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## Chemical Stability Investigations of Low GWP Refrigerants R-1234ze(E), R-450A, R-515B, R-1234yf, R-513A and R-516A with Lubricants

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### ABSTRACT

AHRTI (Air-Conditioning Research Technology Institute) sponsored a research program on developing essential low GWP refrigerant database in collaboration with Oak Ridge National Laboratory (ORNL) and National Institute of Standards and Technology (NIST). In 2019, AHRTI received a US Department of Energy Building Technology Office funding award to carry out this research program. As part of the overall effort, Trane Technologies conducted AHRTI Project 9016 – Chemical Stability of Low GWP Refrigerants with Lubricants.

This paper summarizes the results of highly accelerated life tests (HALT), conducted according to ASHRAE Standard 97 sealed glass tube methodology, for refrigerants R-1234ze(E), R-450A, R-515B, R-1234yf, R-513A, and R-516A with and without lubricants. The lubricants studied were polyalkylene glycol (PAG), polyolester (POE) and polyvinyl ether (PVE). The study also included evaluation of HFC blending components R-227ea and R-152a.

### 1. INTRODUCTION

Heating, ventilation, air-conditioning, and refrigeration (HVACR) equipment life expectancies are typically 15 to 25 years depending on the application. The chemical stability of the refrigerant with materials of construction needs to be durable to ensure equipment operates reliably over these lifespans. AHRTI Project 9016 was an 11 month research effort to conduct chemical and thermal stability assessments of a wide range of new low GWP refrigerants. The information obtained through this project is designed to assist the HVACR industry in identification of potential chemical compatibility and material compatibility concerns that may result from interactions between new refrigerants or new refrigerant blends and materials currently used in refrigeration systems. AHRTI Project 9016 was divided into two phases: Phase 1 - chemical stability evaluations of various system metals on the chemical stability of the refrigerants with or without unadditized lubricants and Phase 2 - chemical stability evaluations to further understand the impact of various factors on chemical stability (e.g., additized lubricants, refrigerant blending components, filter drier materials).

Few chemical stability studies exist in literature that describe the comprehensive investigation of R-1234ze(E), R-450A (42% R-134a/58% R-1234ze(E)), R-515B (91.1% R-1234ze(E)/8.9% R-227ea), R-1234yf, R-513A (56% R-1234yf/44% R-134a), and R-516A (77.5% R-1234yf/8.5% R-134a/14.0% R-152a) with and without various lubricants. Compositions for blends shown are percent by weight. The study also included evaluation of new HFC blending components to the HVACR industry, R-152a and R-227ea, which will be discussed in this paper. The AHRTI 9016 final report provides a literature summary of limited investigations into the stability of these refrigerants (Sorenson et al., 2021). No discussion is provided for the filter drier material exposures in this paper, however little to no reactivity was observed in these experiments likely as a result of the lower temperature conditions (Table 2).

## 2. EXPERIMENTAL

Refrigerants R-1234ze(E), R-450A, R-515B, R-1234yf, R-513A, and R-516A were evaluated in their pure form (100% refrigerant conditions) and with their appropriate lubricants used or proposed to be used with the candidate refrigerant chemistries. Lubricants evaluated included unadditized and additized polyalkylene glycol (PAG), unadditized polyol ester (POE), and unadditized and additized polyvinyl ether (PVE). Typically, POEs are used without any additizes to improve the stability of the lubricant with a refrigerant, while both PAGs and PVEs use additives to stabilize the lubricant with the refrigerant. Table 1 and Table 2 summarize the test conditions used in this study and Figure 1 provides visual examples of the sealed glass tubes containing the various materials.

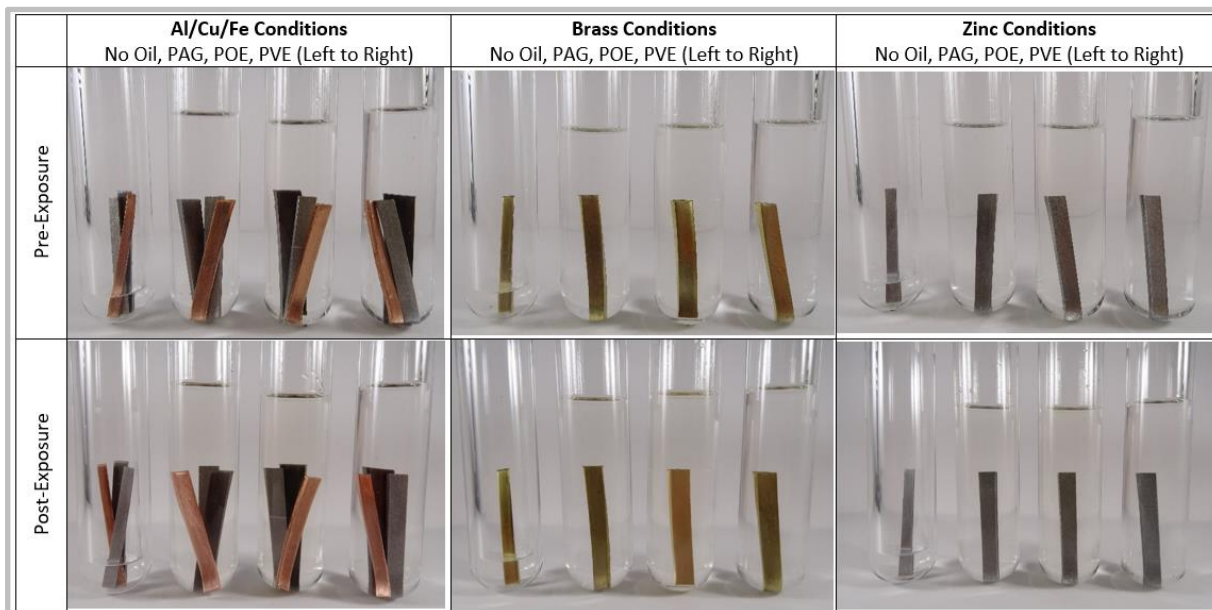
Table 1. Summary of Refrigerant and Lubricant Test Conditions with Metal Coupons.

	No Lubricant	Unadditized PAG	Additized PAG	POE	Unadditized PVE	Additized PVE	Time (days)	Temp
R-1234ze(E)	X	X	X	X	X	X	14	175°C
R-450A	X	X		X	X		14	175°C
R-515B	X	X		X	X		14	175°C
R-1234yf	X	X	X	X	X	X	14	175°C
R-513A	X	X	X	X	X	X	14	175°C
R-516A	X	X		X	X		14	175°C

Table 2. Summary of Refrigerant and Lubricant Test Conditions with Desiccant Materials.

	No Lubricant	Additized PAG	POE	Additized PVE	Time (days)	Temp
R-1234ze(E)	X	X	X	X	28	100°C
R-450A					28	100°C
R-515B	X	X	X	X	28	100°C
R-1234yf	X	X	X	X	28	100°C
R-513A					28	100°C
R-516A	X	X	X	X	28	100°C

All exposures were conducted in the presence of metal coupons or desiccant materials. Metal coupons included a three metal combination of aluminum (AA380), copper (CDA 110), and iron (G1095) and single coupons of brass (C260) and zinc-aluminum alloy (ZA8). Desiccant materials included type 594 3A and 4A molecular sieve and type D-201 activated alumina. The chemical stability assessments were conducted in sealed glass tubes per ASHRAE Standard 97 procedures (ASHRAE 97, 2007) with 100% refrigerant and 20% refrigerant/80% lubricant by weight. The aging conditions for the sealed glass tubes experiments were 175°C (347°F) for 14 days with the metal coupons and 100°C (212°F) for 28 days with the desiccant materials. Analytical assessments for all conditions included visual appearance changes of the fluids, metal coupons or desiccant materials, refrigerant breakdown via anion (fluoride and chloride) analysis, and refrigerant or lubricant breakdown analysis of the sealed glass tube headspace via Gas Chromatography Mass Spectroscopy (GC-MS). Additionally, for the conditions containing lubricant, total acid number (TAN), dissolved metals using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), and where applicable, POE lubricant breakdown via organic acid quantification were completed to provide more insights.



**Figure 1:** Example of before and after exposure sealed glass tubes containing metals coupons for accelerated aging in presence of refrigerant (R-513A) and unadditized lubricants. From left to right, conditions shown are the three-metal combination (aluminum, copper, and iron) and single coupons of brass and zinc-aluminum alloy.

### 3. CHEMICAL STABILITY RESULTS

#### R-1234ze(E) Summary - 14 days at 175°C (347°F)

Table 3 summarizes the results of the R-1234ze(E) evaluations. 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. Analysis of the vapor space after exposure by GC-MS did not detect any significant R-1234ze(E) breakdown products. A unique compound was detected, but not fully identified, in all conditions tested with unadditized and additized PVE lubricants. This compound appeared to result from an interaction between the R-1234ze(E) and PVE chemistry with a possible molecular weight of 76 grams/mole. Elevated TAN and dissolved zinc were detected when in the presence of POE, however these results were consistent when compared to other refrigerants with the same test condition which would indicate this is a zinc/POE reaction and not a refrigerant/zinc/POE reaction. Dissolved silicon was detected in several conditions at low concentrations (<15 ppm). The presence of elevated silicon is potentially a reaction with the glass (silicon boride) in the sealed tubes, but a corresponding presence of boron was not at reportable levels in the analysis.

Table 3. Summary of R-1234ze(E) Chemical Stability with Metal Coupons

Refrigerant	Lubricant	Catalyst	Fluoride (ppm)	Chloride (ppm)	TAN mg KOH/g oil	Dissolved Elements in Lubricants by ICP (ppm)				
						Al	Cu	Fe	Zn	Si
R-1234ze(E)	No Oil	Al/Cu/Fe	<10	<10		n/a				
	PAG	Al/Cu/Fe	<10	<10	<0.05	<3	<1	<1	<1	<3
	Additized PAG	Al/Cu/Fe	<10	<10	<0.05	<3	<1	<1	<1	<3
	POE	Al/Cu/Fe	<10	<10	<0.05	<3	<1	<1	<1	3
	PVE	Al/Cu/Fe	<10	<10	<0.05	<3	<1	<1	<1	8
	Additized PVE	Al/Cu/Fe	<10	<10	<0.05	<3	<1	<1	<1	11
	No Oil	Brass	<10	<10		n/a				
	PAG	Brass	<10	<10	<0.05	<3	<1	<1	<1	<3
	Additized PAG	Brass	12	<10	<0.05	<3	<1	<1	<1	<3
	PVE	Brass	<10	<10	<0.05	<3	<1	<1	<1	7

	Additized PVE	Brass	<10	<10	<0.05	<3	<1	<1	<1	12
	No Oil	Zinc	<10	<10	n/a					
	PAG	Zinc	<10	<10	<0.05	<3	<1	<1	<1	4
	Additized PAG	Zinc	<10	<10	<0.05	<3	<1	<1	<1	<3
	POE	Zinc	10 (13 <sup>1</sup> )	<10	0.20	<3	<1	<1	74	<3
	PVE	Zinc	<10	<10	<0.05	<3	<1	<1	<1	<3
	Additized PVE	Zinc	<10	<10	<0.05	<3	<1	<1	<1	9

<sup>1</sup>Repeated measurements

#### R-450A Summary - 14 days at 175°C (347°F)

Table 4 summarizes the results of the R-450A (42% R-134a/58% R-1234ze(E)) evaluations. As one would expect, results are similar to R-1234ze(E) evaluations. A reaction was seen between the POE and zinc due to elevated concentrations of dissolved zinc. Also, the same unique compound was detected via GC-MS, but not identified, in all conditions tested with unadditized and additized PVE lubricants. The presence of elevated silicon was again observed which is potentially a reaction with the glass (silicon boride) in the sealed tubes, but a corresponding presence of boron was not at reportable levels in the analysis.

Table 4. Summary of R-450A Chemical Stability with Metal Coupons

Refrigerant	Lubricant	Catalyst	Fluoride (ppm)	Chloride (ppm)	TAN mg KOH/g oil	Dissolved Elements in Lubricants by ICP (ppm)				
						Al	Cu	Fe	Zn	Si
R-450A	No Oil	Al/Cu/Fe	<10	<10	n/a					
	PAG	Al/Cu/Fe	<10	<10	0.06	<3	<1	<1	<1	<3
	POE	Al/Cu/Fe	<10	<10	<0.05	<3	<1	<1	<1	3
	PVE	Al/Cu/Fe	<10	<10	0.07	<3	<1	<1	<1	7
	No Oil	Brass	<10	<10	n/a					
	PAG	Brass	<10	<10	<0.05	<3	<1	<1	<1	<3
	POE	Brass	<10	<10	<0.05	<3	<1	<1	<1	<3
	PVE	Brass	<10	<10	0.07	<3	<1	<1	<1	5
	No Oil	Zinc	<10	<10	n/a					
	PAG	Zinc	<10	<10	<0.05	<3	<1	<1	<1	<3
	POE	Zinc	<10	<10	0.21	<3	<1	<1	48	<3
	PVE	Zinc	<10	<10	<0.05	<3	<1	<1	<1	12

#### R-515B Summary - 14 days at 175°C (347°F)

Table 5 summarizes the results of R-515B (91.1% R-1234ze(E)/8.9% R-227ea) evaluations. Fluoride was observed in three test conditions, indicating potential refrigerant decomposition, and follow-on repeat exposures confirmed these observations. In addition, the same unidentified compound was seen by GC-MS in all PVE exposures as previously discussed above. Once again, the reaction of POE with zinc was observed and dissolved silicon was detected which is likely from a reaction with the sealed glass tube material. 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. Results from these evaluations were inconclusive. Pure R-227ea indicated 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.

Table 5. Summary of R-515B Chemical Stability with Metal Coupons

Refrigerant	Lubricant	Catalyst	Fluoride (ppm)	Chloride (ppm)	TAN mg KOH/g oil	Dissolved Elements in Lubricants by ICP (ppm)				
						Al	Cu	Fe	Zn	Si
R-515B	No Oil	Al/Cu/Fe	<10	<10	n/a					
	PAG	Al/Cu/Fe	13 (<10 <sup>1</sup> )	<10	<0.05	<3	<1	<1	<1	4
	POE	Al/Cu/Fe	<10	<10	<0.05	<3	<1	<1	<1	3
	PVE	Al/Cu/Fe	23 (<10 <sup>1</sup> )	<10	<0.05	<3	<1	<1	<1	7
	No Oil	Brass	<10	<10	n/a					

	PAG	Brass	<10	<10	<0.05	<3	<1	<1	<1	<3
	POE	Brass	<10	<10	0.10	<3	<1	<1	8	4
	PVE	Brass	<10	<10	<0.05	<3	<1	<1	<1	5
	No Oil	Zinc	<10	<10	n/a					
	PAG	Zinc	<10	<10	<0.05	<3	<1	<1	1	<3
	POE	Zinc	58 (25 <sup>1</sup> )	<10	0.17	<3	<1	<1	17	5
	PVE	Zinc	<10	<10	<0.05	<3	<1	<1	<1	<3

<sup>1</sup>Repeated measurements

### R-1234yf Summary - 14 days at 175°C (347°F)

Table 6 summarizes the results of R-1234yf evaluations. Elevated levels of fluoride 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 had variability in its ability to reduce the presence of fluoride after aging. GC-MS of the refrigerant vapor did not yield any insights into possible R-1234yf breakdown products. As observed previously, a reaction product was detected and appears to be an interaction between R-1234yf and the PVE. The compound was different than the previously discussed R-1234ze(E)/PVE product and review of the mass spectra suggests a potential empirical formula of C<sub>3</sub>H<sub>7</sub>F<sub>3</sub> (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 from the breakdown of the PVE lubricant. This component was present in all conditions tested with unadditized and additized PVE lubricants. Once again, the reaction of POE with zinc was observed and dissolved silicon was detected which is likely from a reaction with the sealed glass tube material. 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.

Table 6. Summary of R-1234yf Chemical Stability with Metal Coupons

Refrigerant	Lubricant	Catalyst	Fluoride (ppm)	Chloride (ppm)	TAN mg KOH/g oil	Dissolved Elements in Lubricants by ICP (ppm)				
						Al	Cu	Fe	Zn	Si
R-1234yf	No Oil	Al/Cu/Fe	<10	<10	n/a					
	PAG	Al/Cu/Fe	78	<10	<0.05	<3	<1	<1	<1	7
	Additized PAG	Al/Cu/Fe	28	<10	<0.05	<3	<1	<1	<1	4
	POE	Al/Cu/Fe	<10	<10	<0.05	<3	<1	<1	<1	<3
	PVE	Al/Cu/Fe	60	<10	0.07	<3	<1	<1	<1	14
	Additized PVE	Al/Cu/Fe	<10	<10	0.10	<3	<1	<1	<1	6
	No Oil	Brass	<10	<10	n/a					
	PAG	Brass	34	<10	0.06	<3	<1	<1	<1	3
	Additized PAG	Brass	44	<10	<0.05	<3	<1	<1	<1	5
	POE	Brass	<10	<10	0.07	<3	<1	<1	12	<3
	PVE	Brass	49	<10	0.06	<3	<1	<1	<1	4
	Additized PVE	Brass	<10	<10	<0.05	<3	<1	<1	<1	31
	No Oil	Zinc	<10	<10	n/a					
	PAG	Zinc	33	<10	<0.05	<3	<1	<1	1	6
	Additized PAG	Zinc	36	<10	<0.05	<3	<1	<1	<1	<3
	POE	Zinc	<10	<10	0.10	<3	<1	<1	37	<3
	PVE	Zinc	44	<10	0.06	<3	<1	<1	<1	7
	Additized PVE	Zinc	<10	<10	0.07	<3	<1	<1	<1	4

### R-513A Summary - 14 days at 175°C (347°F)

Table 7 summarizes the results of R-513A (56% R-1234yf/44% R-134a) evaluations. As one would expect, results are similar to R-1234yf evaluations. Elevated levels of fluoride 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 had variability in its ability to reduce the presence of fluoride after aging. A reaction was seen between the POE and zinc due to elevated concentrations of dissolved zinc. Also, the same unique compound was

detected by GC-MS, by not identified, in all conditions tested with unadditized and additized PVE lubricants. The presence of elevated silicon was again observed which is potentially a reaction with the glass (silicon boride) in the sealed tubes, but a corresponding presence of boron was not at reportable levels in the analysis. The presence of R-134a did little to either reduce or accelerate the chemical instability of R-1234yf.

Table 7. Summary of R-513A Chemical Stability with Metal Coupons

Refrigerant	Lubricant	Catalyst	Fluoride (ppm)	Chloride (ppm)	TAN mg KOH/g oil	Dissolved Elements in Lubricants by ICP (ppm)				
						Al	Cu	Fe	Zn	Si
R-513A	No Oil	Al/Cu/Fe	<10	<10		n/a				
	PAG	Al/Cu/Fe	89	12	0.06	<3	<1	<1	1	7
	Additized PAG	Al/Cu/Fe	16	<10	<0.05	<3	<1	<1	<1	<3
	POE	Al/Cu/Fe	<10	<10	0.06	<3	1	<1	<1	5
	PVE	Al/Cu/Fe	51	<10	<0.05	<3	<1	<1	<1	7
	Additized PVE	Al/Cu/Fe	<10	<10	<0.05	<3	<1	<1	<1	5
	No Oil	Brass	<10	<10		n/a				
	PAG	Brass	51	<10	0.06	<3	<1	<1	1	5
	Additized PAG	Brass	32	<10	<0.05	<3	<1	<1	<1	<3
	POE	Brass	<10	<10	0.16	<3	<1	<1	53	<3
	PVE	Brass	13	<10	<0.05	<3	<1	<1	<1	4
	Additized PVE	Brass	<10	<10	<0.05	<3	<1	<1	<1	4
	No Oil	Zinc	<10	<10		n/a				
	PAG	Zinc	11	<10	0.07	<3	<1	<1	3	5
	Additized PAG	Zinc	18	<10	<0.05	<3	<1	<1	<1	<3
	POE	Zinc	<10	<10	0.22	4	<1	<1	65	<3
	PVE	Zinc	<10	<10	0.05	<3	<1	<1	<1	<3
	Additized PVE	Zinc	<10	<10	0.05	<3	<1	<1	<1	5

**R-516A Summary - 14 days at 175°C (347°F)**

Table 8 summarizes the results of R-516A (77.5% R-1234yf/8.5% R-134a/14.0% R-152a) evaluations. Once again, results were similar to R-1234yf and R-513A investigations with a few differences as a result of the addition of R-152a. Elevated levels of fluoride 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 had variability in its ability to reduce the presence of fluoride after aging. A reaction was seen between the PVE and zinc due to elevated concentrations of dissolved zinc. Also, the same unique compound was detected by GC-MS, but not identified, in all conditions tested with both unadditized and additized PVE lubricants. The presence of elevated silicon was again observed which is potentially a reaction with the glass (silicon boride) in the sealed tubes, but a corresponding presence of boron was not at reportable levels in the analysis.

Table 8. Summary of R-516A Chemical Stability with Metal Coupons

Refrigerant	Lubricant	Catalyst	Fluoride (ppm)	Chloride (ppm)	TAN mg KOH/g oil	Dissolved Elements in Lubricants by ICP (ppm)				
						Al	Cu	Fe	Zn	Si
R-516A	No Oil	Al/Cu/Fe	<10	<10		n/a				
	PAG	Al/Cu/Fe	22	<10	<0.05	<3	<1	<1	<1	<3
	POE	Al/Cu/Fe	<10	<10	0.10	<3	<1	<1	<1	<3
	PVE	Al/Cu/Fe	14	<10	<0.05	<3	<1	<1	<1	6
	No Oil	Brass	<10	<10		n/a				
	PAG	Brass	11	<10	<0.05	<3	<1	<1	<1	<3
	POE	Brass	<10	<10	0.05	<3	<1	<1	1	4
	PVE	Brass	13	<10	<0.05	<3	<1	<1	<1	16
	No Oil	Zinc	<10	<10		n/a				

	PAG	Zinc	<10	<10	0.05	<3	<1	<1	1	3
	POE	Zinc	<10	<10	0.15	<3	<1	<1	50	<3
	PVE	Zinc	50	<10	0.05	<3	<1	<1	<1	11

Analysis of the vapor space detected vinyl fluoride (R-1141) in the zinc-containing conditions at low concentrations which is a possible breakdown product of R-152a. As a result, pure R-152a was evaluated given this observation. Vinyl fluoride ( $\text{CH}_2=\text{CHF}$ ) could form as the result of a hydrogen fluoride elimination reaction from R-152a ( $\text{CH}_3-\text{CHF}_2$ ). Initial investigations with pure R-152a indicated possible 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 overpressurization would be expected since vinyl fluoride has a boiling point of  $-72^\circ\text{C}$  ( $-98^\circ\text{F}$ ). 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. GC-MS analysis detected elevated levels of vinyl fluoride produced, consistent with GC-MS findings for R-516A. 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/R-152a/R-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.

#### 4. CONCLUSIONS

Highly accelerated life tests (HALT) were conducted according to ASHRAE Standard 97 sealed glass tube methodology for refrigerants R-1234ze(E), R-450A, R-515B, R-1234yf, R-513A, and R-516A with and without lubricants. In addition, R-227ea and R-152a were studied further in their pure form because of possible reactivity seen in blends. The results reveal the role of lubricant chemistry involvement on the breakdown of the various hydrofluoroolefin (HFO) refrigerants. A unique breakdown product was observed in all the HFO-PVE conditions and is suspected to be an interaction of the refrigerant and lubricant. The addition of the additive package in the PVE had no impact on the presence of this unknown compound. An additional indicator of refrigerant decomposition is the generation of fluoride. Fluoride was consistently generated in conditions containing the unadditized PAG and unadditized PVE lubricants, however, the same trend was not observed in conditions containing POE. The addition of the PVE additive package resulted in a reduction in fluoride generation, but the same was not observed with the PAG additive package, which had varying impact on the fluoride generation (Figure 2 and 3).

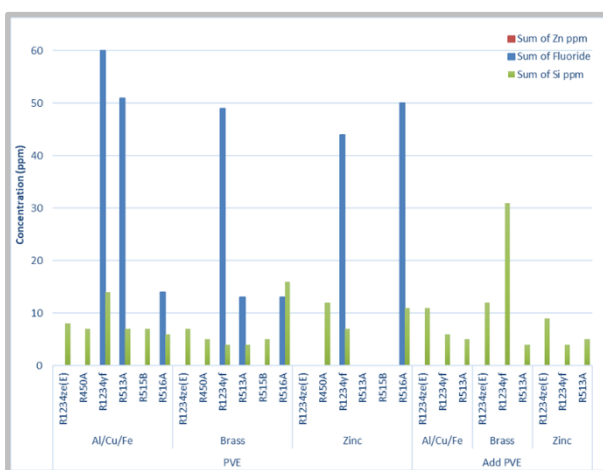


Figure 2: Summary of Dissolved Zinc, Fluoride and Silicon in PVE Evaluations

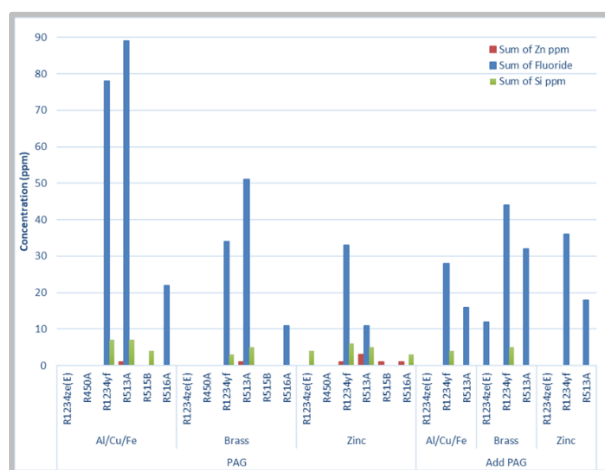


Figure 3: Summary of Dissolved Zinc, Fluoride and Silicon in PAG Evaluations



Zinc-containing materials were observed to accelerate reactivity in numerous conditions, both in driving refrigerant reactions as well as increasing lubricant decomposition. POE lubricant decomposition in the presence of zinc containing materials was observed and indicates caution should be taken when applying zinc containing materials in HVACR systems with HFO refrigerants (Figure 4). Further work was recommended in the AHRTI Project 9016 final report specifically related to the refrigerants presented in this paper. It was recommended to further explore the unique HFO-PVE interactions that were observed in the GCMS analysis, the impact of lubricant additives and/or refrigerant stabilizers on stability, and additional materials of construction that may result in unique interactions given observations with brass and zinc. Additionally, there remains a gap in understanding of refrigerant breakdown products where significant levels of fluoride were detected, but no refrigerant decomposition products were detected in the assessment of the headspace via GC-MS.



Figure 4: Summary of Dissolved Zinc, Silicon and TAN in POE Evaluations. Fluoride was not detected, so it is not shown.

Overall, good chemical stability was observed across the many refrigerants in this study with 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. 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. No stereoisomerization rearrangement, R-1234ze(Z), was seen in the R-1234ze(E) evaluations.

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## REFERENCES

ASHRAE Standard 97-2007, Sealed Glass Tube Method to Test the Chemical Stability of Materials for Use Within Refrigerant Systems, ASHRAE, Inc., Atlanta, GA 30329.

Sorenson, E., Kujak, S., Leehey, M., Robaczewski, C., Stellpflug, T. 2021. Material Compatibility and Lubricants Research for Low GWP Refrigerants – Chemical Stability of Low GWP Refrigerants with Lubricants. Report AHRI 09016. Arlington, VA: Air Conditioning, Heating, and Refrigeration Technology Institute, Inc.

Bier, K., Crone, M., Tuerk, M., Leuckel, W., Christill, M., and Leisenheimer, B., 1990. Studies of the thermal stability and ignition behavior and combustion properties of the refrigerants R-152a and R-134a. DKV-Tagungsbericht 17:169-191.

Hansen, P.E., and Finsen, L. 1992. Lifetime and reliability of small hermetic compressors using a ternary blend HCFC-22/HFC-152a/HCFC-124. International Refrigeration Conference—Energy Efficiency and New Refrigerants, D. Tree, ed. Purdue University, West Lafayette, IN.