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ASHRAE Guideline 38 Methodology Material Compatibility Testing of R-473A

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ABSTRACT

The development of non-flammable refrigerants with a lower global warming potential (GWP) for ultra-low temperature refrigeration is desired because existing refrigerants used in this application range have very high GWP. A new blend refrigerant R-473A has been developed by Koura, which offers high energy efficiency and low global warming potential (GWP), resulting in low overall environmental impact. It has been classified by ASHRAE as an A1 refrigerant. The material compatibility and reactivity of this refrigerant has been studied with lubricants that are commonly used in this application with R-23 refrigerants. In this paper, ASHRAE Guideline 38 methodology for (R-473A) materials compatibility test of select metals and rubbers been evaluated by using various commercially available POE and PAG lubricants. Results will be reported and compared with those obtained using R-23 as a reference refrigerant.

1. INTRODUCTION

In Europe, F-Gas regulations (2014) limit the Global Warming Potential (GWP) to 750 in single split unitary air conditioning systems with refrigerant charge less than 3 kg. Although there are no limits on GWP for ultra-low temperature refrigeration applications there is still an industry desire for fluids with lower GWP in this application sector. In this context, several lower-GWP refrigerant replacements are under evaluation by the industry. Ethane (R-170) is a good refrigerant for small systems, but its flammability restricts applicability. The industry is investing heavily in understanding the use of flammable refrigerants, but some low temperature systems still need refrigerants with low or no flammability. With a viable option of non-flammable lower-GWP refrigerants with equivalent or better energy efficiency, actions can be implemented in the refrigeration segment with the potential to ensure carbon footprint reduction[1].

This study focuses on non-flammable R-473A as replacement refrigerant, R-473A (R-744/R-1132a/R-23/R-125 60%/20%/10%/10%). This blend is non-flammable and is classified as A1 according to ASHRAE Standard 34[2]. It has GWP of 1830, an 85% reduction compared to R-23. Starting from this background, a target of this paper is to present performance of R-473A and material compatibility results with polyol ester (POE/ PAG) lubricants by Koura to be appropriate to accommodate possible future reduction requirements. The recent study of R-1132a as a refrigerant blend component[3] allows further air-conditioning refrigerant development for the applications and outlined the body of this paper.

2. MATERIAL COMPATIBILITY TEST OF R473A REFRIGERANT

2.1. The design of the system

The oven been designed to accelerate the lifetime of the material and study the compatibility of the R-473A with different lubricant types. As it is shown from the figure below, this system has 8x 300ml Parr Autoclave Pots which are charged with a mixture of refrigerant blend, lubricant, and testing coupons/ rubber. The pots are then placed in a 3kW temperature-controlled oven and heated to a normal operating temperature up to 175°C and held at this temperature for several days. The oven has a temperature trip as a primary control measure which has been tested at both operating temperatures. The Nitrogen acts as a continuous supply, purging the system throughout the experiment, exact quantities are directly charged to the autoclaves via a sample cylinder. To limit the normal operating pressure to 70 bar at the operational temperature of 80-175°C, a maximum fill limit of 30 g for all fluids has been defined bar. Each autoclave pot has a design pressure of 207 bar and has its own bursting disc rated for 207barg. All 8 pots in use will relieve via a common header into a 61L dump tank.

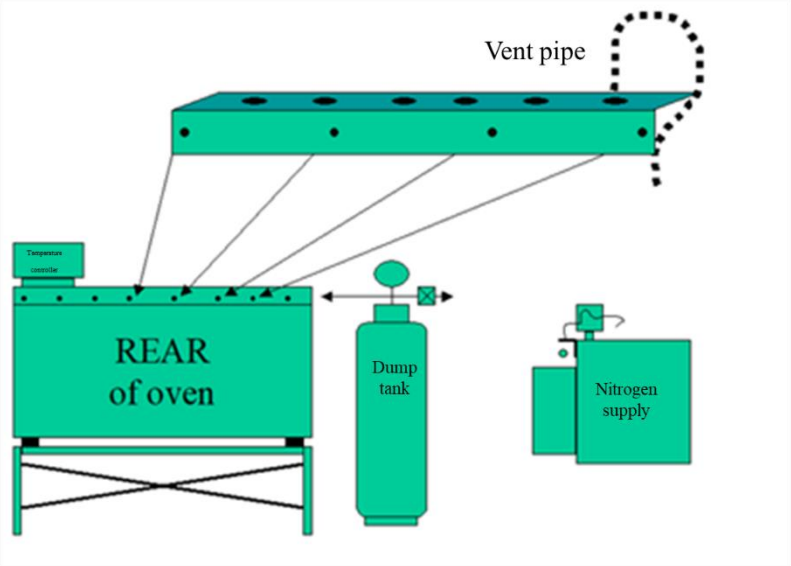


Figure 1: The compatibility test system

The autoclaves are fitted with 3000 psi bursting discs with a vent pipe going to a dump tank. The bursting disc rating was chosen to protect the equipment. It is important to maintain Nitrogen purge into the ovens when using flammable materials. It is used dump tank in case the temperature goes up. The dump tank is connected via this manifold (mounted on angle-iron at the back of the oven) and via Swagelok flexis to the autoclave burst disc exit fitting. The dump tank has a gauge fitted, and its valve modified to ensure it cannot be closed. The hand wheel is then removed, and the cylinder labelled to that effect. A separate leg off the line has a ball valve to allow venting in the event of a burst disc.

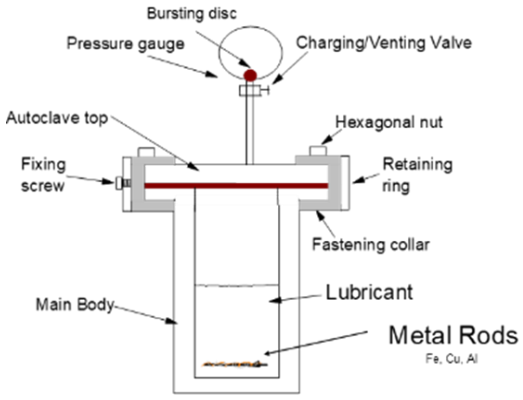


Figure 2: The autoclave vessel design

2.2. Experimental Procedure

ASHRAE Standard 97 tube testing[4] and ASHRAE Guideline 38[5] was performed of R-473A & R-23 with (POE/ PAG) lubricants from 1- 2 weeks at the range of Temp. 80-175 °C. The test was performed with 50/50 wt.% ratio of refrigerant/lubricant for the metal materials test and 33/66 wt.% ratio of refrigerant/lubricant for the rubber materials test. Elevated levels of moisture (1000 ppm) were included, chosen as they exceed levels normally found in real A/C equipment. The lubricants were dried using cylinder nitrogen passing through it overnight then tested for moisture content by Karl Fischer. Those oils were wetted by taking a small amount and first analyzing it for the moisture then adding (1000 ppm) distilled water from a microliter syringe. The oil was shaken to mix it, and then the moisture analysis was repeated. This was done until the desired level was achieved. The (POE/ PAG) lubricants were added to each glass liner approx. 30gm containing the metals in the autoclaves before being sealed and evacuated. The required amount of refrigerant 30 g was added via vacuum. While the addition of the R-473A & R-23 for the rubber was 15 gm in 33/66 wt% ratio of refrigerant/lubricant as mentioned above.

The oil was also tested without the metal coupons. The autoclaves were aged in temperature-controlled ovens. After aging the tube contents were again analyzed for moisture, IC, and TAN. Copper, iron, and aluminum coupons were used as representative metals. To compare the results, it has been used R-473A & R23. The metals used for this compatibility study were copper 110 (99.9% pure), aluminum 1200 (>99% Pure) and steel 1020 (low carbon steel). In addition, the rubbers were used for this test is (NBR, HNBR, VITON, EPDM & NATURAL) (15 mm Width x 1.5 mm Thickness x 75mm Length). For the autoclaves, the material samples were used in glass tubes, there is no direct contact between the tested materials & the steel autoclave surface. At normal test temperature between 80 °C, and 175 °C, there was not a liquid refrigerant phase, only vapour phase. After aging, the exposed materials are assessed for changes in lubricant condition and appearance of metal coupons.

Figure 3: Glass Tube Preparation

3. THERMAL STABLITY

3.1. Analytical Equipment used

Following is the list of analysis done on the oils before and after the experiments

1	KF Karl Fisher moisture meter for the determination of water content in Oils
2	TAN Total Acidity Number for the determination of acidity content in Oils
3	IC Ionic Chromatography for the determination of fluoride content in Oils
4	GC/GCMS to identify the breakdown of the refrigerants
5	Tensiometer for the determination of the Tensile property changes of the tested polymers
6	IRHD for the determination of the hardness change of the elastomers

3.2. Test Condition

Material compatibility evaluations were conducted in parr pressure vessels using R-473A and R-23 and POE/ PAG lubricants. No additives were present in the POE/ PAG lubricant in the ID number 1-19 whereas ID number 20,22 & 24 has 1000 ppm of water as shown in the table below. Materials evaluated included metal coupons and 5 different rubbers. The testing for ID number 1-3 was carried out at 50/50 wt.% ratio of refrigerant/lubricant conditions whereas for ID number 4 to 24 was carried out at 33% refrigerant and 66% lubricant (by weight) conditions. Samples were aged for 5 - 14 days at temp. set from 80˚C to 175 ˚C. The test conditions are shown in Table 1. GC analyses indicated the stability of the refrigerants to show that in all units the R-473A & R-23 had not decomposed through the test heating time.

Table 1: Refrigerant Compatibility Test Matrix

ID	Condition	Materials	Temp. °C	Period hour	Purity GC%
1	50% R-473A + 50% Emkarate RL32.3MAF	Cu, Fe, Al	175	336	98.9
2	50% R-473A+ 50% Emkarate RL32H	Cu, Fe, Al	175	336	98.9
3	50% R-473A+ 50% Zerol HD46	Cu, Fe, Al	175	336	98.9
4	33% R-473A+ 66% Emkarate RL32.3MAF	NBR	160	120	98.9
5	33% R-473A+ 66% Emkarate RL32.3MAF	EPDM	160	120	98.9
6	33% R-473A+ 66% Emkarate RL32.3MAF	Natural	160	120	98.9
7	33% R-23+ 66% Emkarate RL32.3MAF	NBR	160	120	98.9
8	33% R-23+ 66% Emkarate RL32.3MAF	EPDM	160	120	98.9
9	33% R-23+ 66% Emkarate RL32.3MAF	Natural	160	120	98.9
10	33% R-473A+ 66% RENISO SEZ32	NBR	160	120	98.9
11	33% R-473A+ 66% RENISO SEZ32	EPDM	160	120	98.9
12	33% R-473A+ 66% RENISO SEZ32	Natural	160	120	98.9
13	33% R-473A+ 66% RENISO C85 E	NBR	130	120	98.9
14	33% R-473A+ 66% RENISO C85 E	EPDM	130	120	98.9
15	33% R-473A+ 66% RENISO C85 E	Natural	130	120	98.9
16	33% R-473A+ 66% Emkarate RL68H	VITON	80	720	98.9
17	33% R-473A+ 66% Emkarate RL68H	HNBR	80	720	98.9
18	33% R-473A+ 66% Emkarate RL68H	EPDM	80	720	98.9
19	33% R-473A+ 66% Zerol HD46	HNBR	130	120	98.9
20	33% R-473A+ 66% Zerol HD46+1000 ppm H2O	HNBR	130	120	98.9
21	33% R-473A+ 66% Zerol PE32-X	HNBR	130	120	98.9
22	33% R-473A+ 66% Zerol PE32-X+1000 ppm H2O	HNBR	130	120	98.9
23	33% R-473A+ 66% Emkarate RL32H	HNBR	130	120	98.9
24	33% R-473A+ 66% Emkarate RL32H+1000 ppm H2O	HNBR	130	120	98.9

4. RESULTS AND DISCUSSION

Refrigerant/lubricant stability testing was undertaken for the R-473A and R-23 using ASHRAE Standard 97 conditions for ID number 1-3 at 175°C test temperature for 14 days. Equal masses of refrigerant and selected POE and PAG lubricants were tested using stainless steel autoclaves with internal glass liners. Coupons of copper, steel and aluminum of known size, thickness and weight were suspended from a glass support into the lubricant phase for each test. While the ID number 4-24 were used for rubber materials with 33% refrigerants (R-473A & R-23) and 66% lubricant and POE/ PAG (by weight) at normal operating temperature of 80 - 160°C. Typical test results are shown in Table 2, Results of Moisture, total acid number and fluoride content of lubricants after thermal stability test were

indicated and been summarized in the table below. Also, the visual appearance of the oils was recorded (Figure 4). The results as shown in Table 2 indicate that the stability of the oils is very high, as illustrated by very low levels of anions (fluoride), low level of metals, and no detectable increase in total acid number. The results for R-473A with lubricants are very similar to baseline refrigerant R-23. This suggests that the combination of R-473A with POE/ PAG oil would be satisfactory for use in systems. Testing is ongoing and furthermore results will be presented in the conference presentation.

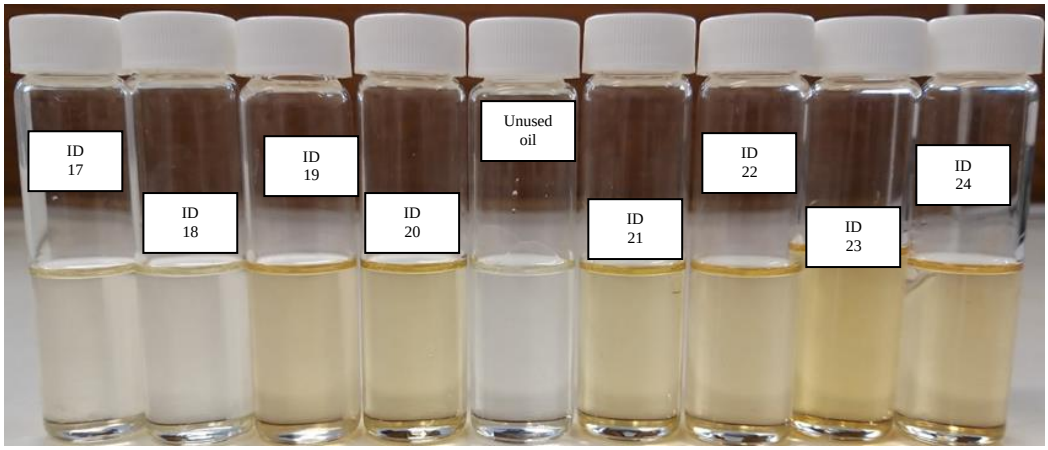


Figure 4: Example photo of the tested POE/ PAG lubricants

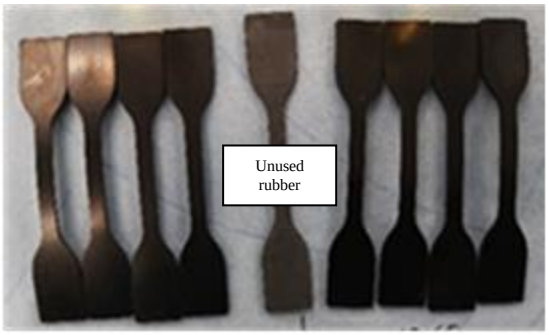
Table 2: The results of the exposure tests with lubricants

ID	Metal Elastomers	Moisture	TAN (mg KOH/g)	Fluoride (ppm)	ICP mg	Visual Oil appearance
1	Cu, Fe, Al	Dry	<0.1	<0.1	<1	Clear; light discoloration
2	Cu, Fe, Al	Dry	<0.1	<0.1	<1	Clear; light discoloration
3	Cu, Fe, Al	Dry	<0.1	<0.1	<1	Clear; light discoloration
4	NBR	Dry	<0.1	0	-	Clear; light discoloration
5	EPDM	Dry	<0.1	0	-	Clear; light discoloration
6	Natural	Dry	<0.1	0	-	Clear; light discoloration
7	NBR	Dry	<0.1	0	-	Clear; light discoloration
8	EPDM	Dry	<0.1	0	-	Clear; light discoloration
9	Natural	Dry	<0.1	0	-	Clear; light discoloration
10	NBR	Dry	<0.1	0	-	Clear; light discoloration
11	EPDM	Dry	<0.1	0	-	Clear; light discoloration
12	Natural	Dry	<0.1	0	-	Clear; light discoloration
13	NBR	Dry	<0.1	0	-	Clear; light discoloration
14	EPDM	Dry	<0.1	0	-	Clear; light discoloration
15	Natural	Dry	<0.1	0	-	Clear; light discoloration
16	VITON	Dry	0	0	-	Clear; light discoloration
17	HNBR	Dry	0	0	-	Clear; very light discoloration
18	EPDM	Dry	0	0	-	Clear; very light discoloration
19	HNBR	Dry	<0.1	0	-	Clear; light discoloration
20	HNBR	Wet	<0.1	0	-	Clear; light discoloration
21	HNBR	Dry	<0.1	0	-	Clear; light discoloration
22	HNBR	Wet	<0.1	0	-	Clear; light discoloration
23	HNBR	Dry	<0.1	0	-	Clear; light discoloration
24	HNBR	Wet	<0.1	0	-	Clear; light discoloration

It seems that R-473A and R-23 exhibits similar behavior with same oils under the same conditions as the results are shown in Table 2. In addition, it is indicated that as illustrated by very low levels of anions (fluoride), low level of metals, and no detectable increase in total acid number. The results for R-473A with additives are very similar to baseline refrigerant R23. Refrigerant/lubricant combinations, testing the material compatibility of metallic/ rubber refrigeration components in the presence of refrigerant gas. This test was carried out using the POE & PAG oils and refrigerant R473A & R-23.

ID-3
Before test

ID-3
After test



ID- 21,22

ID- 23,24

Figure 5: Example photo of the tested metal/ rubber materials

Figure 5 above is showing an example photo of some of tested materials metal and rubber before the test and after ID 3 metal/ ID 21- 24 HNBR rubber which are carried out at different parameters with different POE/ PAG oils Zerol HD46 & Emkarate RL32H, the observation would tell that there are no changes have been appeared to the material after the test. Table 3 below is summarizing the post-exposure assessments of the elastomer and polymer materials which included evaluating the materials for changes in physical properties such as appearance, weight, volume, and hardness. The materials compatibility of elastomers (Table 3) with R-473A & R-23 with POE/PAG lubricants was similar to results you would see with R-23 with the same lubricant. Only small changes in weight, volume and hardness were observed in the samples, which contains both R-473A and R-23 exhibits similar behavior.

Table 3: Autoclave stability test results of the materials

ID	Materials	Appearance changes	Material weight changes	Hardness changes (elastomers)	Tensile property changes (polymers)
1	Cu, Fe, Al	No notable material changes	0%–20% increase	-	-
2	Cu, Fe, Al	No notable material changes	0%–20% increase	-	-
3	Cu, Fe, Al	No notable material changes	0%–20% increase	-	-
4	NBR	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
5	EPDM	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
6	Natural	No notable material changes	0%–20% increase	0%–10% decrease	0%–25% decrease
7	NBR	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
8	EPDM	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
9	Natural	No notable material changes	0%–20% increase	0%–10% decrease	0%–25% decrease
10	NBR	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
11	EPDM	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
12	Natural	No notable material changes	0%–20% increase	0%–10% decrease	0%–25% decrease
13	NBR	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
14	EPDM	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
15	Natural	No notable material changes	0%–20% increase	0%–10% decrease	0%–25% decrease
16	VITON	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
17	HNBR	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
18	EPDM	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
19	HNBR	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
20	HNBR	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
21	HNBR	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
22	HNBR	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
23	HNBR	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease
24	HNBR	No notable material changes	0%–20% increase	0%–10% increase	0%–25% decrease

5. CONCLUSION

This paper discusses the material compatibility and refrigerant/lubricant interactions of R-473A and presented comparative testing with R-23. R-473A has been identified as a non-flammable refrigerant with 85% lower GWP than R-23 and showed acceptable performance of the thermal stability with typical materials of construction used in refrigeration systems today. R-473A is also compatible with most of the elastomers/ metals which are commonly used today. The solubility results indicate that, when using both POE & PAG lubricants with R-473A under same reaction conditions, the working analysis provided to them will be similar. Experimental system reliability evaluation of R-473A shows satisfactory lubricant stability and refrigerant stability. Approach was developed to estimate the lifetime of the system operating with R-473A.

6. REFERENCES

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