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ABSTRACT

Understanding the compatibility of system materials with HFO-1234yf and corresponding compressor lubricants is critical to long term operation of mobile air conditioning systems. Today's regulatory climate of reporting and eliminating system leaks leaves very little margin of error when approving elastomeric materials to seal compressor and tube connection joints over the lifetime of the system. Polymeric O-ring materials and metals used in several automotive compressor manufacturers have been tested in accelerated conditions to determine volume change, strength change, extraction of plasticizers or dyes, and chemical compatibility of the lubricant and refrigerant. Additionally, information on the effects of water and air contamination on system lifetime are critical to allow OEs and service techs to design proper construction and service methodologies. This study focuses on the use of polymers with PAG lubricants with HFC-134a and HFO-1234yf, and with the effects of air and water on POE in HFC-134a and HFO-1234yf with standard metal catalysts. Results and conclusions are presented in graphical and tabular format along with conclusions on polymeric types and metals that are suited for continued development as long-term system sealing and functional life.

1. INTRODUCTION

In the push to replace the current high global warming potential (GWP) refrigerants, we are constantly looking to new developments in technology and science to drive us forward to make our environmental footprint as small as possible. One of the initiatives happening in the automotive industry is the replacement of HFC-134a as the primary refrigerant with HFO-1234yf in mobile air conditioning compressor systems. HFC-134a is known to have a high GWP of 1430 while the new replacement has a GWP of 4. Though converting to HFO-1234yf would be a significant improvement in GWP we still need to confirm that this new refrigerant is compatible with all the materials and lubricants used in current day automotive compressors. Material compatibility is an essential tool in the refrigeration industry due to the continuous development of new lubricants and refrigerants. HFC-134a is slated to be officially phased out of all light duty motor vehicles in the U.S. by model year 2021. To comply with this new upcoming regulation a study must occur to verify that the new refrigerant and materials are compatible. In this study the elastomers and metals will be exposed to an environment simulating operating conditions seen in automotive compressors. The two refrigerants will be compared by the amount of physical property change between before and after exposure along with any visual change in the metal coupons and total acid number (TAN). The metrics used will be weight, density, volume, micro hardness, max stress, ultimate elongation, TAN and visual observations to make sure the material is compatible with HFO-1234yf and its co-existing lubricant.

2. EXPOSURE CONDITIONS

2.1 Elastomers

The elastomers that will be compared for this compatibility study are NBR, VITON, and EPDM. NBR and Viton were selected because of their poor property stability and performance when exposed to current HFC refrigerants; unlike EPDM which performs very well and is the go-to material for seal material in current HFC-134a automotive compressors. The conditions for the accelerated testing were as follows: 50g of Refrigerant to 50g of Lubricant in a 600 ml pressure vessel at 100°C for 168hrs. Size 214 O-rings were all exposed in replicates of 5 units and separated by copper wire loops designed to keep them separated as well as in a specified order to ensure the before and after measurements were made with the same O-ring. Replicates of 5 were tested to consider the variability between different samples of elastomers within the same batch. The tensile testing was performed 24 hrs after exposure allowing the refrigerant to degas, and all other test were done within one hour of removal from the pressure vessel.

2.2 Metals

The metals used for this compatibility study were copper 110 (99.9% pure), aluminum 1100 (>99% Pure) and steel 1010 (low carbon steel). The sealed glass tubes were prepared by weighing out 4 grams of oil (POE) and adding 2 grams of refrigerant as laid out in ASHRAE Standard 97. The tests were carried out with 3 different parameters: 1) no air, low water (<50 ppm water); 2) no air, high water (200 ppm water); and 3) air and water (1000ppm air, 200 ppm water). The glass tubes were then placed in secondary containment and placed in the oven for 2 weeks at 175˚C. After aging, the exposed materials are assessed for changes in lubricant condition and appearance of metal coupons. The exposed lubricant is then tested for total acid number.

3. RESULTS

3.1 Elastomers

By monitoring the change in physical properties of the O-rings, we can compare the results between the different refrigerants to see if the effects of exposure to 1234yf had a similar or different effect on the elastomeric material than 134a. In doing so we could do a direct comparison to see if 1234yf could be a suitable replacement and have a conclusion on best performing elastomers.

Volume & Weight change	0 to 15%
Elongation change at break	-50% max
Tensile Strength change	± 30% max
Hardness change	± 15% max

Table 2: Typical Automotive OEM Requirements

Nitrile butadiene rubber (NBR) is an oil-resistant rubber typically used in the automotive industry for fuel hoses and gaskets that are not exposed to refrigerants. Figure 1 shows the percent change in physical properties after the exposure to HFC-134a and HD46 (automotive OEM double end-capped PAG lubricant) refrigerant. The HFC-134a data displays signs of slight hardening and loss of pliability of the elastomeric material shown by the increase in hardness and stress along with the decrease in elongation. The HFO-1234yf exposure in Figure 2 shows a very similar trend as compared to HFC-134a with increase in hardness, stress and decrease in elongation. The NBR material was the only one of the three elastomers tested that had color in the lubricant, which is an indication of leaching. The leaching can be backed up by the slight weight loss and increase of density which indicates a small amount material loss and some shrinkage. In this application, shrinkage is an undesirable effect of aging being that the sealing material could end up not large enough to fill the gap and could result in the leaking of refrigerant into the atmosphere, therefore, damaging the compressor and its long-term function. Overall the NBR reacts similarly with HFC-134a and HFO-1234yf.

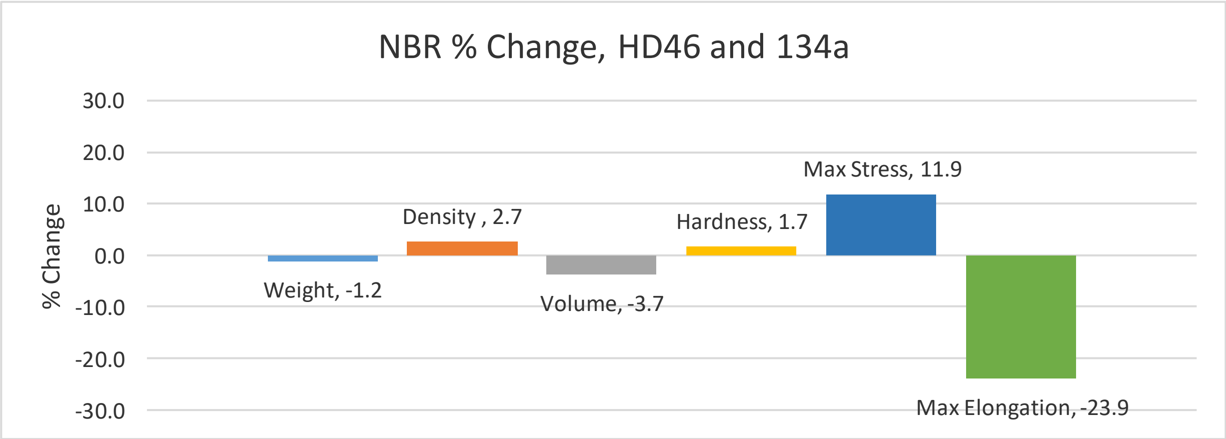

Figure 1: NBR Percent Change after exposure to HD46 and HFC-134a for 7 days at 100°C

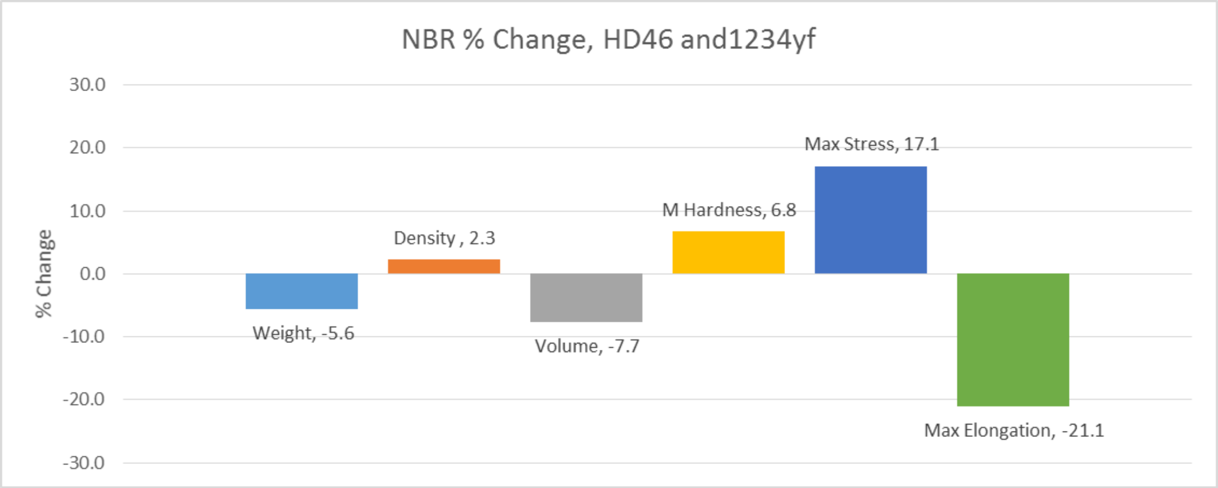

Figure 2: NBR Percent Change after exposure to HD46 and HFO-1234yf for 7 days at 100°C

Viton is a fluoropolymer that is typically known for its chemical resistance. However, in the HVAC&R application, Viton is inherently incompatible with refrigerants because they are both fluorine containing compounds. The effect of the refrigerant breaking down the fluoropolymer can be seen in the results from the Viton exposure charts below in Figures 3 and 4. Viton had the least desirable results of all three of the materials tested. Viton failed in all aspects of what is ideal for a sealing material in this application. It had the largest increase of volume and had the largest percent loss in tensile max strength and max elongation. The decrease in tensile properties indicate the O-rings inability to maintain its form. The decrease in hardness in conjunction with the large volume increase could be an indication that the O-ring could possibly extrude from the gap and fail to seal the compressor. However, in both instances the elastomer preformed the same in either refrigerant.

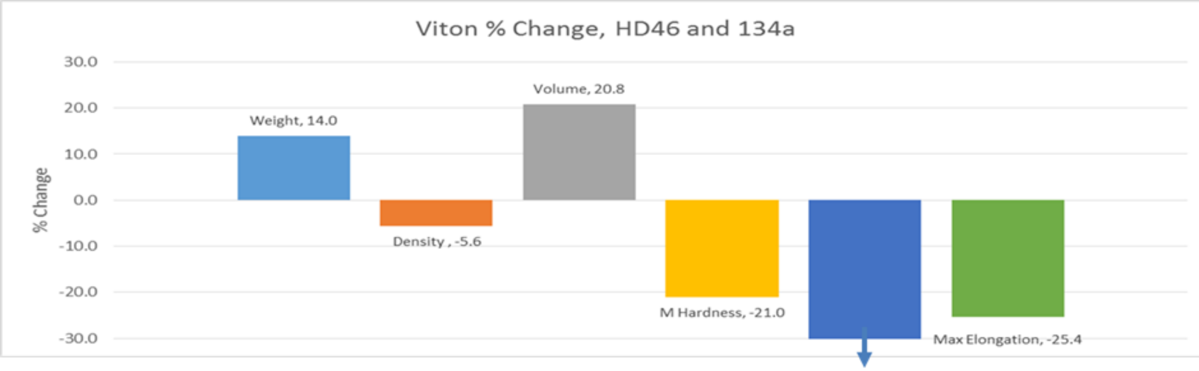

Figure 3: Viton Percent Change after exposure to HD46 and 134a for 7 days at 100°C

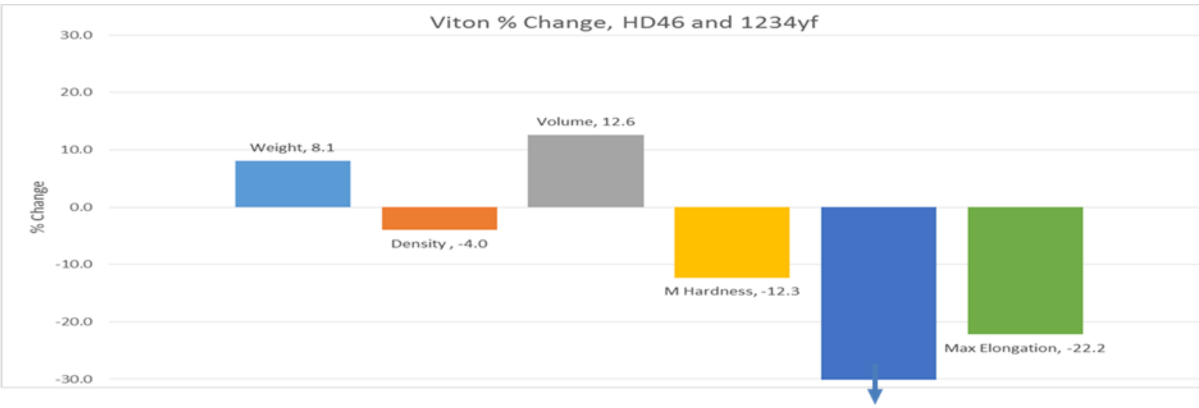

Figure 4: Viton Percent Change after exposure to HD46 and 1234yf for 7 days at 100°C

Ethylene Propylene Diene monomer (EPDM) is a very versatile synthetic elastomer that is used in application from roofing paper to automotive applications. However, EPDM is not a typical material used in HVAC&R systems as HCFC-22 typically used mineral oils and alkylbenzene lubricants that dramatically softened the elastomer. However, in the system of HFC and HFO refrigerants with PAG lubricant, EPDM can perform well. The results which can be seen in Figures 5 and 6 show an excellent chemical compatibility for both refrigerants. In both cases the percent change was very minimal. They both had a slight increase in volume which is ideal to further fill the gap; providing a better seal.

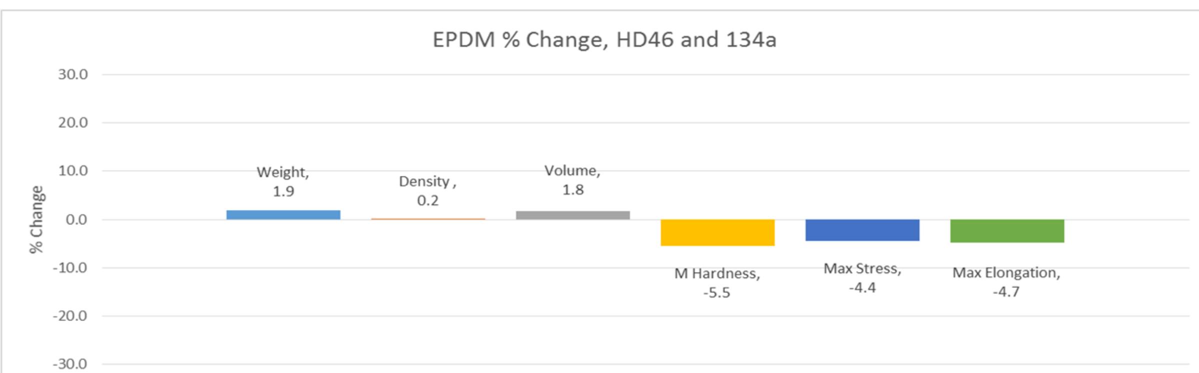

Figure 5: EPDM Percent Change after exposure to HD46 and 134a for 7 days at 100°C

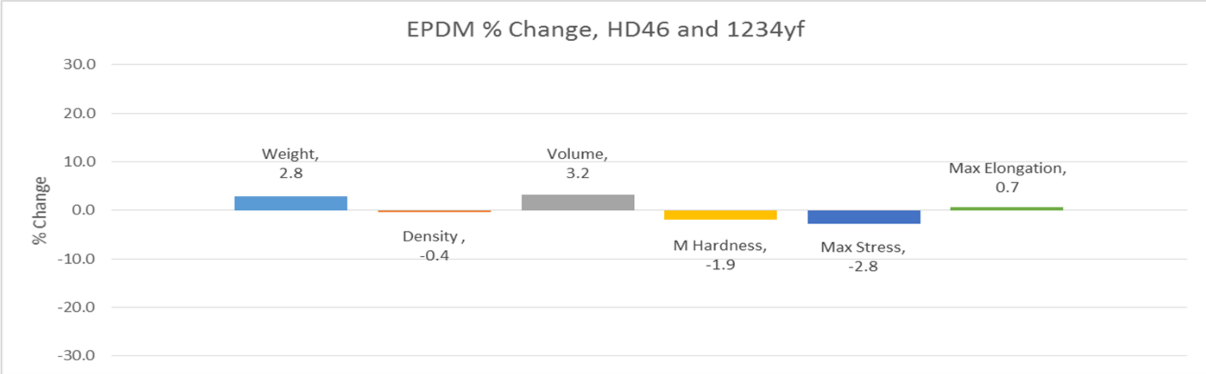

Figure 6: EPDM Percent Change after exposure to HD46 and 1234yf for 7 days at 100°C

3.2 METALS

Thermal stability was tested on 6 samples with the formulation displayed in Table1 1. Samples 13, 15, & 16 used a POE32 oil with HFC-134a and samples 17, 19, & 20 used POE32 oil with HFO-1234yf. Visual evaluations were done to compare the exposure effects of the two refrigerants on the oil and the metal coupons. The unexposed POE32 is of a clear water-white to slightly yellow color with a low acid number (< 0.05 mg KOH/g). Figure 7 shows unexposed metals as a reference.

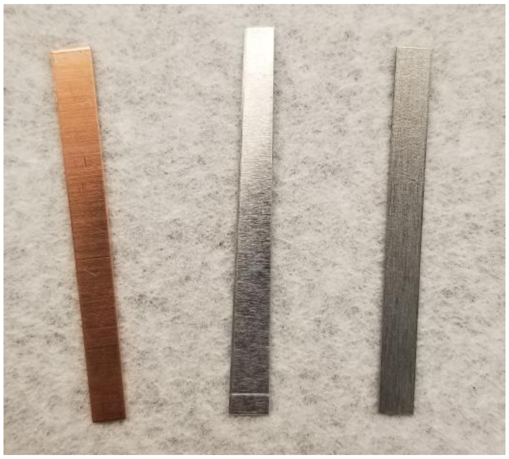

Figure 7: Reference (New unexposed Coupons)

Samples 13, 15, and 16 all used POE32 with HFC-134a, but had different exposure parameters with some containing amounts of water and/or air, Table 1. As can be seen in Figure 8, sample 13 (containing no air or water) had a very faint pale-yellow tint, and sample 15 (containing water) slightly more yellow in color. However, sample 16 (containing water and air) was a very dark yellow/orange color. Acid number on 13 and 15 were relatively low (<0.25 mg KOH/g), while sample 16 had a slightly elevated TAN of 0.33 mg KOH/g. The same parameters were done on a separate set of samples with the same oil, but using HFO-1234yf (samples 17, 19, 20). Figure 9 shows sample 17 (containing no air or water) was colorless, sample 19 (containing water) was a faint pale-yellow color, and sample 20 (containing water and air) was a very dark yellow/orange color. Samples 17 and 19 also had low acid numbers of <0.25 mg KOH/g while sample 20 had an acid number of 1.2 mg KOH/g.

Sample	Oil	Refrigerant	Air	Water
13	POE	HFC-134a	-	<50ppm
15			-	200ppm
16			1000ppm	200ppm
17		HFO-1234yf	-	<50ppm
19			-	200ppm
20			1000ppm	200ppm

Table 1: Refrigerant Compatibility Test Matrix

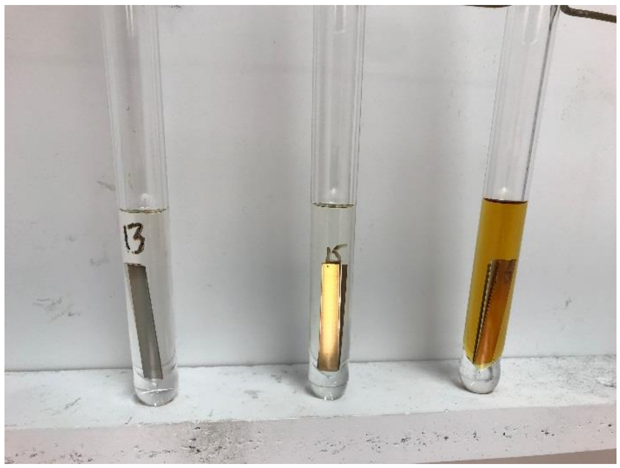

Figure 8: Exposed Oil Samples using HFC-134a (left to right: 13, 15, and 16)

Figure 9: Exposed Oil Samples using HFO-1234yf (left to right: 17, 19, and 20)

When looking at the exposed metals of the samples tested in Figure 10, metals from sample 13 showed no change to the aluminum, slight lightening in color of the copper coupon, and a small amount of darkening/copper coloring on the tip of the steel coupon. Sample 15 showed discoloring of copper on both sides of the coupon, no change to the aluminum coupon, and darkening with copper coloring on both sides of the steel coupon. Metals from sample 16 showed discoloring of the copper coupon on both sides, no aluminum change, and a dark copper coloring on the steel coupon. The samples using HFO-1234yf had similar findings. Figure 11 shows metals from sample 17 had no visible changes to any coupons. Sample 19 had minor discoloring to one side of the copper coupon, no changes to the aluminum coupon, and darkening to the steel coupon with what appeared to be a copper coloring. Metals from sample 20 showed greater discoloring of the copper coupon, discoloring of the aluminum coupon, and darkening as well as color leeching from the steel coupon.

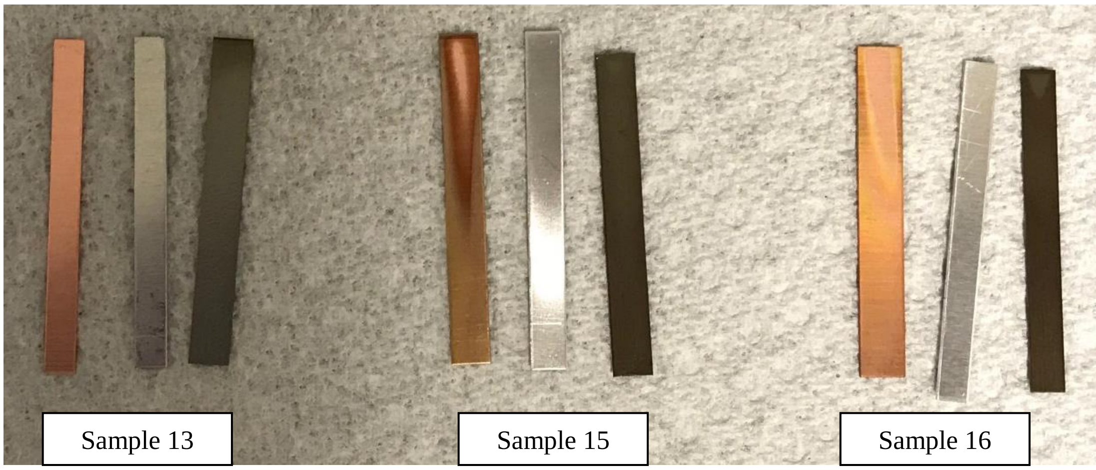

Figure 10: Exposed Metal Coupons using HFC-134a

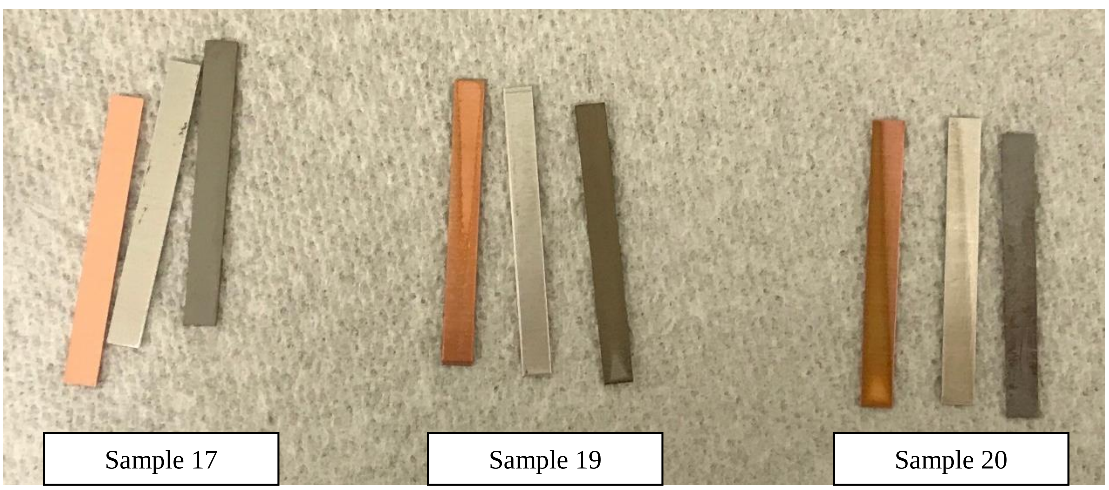

Figure 11: Exposed Metal Coupons using HFO-1234yf

Based on changes of the exposed oils as well as the metal coupons, samples using HFC-134a and samples using HFO-1234yf had similar trends. Neither oil/refrigerant combination reacted much beyond expectations in samples containing no air or water (samples 13 and 17). When adding a small amount of water to the oil/refrigerant combination (samples 15 and 19), samples containing either refrigerant changed slightly to a pale yellow in color, and although the metals tested had a little more discoloration of the copper coupon and darkening of the steel coupon, these results were also within the expected thermal stress parameters. However, when adding air and water to the oil/refrigerant combination (samples 16 and 20), samples containing either refrigerant were of a dark yellow/orange color. For sample 16, using HFC-134a, the dark color of the oil, discoloration of the copper coupon and darkening of the steel coupon, as well as the increased acid number of 0.33 mg KOH/g indicates some degradation of the POE. While for sample 20, containing HFO-1234yf, the discoloring of the oil and the metal coupons were similar, however, a significant increase in acid number (1.2mg KOH/g), shows a breakdown of not only the POE but also the refrigerant as well. This indicates that POE hydrolysis to create the constituent acids and alcohols (-OH terminating molecules) will react with the HFO refrigerant molecule.

6. CONCLUSION

Accelerated exposure testing can be an excellent way to discover how different materials perform in various environments for long term applications. In this study NBR, Viton and EPDM in exposure to HFC-134a and HFO-1234yf in conjunction with an OE PAG lubricant were tested and compared. All polymeric materials displayed very similar results whether they were exposed to HFC-134a or HFO-1234yf. Both refrigerants experienced negative effects on the NBR and Viton O-rings, while excellent results were seen with EPDM. Another testing program was also undertaking to test copper, aluminum, and steel metal catalysts with varying amounts of air and water with POE32 lubricant with HFC-134a and HFO-1234yf. When air and water were nonexistent, the samples had expected results of very minimal change to the oil coloring and metals. However, when water and air were incorporated into the equation, HFO-1234yf showed a significant breakdown. Given that both refrigerants had very similar results in compatibility with elastomers as well as with metals in low water and no air, HFO-1234yf shows to be a very suitable replacement to HFC-134a in current mobile air conditioning systems. Directional efforts should be given towards efforts to minimize and possibly eliminate air in system.

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