrigerant-Oil (right)	100% Refrigerant (left)	), Refrigerant-Oil (right)	
Pre-Exposure	Post-Exposure	Pre-Exposure	Post-Exposure	Pre-Exposure	Post-Exposure	
W W				100 - 100	0	

Refrigerant	Material	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Material Appearance
	24 Malagular Sigura	No Oil	-	Faint Particles <sup>1</sup>	-
	SA MOIECUIAI SIEVE	Mineral Oil	-	-	-
D 1224	4A Molecular Sieve	No Oil	-	Faint Particles <sup>1</sup>	-
K-1224ya(2)		Mineral Oil	-	-	-
	Activated Alumina	No Oil	-	Faint Particles <sup>1</sup>	-
	Activated Alumina	Mineral Oil	-	-	Yellowed

Table 5.84: Appearance Changes for R-1224yd(Z) Phase IIE Evaluations

<sup>1</sup>Faint particles observed pre and post exposure.

#### Table 5.85: Pre and Post Exposure Photographs for R-1224yd(Z) Phase IIE Evaluations

<b>3A Molecular S</b> 100% Refrigerant (left)	ieve Conditions ), Refrigerant-Oil (right)	<b>4A Molecular S</b> 100% Refrigerant (left	<b>Sieve Conditions</b> ), Refrigerant-Oil (right)	Activated Alumina Conditions 100% Refrigerant (left), Refrigerant-Oil (right)		
Pre-Exposure	Post-Exposure	Pre-Exposure	Post-Exposure	Pre-Exposure	Post-Exposure	
	and the second		w w	100 - 730	100 M	

Table 5.86: Appearance	<b>Changes for</b>	R-514A Phase III	E Evaluations
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Refrigerant	Material	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Material Appearance
		No Oil	-	Faint particles <sup>1</sup>	-
	24 Malagular Sigura	Additized PAG	Pale yellow	Faint particles <sup>1</sup>	-
	SA WOIECUIAI SIEVE	POE	Pale yellow	Faint particles <sup>1</sup>	-
		Additized PVE	-	Faint particles <sup>1</sup>	-
	4A Molecular Sieve	No Oil	-	Faint particles <sup>1</sup>	Dulled
R-514A		Additized PAG	Pale yellow	-	Dulled
25.3% R-1130(E) 74.7% R-1336mzz(Z)		POE	Pale yellow	Faint particles <sup>1</sup>	Dulled
		Additized PVE	-	Faint particles <sup>1</sup>	-
		No Oil	-	Faint particles <sup>1</sup>	Slight yellowing
	Activated Alumina	Additized PAG	Pale yellow	Faint particles <sup>1</sup>	Slight yellowing
	Activated Alumina	POE	Pale yellow	Faint particles <sup>1</sup>	Slight yellowing
		Additized PVE	-	Faint particles <sup>1</sup>	-

Table 5.87: Pre an	nd Post Exposur	e Photographs	for R-514A Phase	IIE Evaluations
10010 01071110 01	ia i ost Exposai	c i notograpiis		



Table 5.88: Appearance	Changes for R-1336	mzz(Z) Phase IIE Evaluations
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Refrigerant	Material	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Material Appearance
		No Oil	-	Faint particles <sup>1</sup>	-
		Additized PAG	Pale yellow	Faint particles <sup>1</sup>	-
	3A Molecular Sleve	POE	Pale yellow	Faint particles <sup>1</sup>	-
		Additized PVE	-	-	-
	4A Molecular Sieve	No Oil	-	Faint particles <sup>1</sup>	-
D 4000		Additized PAG	Pale yellow	Faint particles <sup>1</sup>	-
R-1336m22(2)		POE	Pale yellow	Faint particles <sup>1</sup>	-
		Additized PVE	-	-	-
		No Oil	-	Faint particles <sup>1</sup>	-
		Additized PAG	Pale yellow	Faint particles <sup>1</sup>	Slight yellowing
	Activated Alumina	POE	Pale yellow	Faint particles <sup>1</sup>	-
		Additized PVE	-	Faint particles <sup>1</sup>	-

<sup>1</sup>Faint particles observed pre and post exposure.

# Table 5.89: Pre and Post Exposure Photographs for R-1336mzz(Z) Phase IIE Evaluations

	3A Molecular Sieve Conditions	4A Molecular Sieve Conditions	Activated Alumina Conditions
	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)
Pre-Exposure			
Post-Exposure			

Table 5.90: Appearance	Changes for	R-1336mzz(E)	Phase IIE Evaluations
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Refrigerant	Material	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Material Appearance
		No Oil	-	Faint particles <sup>1</sup>	-
	24 Malagular Sigura	Additized PAG	Pale yellow	Faint particles <sup>1</sup>	-
	3A Wolecular Sieve	POE	Pale yellow	Faint particles <sup>1</sup>	-
		Additized PVE	-	-	-
	4A Molecular Sieve	No Oil	-	Faint particles <sup>1</sup>	-
D 122(		Additized PAG	Pale yellow	Faint particles <sup>1</sup>	-
R-1336m22(E)		POE	Pale yellow	Faint particles <sup>1</sup>	-
		Additized PVE	-	-	-
		No Oil	-	Faint particles <sup>1</sup>	-
	Activated Alumina	Additized PAG	Pale yellow	Faint particles <sup>1</sup>	Slight yellowing
	Activated Alumina	POE	Pale yellow	Faint particles <sup>1</sup>	-
		Additized PVE	-	-	-





Table 5.92: Appearanc	e Changes for R-1234	ze(E) Phase IIE Evaluations
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Refrigerant	Material	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Material Appearance
		No Oil	-	Faint particles <sup>1</sup>	-
	24 Malagular Sigua	Additized PAG	-	Faint particles <sup>1</sup>	-
	3A Molecular Sleve	POE	-	Faint particles <sup>1</sup>	-
		Additized PVE	-	-	-
	4A Molecular Sieve	No Oil	-	Faint particles <sup>1</sup>	-
D 4004 (5)		Additized PAG	-	Faint particles <sup>1</sup>	-
R-1234Ze(E)		POE	-	Faint particles <sup>1</sup>	-
		Additized PVE	-	-	-
		No Oil	-	Faint particles <sup>1</sup>	Yellowed
		Additized PAG	-	Faint particles <sup>1</sup>	Yellowed
	Activated Alumina	POE	-	Faint particles <sup>1</sup>	-
		Additized PVE	-	Faint particles <sup>1</sup>	-

Table 5.93: Pre and Post Ex	posure Photographs for R	R-1234ze(E) Phase IIE Evaluations
TUDIC 5.55. TTC UTU T OST EX	posure i notographs for h	

	3A Molecular Sieve Conditions	4A Molecular Sieve Conditions	Activated Alumina Conditions
	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)
<sup>o</sup> re-Exposure			
	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	<b>M M M</b>	100 W W W
-Exposure			
Post-			······································

Table 5.94: Appearance	Changes for	R-515B Phase I	IE Evaluations
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Refrigerant	Material	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Material Appearance
		No Oil	-	Faint particles <sup>1</sup>	-
		Additized PAG	-	Faint particles <sup>1</sup>	-
	3A Molecular Sieve	POE	-	Faint particles <sup>1</sup>	-
		Additized PVE	-	Faint particles <sup>1</sup>	-
		No Oil	-	Faint particles <sup>1</sup>	-
R-515B		Additized PAG	-	Faint particles <sup>1</sup>	-
8.9% R-227ea 91 1% R-1234ze(F)	4A Molecular Sieve	POE	-	Faint particles <sup>1</sup>	-
5112/01/12/07/20(2)		Additized PVE	-	Faint particles <sup>1</sup>	-
		No Oil	-	Faint particles <sup>1</sup>	Yellow-Orange
		Additized PAG	-	Faint particles <sup>1</sup>	Yellowed
	Activated Alumina	POE	-	Faint particles <sup>1</sup>	-
		Additized PVE	-	Faint particles <sup>1</sup>	-

Table 5.95: Pre and Post F	xposure Photogra	phs for R-515B Phase	IF Evaluations
1051C 3.33.11C 010 1 050 E	Aposare i notogra		

	3A Molecular Sieve Conditions	4A Molecular Sieve Conditions	Activated Alumina Conditions
Pre-Exposure	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)
Post-Exposure			

Table 5.96: Appearance	ce Changes for R-1234	f Phase IIE Evaluations
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Refrigerant	Material	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Material Appearance
		No Oil	-	Faint particles <sup>1</sup>	-
		Additized PAG	-	Faint particles <sup>1</sup>	-
	3A Molecular Sieve	POE	-	Faint particles <sup>1</sup>	-
		Additized PVE	-	-	-
	4A Molecular Sieve	No Oil	-	Faint particles <sup>1</sup>	-
D 1224.4		Additized PAG	-	Faint particles <sup>1</sup>	-
K-1234yt		POE	-	Faint particles <sup>1</sup>	-
		Additized PVE	-	-	-
	Activated Alumina	No Oil	-	Faint particles <sup>1</sup>	-
		Additized PAG	-	Faint particles <sup>1</sup>	Yellowed
		POE	-	Faint particles <sup>1</sup>	-
		Additized PVE	-	-	-

<sup>1</sup>Faint particles observed pre and post exposure.

# Table 5.97: Pre and Post Exposure Photographs for R-1234yf Phase IIE Evaluations

	3A Molecular Sieve Conditions	4A Molecular Sieve Conditions	Activated Alumina Conditions
	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)
Pre-Exposure			
		****	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
Exposure			
Post-E			

Table 5.98: Appearance	Changes for	R-516A Phase IIE	Evaluations
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Refrigerant	Material	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Material Appearance
		No Oil	-	Faint particles <sup>1</sup>	-
		Additized PAG	-	Faint particles <sup>1</sup>	-
	3A Molecular Sieve	POE	-	-	-
		Additized PVE	-	-	-
D E16A	4A Molecular Sieve	No Oil	-	Faint particles <sup>1</sup>	-
<b>K-510A</b> 77.5% R-1234vf		Additized PAG	-	Faint particles <sup>1</sup>	-
8.5% R-134a		POE	-	Faint particles <sup>1</sup>	-
14.0% R-152a		Additized PVE	-	-	-
		No Oil	-	Faint particles <sup>1</sup>	Yellow-Orange
		Additized PAG	-	Faint particles <sup>1</sup>	Yellowed
	Activated Alumina	POE	-	Faint particles <sup>1</sup>	-
		Additized PVE	-	Faint particles <sup>1</sup>	-

Table 5.99: Pre and Post E	xposure Photographs	for R-516A Phase IIE Evaluations

	3A Molecular Sieve Conditions	4A Molecular Sieve Conditions	Activated Alumina Conditions
	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)	No Oil, PAG, POE, PVE (Left to Right)
<sup>o</sup> re-Exposure			
		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	100 00 00 V
xposure			
Post-E)			

Refrigerant	Material	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Material Appearance
		Additized PAG	-	Faint particles <sup>1</sup>	-
	3A Molecular Sieve	POE	-	-	-
		Additized PVE	-	-	-
R-455A	4A Molecular Sieve	Additized PAG	-	Faint particles <sup>1</sup>	-
3.0% R-744		POE	-	Faint particles <sup>1</sup>	-
21.5% R-32 75.5% R-1234yf		Additized PVE	-	-	-
		Additized PAG	-	Faint particles <sup>1</sup>	Yellowed
	Activated Alumina	POE	-	Faint particles <sup>1</sup>	-
		Additized PVE	-	Faint particles <sup>1</sup>	-





Table 5.102: Appearance C	Changes for R-468A	<b>Phase IIE Evaluations</b>
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Refrigerant	Material	Lubricant	Liquid Color	Cloudiness, Particulate or Film	Material Appearance
		Additized PAG	-	Faint particles <sup>1</sup>	-
	3A Molecular Sieve	POE	-	Faint particles <sup>1</sup>	-
		Additized PVE	-	Faint particles <sup>1</sup>	-
R-468A	4A Molecular Sieve	Additized PAG	-	Faint particles <sup>1</sup>	-
3.5% R-1132a		POE	-	-	-
75.0% R-1234yf		Additized PVE	-	Faint particles <sup>1</sup>	-
		Additized PAG	-	Faint particles <sup>1</sup>	Yellowed
	Activated Alumina	POE	-	Faint particles <sup>1</sup>	-
		Additized PVE	-	Faint particles <sup>1</sup>	-

<sup>1</sup>Faint particles observed pre and post exposure.

#### Table 5.103: Pre and Post Exposure Photographs for R-468A Phase IIE Evaluations



Refrigerant	Lubricant	Material	Liquid Color	Cloudiness, Particulate or Film	Material Appearance
R-466A	R-466A 49.0% R-32 11.5% R-125 39.5% R-1311 Additized POE	3A Molecular Sieve	-	Faint particles <sup>1</sup>	-
49.0% R-32		4A Molecular Sieve	-	Faint particles <sup>1</sup>	-
11.5% R-125 39.5% R-13I1		Activated Alumina	-	Faint particles <sup>1</sup>	Slight yellowing

#### Table 5.104: Appearance Changes for R-466A Phase IIE Evaluations

'-' indicates no detected change

<sup>1</sup>Faint particles observed pre and post exposure.

## Table 5.105: Pre and Post Exposure Photographs for R-466A Phase IIE Evaluations



	Lubricant	erial	Inorganic Anions (ppm in refrigerant)			Lubricant Organic Acids (ppm, ug/g)			Dissolved Elements in Lubricant (ppm)				
Refrigerant		Mat	Б Fluoride Chloride оil	KOH/ g oil	Valeric	Heptanoic	Branched Nonanoic	AI	Cu	Fe	Zn	Si	
		3A	<10	<10									
R-1233zd(E)	No Oil	4A	<10	<10									
		AA	<10	<10		_							
100°C		3A	<10	<10	0.13	_			<3	<1	<1	<1	<3
28 days	Mineral Oil	4A	<10	<10	0.10				<3	<1	<1	<1	<3
		AA	Inorganic Anions (ppm in refrigerant)           Fluoride         Chloride           <10	0.12				<3	<1	<1	<1	<3	
		3A	<10	<10									
R-1224vd(Z)	No Oil	4A	<10	<10									
1.01		AA	<10	<10		1			r	r	r	r	r
100°C 28 days	Mineral Oil	3A	<10	<10	<0.05	-			<3	<1	<1	<1	<3
		4A	<10	<10	<0.05	-			<3	<1	<1	<1	<3
		AA	<10	<10	<0.05				<3	<1	<1	<1	<3
	No Oil	3A	<10	<10									
		4A	<10	<10									
		AA	<10	<10		1							
	Additized PAG	3A	<10	<10	<0.05	-			<3	<1	<1	<1	<3
R-514A		4A	<10	<10	<0.05	-			<3	<1	<1	<1	4
25.3% R-1130(E)		AA	<10	<10	<0.05		1	I	<3	<1	<1	<1	3
74.7% R-1336mzz(2)		3A	<10	<10	0.06	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
100°C 28 days	POE	4A	<10	<10	0.07	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
		AA	<10	<10	0.20	<200 <sup>ND</sup>	<200 (~160 <sup>A</sup> )	<200 (~110 <sup>A</sup> )	<3	<1	<1	<1	<3
		3A	<10	<10	<0.05				<3	<1	<1	<1	12
	P\/F	4A	<10	<10	0.05				<3	<1	<1	<1	15
	F V L	AA	<10	<10	<0.05				<3	<1	<1	<1	11

Table 5.106: Summary of Analytical Results of Aged Sealed Tubes from Phase IIE

<sup>A</sup>Organic acids were detected at concentrations lower than the verified quantitation limit. Results are reported for informational purposes.

NDNot Detected

Refrigerant	Lubricant	erial	Inorganic Anions (ppm in refrigerant)		TAN mg	Lubricant Organic Acids (ppm, ug/g)			Dissolved Elements in Lubricant (ppm)					
		Mat	Fluoride	Chloride	KOH/ g oil	Valeric	Heptanoic	Branched Nonanoic	AI	Cu	Fe	Zn	Si	
		3A	<10	<10										
	No Oil	4A	<10	<10										
		AA	<10	<10		_								
	Additized	3A	<10	<10	<0.05	_			<3	<1	<1	<1	<3	
	PAG	4A	<10	<10	<0.05				<3	<1	<1	<1	<3	
R-1336mzz(Z)	FAG	AA	<10	<10	<0.05				<3	<1	<1	<1	<3	
100°C		3A	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3	
28 days	POE	4A	<10	<10	0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	8	
		AA	<10	<10	0.16	<200 (~120 <sup>A</sup> )	490	230	<3	<1	<1	<1	<3	
	Additized PVE	3A	<10	<10	<0.05				<3	<1	<1	<1	22	
		4A	<10	<10	<0.05				<3	<1	<1	<1	13	
		AA	<10	<10	<0.05				<3	<1	<1	<1	9	
	No Oil	3A	<10	<10										
		4A	<10	<10										
		AA	<10	<10		_								
	Additized PAG	3A	<10	<10	<0.05				<3	<1	<1	<1	<3	
		4A	<10	<10	<0.05				<3	<1	<1	<1	3	
R-1336mzz(E)		AA	<10	<10	<0.05				<3	<1	<1	<1	3	
100°C 28 days	POE	3A	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3	
		4A	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	4	
		AA	<10	<10	0.60	<200 <sup>ND</sup>	<200 (~160 <sup>A</sup> )	<200 (~100 <sup>A</sup> )	<3	<1	<1	<1	<3	
	Additized	3A	<10	<10	<0.05				<3	<1	<1	<1	20	
	PVE	4A	<10	<10	<0.05				<3	<1	<1	<1	11	
		AA	<10	<10	<0.05				<3	<1	<1	<1	10	

Table 5.107: Summary of Analytical Results of Aged Sealed Tubes from Phase IIE

<sup>A</sup>Organic acids were detected at concentrations lower than the verified quantitation limit. Results are reported for informational purposes.

NDNot Detected

Defiinment	Lubricant	erial	Inorganic Anions (ppm in refrigerant)		TAN	Lubricant Organic Acids (ppm, ug/g)			Dissolved Elements in Lubricant (ppm)					
Refrigerant		S Fluorid	Fluoride	Chloride	KOH/g oil	Valeric	Heptanoic	Branche d Nonanoic	AI	Cu	Fe	Zn	Si	
		3A	<10	<10										
	No Oil	4A	<10	<10										
		AA	<10	<10										
	م . ا . ا : + : ا	3A	<10	<10	0.08				<3	<1	<1	<1	<3	
P 122470(E)	Additized	4A	<10	<10	<0.05				<3	<1	<1	<1	3	
K-123428(C)	140	AA	<10	<10	<0.05				<3	<1	<1	<1	4	
100°C		3A	<10	<10	0.10	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3	
28 days	POE	4A	<10	<10	0.07	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3	
		AA	<10	<10	0.32	<200 <sup>ND</sup>	300	200	<3	<1	<1	<1	3	
	Additized PVE	3A	<10	<10	<0.05				<3	<1	<1	<1	8	
		4A	<10	<10	<0.05				<3	<1	<1	<1	26	
		AA	<10	<10	<0.05				<3	<1	<1	<1	14	
	No Oil	3A	<10	<10										
		4A	<10	<10										
		AA	<10	<10										
	Additized PAG	3A	<10	<10	<0.05				<3	<1	<1	<1	<3	
R-515B		4A	<10	<10	<0.05				<3	<1	<1	<1	<3	
8.9% R-227ea		AA	<10	<10	<0.05				<3	<1	<1	<1	4	
91.1% R-1234ze(E)		3A	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	8	
100°C 28 days	POE	4A	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	6	
		AA	<10	<10	0.32	<200 <sup>ND</sup>	320	<200 (~170 <sup>A</sup> )	<3	<1	<1	<1	<3	
		3A	<10	<10	<0.05				<3	<1	<1	<1	38	
	Additized	4A	<10	<10	<0.05				<3	<1	<1	<1	18	
	FVE	AA	<10	<10	<0.05				<3	<1	<1	<1	16	

Table 5.108: Summary of Analytical Results of Aged Sealed Tubes from Phase IIE

<sup>A</sup>Organic acids were detected at concentrations lower than the verified quantitation limit. Results are reported for informational purposes.

 ${}^{\mathsf{ND}}\mathsf{Not}$  Detected
Refrigerant	Lubricont	erial	Inorgani (ppm in re	c Anions efrigerant)		Lub	ricant Organi (ppm, ug/g	c Acids ;)	Di	ssolve Lubri	d Ele cant	ment (ppm)	s in
Kerngerant	Lubricant	Mat	Fluoride	Chloride	KOH/ g oil	Valeric	Heptanoic	Branched Nonanoic	AI	Cu	Fe	Zn	Si
		3A	<10	<10									
	No Oil	4A	<10	<10									
		AA	<10	<10		_							
	م المانية م ما	3A	<10	<10	<0.05				<3	<1	<1	<1	<3
R-1234vf	PAG	4A	<10	<10	<0.05				<3	<1	<1	<1	8
N-1234y1	FAG	AA	<10	<10	<0.05				<3	<1	<1	<1	3
100°C		3A	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
28 days	POE	4A	<10	<10	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
		AA	<10	<10	0.28	<200 <sup>ND</sup>	320	200	<3	<1	<1	<1	<3
		3A	<10	<10	<0.05				<3	<1	<1	<1	12
	Additized	4A	<10	<10	<0.05				<3	<1	<1	<1	31
	FVL	AA	<10	<10	<0.05				<3	<1	<1	<1	20
		3A	<10	<10									
	No Oil	4A	<10	<10									
		AA	<10	<10									
	م المانية م ما	3A	<10	<10	<0.05				<3	<1	<1	<1	5
R-516A	PAG	4A	<10	<10	<0.05				<3	<1	<1	<1	4
77.5% R-1234yf 8.5% R-134a	170	AA	<10	<10	<0.05				<3	<1	<1	<1	3
14.0% R-152a		3A	<10	<10	0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	7
100°C	POF	4A	<10	<10	0.07	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	4
28 days		AA	<10	<10	0.64	<200 (~180 <sup>A</sup> )	610	320	<3	<1	<1	<1	<3
	A alalitin a al	3A	<10	<10	<0.05				<3	<1	<1	<1	11
	Additized PVF	4A	<10	<10	<0.05				<3	<1	<1	<1	17
		AA	<10	<10	<0.05				<3	<1	<1	<1	32

Table 5.109: Summary of Analytical Results of Aged Sealed Tubes from Phase IIE

<sup>A</sup>Organic acids were detected at concentrations lower than the verified quantitation limit. Results are reported for informational purposes.

NDNot Detected

Refrigerant	Lubricont	erial	Inorgani (ppm in r	ic Anions efrigerant)	TAN	Lubric	ant Organic / (ppm, ug/g)	Acids	Dissolved Elements in Lubricant (ppm)				
Refrigerant	Lubricant	Mate	Fluoride	Chloride	mg KOH/ g oil	Valeric	Heptanoic	Branche d Nonanoic	AI	Cu	Fe	Zn	Si
	A dditiaed	3A	<10	<10	<0.05				<3	<1	<1	<1	<3
	PAG	4A	<10	<10	<0.05				<3	<1	<1	<1	5
R-455A	170	AA	<10	<10	0.07				<3	<1	<1	<1	4
3.0% R-744		3A	<10	<10	0.08	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	3
21.5% R-32 75 5% R-1234vf	POF	4A	<10	<10	0.07	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	5
100°C	102	AA	<10	<10	0.67	<200 (~90 <sup>A</sup> )	610	350	<3	<1	<1	<1	<3
28 days	۵ ما ما : ۵: ۰ م ما	3A	<10	<10	<0.05				<3	<1	<1	<1	18
	Additized PVF	4A	<10	<10	<0.05				<3	<1	<1	<1	37
	1 .	AA	<10	<10	0.08				<3	<1	<1	<1	11
	A dditia o d	3A	<10	<10	<0.05				<3	<1	<1	<1	<3
	PAG	4A	<10	<10	<0.05				<3	<1	<1	<1	3
R-468A	170	AA	<10	<10	<0.05				<3	<1	<1	<1	<3
3.5% R-1132a		3A	<10	<10	0.06	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
21.5% R-32	POF	4A	<10	<10	0.07	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	<3
75.0% R-1234yf 100°C	102	AA	<10	<10	0.66	<200 (~90 <sup>A</sup> )	790	450	<3	<1	<1	<1	3
28 days	م مامانه: - م دا	3A	<10	<10	0.05				<3	<1	<1	<1	46
	Additized	4A	<10	TAN         TAN           spm in refrigerant)         TAN           uoride         Chloride         g oil         Vale           <10				<3	<1	<1	<1	21	
		AA	<10	<10	<0.05				<3	<1	<1	<1	6

### Table 5.110: Summary of Analytical Results of Aged Sealed Tubes from Phase IIE

<sup>A</sup>Organic acids were detected at concentrations lower than the verified quantitation limit. Results are reported for informational purposes.

<sup>ND</sup>Not Detected

#### Table 5.111: Summary of Analytical Results of Aged Sealed Tubes from Phase IIE

Refrigerant	Lubricant	erial	Inorganic Anions (ppm in refrigerant)			TAN mg	Lubricant Organic Acid (ppm, ug/g)				Dissolved Elements in Lubricant (ppm)					
	Lubricant	Mat	Fluoride	Chloride	lodide	KOH/ g oil	Valeric	Heptanoic	Branche d Nonanoic	AI	Cu	Fe	Zn	Si		
<b>R-466A</b> 49.0% R-32		3A	<10	<10	<100	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	3		
11.5% R-125 39.5% R-13l1	Additized POE	4A	<10	<10	<100	<0.05	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<200 <sup>ND</sup>	<3	<1	<1	<1	4		
100°C 28 days		AA	<10	<10	<100	0.22	<200 <sup>ND</sup>	310	<200 (~100 <sup>A</sup> )	<3	<1	<1	<1	<3		

<sup>A</sup>Organic acids were detected at concentrations lower than the verified quantitation limit. Results are reported for informational purposes.

NDNot Detected

	Propose	d Identification	R-1233zd(Z)	3,3,3-trifluoro-1-propyne	3,3,3-trifluoropropene
	R-1233zd(E), a	s rec'd	220	-	-
		3A	100	320	-
	No Oil	4A	100	<100	-
R-1233zd(E)		Alumina	<100	<100	-
		3A	<100	-	-
	Mineral Oil	4A	190	-	-
		Alumina	<100	-	=

### Table 5.112: Qualitative Summary of Key Species in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

'-' indicates not detected.

# Table 5.113: Qualitative Summary of Key Species in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

	Proposed	Identification	R-1224yd(E)	3,3,3-trifluoro-1-propyne	3,3,3-trifluoropropene
	R-1224yd(Z), a	s rec'd		-	-
		3A		-	-
	No Oil	4A		-	-
D 1004.d(7)		4A     -     -       Alumina     changes     -	-		
R-1224ya(2)		3A	changes	-	-
	Mineral Oil	4A		-	-
		Alumina		-	-

	h	Proposed dentification	R-1336mzz(Z)	R-1336mzz(E)	1,1,1,4,4,4- Hexafluorobutane	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol	R-1336mzz-PVE Unknown
	R-514A, as	rec'd		4150	610	-	-	-	-	-	-	-
		3A		1220	200	-	-	-	-	-	-	-
	No Oil	4A		1440	210	-	-	-	-	-	-	-
		Alumina		6330	180	-	-	-	-	-	-	-
		3A		400	<100	-	-	-	-	-	-	-
D 514A	Additized	4A		360	<100	-	-	-	-	-	-	-
25.3% R-1130(E)	PAG	Alumina	-	310	<100	-	-	-	-	-	-	-
74.7% R-1336mzz(Z)		3A		200	<100	-	-	-	-	-	-	-
	POE	4A	-	310	<100	-	-	-	-	-	-	-
R-514A 25.3% R-1130(E) 74.7% R-1336mzz(Z) R-1336mzz(Z)	_	Alumina	-	280	<100	-	-	-	-	-	-	-
		3A	-	200	110	-	-	-	-	-	-	-
	Additized	4A	-	440	140	-	-	-	-	-	-	-
	PVE	Alumina	-	440	120	-	-	-	-	-	-	-
	R-1336mzz	z(Z). as rec'd		4400	270	-	-	-	-	-	-	-
		3A	-	7600	190	-	-	-	-	-	-	-
	No Oil	4A	-	6400	210	-	-	-	-	-	-	-
		Alumina	-	9500	210	-	-	-	-	-	-	-
		3A	-	1200	<100	-	-	-	-	-	-	-
	Additized	4A	-	950	<100	-	-	-	-	-	-	-
R-1336mzz(Z)	PAG	Alumina	-	1900	<100	-	-	-	-	-	-	-
		3A	-	480	<100	-	-	-	-	-	-	-
	POF	4A	-	1000	<100	-	-	-	-	-	-	-
		Alumina	-	1500	<100	-	-	-	-	-	-	-
		34	-	620	<100	-	-	-	_	-	-	-
	Additized	44	-	1200	<100	_	_	-	_	_	-	_
	PVE	Alumina	-	1300	<100	-	-	-	_	-	-	-
	R-1336mz	(F) as rec'd	1362	1000	-	-	-	-	_	-	-	-
	11 10001121	3A	<100		_	-	-	-	-	-	-	-
	No Oil	44	<100	-	-	-	-	-	-	-	-	-
		Alumina	<100	-	_	-	-	-	-	-	-	-
		34	<100		_	-	3370	-	_	-	-	-
	Additized	44	<100		_	-	-	-	_	-	-	-
B-1336mzz(F)	PAG	Alumina	<100	-	_	_	_	-	_	_	-	_
		3A	160	-	-	-	2500	-	-	-	-	-
	POF	44	<100	-	-	-	-	-	-	-	-	-
		Alumina	130	-	-	-	_	-	-	-	-	-
		34	<100	-	-	-	<100	-	-	-	-	-
	Additized	44	<100	-	-	-	-	-	-	-	-	-
	PVE	Alumina	<100	-	-	-	-	-	-	-	-	-
1	1	1		I	1	I	1	I	1	1	I.	1

Table 5.114: Qualitative Summary of Key Species in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

		Proposed Identification	R-1234ze(Z)	3,3,3- trifluoropropene	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol	R-1234ze-PVE Unknown
	R-1234ze(	E), as rec'd	<100	.:	-	-	-	-	-	-	-
		3A	-	ouc	-	140	-	-	-	-	-
	No Oil	4A	-	u L	-	260	-	-	-	-	-
		Alumina	<100	ge i	-	-	-	-	-	-	-
	Additized	3A	-	้นยน	-	-	-	-	-	-	-
	Additized	4A	-	d q c	-	-	-	-	-	-	-
R-1234ze(E)	FAG	Alumina	-	cteo	-	<100	-	-	-	-	-
		3A	-	etec	-	-	-	-	-	-	-
	POE	4A	-	b de	-	-	-	-	-	-	-
		Alumina	-	Ŭ,	-	-	-	-	-	-	-
	Additized	3A	-	ent	-	-	-	-	-	-	-
	Auditizeu DVF	4A	-	res	-	-	-	-	-	-	-
	F V L	Alumina	-	<u>م</u>	-	-	-	-	-	-	-
	R-515B, as	rec'd	G	G	-	-	-	-	-	-	-
		3A	ouo	ouo	-	-	-	-	-	-	-
	No Oil	4A	u L	u L	-	-	-	-	-	-	-
		Alumina	ge	ge	-	-	-	-	-	-	-
	A dditized	3A	าลท	Jan	-	-	-	-	-	-	-
R-515B	PAG	4A	с с	d Ct	-	-	-	-	-	-	-
8.9% R-227ea	FAG	Alumina	cteo	cteo	<100	-	-	-	-	-	-
91.1% R-1234ze(E)		3A	eteo	etec	-	-	-	-	-	-	-
	POE	4A	p d	р о	-	-	-	-	-	-	-
		Alumina	ŭ	ŭ	-	-	-	-	-	-	-
	Additized	3A	ent	ent	-	-	-	-	-	-	-
	PVF	4A	res	res	-	-	-	-	-	-	-
	F V L	Alumina	<u>م</u>	<u>م</u>	-	-	-	-	-	-	-

Table 5.115: Qualitative Summary of Key Species in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

		Proposed Identification	3,3,3- trifluoropropene	Vinyl Fluoride	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol	R-1234yf-PVE Unknown																			
	R-1234yf, a	s rec'd		-	-	-	-	-	-	-	-																			
		3A	ouc	-	-	-	-	-	-	-	-																			
	No Oil	4A	ŭ	-	-	-	-	-	-	-	-																			
		Alumina	ge i	-	-	-	-	-	-	-	-																			
		3A	ang	-	-	-	-	-	-	-	-																			
	Additized	4A	l ch	-	-	-	-	-	-	-	-																			
R-1234yf	PAG	Alumina	cteo	ted	-	-	-	-	-	-	-	-																		
к-1234ут		3A	stec	-	-	-	-	-	-	-	-																			
	POE	4A	de	-	-	-	-	-	-	-	-																			
		Alumina	ů, no	-	-	-	-	-	-	-	-																			
		3A	ent	-	-	-	-	-	-	-	-																			
	Additized	4A	res	-	-	-	-	-	-	-	-																			
	PVE	Alumina	4	-	-	-	-	-	-	-	-																			
	R-516A, as	rec'd		-	-	-	-	-	-	-	-																			
		3A		-	-	-	-	Ethan         Action         Action </td <td>-</td> <td>-</td>	-	-																				
	No Oil	4A		-	-	-	-	-	-	-	-																			
		Alumina	52a	52a	52 <i>a</i>	52 <i>a</i>	52a	52a	52a	52a	52a	.52a	.52a	52a	52a	52a	.52a	.52a	52a	52a	52a	52a	520	-	-	-	-	-	-	-
	۵ مامانه:	3A	۲-1	<100	-	-	-	-	-	-	-																			
R-516A	Additized	4A	th	-	-	-	-	-	-	-	-																			
77.5% R-1234yf	PAG	Alumina	Ň	<100	-	-	-	-	-	-	-																			
8.5% R-1340 14.0% R-152a		3A	ion	-	-	-	-	-	-	-	-																			
	POE	4A	elut	-	-	-	-	-	-	-	-																			
		Alumina	0	-	-	-	-	-	-	-	-																			
	Additized	3A	Ŭ	-	-	-	-	-	-	-	-																			
	Additized	4A	-	- +	-	-	-	1		1	-	-	-	-	-	-	-	-												
	F'VL	Alumina		<100	-	-	-	-	-	-	-																			

Table 5.116: Qualitative Summary of Key Species in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

		Proposed Identification	3,3,3- trifluoropropene	2-methyl-1- propene	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol	R-1234yf-PVE Unknown															
	R-455A, as	rec'd		-	-	-	-	-	-	-	-															
	Additized	3A	~	-	-	-	-	-	-	-	-															
	Additized	4A	C. Cte	-	-	-	-	-	-	-	-															
R-455A	PAG	Alumina	o detec in conc	etec	etec	etec	etec	etec	-	-	-	-	-	-	-	-										
3.0% R-744		3A		-	-	-	-	-	-	-	-															
21.5% R-32	POE	4A	ge	-	-	-	-	-	-	-	-															
75.5% R-1234yf		Alumina	ent	-	-	-	-	-	-	-	-															
		3A	ch	-	-	-	-	-	-	-	-															
	Additized	4A	_ ₽_	-	-	-	-	-	-	-	-															
	PVE	Alumina		-	-	-	-	-	-	-	-															
	R-468A, as	rec'd		-	-	-	-	-		-	-															
	٥ ما ما نه : ٩ ما	3A	~	-	-	-	-	-	.2a	-	-															
	Additized	4A	cted:	c tec	cteo	c. ctec	ctec	cted c.	cted c.	cted c.	cted c.	cted c.	cted c.	cted C.	cted c.	cted -	cted -	cted	-	-	-	-	-	113	-	-
R-168A	PAG	Alumina	etec	-	-	-	-	-	Ľ.	-	-															
3.5% R-1132a		3A	in c	-	-	-	-	-	ith	-	-															
21.5% R-32	POE	4A	, no Be	-	-	-	-	-	≤ ≤	-	-															
75.0% R-1234yf		Alumina	ent	-	-	-	-	-	tio	-	-															
	م ما مانغات م ا	3A	res ch	-	-	-	-	-	-elu	-	-															
	Additized	4A	_ ₽_	-	-	-	-	-	Ś	-	-															
	PVE	Alumina		-	-	-	-	-		-	-															

### Table 5.117: Qualitative Summary of Key Species in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

'-' indicates not detected.

# Table 5.118: Qualitative Summary of Key Species in GC-MS Headspace Analysis of Aged Sealed Tubes, in Peak Area (ppm)

Propose Identificatio		Proposed Identification	Trifluoromethane (R-23)	Fluoroethane	Difluoroiodo- methane	Pentafluoro- ethyliodide	Propanal	Acetone	Isobutane	Acetaldehyde	Ethane	Ethanol	lodoethane
R-466A	R-466A, as	rec'd	-	-	-	-	-	-	-	-	-	-	-
49.0% R-32	9.0% R-32	3A	433	-	-	-	-	-	-	-	-	-	-
11.5% R-12		4A	148	-	-	-	-	-	-	-	-	-	-
39.5% R-13		Alumina	130	-	-	-	-	-	-	-	-	-	-

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