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ABSTRACT

Recently a new blend, R-466A, utilizes R-13I1 (trifluoroiodomethane, CF_3I) in a blend with R-32 and R-125 that ASHRAE Standard 34 classified as A1 (lower toxicity and nonflammable) which is the same safety classification as R-410A. R-466A has been shown to have similar performance and capacity to R-410A, but with only 1/3 of the GWP as compared to R-410A.

R-13I1 is not a new molecule. It was considered in the CFC (chlorofluorocarbon)/HCFC (hydrochlorofluorocarbon) to HFC (hydrofluorocarbon) transition period, but was abandoned because of chemical stability concerns. The iodine atom in the molecule drives the instability concerns. Halogenated refrigerant chemical stability generally follows the rule that fluoride substitutions are more stable than chlorine than bromine and finally iodine. HFCs that later replaced the CFCs and HCFCs were generally found to be more chemically stable with materials.

In this paper, the authors will summarize highly accelerated life test results (HALT), ASHRAE 97 sealed glass tube methodology, for R13I1 and materials compatibility of select elastomers and polymers. Also provided are the chemical stability of R-466A results of accelerated life test equipment (ALT) testing using optimized materials and additives that show R-466A is a viable option for use.

1. INTRODUCTION

HVAC&R (Heating Ventilation Air-Conditioning and Refrigeration) equipment life expectancies are typically 15 to 25 years depending on the application. The authors are aware of water cooled chiller equipment operating in excess of 50 years. 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 decades. 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 sealed glass tubes per ASHRAE Standard 97 procedures with various system materials at highly accelerated temperatures instead of running equipment (ASHRAE 97, 2007). Typical accelerated conditions for sealed glass tubes experiments can vary with temperatures ranging from 130°C to 200°C for durations of 1 to 4 weeks, with a more common test point established at 175°C for 2 weeks. Such temperatures often exceed the inherent thermal capabilities of many organic materials and results from these evaluations may not be relevant to the performance in HVACR equipment. Kujak and Sorenson proposed an analytical methodology to translating small scale HALT results to real life HVACR operational conditions using a simple thermodynamic model and climate zone data (Kujak, Sorenson, 2019)

The new refrigerant blend, R-466A which is a blend of R-32/R-125/R-13I1, has been developed with thermodynamic properties that potentially could make it a design compatible replacement for R-410A. Schultz presented that the capacity and efficiency were very close to R-410A in soft optimized testing in a wide variety of applications. (Schultz, 2019). Limited data exists on the chemical stability of pure R-13I1 or in combination with other refrigerants, lubricants and a wide variety of HVACR system materials. Kujak et. al conducted a review of past work looking at the chemical stability of R-13I1 and proposed possible breakdown reaction mechanisms (Kujak, et. al, 2019). Authors also summarized Arrhenius chemical stability studies with R-13I1 and R-13I1 with polyolester lubricant systems. The authors validated that R-23 generation as the primary breakdown mechanism for R-13I1. The chemical stability work summarized in this paper is a further extension of this initial work. Next, the chemical stability of R-13I1 in R-466A was evaluated at ALT conditions in R-410A designed residential split systems and in unitary rooftop units (RTUs) in both cooling and heating modes to determine the R-13I1 breakdown rates under various operating conditions and materials.

2. HIGHLY ACCELERATED LIFE TESTING (HALT) OF R-466A

Multiple sealed glass tube chemical stability evaluations were conducted using R-466A to understand R-13I1's chemical reaction kinetics and potential for catalytic breakdown with specific system metals. Initial stability evaluations were performed to evaluate the Arrhenius 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 an unadditized and additized 32 cst polyolester (POE) lubricant at a 50% concentration by weight to study the chemical stability in this manner. Accelerated studies were carried out at 4 different temperatures and times, from 80°C to 150°C, and utilized three metal catalysts (iron, aluminum, copper). Table 1 summarizes the results of these evaluations.

The targeted breakdown product, R-23 (CF_3H), was used as the indicator of breakdown to evaluate the Arrhenius relationships. While other species can be formed during the breakdown of CF_3I, such as fluoride and iodide, these species are reactive with the metal catalysts, and therefore do not obey first order rate kinetics.

Table #1: Arrhenius Test Results Summary

		Purity (%)	*R-23 (ppm)*
R466A (Unexposed) Baseline		99.9	10
100% R466A	80˚C, 238 days	99.9	37
	100˚C, 106 days	99.9	82
	120˚C, 49 days	99.9	98
	150˚C, 14 days	99.9	206
50% R466A 50% Unadditized POE	80˚C, 238 days	99.9	601
	100˚C, 106 days	99.7	1350
	120˚C, 49 days	99.2	6464
	150˚C, 14 days	97.9	19,800
50% R466A 50% Additized POE	80˚C, 238 days	99.8	1315
	100˚C, 106 days	99.7	1074
	120˚C, 49 days	99.8	1635
	150˚C, 14 days	99.8	1580

Figure 1 summaries the data from Table 1 to evaluate where the reaction mechanisms and rates follow an Arrhenius relationship. Good Arrhenius correlations were found in the data when plotted using as Arrhenius relationship. This is meaningful, as it enables the use of alternative temperatures in the accelerated study of R-13I1 chemical stability due to the understanding that the rate law is followed within the temperature range of 80-150°C. Use of temperatures above 150°C would necessitate validation using this same practice.

The evaluation of initial chemical stability yielded insight to differing reaction rates initially studied in the 3 refrigerant and lubricant systems. First, it was found that the neat refrigerant exhibits elevated chemical stability compared to its stability in a lubricated system. This finding is consistent with prior knowledge of lubricants promoting CFC refrigerant breakdown via their nature as a hydrogen-donor.

Completion of the Arrhenius testing allowed for the selection of a test temperature and time for further HALT studies of stability with additional materials of interest. A test temperature and time of 150ºC and 14 days was selected for further review of chemical stability with five materials of interest.

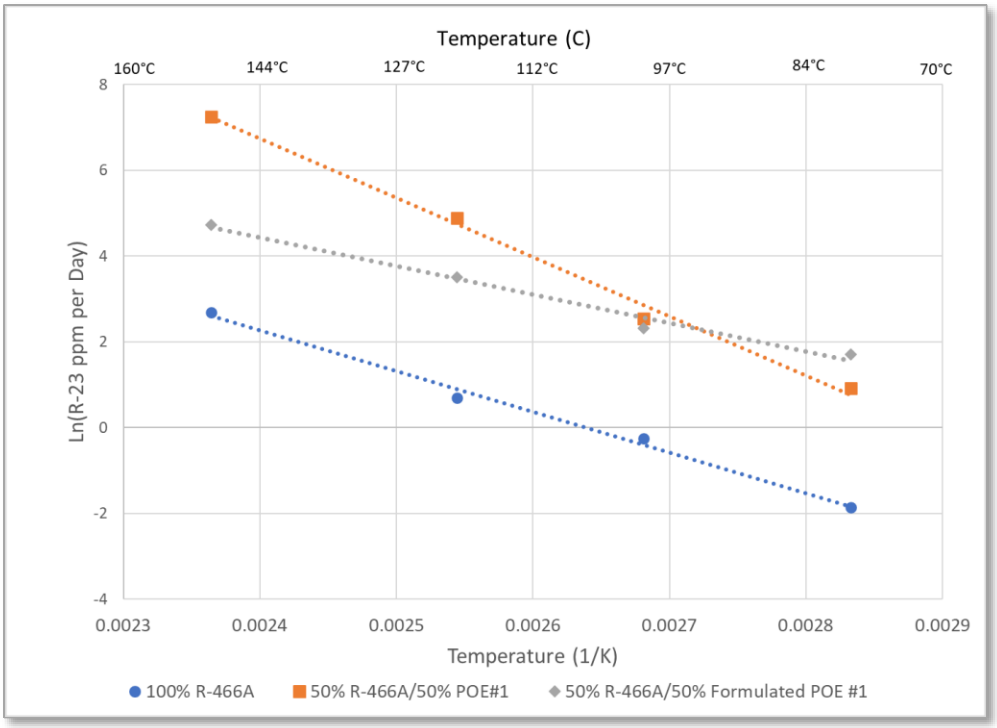

Figure #1: Arrhenius plot of R-466A evaluations from Table 1

Further understanding was needed to understand individual catalyst reaction rates rather the combination of copper, iron and aluminum catalysts together. Individual catalysts of copper, iron, aluminum as well as brass and zinc were exposed to pure R-466A and R-466A with a more stable formulation of POE for 14 days at 150ºC. Brass and zinc were identified as promoting the accelerated breakdown of R-13I1 in the presence of POE. In addition, additives (#1 and #2) were evaluated to promote the chemical stabilization of the R-13I1.

Table #2: Chemical Stability screening with Individual Metals

Condition	**Catalyst**	**% Purity**	**R-23 (ppm)**
100% R466A	Copper UNS C12200	99.9	58
	Iron UNS G10100	99.9	162
	Aluminum UNS A03800	99.9	126
	Brass C360	99.8	309
	Zinc-Al Alloy	99.9	211
50% R466A 50% Unadditized POE	Copper UNS C12200	99.8	1749
	Iron UNS G10100	99.9	933
	Aluminum UNS A03800	99.9	569
	Brass C360	99.7	2357
	Zinc-Al Alloy	78.6	208,100

Table #3: Chemical Stability evaluation with key metals with additives

Condition	POE	Catalyst	% Purity	R-23 (ppm)
50% R466A 50% More Stable POE	Baseline POE	Cu/Al/Fe	99.6	3584
	POE Additive #1	Cu/Al/Fe	99.9	118
	POE Additive #2	Cu/Al/Fe	99.9	773
50% R466A 50% More Stable POE	Baseline POE	Brass C360	99.7	2343
	POE Additive #1	Brass C360	99.9	120
	POE Additive #2	Brass C360	99.9	713
50% R466A 50% More Stable POE	Baseline POE	Zinc-Al Alloy	98.9	9771
	POE Additive #1	Zinc-Al Alloy	99.9	54
	POE Additive #2	Zinc-Al Alloy	99.9	492

The more stable POE improved the stability of R-13I1 by 5 times (19,800 ppm, Table 1 vs 3584 ppm, Table 3) in the prescence of copper, iron and aluminum catalysts. Both POE's are 32 cst lubricants that are commonly used in todays HVAC&R equipment and differ only in small chemical differences and additives. This result points to the selection of lubricant is likely a primary factor that needs to be considered when using R-13I1. Not shown, but the authors obtained similar results between both lubricants when additized with Additive #1 and #2, which would indicate that the lubricants impacts can be mitigated without changing lubricants.

Table 3 summarizes the results of two additives that were evaluated to reduce the reactivity of R-13I1, catalysts or both. Each additive was selected for its ability to either radical scavange or perform as a surface corrosion inhibitor. Both additives were effective at improving the chemical stability of R-13I1, especially in the prescence of brass and zinc alloys.

3. R-466A MATERIALS COMPATIBILITY SUMMARY

Material compatibility evaluations were conducted in Parr pressure vessels with R-466A and a 32 cst polyol ester (POE) based lubricant. No additives were present in the POE lubricant. Materials evaluated included 6 elastomers and 5 polymers. Testing was carried out at 100% refrigerant condition as well at 50% refrigerant/50% lubricant (by weight) conditions. Samples were aged for 7 days at 60˚C.. Table 4 and 5 summarize 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.

Table #4: Elastomer compatibility test results summary

Material	Exposure Condition	Post-Exposure Change (%)		
		Volume	Weight	Shore A Hardness
Neoprene	100% R-466A	5.0	7.1	0
	50% R-466A/POE	4.1	5.4	0
Nitrile-based NBR	100% R-466A	35.7	48.3	-7
	50% R-466A/POE	36.0	38.7	-12
EPDM	100% R-466A	9.6	13.3	-6
	50% R-466A/POE	11.4	13.2	-10
Epichlorohydrin	100% R-466A	12.7	12.2	-10
	50% R-466A/POE	16.1	12.7	-12
Neoprene	100% R-466A	9.1	11.4	-1
	50% R-466A/POE	11.5	10.8	-4
Fluorocarbon	100% R-466A	59.9	45.4	-8
	50% R-466A/POE	54.1	34.2	-12

Table #5: Plastic compatibility test results summary

Material	Exposure	Post-Exposure Change (%)		
		Volume	Weight	Shore D Hardness
Nylon 6,6	100% R-466A	0.1	0.1	2.4
	50% R-466A/POE	-0.1	-0.1	2.4
Polycarbonate	100% R-466A	6.9	11.3	-1.2
	50% R-466A/POE	2.6	3.6	-3.8
PEEK	100% R-466A	0.3	0.3	1.2
	50% R-466A/POE	0.3	0.3	2.4
Polypropylene	100% R-466A	4.4	6.2	-7.7
	50% R-466A/POE	2.5	3.6	-5.1
PTFE	100% R-466A	2.9	1.5	-4.8
	50% R-466A/POE	1.8	1.8	-4.8

The materials compatibility of elastomers (Table 4) with R-466A with and without POE lubricant was similar to results you would see with R-410A with and without POE lubricant. Only small changes in weight, volume and hardness were observed in the samples. The fluoropolymers showed significant weight and volume change but R-466A contains HFCs R-32 and R-125 and R-410A, which contains both R32 and R125, exhibits similar behavior.

The materials compatibility of polymers (Table 5) with R-466A with and without POE lubricant was similar to results you would see with R-410A with and without POE lubricant. Only small changes in weight, volume and hardness were observed in the samples.

4. EQUIPMENT ACCELERATED LIFE TESTING (ALT) OF R-466A

Two residential splits and two unitary rooftop R-410A units were floor tested in cooling mode and were modified to increase the temperatures on the compressor and condenser. The compressor discharge temperatures were kept greater than 130ºC and the condenser discharge air temperatures were held above 50°C for at least 2000 hours or as long as they could operate. Each unit was first run on R-410A to see if the modifications would hold the specified temperatures and then each unit was converted to R-466A. Each unit had a certain materials of construction. One residential split was tested unmodified except for the just changing refrigerant. The other residential split was evaluated with optimized compatible materials for use with R-13I1 which included additive 2. The two RTUs contained optimized materials for use with R-13I1 and additive 1 with either copper round tube heat exchangers or aluminum microchannel heat exchangers in both the evaporator and condenser. The heat exchangers differences were evaluated to see the impact of copper and aluminum heat exchanger materials. The optimized materials and additives used in these evaluations are standard off the shelf materials which have been used by the industry for many years in various applications. Figure 2 summarizes the results of the ALT evaluations. R-23 was measured at various interval to track the breakdown rates of R-13I1.

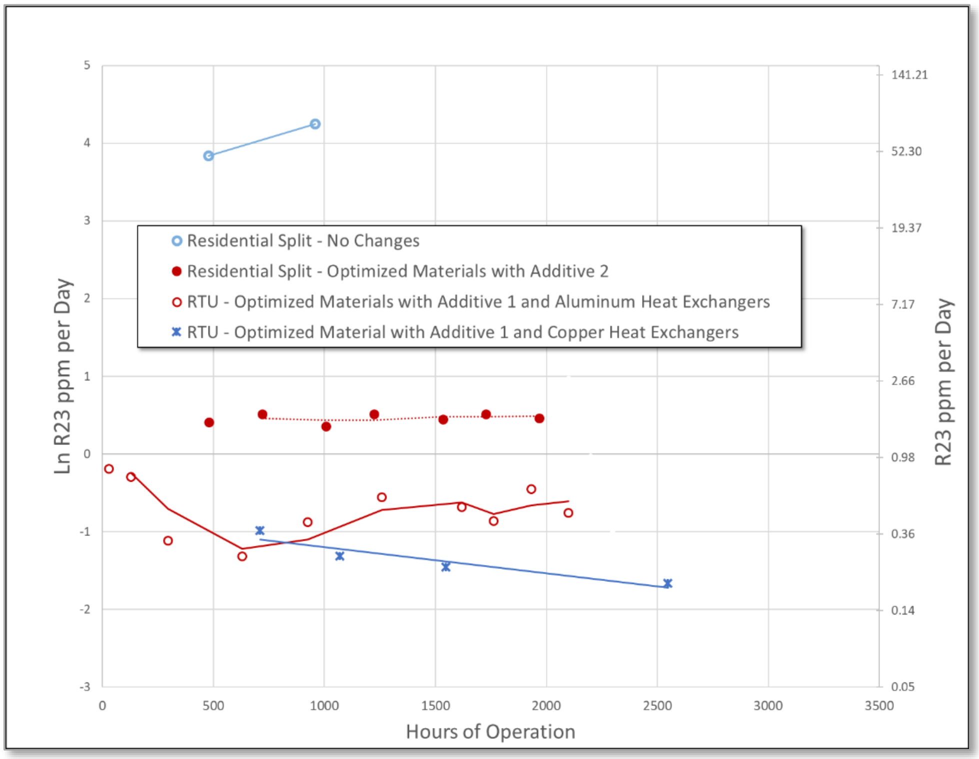

Figure #2: Summary of R-23 generationg rates for ALT units versus operational hours

The residential split with no changes experienced high R-23 generation rates (>50 ppm per day) and the reaction rate continued to increase. The unit was stopped early since this was expected behavior based on HALT testing evaluations with various materials and lubricants without the present of additives.

The remaining units with optimized materials and additive experienced low R-23 generation rates with the reaction rate being stable over time. There is some scatter in the data but this is as a result that the measured R-23 were very low and only small differences were seen from sample to sample. The acceptance goal was to obtain a reaction rates of <1 ppm per day on average. 2 out of 3 ALT units obtained a R-23 generation rate of <1 ppm with only 1 unit slightly above this goal or about 1.5 ppm per day.

After the evaluations, the units were opened and examined for damage or changes in components. The compressors used in the optimized units with additives appeared unchanged and were similar to a R-410A run units. Examination of expansion devices and other components in the optimized unit either indicated no appearance changes or very slight surface effects. More ALT testing is planned to further evaluate materials and optimize additives, but these results indicate that R-466A is a viable option and could be used by the industry as a nonflammable less than 750 GWP alternative to replace R-410A.

6. CONCLUSIONS

A series of HALT sealed glass tube evaluations were conducted with R-466A to understand its chemical reaction kinetics and potential for catalytic breakdown with specific system materials like metals and lubricant. Reaction mechanisms followed a proposed mechanism with the generation of the targeted breakdown product, R-23 (CF_3H), and rates followed an Arrhenius relationship. This is work was meaningful in that it enabled the ability to select alternative temperatures and times in highly accelerated studies of R-13I1.

R-466A HALT evaluations of materials with various POE lubricant chemistries, materials and additives showed the optimization of lubricants, materials and additives is possible to reduce the reaction rates of R-13I1 to potentially acceptable levels. Equipment ALTs were conducted with the optimization of materials and additives to verify the

HALT results. The optimized units with various additives and heat exchanger materials experienced low R-23 generation rates that were stable. The acceptance goal was to obtain a reaction rates of <1 ppm per day on average. 2 out of 3 ALT units obtained a R-23 generation rates of <1 ppm with only 1 unit slightly above this goal or about 1.5 ppm per day. After the evaluations, the units were opened and examined for damage or changes in components and no significant changes were observed in any of the components. The optimized materials and additives used in these evaluations are standard off the shelf materials which have been used by the industry for many years in various applications and should enable an orderly transition.

The sealed glass tube HALT and equipment ALT evaluations indicate that R-466A is a viable option for using HVAC&R equipment. R-466A is a design compatible less than 750 GWP alternative to replace R-410A and it would be a preferred alternative of choice than having to consider flammable options, like R-32 or R-454B.

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