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1,1-Difluoroethylene Thermal Stability, Material Compatibility and Refrigerant/Lubricant Interactions Study

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ABSTRACT

Hydrofluoroolefins (HFOs) play an important role in industry, it is recognized that (HFOs) containing unsaturated bonds in their molecular structure have a shorter atmospheric lifetime than hydrofluorocarbons (HFCs) and thus have a lower global warming potential (GWP) and due to increasing concerns about global warming and ozone depletion, the development of Refrigerants is becoming increasingly important and highly attraction for air-conditioning applications in the international community. which offers high energy efficiency and low global warming potential (GWP), resulting in low overall environmental impact and improved energy efficiency. In this paper, the authors will summarize thermal stability test results, ASHRAE Standard 97 and ASHRAE Guideline 38 accelerated compatibility testing methodologies, for R1132a and materials compatibility of select Metals. We conducted an experimental study on the design parameters that are important for life temperature, contamination (moisture, and Air) with various polyolester (POE) and polyether (PAG) lubricants.

Keywords: R-1132a, Chemical Stability, Material Compatibility

1. INTRODUCTION

1,1-Difluoroethylene (R-1132a or vinylidene fluoride) is stable under recommended storage conditions, Chemical stability of the refrigerant containing systems needs to be designed to be stable enough without being replaced over the above time periods. The ability to assess the chemical stability of refrigerants in the laboratory has been a dilemma in industry for decades¹. Investigators are challenged to correlate tens of thousands of system operation hours to data from laboratory scale tests performed over durations of days and weeks. Highly accelerated laboratory testing is required because of the impracticality and cost of running equipment for years. It is common practice in the industry to assess chemical stability of refrigerants using glass tubes per ASHRAE Standard 97² and ASHRAE Guideline 38³ procedures with various system materials at highly accelerated temperatures instead of running equipment (ASHRAE 97, 2007). The recent study⁴ of R-1132a as a refrigerant blend component (Low, 2018) allows further air-conditioning refrigerant development in both stationery and EV thermal management applications. Typical accelerated conditions for sealed glass tubes experiments can vary with temperatures ranging from 80°C to 175°C for durations of 1 to 4 weeks, with a more common test point established at 175°C for 2 weeks. Limited data exists on the chemical stability of pure R-1132a or in combination with other refrigerants, lubricants^{5,6}. Authors also summarized the chemical stability studies with R-1132a with polyol ester lubricant systems. The chemical stability work summarized in this paper is a further extension of this initial work. The chemical stability of R-1132a was evaluated at Accelerated Compatibility Testing (ACT) conditions in R-1132a.

2. CHEMICAL STABILITY OF NEAT R-1132a

Generally, a common free-radical polymerization (FRP)⁷ is a method of polymerization, by which a polymer forms by the successive addition of free-radical building blocks. Free radicals can be formed by several different mechanisms, usually involving separate initiator molecules. Following its generation, the initiating free radical adds (nonradical) monomer units, thereby growing the polymer chain. Neat R-1132a (also known as VDF, vinylidene fluoride) is used as the feed stock for PVDF (polyvinylidene fluoride) a polymer used in lithium-ion batteries.

During polymerization, a polymer spends most of its time in increasing its chain length, or propagating. After the radical initiator is formed, it attacks a monomer (Figure 1). In an ethene monomer, one electron pair is held securely between the two carbons in a sigma bond. The other is more loosely held in a pi bond. The free radical uses one electron from the pi bond to form a more stable bond with the carbon atom. The other electron returns to the second carbon atom, turning the whole molecule into another radical. This begins the polymer chain. Figure shows how the orbitals of an ethene monomer interact with a radical initiator.

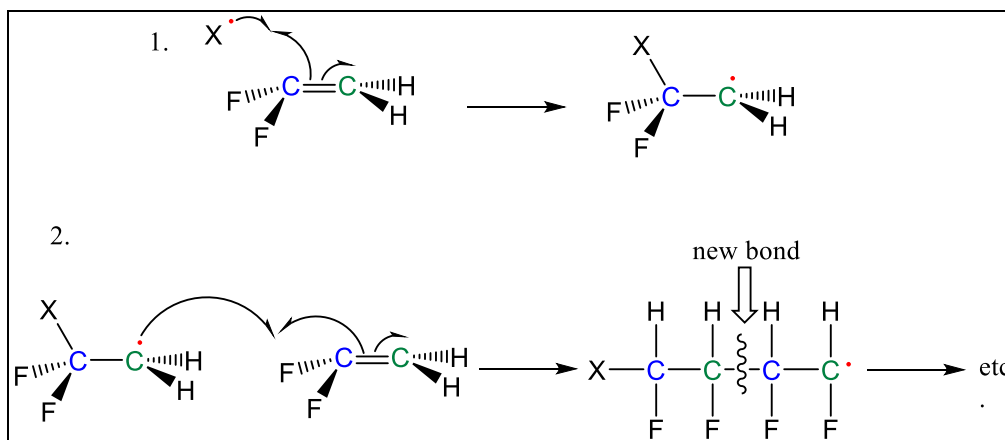


Figure 1: General Free-radical polymerization (FRP) mechanism

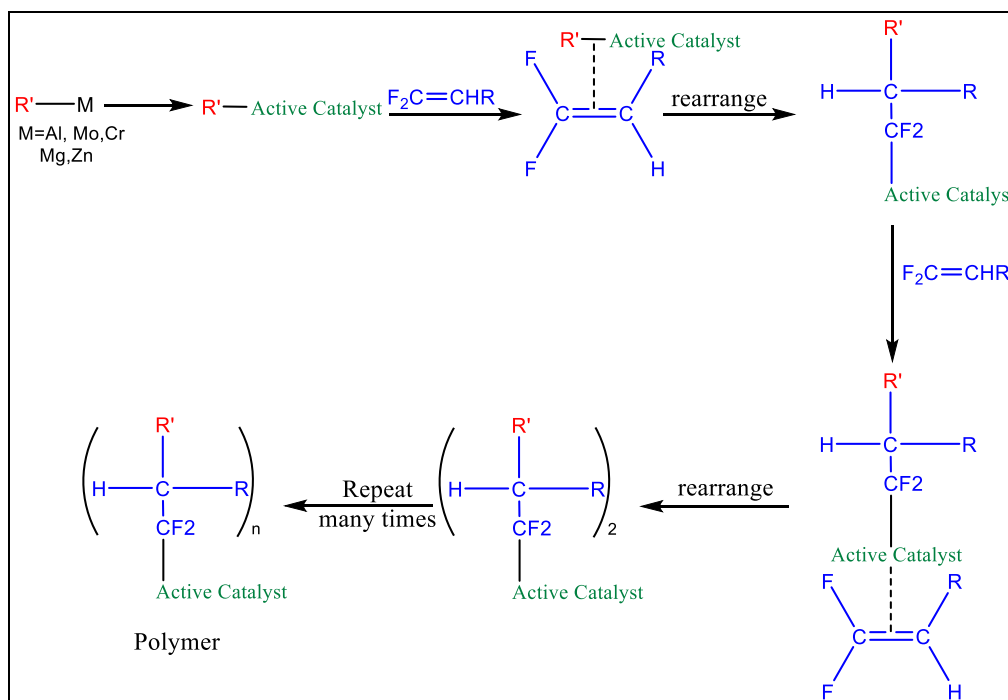
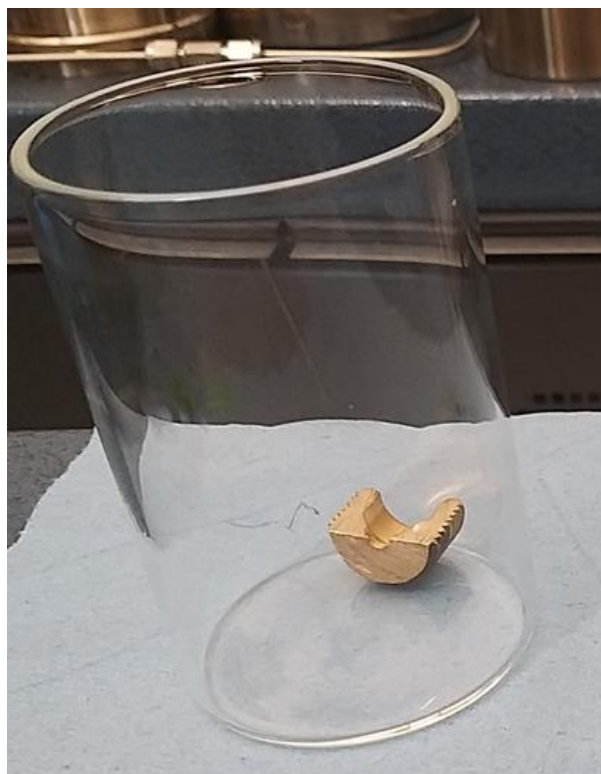


Figure 2: The possible Catalyst Transfer Polymerization (CTP) mechanism of forming PVDF in present of air at 80 °C /6 weeks ID number 22, 23 &24

As Figure 2 showed, one of the possible mechanisms for the polymerization reaction that happened is the Catalyst Transfer Polymerization (CTP)⁸, which is a type of living chain-growth polymerization that is used for synthesizing conjugated polymers. Initiation from a metal (II) species involves two monomers trans metalating onto the metal center to form a complex that can undergo reductive elimination. The complex formed after reductive elimination is referred to as a π -complex because the catalyst bound to the π system of the monomer. The catalyst can isomerize to other π -complexes via a process known as "ring-walking" to the π -bond adjacent to a C-X bond at the end of the chain allowing oxidative addition to occur. The product of oxidative addition is an active polymer-metal (II)-halide, and it can react with monomers in the propagation reaction. This metal-initiated polymerization may take the form of two types of commonly used materials found in the HVAC&R trade: CrMo steel (cylinders and components) and brass (valves, swash plates, copper piping connections, etc)



(a) Brass
19,20&21
4 weeks at 80 °C
No oil/no Air



(b)CrMo + Brass + Al wire
22,23&24
6 weeks at 80 °C
No oil/ 100 or 1000 ppm Air

Figure 3: Example photo of neat R1132a with Brass and CrMo+brass corresponding to ID numbers (19-24)

For brass by itself, Figure 3a, above shows that it seems nothing is happened to the material through the test conditions with no oil/ nor air additives for the ID number (19,20&21) and all the R-1132a was recovered to give peaks of the refrigerant only via GC. In this study, it was amid to build an initial understanding of the possible reaction mechanism that could happen in present or absent of the POE/ PAG oils.

In the combination of CrMo steel, Brass, and an aluminum binding wired, Figure 3b and test ID numbers (22,23&24) the test was carried out without oil in present of air at 80 °C. over 6 weeks, the observation of the pots was interesting. A white solid material was covering all the pots and the glass liner inside the pots which was the first indication of the polymerization of VDF (R-1132a) into PVDF. Also, the GC analysis of the refrigerant before taken out the pots showed some new peaks compare to those one that been analyzed for the R-1132a before running the test table1. Table 3 showed increase of metal weight change results as 1% wt. compared to the metal weight before the test.

Further analysis for the solid sample was taken to study and identify the chemical structure of the new formed material. The IR (Infrared spectroscopy) and XRD (X-ray diffractometers) allow for identification of the new formed PVDF of the pots sample and a commercial PVDF. The results showed that the interpretation of IR shows the alkenyl C-H bond is clearly visible in the region of 3000-3100 cm^{-1} . There is an indication of C=O stretch for ester in the pot sample around 1747 region which could be from traces of oil. C=C bond is clearly visible in the individual graphs in the region of 1680- 1750 cm^{-1} . All in all, the absorption replicates quite well with the commercial sample. In addition, the interpretation of XRD As the nature of the Bragg's peaks tell us the commercial material is semicrystalline, ours was flaky even after grinding. The X-ray intensities were recorded at 2θ with the intensity values. For both commercial sample and the pot samples, the reference patterns for PVDF (exported from the instrument library) are a match.

3. CHEMICAL STABILITY AND MATERIALS COMPATIBILITY OF R-1132a WITH LUBRICANTS

3.1. Inhibiting Effect of Lubricant in the VDF polymerization

With the concern of R-1132a reacting to form PVDF, a study was undertaken to investigate the polymerization reaction with lubricants to determine if the lubricant formulations offered a reaction inhibiting effects as postulated in Figure 4.

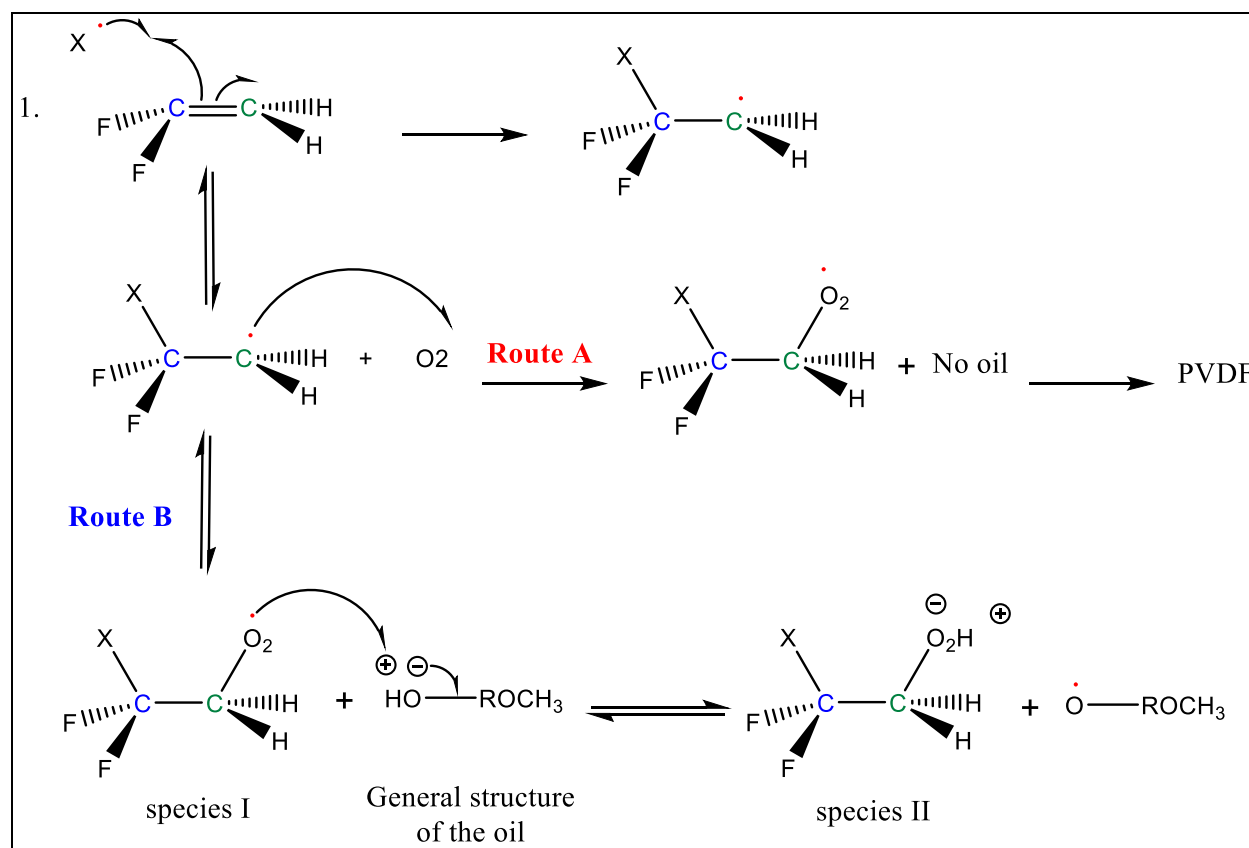


Figure 4: The possible reaction mechanism of the VDF in present of oils

In Figure 4, the possible anti-polymerization mechanism has been suggested to explain the step that VDF does not form PVDF in ID number 1-18. Initiation from the first step, the route is started the same way as for the mechanism

above, Figure 1. The π -bond adjacent to a C-X bond at the end of the chain allowing oxidative addition to occur, Figure 4 step 1& Route A. But it seems that the oil has inhibited the polymerization reaction step (Route B) by forming the H- bond and driving the reaction equilibrium towards (species I). Therefore, inhibiting the polymerization, it is controlled as it ensures that the catalyst cannot associate from the polymer chain (and start new chains). It is believed the oil be added, such as a strong acid to protonate the polymer, or a nucleophile to add an end cap the polymer. Also, If the π -complex is too weakly bound, termination of polymer chains can occur. over the test time at high temperature 175 °C in present of different type of POE/ PAG oils.

3.2. Highly Accelerated Compatibility Testing (HACT) of R-1132a

Multiple glass tube chemical stability evaluations were conducted using to understand R-1132a's chemical reaction and potential for catalytic breakdown/ polymerized product with specific system metals. Initial stability evaluations were performed to evaluate the behavior of the refrigerant, to enable the development of an acceptable means of accelerated testing. The refrigerant was tested alone, and also in the presence of polyol ester (POE) & polyether (PE) lubricants at a 50% concentration by weight to study the chemical stability in this manner. Accelerated studies were carried out at a different temperatures and times, from 80°C to 175°C, and utilized three metal catalysts (Iron, Aluminum, Copper& Brass). Table 1 summarizes the thermal stability test condition of HFO-R1132a.

3.3. Test Condition

The test conditions are shown in Table 1 of HFO-R1132a, this table summarizes the results of two additives (moisture / air) that were evaluated to find out the reactivity of R-1132a, catalysts or both. Each additive was selected for its ability to either radical reaction or perform as a metal surface deactivator. Both additives were effective at improving the chemical stability of R-1132a, especially in the presence of metal coupons (Cu, Fe, Al), brass and Cr Mo alloys.

Table 1: Refrigerant/ Lubricants Compatibility Test Matrix

ID	Condition	Metal	Temp. °C	P Bar	Period hour	Final Purity GC%
1	50% R1132a + 50% EMKARATE RL32.3MAF	Cu, Fe, Al	175	35	336	99.9
2	50% R1132a + 50% EMKARATE RL32H					
3	50% R1132a + 50% RENISO TRITON SEZ32	*CrMo 4130 alloy	175	70	336	99.9
4	50% R1132a + 50% EMKARATE RL68H					
5	50% R1132a + 50% EMKARATE RL32H					
6	50% R1132a + 50% EMKARATE RL32.3MAF					
7	50% R1132a + 50% Zerol HD46					
8	50% R1132a + 50% Zerol PE32-X					
9	50% R1132a + 50% RENISO C85E					
10	50% R1132a + 50% RENISO TRITON SEZ22					
11	50% R1132a + 50% RENISO TRITON SEZ32(Wet)					
12	50% R1132a + 50% EMKARATE RL68H(Wet)					
13	50% R1132a + 50% EMKARATE RL32H(Wet)					
14	50% R1132a + 50% EMKARATE RL32.3MAF(Wet)					
15	50% R1132a + 50% Zerol HD46(Wet)					
16	50% R1132a + 50% Zerol PE32-X(Wet)					
17	50% R1132a + 50% RENISO C85E(Wet)					
18	50% R1132a + 50% RENISO TRITON SEZ22(Wet)					
19	100% R1132a	Brass	80	140	720	99.9

20	100% R1132a	C360				
21	100% R1132a					
22	100% R1132a	*CrMo	80	177	1008	~ 96:4
23	99.99% R1132a+ 0.01 %Air	+				
24	99.90% R1132a+ 0.1% Air	Brass				

*Chromium-Molybdenum Alloy Steel

3.4. The standard operating protocol

This test was carried out in reaction conditions: dry oil (within manufacturers specification limits) and with moisture added (POEs and polyethers at 1000 ppm). The oils were prepared by weighing out (30 g) and refrigerant R-1132a as laid out in ASHRAE Standard 97² and ASHRAE Guideline 38³ (30 g) at different parameters; temperature, time, and pressure as it has been shown in Table 1. The lubricants were dried using nitrogen passing through them overnight then tested for moisture content by Karl Fischer (KF), acidity of the oil was tested using the Total Acid Number (TAN) and Ionic Chromatography (IC) was used to indicate the fluorine content of the oil. For the autoclaves, the material samples were used in glass tubes, there is no direct contact between the tested materials & the steel autoclave surface.

Screening tests were conducted with copper (Cu CDA110), steel (Fe C1020) and aluminum (C1020, Al 1200) with two typical ISO 32 grade POEs. However, we focused the investigation on 4130 CrMo alloy as no literature information was available for this refrigerant + lubricant + catalyst combination. Testing was conducted at the typical 175°C, 35 and 70 bara for a period of two weeks.

For the testing with pure R-1132a (representing the cylinder + valve), brass and CrMo alloy were exposed to pure R-1132a and R-1132a with a small amount of air at an accelerated storage condition of 80°C, 140 and 175 bara for a 4-week period. For the targeted breakdown or polymerized of R-1132a, the constant pressure study was used as the indicator of polymerizing to evaluate the test. While the decomposing of R1132a was indicated by using the analytical study such as GC and GCMS spectra. Table 2 summarizes the chemical and the physical properties results of these experiments.

Table 2: Refrigerant/ Lubricants Compatibility Test Results

ID	Condition	TAN mgKOH	Fluoride (ppm)	ICP mg/kg
1	50% R1132a + 50% EMKARATE RL32.3MAF	0.16	130	<1
2	50% R1132a + 50% EMKARATE RL32H	0.14	87	<1
3	50% R1132a + 50% RENISO TRITON SEZ32	0.08	16	<1
4	50% R1132a + 50% EMKARATE RL68H	0.13	37	<1
5	50% R1132a + 50% EMKARATE RL32H	0.19	93	<1
6	50% R1132a + 50% EMKARATE RL32.3MAF	0.38	14	<1
7	50% R1132a + 50% Zerol HD46	0.13	17	<1
8	50% R1132a + 50% Zerol PE32-X	0.11	10	<1
9	50% R1132a + 50% RENISO C85E [#]	>2	165	Fe 550
10	50% R1132a + 50% RENISO TRITON SEZ22	0.54	146	<1
11	50% R1132a + 50% RENISO TRITON SEZ32(Wet)	0.11	~0	<1
12	50% R1132a + 50% EMKARATE RL68H(Wet)	0.19	128	<1
13	50% R1132a + 50% EMKARATE RL32H(Wet)	0.25	47	<1
14	50% R1132a + 50% EMKARATE RL32.3MAF(Wet)	0.63	52	<1
15	50% R1132a + 50% Zerol HD46(Wet)	0.51	27	<1
16	50% R1132a + 50% Zerol PE32-X(Wet)	0.12	7	<1
17	50% R1132a + 50% RENISO C85E(Wet) [#]	>2	158	Fe 300
18	50% R1132a + 50% RENISO TRITON SEZ22(Wet)	0.60	240	<1

* Cu+ Al+ Steel coupons for tests 1&2; Chromium-Molybdenum Alloy 4130 Steel for tests 3-18

C85E is designed for CO₂ service, it is not necessarily formulated for fluorocarbon service

In table 2, the data analysis of TAN, IC & ICP for the tested samples showed a good, acceptable, and reasonable results in the industry and none of the lubricants experienced any difficulty with R-1132a at the testing conditions. However, the results for the ID numbers (9, 17 & 18) were completely different for the same testing reaction parameters of temperature, pressure, and duration time. On the other hands, all the ID numbers (1-21) showed in the testing of pure R-1132a in storage conditions no indication of refrigerant breakdown in the GC results, nor an indication of polymerization or residue in the cells when removed from test.

Photos of the lubricants are shown in Figure 5 and described in Table 3 showed that the slight yellowing color of the lubricants is normal and indicative of the severity of the test conditions up to 175 deg. Also, the results showed a strong chemical stability of R 1132a with both current POE/ PAG lubricants as mentioned above. There was not a noticeable change of the metal weight. In opposite, those samples with the ID numbers (9, 17 & 18) gave a very high TAN, IC, ICP and decrease of metal weight change results compare to the others. That could be evidence of the oil's degradation to indicate the incompatibility of those materials with R-1132a at these set parameters of temperature & pressure.

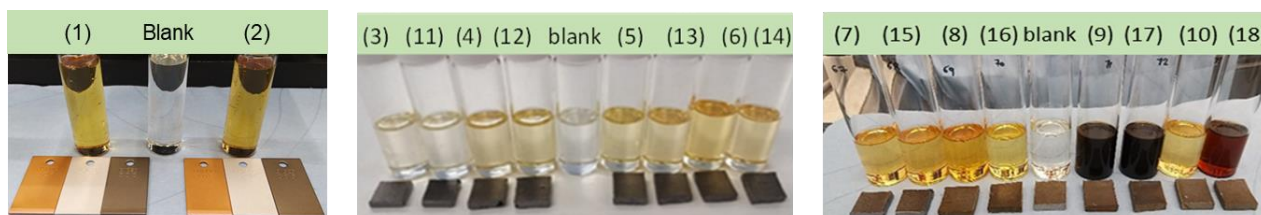


Figure 5: The tested POE/ PAG lubricants & metals with R1132a

Table 3: The Visual appearance of the materials of the test with/ without oil charged

ID	Conditions	Metal	Oil Visual appearance	Metal weight change
1	50% R1132a +	Cu CDA110, Fe C1020, Al 1200	Clear; light discoloration	Negligible
2	50% POE			
3				
4	50% R1132a + 50% POE Or 50% PAG	*Cr Mo alloy	Clear; light coloration	Negligible
5				
6				
7				
8				
9	50% R1132a +50% RENISO C85E		Dark brown	1% decrease
10	50% R1132a +50% RENISO TRITON SEZ22		Clear; Yellow	Negligible
11				
12	50% R1132a + 50% POE Or 50% PAG	*Cr Mo alloy	Clear; light coloration	Negligible
13				
14				
15				
16				
17	50% R1132a +50% RENISO C85E wet		Dark brown	1% decrease
18	50% R1132a +50% RENISO TRITON SEZ22 wet		Clear; Red	Negligible
19				

20	100% R1132a	Brass C360	No oil	Negligible
21				
22	100% R1132a	*CrMo +	No oil	Negligible
23	99.99% R1132a+ 0.01 % Air			1% increase
24	99.90% R1132a+ 0.1% Air			1% increase

4. CONCLUSIONS

This paper presented some initial results of materials compatibility and stability testing of R-1132a. We found that it was possible for R-1132a to from PVDF in the presence of CrMo steel, brass and aluminum with a small amount of air present. Highly accelerated tests were carried out in accordance with ASHRAE Guideline 38 to understand if the lubricant formulations offered an inhibiting effect in the potential breakdown or polymerization with these system materials, lubricant, and moisture. Different types of polyol ester (POE) & polyether (PE) lubricants were selected for further review of chemical stability of the R-1132a with materials of interest. Except for one lubricant product (in defense, it was designed for service with CO₂ and not with fluorocarbons), all the test results indicated that R-1132a exhibits TAN, IC, color and metals results that are similar to other refrigerants currently in the marketplace. R-1132a may be considered as viable option for use in HVAC&R equipment with common materials of construction. Future research will focus on blends containing R-1132a to further investigate the effect of other fluorocarbon inhibiting effects on potential polymerization reactions.

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