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New Lubricants to Enable Performance, Reliability, and Efficiency of Equipment using Low GWP Refrigerants

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ABSTRACT

This paper will highlight case studies of physical and chemical interactions between refrigerants, lubricants, and components in HVACR systems from recent evaluations of new low GWP refrigerants, and will emphasize the value of including lubricants as an integral component of technology and product development roadmaps.

Refrigerant/lubricant mixture properties, such as miscibility, solubility, and viscosity, are critical to understand to meet design, operation, and reliability goals of HVACR equipment. In this paper, we will discuss miscibility and solubility challenges of specific new refrigerants, and review how these challenges have been addressed using advanced capabilities and deep understanding. Working viscosity is one of the most important factors to understand for optimal compressor efficiency and reliability, and is typically determined through Pressure/Viscosity/Temperature (PVT) measurements and corresponding models. We will compare working viscosities of current and new refrigerants, and discuss other factors to consider when defining lubrication requirements for alternative refrigerants.

Relative to incumbent refrigerants, some of the new low GWP refrigerants will have fundamental differences in their chemical stability, or will be exposed to more demanding application conditions such as higher discharge temperature - both of which may contribute to reliability concerns. We will review some of these considerations and provide examples of lubricant selection and formulation approaches to mitigate potential reliability issues.

This paper will highlight examples of physical and chemical interactions that should be considered early in the development of product applications for new low GWP refrigerants, and will illustrate the benefits that optimized lubricants may have on the performance, efficiency, and reliability of equipment.

1. INTRODUCTION

As the industry aims to lower the environmental impact of HVAC and refrigeration applications, there is significant focus on controlling factors that have the potential to contribute to global warming. Major efforts have been underway over the past several years to identify and test lower GWP refrigerant alternatives for today's high global warming hydrofluorocarbon (HFC) refrigerants. In addition to establishing refrigerant options to meet different environmental, regulatory, and safety targets, the performance of these new fluids has been evaluated in test programs such as AHRI's Low GWP Alternative Refrigerant Evaluation Program (Low GWP AREP) to ensure that the alternatives have similar or better efficiency in their target applications relative to the baseline. This is important

to bear in mind when discussing refrigerant transitions because both the direct and indirect environmental impacts must be considered as part of the overall global picture.

In this paper, we consider the role that lubrication and lubricants play in enabling the industry to reduce its direct and indirect environmental impacts. Lubricant technology and associated engineering information are integral and critical components to facilitate the transition to lower GWP refrigerants, to maintain the design and application of reliable equipment, and to enable performance and efficiency targets to be achieved.

Table 1 is a summary of hydrochlorofluorocarbon (HCFC) and HFC refrigerants that have been and may still be commonly used, and categorizes them into three pressure classes. R-410A is categorized as a high pressure refrigerant. R-507A, R-404A, R-502, R-22, and R-407C are designated as medium pressure, and R-134a, R-245fa, and R-123 are referred to as low pressure refrigerants. R-22 and all of the tabulated low pressure refrigerants are single-component fluids and thus each have the same bubble point and dew point values.

Table 1: Relevant Information for Commonly Used HCFC and HFC Refrigerants

Pressure Category	Refrigerant	Bubble Point at 1 atm (°C)	Dew Point at 1 atm (°C)	Critical Temperature (°C)	GWP ¹
High	R-410A	-51.4	-51.4	71.3	1924
Medium	R-507A	-47.1	-47.1	70.9	3900
	R-404A	-46.2	-45.5	72.0	3943
	R-502	-45.3	-45.1	81.5	4600
	R-22	-40.8	-40.8	96.1	1760
	R-407C	-43.6	-36.6	86.0	1624
Low	R-134a	-26.1	-26.1	101.1	1300
	R-245fa	15.1	15.1	154.0	858
	R-123	27.8	27.8	183.7	79

¹GWPs determined from Intergovernmental Panel on Climate Change (IPCC) 5th Assessment Report

Lubrication and lubricant considerations for R-134a, R-404A, and R-410A alternatives will be reviewed in this paper, and specific examples will be given to highlight the benefits of newly developed lubricant platforms optimized for R-1234ze(E) and R-32.

2. LUBRICATION CONSIDERATIONS FOR REFRIGERANT ALTERNATIVES

2.1 Low Pressure R-134a Alternatives

Table 2 contains information on R-134a and a number of proposed alternatives. Several of the alternatives, such as R-1234yf, R-513A, and R-450A have similar vapor pressures compared to R-134a. However, alternatives such as R-515A, R-1234ze(E), and R-600a operate at significantly lower pressures. In general, and especially in these cases, it is important to make solubility and viscosity comparisons at fixed saturation temperatures that reflect the different operating pressures of the refrigerants in the application; otherwise misleading conclusions can be drawn that are irrelevant to the end use. This approach is applied for the solubility and viscosity comparisons throughout this paper.

Table 2: Relevant Information on R-134a and Potential R-134a Alternatives

Refrigerant	Composition	Average Molar Mass (g/mole)	Bubble Point at 1 atm (°C)	Dew Point at 1 atm (°C)	Critical Temp. (°C)	GWP	ASHRAE Classification
R-134a	R-134a (100)	102.0	-26.1	-26.1	101.1	1300	A1
R-513A	R-134a/R-1234yf (44/56)	108.4	-29.3	-29.2	96.5	573	A1
R-450A	R-134a/R-1234ze(E) (42/58)	108.7	-23.4	-22.8	105.6	546	A1
R-515A	R-1234ze(E)/R-227ea (88/12)	118.7	-19.0	-19.0	108.7	402	A1
R-1234yf	R-1234yf (100)	114.0	-29.5	-29.5	94.7	<1	A2L
R-1234ze(E)	R-1234ze(E) (100)	114.0	-19.0	-19.0	109.4	<1	A2L
R-600a	R-600a (100)	58.1	-11.7	-11.7	134.7	3	A3

Many of the R-134a alternatives laid out in Table 2 have been extensively tested (Low GWP AREP) and some have been commercialized for use. For example, the lower GWP Class A1 alternatives R-513A and R-450A are being offered as options for use in commercial HVAC applications that were originally designed for R-134a. In these cases, the refrigerants are generally being applied in the same equipment that was used with R-134a, with only minor control or valve setting changes to adapt to slight differences in the refrigerant properties. Significant work has been done by lubricant technology companies, refrigerant manufacturers, original equipment manufacturers (OEMs), and the industry overall to verify suitability of these lower GWP nonflammable options in existing equipment designs with existing lubricants. For example, AHRI's Low GWP AREP and Material Compatibility and Lubricants Research (MCLR) program, as well as several research studies sponsored through ASHRAE and other organizations, have resulted in a robust knowledge base to enable the industry to transition quickly to viable options with 50-60% lower GWP than R-134a.

For the flammable lower GWP R-134a alternatives, there have been larger implementation hurdles, especially for applications with significant refrigerant charge sizes; however, the industry continues to close knowledge gaps (Cundy, 2017; Goetzler, 2013; Goetzler, 2016; Kim, 2017) and develop solutions that enable implementation of these very low GWP refrigerants; for example, R-1234yf in mobile air conditioning, R-600a (isobutane) in residential appliances, and R-1234ze(E) in commercial HVAC applications. For these three very low GWP flammable options, lubricants originally designed for use with R-134a may need to be optimized slightly or completely overhauled depending on the refrigerant and the application requirements.

R-1234ze(E), and R-1234ze(E)-rich blends such as R-515A, present challenges for use with conventional lubricants. R-1234ze(E) is physically compatible and miscible with lubricants that have been applied with R-134a, but it has significantly higher solubility than R-134a (Figure 1). To address the higher solubility and lower working viscosity of R-1234ze(E) relative to R-134a, one option for an equipment designer would be to increase the viscosity grade of the lubricant to achieve higher working viscosity under the same conditions. The tradeoff to this approach would be a negative efficiency impact from the additional electrical power required to move the higher viscosity lubricant. Another approach that could be considered is the use of hardware to separate the refrigerant and lubricant so that higher quality lubricant returns to the compressor sump. The tradeoff to this approach is the cost of additional or optimized components, and potentially significant resource investments required for equipment redesign. Another potential approach is to limit the equipment operating map so that low viscosity or high solubility conditions of concern cannot be reached in the application. The tradeoff with this approach is that without taking on higher reliability risks, the equipment will have a reduced application range relative to its original design intent - potentially limiting its commercial viability.

Another approach that can be considered is to change the lubricant chemistry such that the new refrigerant and lubricant combination behaves similarly to or better than the baseline refrigerant that the equipment was originally designed around. One tradeoff to this approach is that to achieve this goal, new and different lubricant chemistries may be required that bring along technical, commercial, or regulatory unknowns that need to be fleshed out.

Another tradeoff is that as lubricants are changed to address a challenge with a specific new refrigerant, there is higher potential for them to become less optimized for the incumbent refrigerant. In this case, a decision needs to be made on whether to take on the complexity of an additional lubricant, or to potentially sub-optimize lubrication for one or both refrigerants to maintain use of a single lubricant.

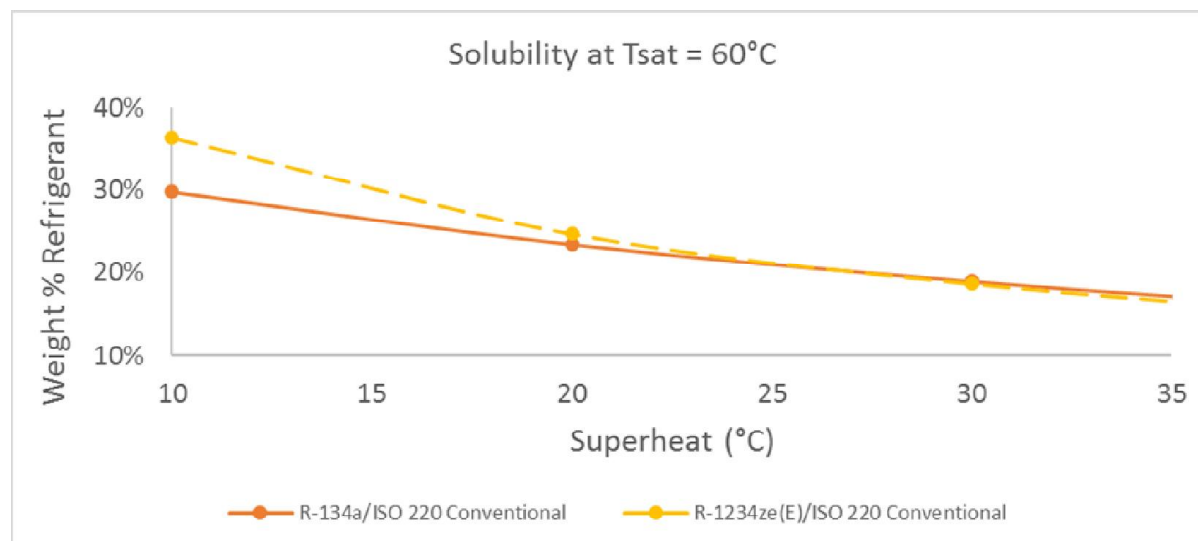


Figure 1: Solubility comparison of R-134a and R-1234ze(E) with the same conventional ISO 220 polyol ester lubricant at a saturation temperature of 60°C. R-1234ze(E) exhibits higher solubility than R-134a.

Because of the tradeoffs associated with any of these scenarios, two-way exchanges between the lubricant technology company and OEM or end user need to take place early and often to ensure there is mutual understanding of technology readiness and design flexibility, and to realize the best possible outcome in the timeframe of interest with the lowest possible investment.

In the case of R-1234ze(E), a new lubricant platform has been developed that addresses the solubility challenges with conventional lubricants. As shown in Figure 2, the optimized chemistry provides similar or slightly improved solubility with R-1234ze(E) compared to R-134a with conventional POEs of the same viscosity grade. This solution enables system designers to apply the low GWP refrigerant 1234ze(E) with the same or lower viscosity grade lubricant as R-134a - eliminating an efficiency penalty - and removes the need to implement new hardware or operating map restrictions.

As part of the lubricant qualification process, elastomer compatibility and chemical stability assessments with R-1234ze(E) have been performed. Figure 3 shows the elastomer volume change results after exposure to a 50/50 (weight %) refrigerant/lubricant mixture for 1 week at 90°C. Results indicate acceptable elastomer compatibility with all of the materials except the fluorocarbon material. It is worth noting that this same material has been previously determined to be high risk for HVACR applications due to its tendency to excessively swell after refrigerant exposures and potentially deform during use (Majurin, 2014).

Chemical stability assessments were carried out according to ASHRAE 97 by exposing R-1234ze(E) and the ISO 220 optimized lubricant with aluminum, copper, and steel coupons in sealed glass tubes for two weeks at 175°C. Image 1 is a post-exposure image of the tubes and catalysts. Tube contents were evaluated for appearance changes of the fluids and catalysts, and lubricant samples were analyzed for changes in color, total acid number (TAN), and dissolved elements. Results demonstrate acceptable chemical stability, with a post-exposure TAN change of +0.05 mg KOH/g of lubricant, no detection of dissolved aluminum, copper, or iron, and no notable visual changes to the fluids or catalysts.

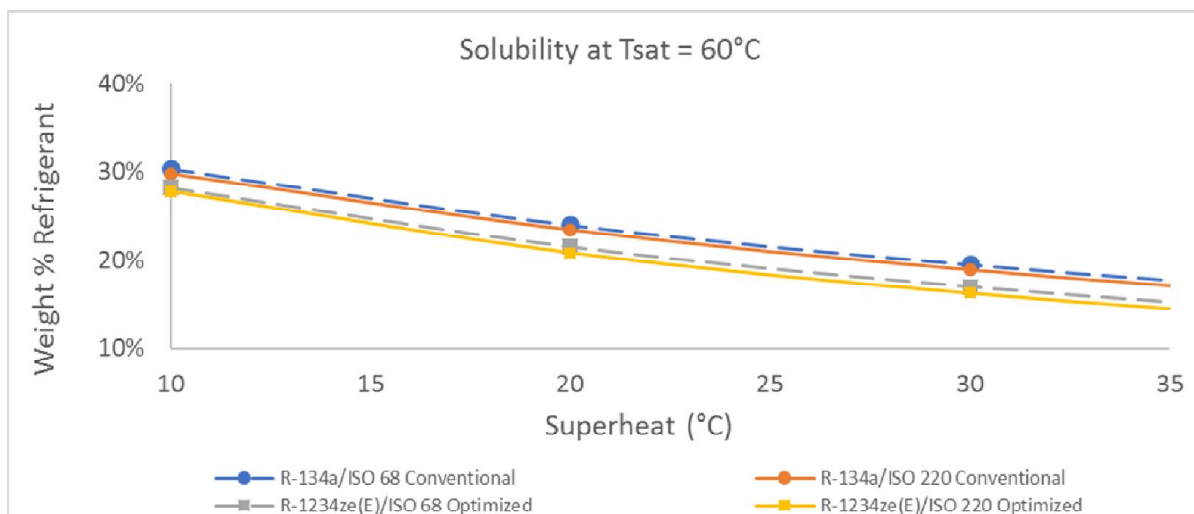


Figure 2: Solubility comparison of R-134a with ISO 68 and ISO 220 conventional polyol ester lubricants and R-1234ze(E) with ISO 68 and ISO 220 optimized lubricant chemistry at saturation temperatures of 60°C. The optimized lubricants applied with R-1234ze(E) result in similar or slightly lower solubility than the baseline conventional lubricants applied with R-134a.

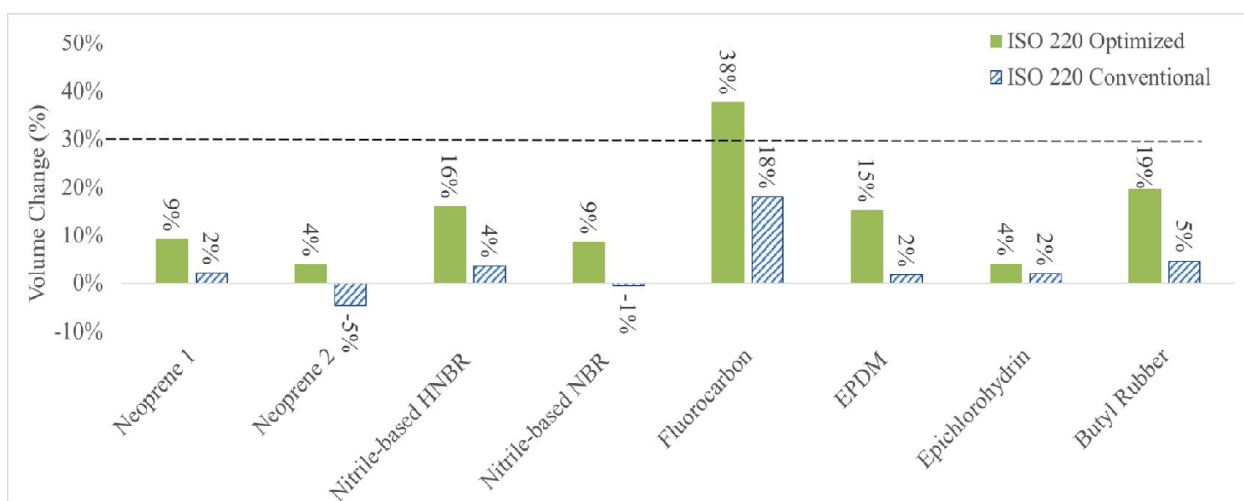


Figure 3: Elastomer volume changes after exposure to 50% R-1234ze(E)/50% lubricant for 1 week at 90°C.

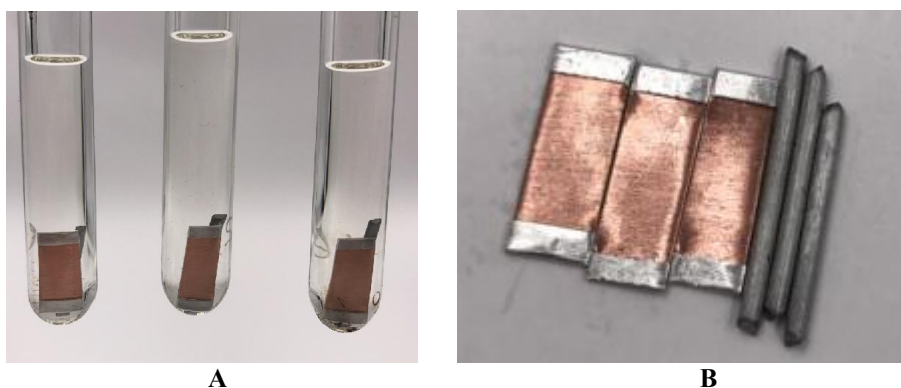


Image 1: Post-exposure images of (A) the sealed glass tubes with 20% R-1234ze(E)/80% ISO 220 optimized lubricant exposed with catalysts for 2 weeks at 175°C, and (B) catalysts after removal from the tubes.

Sometimes, lubricant chemistry changes can result in intended or unintended benefits that are confirmed or discovered during qualification processes. One of the benefits of the new lubricant platform is that it is less hygroscopic compared to conventional POEs (and other synthetics including polyvinyl ether (PVE) and polyalkylene glycol (PAG) lubricants). As shown in Figure 4, the new lubricant chemistry saturates at about 25% lower moisture content compared to conventional POEs of the same viscosity grade, and has a lower moisture absorption rate. This is anticipated to result in lower energy costs to keep the lubricant dry, and potentially shorter evacuation times on the equipment assembly line.

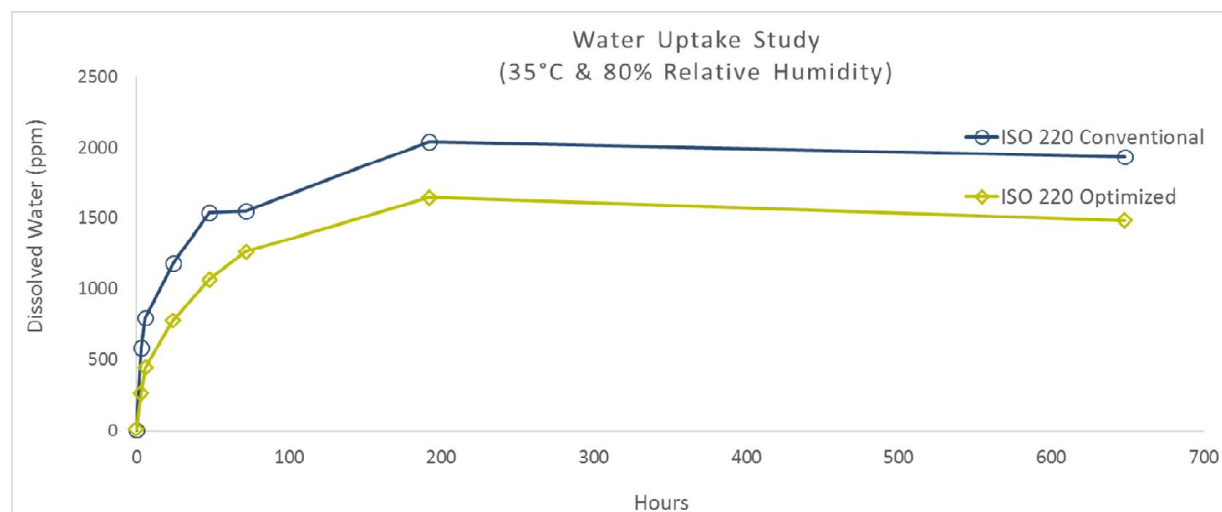


Figure 4: Moisture uptake comparison of optimized lubricant chemistry and conventional polyol ester lubricant chemistry, at 35°C and 80% relative humidity.

Another significant benefit of the new lubricant platform is a higher pressure-viscosity coefficient than conventional POEs (Table 3). Pressure-viscosity coefficient (alpha coefficient, α^*) refers to the relationship between the load placed on the oil film (pressure) at the dynamic load zone and the thickness of the oil film (viscosity) at that load. This is of particular importance in the lubrication of heavily loaded concentrated contacts such as those found in rolling contact bearings and gears. In commercial HVAC applications, R-134a and R-1234ze(E) are frequently applied in screw compressors with rolling element bearings that operate under very high contact pressures (up to a gigapascal, or 10,000 bar); alpha coefficient is a critical parameter to understand for these applications.

Alpha coefficient determinations were conducted by measuring viscosities at three different temperatures with an in-house high pressure viscometer that was developed to enable the measurement of contact pressure viscosities in the presence of refrigerant. As shown in Table 3, the optimized neat lubricant's empirically derived alpha coefficient was consistently 10% higher than a conventional POE lubricant of the same viscosity grade.

Table 3: Relative Pressure-Viscosity Coefficient of the ISO 220 Optimized Lubricant Relative to ISO 220 Conventional POE

Temperature (°C)	Relative α^* of ISO 220 Optimized Lubricant Compared to ISO 220 Conventional
40	1.12
60	1.09
80	1.11

Figure 5 shows the impact of refrigerant and temperature on the measured alpha coefficient of the lubricant relative to the neat lubricant measured at the same temperature. It is observed that dilutions in the range of 25% cause about a 35-40% reduction in alpha coefficient, and dilutions in the range of 10% cause a 15-20% reduction relative to the neat lubricant.

It is believed that a cumulative lubrication benefit can be realized by simultaneously reducing refrigerant solubility and increasing alpha coefficient for refrigeration lubricant applications with rolling element bearings.

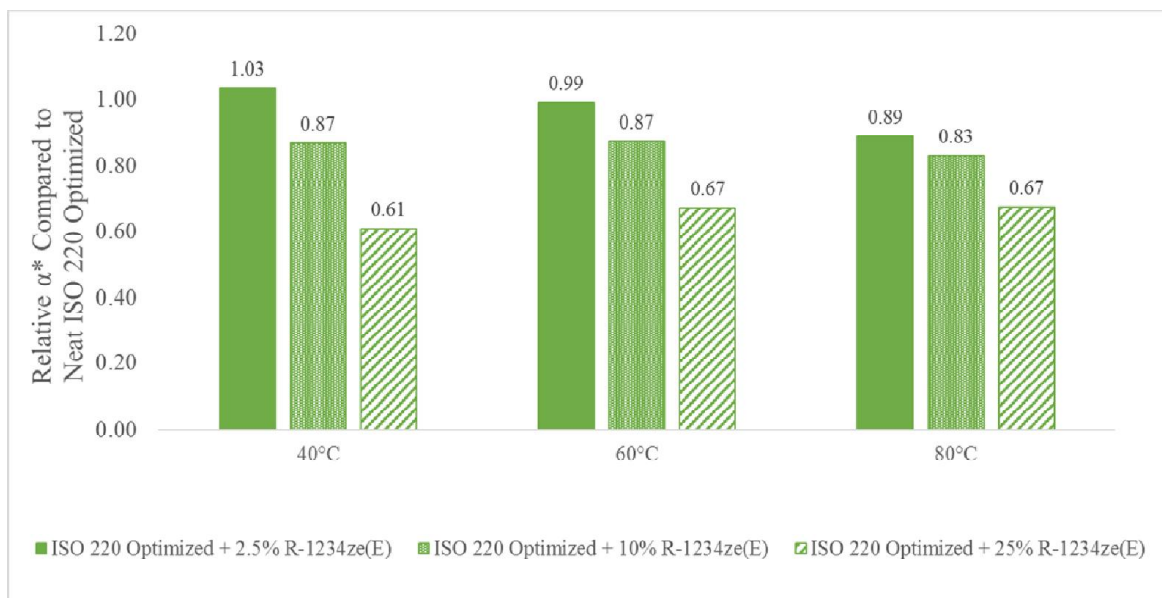


Figure 5: Relative pressure-viscosity coefficient as a function of refrigerant concentration and temperature. Values are determined relative to the ISO 220 optimized neat lubricant values at the corresponding temperature.

In summary, a new lubricant platform has been developed for R-1234ze(E) and other refrigerants with high POE lubricant solubility. In addition to lower solubility, the new lubricant platform exhibits higher pressure-viscosity coefficient and lower moisture uptake relative to conventional POEs. Screening tests indicate acceptable chemical stability and material compatibility.

This example illustrates how lubricant chemistry may be modified to enable the implementation of highly soluble low GWP refrigerants without negatively impacting efficiency or reliability. It also demonstrates the role lubricant technology plays in allowing equipment to be operated throughout a target application range, while minimizing additional design and manufacturing costs.

2.2 Medium Pressure R-404A Alternatives

Because of the very high GWP of R-404A, nonflammable lower GWP R-404A alternatives such as R-452A, R-448A, and R-449A have had the earliest adoption and most experience in the field. Hundreds if not thousands of stationary and transport refrigeration systems are using these refrigerants with existing equipment and existing lubricants applied with R-404A. The rationale is clear since relative to R-404A, these design-compatible refrigerants provide a means to achieve 50-70% lower GWP than R-404A. In addition to nonflammable HFC/HFO blend options for the medium pressure space, lower GWP nonflammable HFC blends in the R-407 series are also being proposed and applied. These R-407 series blends are all compatible with existing lubricants applied for decades with HFC refrigerants including R-407C. As the industry considers the flammable lower GWP options, there are generally two categories proposed and evaluated to date 1) HFO/HFC blends with GWP <300 including but not limited to R-454A, R-454C, R-455A, R-444B, and R-457A, and 2) the hydrocarbon R-290 (propane). Lubricants are available that meet the needs of all of these refrigerant options for today's applications and will be reviewed separately.

2.3 High Pressure R-410A Alternatives

Table 4 includes information on select R-410A alternatives. The three lower GWP options in this table are all classified as ASHRAE Class A2L, and are slightly flammable. Other slightly flammable options with larger temperature glides, including R-446A, R-447A, R-447B, and R-459B have also been developed and evaluated. Nonflammable alternatives are also under consideration through ASHRAE Standard 34, or are potentially still under development, and are not reviewed here.

Table 4: Relevant Information on R-410A and Select Alternatives

Refrigerant	Composition	Average Molar Mass (g/mole)	Bubble Point at 1 atm (°C)	Dew Point at 1 atm (°C)	Critical Temp. (°C)	GWP	ASHRAE Classification
R-410A	R-32/R-125 (50/50)	72.6	-51.4	-51.4	71.3	1924	A1
R-32	R-32 (100)	52.0	-51.7	-51.7	78.1	677	A2L
R-452B	R-32/125/1234yf (67/7/26)	63.5	-51.0	-50.2	79.7	675	A2L
R-454B	R-32/1234yf (68.9/31.1)	62.6	-50.9	-49.9	80.9	466	A2L

Of the options presented in Table 4, R-32 has the most challenges with lubricants currently applied with R-410A. As illustrated in Figure 6, R-32 has miscibility challenges relative to R-410A and R-452B with conventional lubricants. The challenge with limited miscibility of this nature is concern that circulating lubricant may become trapped in the heat exchanger and not return to the oil sump where it is required to feed compressor bearings and other moving parts.

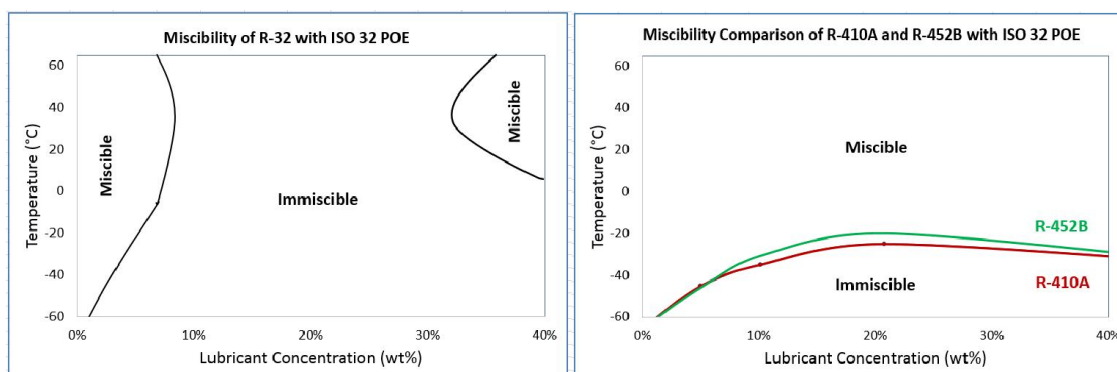


Figure 6: Miscibility of R-32 with an ISO 32 conventional POE lubricant (left), and miscibility of R-452B and R-410A with the same ISO 32 conventional POE lubricant (right).

To address this miscibility challenge, the POE lubricant chemistry was changed so that the R-32 miscibility with the optimized lubricant matches the miscibility profile of R-410A with the baseline lubricant (Figure 7). The value that this solution provides is similar miscibility performance with R-32 compared to the baseline R-410A, the refrigerant for which the equipment was originally designed and for which decades of application experience exist.

New lubricant chemistries optimized for R-32 have been developed in viscosity grades up to ISO 100 and are compatible with R-452B, R-454B, and the baseline R-410A. These solutions enable the OEM or end user to identify a single lubricant that may be applied with a range of potential R-410A alternative refrigerants.

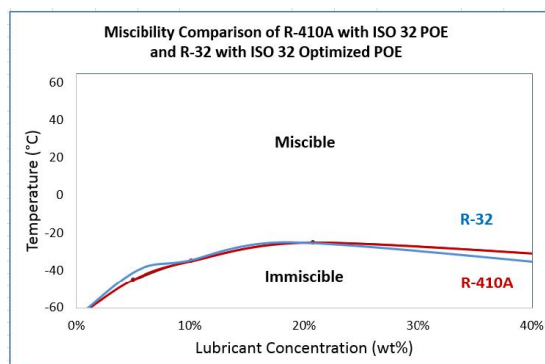


Figure 7: Miscibility comparison of ISO 32 optimized POE and R-32 compared to ISO 32 conventional POE and R-410A.

3. CHEMICAL STABILITY

One of the topics of interest in the industry is chemical stability of the new refrigerants. Extensive internal and industry-sponsored studies (Rohatgi et al., 2012; Majurin et al., 2014) on thermal and chemical stability have been carried out on HFO refrigerants and blends of these refrigerants with R-32. Results from these studies generally conclude that HFO refrigerants such as R-1234yf and R-1234ze(E) have acceptable chemical stability under typical application conditions. However, they exhibit slightly higher chemical instability than R-134a and R-410A in the presence of high concentrations of air and in some cases, air and water. At this stage, the industry has not reached consensus that refrigerant or lubricant additives are required to manage some marginally higher chemical instability of specific low GWP refrigerants in the presence of contaminants. Some of the high pressure refrigerants, such as R-32, will operate at higher discharge temperatures when applied over the same operating map as R-410A or R-22. In general, engineering solutions are in place to limit these excessive temperatures. However, as more experience is gained with low GWP refrigerants throughout a broader range of applications, and as new low GWP refrigerants continue to be developed, it will be important for compressor and system designers to work closely with lubricant technology companies to understand if and when lubricant chemistries or formulations need to change to manage chemical instability, and to understand the potential tradeoffs.

4. CONCLUSIONS

A new lubricant platform has been developed for R-1234ze(E) and other highly soluble refrigerants. The new lubricants exhibit acceptable chemical stability and material compatibility and have less moisture uptake than conventional synthetic lubricants. The new lubricant platform exhibits lower solubility with R-1234ze(E), and has a higher pressure-viscosity coefficient compared to conventional POE lubricants. It is believed that the combination of lower solubility and higher pressure-viscosity coefficient will be particularly advantageous for applications with rolling element bearings.

A new lubricant platform has been developed for R-32 that enables R-32 miscibility to match the baseline R-410A miscibility with conventional lubricants across a range of viscosity grades. The new lubricant platform is compatible with HFO/HFC refrigerant alternatives such as R-452B and R-454B, as well as the baseline R-410A.

These solutions provide examples of the benefits that deep fundamental understanding of lubricant technology, and the end uses that they are applied to, can bring to the industry as we navigate through the low GWP refrigerant landscape.

NOMENCLATURE

AHRI	Air Conditioning, Heating and Refrigeration Institute
AREP	Alternative Refrigerants Evaluation Program
ASHRAE	American Society of Heating, Refrigerating and Air Conditioning Engineers
GWP	Global Warming Potential
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HFO	hydrofluoroolefin
HVACR	Heating, Ventilation, Air Conditioning and Refrigeration
ISO	International Standards Organization Viscosity Grade
MCLR	Material Compatibility and Lubricants Research
OEM	Original Equipment Manufacturer
PAG	polyalkylene glycol
POE	polyol ester
PVE	polyvinyl ether
PVT	Pressure/Viscosity/Temperature
TAN	Total Acid Number

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