COMPATIBLE REFRIGERATION OILS FOR VARIOUS NEXT-GENERATION REFRIGERANTS

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ABSTRACT

Various refrigerants have been proposed as countermeasures against global warming and climate change. Fluorine-containing refrigerants, techniques have been developed to reduce their global warming potential. However, maintaining the stability of such refrigerants within a refrigeration cycle remains a challenge. Hydrocarbon refrigerants, which inherently have low global warming potential, require safety measures due to their flammability. This report presents recent studies on the responce of refrigeration oils to these emerging refrigerant trends.

Keywords: Refrigeration Oil, Refrigerant, Refrigeration cycle, Miscibility

INTRODUCTION

Currently, efforts to maintain and improve global environments are being made in various industrial fields, and in the field of refrigeration and air conditioning, energy saving of various devices and facilities and switching to refrigerants having a low global warming potential (GWP) are being promoted in order to suppress global warming and climate change. In addition, there is a possibility that R1234yf (2333 - tetrafluoropropene), which is a hydrofluoroolefin (HFO) refrigerant that is a main component of a low GWP refrigerant, cannot be adopted in some regions due to strengthening of regulations on chemical substances throughout the world. In particular, in Europe, hydrocarbon refrigerants containing no fluorine have been attracting attention because of considering the legislation of PFAS regulations for strengthening the regulation of fluorine compounds has been studied since the last year.

Although the hydrocarbon-based refrigerant has very high combustibility, R600a (isobutane), which is a hydrocarbon-based refrigerant, has been adopted in the field of household refrigerators in the past and is currently the mainstream refrigerant in Europe and Asia. And R290 (propane), which has a slightly higher saturated vapor pressure than R600a, has also been used as an environment-friendly refrigerant in the field of small-sized air conditioning, the field of freezing and refrigeration, and the field of hot water heating in recent years, but there is a technical problem that it is necessary to reduce the amount of the refrigerant to be sealed as much as possible as a part of ensuring safety against high combustibility.

In order to contribute to such a problem from the viewpoint of the refrigeration oil, there is a means of suppressing the solubility with the refrigerant. Since R12 (dichlorodifluoromethane) started to be used as a refrigerant in 1930, the fact that the refrigerant and the refrigeration oil are easily dissolved in each other has become the center of the technology of the refrigeration oil in the refrigeration cycle, in view of the fact that the solubility with the naphthenic mineral oil, which is the main refrigeration oil at that time, was good. But the solubility between the refrigerant and the refrigeration oil was not considered before that, and even today, a combination of R717, which is operated all over the world, and the naphthenic mineral oil or white oil, which are not dissolved in each other, shows that. [1-3] In addition, a combination of a hydrofluorocarbon (HFC) refrigerant such as R410A (difluoromethane / penta-fluoroethane) or R32 (difluoromethane) and an alkyl-benzene oil, a combination of R32 and a polyolester (POE) oil for R410A, and the like, which are adopted by some manufacturers in household air conditioners, are the same, and it is shown that the operation is possible even with a combination in which the refrigerant and the refrigeration oil are not easily dissolved depending on the use, the cycle design, and the control.

The reason why solubility between refrigeration oil and refrigerant is required, is said to be due to the ``oil return" performance, in which the small amount of refrigeration oil discharged from the compressor along with the refrigerant returns to the compressor through the refrigeration cycle. [4-5]

However, the refrigerant returning to the compressors is basically vaporized, and returning in a liquid state is considered to be a specific operation condition such as defrosting depending on the application. Therefore, it is considered that the "low solubility" that has started to be required for the operation of the flammable refrigerant can be effectively utilized by grasping not only the "two phase separation temperature", which is the ratio and temperature at which the liquid refrigerant and the refrigeration oil are uniformly dissolved, but also the relationship between the refrigerant and the refrigeration oil in the environment of returning from the evaporator to the compressor, and the difference in solubility between the refrigeration oil and the refrigerant is reported on the basis of several evaluation items.

Furthermore, the compatibility between an HFO -based mixed refrigerant containing the latest R-1132 (E) and a refrigeration oil is also introduced.

REFRIGERANT SOLUBILITY OF REFRIGERATION Oil

REFRIGERANT AND REFRIGERATION OIL

First, the evaluation of the refrigerant solubility of the refrigeration oil will be described. As the refrigerant, the R32 of the HFC refrigerant for air conditioning and the R1234yf of the HFO refrigerant for vehicular air conditioning, cold insulation cars, and turbo refrigerators were taken up from the "fluorine-containing refrigerant" such as the HFC refrigerant and the HFO refrigerant, and the R290 was selected from the "hydrocarbon-based refrigerant" containing no fluoride.

As the evaluation oil, an oil that was easily compatible with the target refrigerant and an oil that was hardly compatible with the target refrigerant were selected from the refrigerator oils applied to the respective refrigerants. The refrigeration oils to be combined with the R32 were “POE for R32” having high solubility, “POE for R410A” having low solubility, and “Development Oil” [6-8] having poor solubility. The refrigeration oils to be combined with the R1234yf were “PAG for R1234yf” used for vehicular air conditioning, “POE for R410A” and “Development Oil” having poor solubility with HFC refrigerants and HFO refrigerants, such as R1234yf R32 as described above. Table 1 lists the respective properties. As the refrigeration oil to be combined with the R290, naphthenic mineral oils and POE for R410A, which have very high solubility, and PAG, which has low solubility with R290, were selected. Table 2 lists the respective properties.

Table 1 Properties of Test Oils

		POE VG68 for R32	POE VG68 for R410A	PAG VG46 for R1234yf	Developed Oil VG46
Density, @15℃	g/cm^3	0.986	0.960	1.013	0.925
Color, ASTM		L0.5	L0.5	L0.5	L1.0
Flash Point, COC	℃	264	256	220	190
Pour Point,	℃	-40	-40	-42.5	-40
Kinematic Viscosity, @40℃	mm^2/s	62.6	66.2	46.5	41.5
Kinematic Viscosity, @100℃	mm^2/s	8.01	8.19	9.06	5.67
Acid Number,	mgKOH/g	0.01	0.01	0.01	0.01
Water Content,	ppm	35	35	100	30
Volume Resistivity, @25℃	Ω･cm	2×10^{13}	5×10^{14}	5×10^{10}	4×10^{13}

Table 2 Properties of Test Oils

		Naphthenic Mineral Oil VG100 for R290	POE VG68 for R410A	PAG VG60 for R290
Density, @15℃,	g/cm^3	0.919	0.960	1.012
Color, ASTM		L1.5	L0.5	L0.5
Flash Point, COC,	℃	234	256	234
Pour Point,	℃	-27.5	-40	-40
Kinematic Viscosity, @40℃,	mm^2/s	96.3	66.2	63.9
Kinematic Viscosity, @100℃,	mm^2/s	8.97	8.19	10.3
Acid Number,	mgKOH/g	0.01	0.01	0.01
Water Content,	ppm	20	35	100
Volume Resistivity, @25℃	Ω･cm	1×10^{15}	5×10^{14}	1×10^{10}

COMPARISON RESULTS

Two phase separation temperature (critical solution temperature)

Table 3 shows the two phase separation temperature at an oil fraction of 20% by weight, which is close to the lower critical solution temperature of each refrigeration oil.
It can be seen that a combination which is easily compatible shows a low value, but a combination which is hardly compatible shows a high value or shows two phase separation.
However, actually, since the refrigerant has already been vaporized on the suction side of the compressor, the oil fraction is usually high. For example, the two phase separation temperature at an oil fraction of 90% by weight is shown in Table 4. Even in a combination in which the refrigerant is separated into two phases at an oil fraction of 20% by weight, the two phase separation temperature is a somewhat low value at an oil fraction of 90% by weight, and it can be seen that the refrigerant is dissolved in the refrigeration oil.

Pressure temperature solubility / temperature viscosity solubility

Although the conditions vary depending on the application and the apparatus, the solubility of refrigeration oil with refrigerant and its viscosity at that time when the pressure at the outlet of the evaporator is set to 0.1 MPa and the temperature is set to -20 ° C. are shown in Table 5. When the viscosities of the respective combinations are compared with each other, it can be seen that the viscosity is not so large even in a combination in which the refrigerant and the refrigeration oil are hardly compatible with each other. In particular, the viscosity of the combination with R32, which is a refrigerant that is not easily dissolved in the refrigeration oil, shows the equivalent value for all refrigeration oils, and if the oil return to the compressor is sufficient with this viscosity, it is considered that sufficient oil return is ensured even with other combinations.

Table 3 Two Phase Separation Temperature (Lower Temp. side)

	POE VG68 for R32	POE VG68 for R410A	Developed Oil VG46
Oil/R32, Oil Rate 20 mass%, ℃	+15	Separate	Separate

	POE VG68 for R410A	PAG VG46 for R1234yf	Developed Oil VG46
Oil/R1234yf, Oil Rate 20 mass%, ℃	< -60	< -60	Separate

	Naphthenic Mineral Oil VG100 for R290	POE VG68 for R410A	PAG VG60 for R290
Oil/R290, Oil Rate 20 mass%, ℃	< -60	< -60	Separate

Table 4 Two Phase Separation Temperature (Lower Temp. side, High Oil Fraction)

	POE VG68 for R32	POE VG68 for R410A	Developed Oil VG46
Oil/R32, Oil Rate 90 mass%, ℃	< -60	< -60	+10

	POE VG68 for R410A	PAG VG46 for R1234yf	Developed Oil VG46
Oil/R1234yf, Oil Rate 90 mass%, ℃	< -60	< -60	-24

	Naphthenic Mineral Oil VG100 for R290	POE VG68 for R410A	PAG VG60 for R290
Oil/R290, Oil Rate 90 mass%, ℃	< -60	< -60	< -60

Table 5 Solubility and Viscosity at 0.1MPa and -20℃

	POE VG68 for R32	POE VG68 for R410A	Developed Oil VG46
Solubility, R32 mass% in Oil	3.8	3.2	1.2
Viscosity, mPa･s	2300	3000	3500

	POE VG68 for R410A	PAG VG46 for R1234yf	Developed Oil VG46
Solubility, R1234yf mass% in Oil	13.0	15.0	4.2
Viscosity, mPa･s	700	220	4100

	Naphthenic Mineral Oil VG100 for R290	POE VG68 for R410A	PAG VG60 for R290
Solubility, R290 mass% in Oil	6.2	4.8	4.0
Viscosity, mPa･s	1000	1000	930

From the above, it was found that even when there is a large difference in the solubility between the refrigerant and the refrigeration oil, it is unlikely to have a large influence on the oil return.

COMPATIBILITY BETWEEN HFO-BASED MIXED REFRIGERANTS AND REFRIGER-ATION Oil

R-1132 (E), which is one of the HFO refrigerant components, has an extremely low global warming potential and a saturation pressure close to that of R32, and thus is useful as a refrigerant used in air conditioners in terms of physical properties.

However, since there is a risk of occurrence of a continuous decomposition reaction called "self-decomposition reaction" when used alone, a mixed refrigerant has been studied.

This time, evaluation results of the compatibility of R474 that is currently being considered for use in car air conditioners and other air conditioning equipment and R474B that is being considered for use in the field of food freezing and refrigeration, which are HFO-based mixed refrigerants containing R1132(E), with “POE VG68 for R410A” that is a current refrigeration oil for HFCs are reported.

EVALUATION ITEMS

The basic suitability was assessed by the two phase separation temperature (critical solution temperature) at an oil content of 20% and the thermochemical and hydrolytic stability.

In addition, the mixed volume resistivity of the refrigerant and the refrigeration oil was measured, and the electrical insulation property in a compressor with a built-in electric motor widely used as a refrigerant compressor was confirmed.

For the thermochemical and hydrolytic stabilities, only R474A was the target refrigerant, and the test method used was a sealed tube test in which a refrigeration oil and a refrigerant, and an iron wire, a copper wire, and an aluminum wire having a polished surface as a catalyst for promoting a chemical reaction were sealed in a test tube made of pressure-resistant glass and heated at 175 ° C. for 14 days.

To use R1234yf that is current HFO refrigerant for a car air conditioner as a standard, a comparative test was conducted with R474A and R474B.

EVALUATION RESULTS

Two phase separation temperature (critical solution temperature)

The results of the measured two phase separation temperature are shown in Table 6. It was confirmed that these HFO refrigerant have very good solubility in the POE refrigeration oil similarly to other HFO refrigerants.

Table 6 Two Phase Separation Temperature (Lower Temp. side)

	POE VG68 for R410A
Oil/R474A, Oil Rate 20 mass%, ℃	＜-60
Oil/R474B, Oil Rate 20 mass%, ℃	＜-60

When the solubility is too good, the refrigeration oil causes a decrease in viscosity due to refrigerant dilution, and therefore, it is necessary to select a base oil having an appropriate dynamic viscosity or to reinforce by adding an additive.

Thermochemical Stability / Hydrolytic Stability

Table 7 shows the test results of the thermochemical stability, and Table 8 shows the test results of the hydrolytic stability.
It is considered that there is a high possibility that the existing POE refrigeration oil can also be applied to an HFO-based mixed refrigerant containing R-1132 (E).

Table 7 Thermal-Chemical Stability

Oil	POE VG68 for R410A
Refrigerant	R474A
Temp. / Term	175℃ / 336hrs
Vacuum, Pa	<13
Moisture, ppm	<100
Oil / Refrigerant, mL	1 / 1
Color (ASTM)	L0.5
Catalyst Surface Fe Cu Al	 Good Good Good
Precipitation	None

Table 8 Hydrolytic Stability

Oil	POE VG68 for R410A	
Refrigerant	R474A	
Temp. / Term	175℃ / 336hrs	
Vacuum, Pa	<13	
Oil / Refrigerant, g	5/1	
Moisture, ppm	<100	500
Color (ASTM)	L0.5	L0.5
Acid Number, mgKOH/g	0.03	0.02
Catalyst Surface Fe Cu Al	 Good Good Good	 Good Good Good
Precipitation	None	None

Volume resistivity

The volume resistivity, which is one of the indices of electrical insulating properties, was measured in a mixed state with a refrigeration oil, and the adaptability to a compressor with a built-in electric motor was evaluated, and the results are shown in Figure 1. As compared with the mixed volume resistivity of the existing refrigerant R1234yf and the refrigeration oil POE VG68, both R474A and R474B showed good results, and it could be confirmed that there is no problem with the electrical insulating properties in this combination.

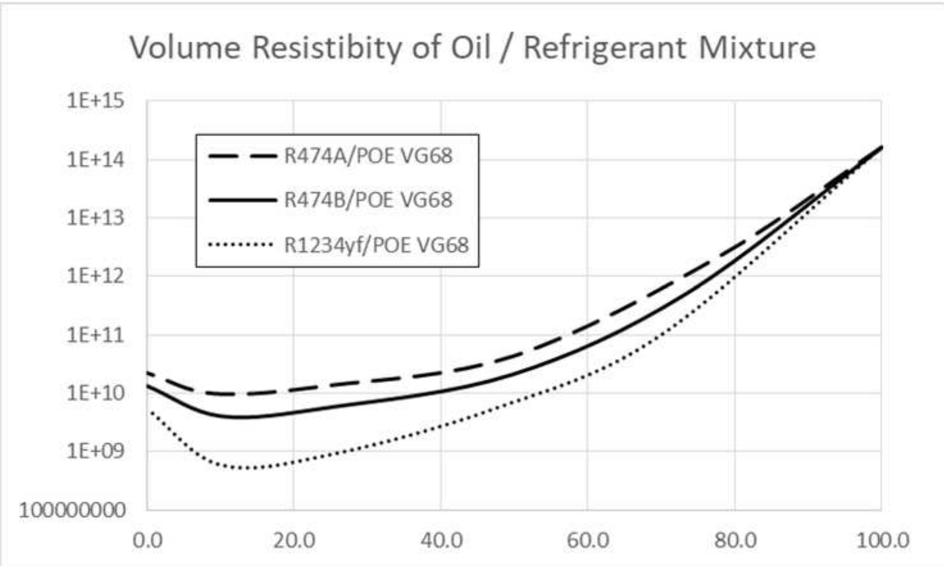

Fig. 1 Volume Resistivity of Refrigeration Oil and Refrigerants

COCLUSIONS

In the present study, as one approach regarding the oil return, there was shown a possibility that the oil returnability cannot be evaluated only by the two phase separation temperature at an oil fraction of 20% from the viscosity of the refrigeration oil of the portion returning to the compressor.
As a matter of course, the conditions of the refrigeration cycle differ depending on the application and the device, and it can be easily assumed that factors other than the pressure and the temperature also become large. However, it is considered that, by increasing the range of selection of the refrigeration oil in an application in which the pipe is not so long, an air-conditioning application dedicated to cooling, or the like, and intentionally selecting a combination in which the

solubility between the refrigerant and the refrigeration oil is low, it is possible to reduce the risk due to the flammability of the refrigerant, and to suppress a decrease in the refrigeration performance due to excessive dissolution of the refrigerant in the refrigeration oil.

In addition, the compatibility of the HFO-based mixed refrigerant containing R-1132 (E), which is the latest refrigerant, with the existing refrigeration oil for HFC could be shown, and the basis of the application policy of the refrigeration oil to such a refrigerant could be shown.

As a member of a group of companies that have been involved in this industry through refrigeration oils since the early days of refrigerating machines, they want to contribute to the development of the refrigerating and air-conditioning industry from the viewpoint of refrigeration oils.

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様々な次世代冷媒と適合する冷凍機油
Compatible Refrigeration Oils for various Next-Generation Refrigerants

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Various refrigerants have been proposed as countermeasures against global warming and climate change. Fluorine-containing refrigerants, techniques have been developed to reduce their global warming potential. However, maintaining the stability of such refrigerants within a refrigeration cycle remains a challenge. Hydrocarbon refrigerants, which inherently have low global warming potential, require safety measures due to their flammability. This report presents recent studies on the responce of refrigeration oils to these emerging refrigerant trends.

Key Word: Refrigeration oil, Refrigerant, Refrigeration cycle, Miscibility

１．はじめに

現在、様々な産業分野で地球環境の維持・改善への取り組みが進められており、冷凍空調分野では、地球温暖化・気候変動抑制のため各種機器や設備の省エネルギー化や地球温暖化係数(GWP)の低い冷媒への転換が進められている。併せて、世界中で化学物質規制の強化が進められており、地域によっては低 GWP 冷媒の主要成分である hydrofluoroolefin (HFO) 冷媒の R1234yf (2,3,3,3-tetrafluoropropene)を採用できない事態になる可能性も現れてきた。特に欧州では昨年よりフッ素化合物の規制を強化する PFAS 規制の法制化検討が進められる中、フッ素を含まない炭化水素冷媒が注目されている。

炭化水素冷媒は非常に高い燃焼性を持つが、過去に家庭用冷蔵庫の分野では炭化水素冷媒である R600a (isobutane)が採用され、現在では欧州やアジアで主流の冷媒となっている。R600a より飽和蒸気圧が少し高い R290 (propane)も近年では環境対応冷媒として、小型空調分野、冷凍冷蔵分野、温水暖房分野で使われるようになってきているが、高い燃焼性に対する安全性確保の一環として冷媒封入量を極力小さくする必要があるという技術課題がある。

こうした課題に冷凍機油の視点で貢献するには、冷媒との相溶性を抑制するという手段がある。1930 年に R12 (dichlorodifluoromethane)が冷媒として使われ始めてから、当時の主力冷凍機油であるナフテン系鉱物油(Naphthenic Mineral Oil)との相溶性が良好だったこともあり、冷媒と冷凍機油が溶け合いやすいことが冷凍サイクルにおける冷凍機油の技術の中心となっていった。しかしそれ以前は冷媒と冷凍機油の相溶性は考慮されておらず、現在でも世界中で運用されている R717 (Ammonia)とナフテン系鉱物油やホワイトオイルの溶け合わない組み合わせがそれを示している。[1-3] 他にも家庭用エアコンで一部のメーカーが採用している R410A (difluoromethane / pentafluoro-ethane)や R32 (difluoromethane)など HFC(Hydro-fluorocarbon) 冷媒とアルキルベンゼン(Alkyl-benzene)油の組み合わせ, R32 と R410A 用ポリオールエステル(polyol Ester, POE)油の組み合わせなども同様であり、用途やサイクル設計、制御によっては冷媒と冷凍機油が溶けにくい組み合わせでも運用は可能となることが示されている。

冷凍機油と冷媒の相溶性が必要とされるのは圧縮機から冷媒とともに吐出した微量の冷凍機油が冷凍サイクルを巡って圧縮機に戻る“油戻り”の性能のためとされている。[4-5] しかし、圧縮機へ戻る冷媒は基本的には気化しており、液体の状態

で戻るのは用途にもよるがデフロストなど特定の運転条件と考えられる。凝縮器では冷媒が液化するが、温度が高いので冷凍機油も粘性が小さく、溶解していなくても流動性が高いため滞留しにくい。従って、液体の冷媒と冷凍機油が均一に溶け合う比率と温度である“二相分離温度”だけでなく、蒸発器から圧縮機に戻る環境での冷媒と冷凍機油の関係を把握することで、可燃性冷媒の運用に要求され始めた“低相溶性”を有効利用することができると考え、幾つかの評価項目を基に冷凍機油と冷媒の相溶性の違いについて報告する。

また、最新の R-1132(E)を含む HFO 系混合冷媒と冷凍機油の適合性についても紹介する。

２．冷凍機油の冷媒溶解性

冷媒と評価油

先ず、冷凍機油の冷媒溶解性の評価について説明する。冷媒は HFC 冷媒や HFO 冷媒などの“含フッ素冷媒”から空調用 HFC 冷媒の R32 と車両空調や保冷車、ターボ冷凍機用 HFO 冷媒の R1234yf を取り上げ、フッ素を含まない“炭化水素冷媒”から R290 を選定した。評価油はそれぞれの冷媒に適用する冷凍機油の中から、対象の冷媒に相溶し易いものと相溶し難いものを選定した。

R32 に組み合わせる冷凍機油は、相溶性が高い R32 用 POE と相溶性が低い R410A 用 POE、相溶し難い開発油 [6-8] とした。R1234yf に組み合わせる冷凍機油は車両用空調に用いられている R1234yf 用 PAG と R410A 用 POE、及び上記と同じ R32 や R1234yf などの HFC 冷媒や HFO 冷媒に相溶し難い開発油とした。Table 1 にそれぞれの性状を記載する。

R290 に組み合わせる冷凍機油としては非常に相溶性の高いナフテン系鉱物油及び R410A 用 POE、R290 との相溶性を低くした PAG を選定した。Table 2 にそれぞれの性状を記載する。

比較結果

・二相分離温度（臨界溶解温度）

Table 3 に各冷凍機油の低温側臨界溶解温度に近い、油分率 20 重量%での二相分離温度を示す。

相溶し易い組み合わせでは低い値を示すが、相溶し難い組み合わせでは高い値を示すか二相分離していることが分かる。

しかし実際は、圧縮機吸入側では既に冷媒が気化しているため、通常は高い油分率になっている。例えば油分率 90 重量%での二相分離温度を Table 4 に示す。油分率 20 重量%では二相分離している組み合わせでも油分率 90 重量%では二相分離温

Table 1　Properties of Test Oils

		POE VG68 for R32	POE VG68 for R410A	PAG VG46 for R1234yf	Developed Oil VG46
Density, @15℃	g/cm^3	0.986	0.960	1.013	0.925
Color, ASTM		L0.5	L0.5	L0.5	L1.0
Flash Point, COC	℃	264	256	220	190
Pour Point,	℃	-40	-40	-42.5	-40
Kinematic Viscosity, @40℃	mm^2/s	62.6	66.2	46.5	41.5
Kinematic Viscosity, @100℃	mm^2/s	8.01	8.19	9.06	5.67
Acid Number,	mgKOH/g	0.01	0.01	0.01	0.01
Water Content,	ppm	35	35	100	30
Volume Resistivity, @25℃	Ω･cm	2×10^{13}	5×10^{14}	5×10^{10}	4×10^{13}

Table 2 Properties of Test Oils

		Naphthenic Mineral Oil VG100 for R290	POE VG68 for R410A	PAG VG60 for R290
Density, @15℃,	g/cm^3	0.919	0.960	1.012
Color, ASTM		L1.5	L0.5	L0.5
Flash Point, COC,	℃	234	256	234
Pour Point,	℃	-27.5	-40	-40
Kinematic Viscosity, @40℃,	mm^2/s	96.3	66.2	63.9
Kinematic Viscosity, @100℃,	mm^2/s	8.97	8.19	10.3
Acid Number,	mgKOH/g	0.01	0.01	0.01
Water Content,	ppm	20	35	100
Volume Resistivity, @25℃	Ω･cm	1×10^{15}	5×10^{14}	1×10^{10}

度がある程度低い値になっており、冷凍機油に冷媒が溶け込んだ状態になっていることが分かる。

・圧力温度溶解度／温度粘度溶解度

用途や装置によって条件は異なるが、仮に蒸発器出口の圧力を 0.1 MPa、温度を-20℃とした場合の冷媒溶解度とそのときの粘性を Table 5 に示す。それぞれの組み合わせの粘性を比較すると、冷媒と冷凍機油が相溶し難い組み合わせでもそれほど粘性は大きくないことがわかる。特に冷凍機油に溶けにくい冷媒である R 32 との組み合わせでの粘性はどの冷凍機油でも同等の値を示しており、圧縮機への油戻りがこの粘性で十分であるなら、他の組み合わせでも十分油戻りは確保されると考えられる。

以上より、冷媒と冷凍機油の相溶性にある程度大きな差がある場合でも、油戻りに大きな影響を与えるとは考えにくいことが分かった。

Table 3 Two Phase Separation Temperature (Lower Temp. side)

	POE VG68 for R32	POE VG68 for R410A	Developed Oil VG46
Oil/R32, Oil Rate 20 mass%, ℃	+15	Separate	Separate

	POE VG68 for R410A	PAG VG46 for R1234yf	Developed Oil VG46
Oil/R1234yf, Oil Rate 20 mass%, ℃	＜-60	＜-60	Separate

	Naphthenic Mineral Oil VG100 for R290	POE VG68 for R410A	PAG VG60 for R290
Oil/R290, Oil Rate 20 mass%, ℃	＜-60	＜-60	Separate

Table 4 Two Phase Separation Temperature (Lower Temp. side, High Oil Fraction)

	POE VG68 for R32	POE VG68 for R410A	Developed Oil VG46
Oil/R32, Oil Rate 90 mass%, ℃	< -60	< -60	+10

	POE VG68 for R410A	PAG VG46 for R1234yf	Developed Oil VG46
Oil/R1234yf, Oil Rate 90 mass%, ℃	< -60	< -60	-24

	Naphthenic Mineral Oil VG100 for R290	POE VG68 for R410A	PAG VG60 for R290
Oil/R290, Oil Rate 90 mass%, ℃	< -60	< -60	< -60

Table 5 Solubility and Viscosity at 0.1MPa and -20℃

	POE VG68 for R32	POE VG68 for R410A	Developed Oil VG46
Solubility, R32 mass% in Oil	3.8	3.2	1.2
Viscosity, mPa･s	2300	3000	3500

	POE VG68 for R410A	PAG VG46 for R1234yf	Developed Oil VG46
Solubility, R1234yf mass% in Oil	13.0	15.0	4.2
Viscosity, mPa･s	700	220	4100

	Naphthenic Mineral Oil VG100 for R290	POE VG68 for R410A	PAG VG60 for R290
Solubility, R290 mass% in Oil	6.2	4.8	4.0
Viscosity, mPa･s	1000	1000	930

３．HFO 系混合冷媒と冷凍機油の適合性

HFO 冷媒成分のひとつである R-1132(E)は地球温暖化係数が極めて低く、飽和圧力が R32 に近いため、物性としては空調機器に用いる冷媒成分として有用である。しかし、単独では「自己分解反応」と呼ばれる連続的な分解反応が生じるリスクがあるため、混合冷媒としての検討が進められている。

今回は、R-1132(E)を含む HFO 系混合冷媒としてカーエアコンなどの空調機器に適用が進められている R474A や食品冷凍冷蔵分野への適用が検討されている R474B と HFC 用の既存冷凍機油である R410A 用 POE VG68 の適合性について評価結果を報告する。

評価項目

油分率 20%の二相分離温度(臨界溶解温度)と熱化学安定性及び加水分解安定性にて基本的な適

合性を評価した。また、冷媒と冷凍機油の混合体積抵抗率を測定し、冷媒圧縮機として広く使われている電気モーター内蔵圧縮機での電気絶縁性について確認した。

熱化学安定性と加水分解安定性については、R474A のみを対象冷媒とした。試験方法は、耐圧ガラス製の試験管に冷凍機油と冷媒、そして化学反応を促進する触媒として表面を磨いた鉄線、銅線、アルミニウム線を封入し、175℃で 14 日間加熱するシールドチューブ試験を用いた。

体積抵抗率は電気絶縁性の指標のひとつである。R474A、R474B 及び、カーエアコン用既存 HFO 冷媒 R1234yf を標準として比較試験を行った。

評価結果

・二相分離温度（臨界溶解温度）

Table 6 に測定した二相分離温度の結果を示す。他の HFO 冷媒と同様に POE 冷凍機油とは非常に良く溶け合うことを確認した。

相溶性が良すぎると、冷凍機油は冷媒希釈による粘度低下を引き起こすため、適切な動粘度を持つ基油の選定や添加剤の添加による補強が必要になる。

Table 6 Two Phase Separation Temperature (Lower Temp. side)

	POE VG68 for R410A
Oil/R474A, Oil Rate 20 mass%, ℃	< -60
Oil/R474B, Oil Rate 20 mass%, ℃	< -60

・熱化学安定性／加水分解安定性

Table 7 に熱化学安定性、Table 8 に加水分解安定性の試験結果を示す。熱化学安定性、加水分解安定性のどちらも特に問題ない結果が得られた。

既存の POE 冷凍機油は、R-1132(E)を含む HFO 系混合冷媒にも適用できる可能性が高いと考える。

Table 7 Thermal-Chemical Stability

Oil	POE VG68 for R410A
Refrigerant	R474A
Temp. / Term	175℃ / 336hrs
Vacuum, Pa	<13
Moisture, ppm	<100
Oil / Refrigerant, mL	1 / 1
Color (ASTM)	L0.5
Catalyst Surface	
Fe	Good
Cu	Good
Al	Good
Precipitation	None

Table 8 Hydrolytic Stability

Oil	POE VG68 for R410A	
Refrigerant	R474A	
Temp. / Term	175℃ / 336hrs	
Vacuum, Pa	<13	
Oil / Refrigerant, g	5/1	
Moisture, ppm	<100	500
Color (ASTM)	L0.5	L0.5
Acid Number, mgKOH/g	0.03	0.02
Catalyst Surface		
Fe	Good	Good
Cu	Good	Good
Al	Good	Good
Precipitation	None	None

・体積抵抗率

電気絶縁性の指標の一つである体積抵抗率を冷凍機油との混合状態で測定し、電気モーター内蔵圧縮機への適合性を評価した。結果を Fig.1 に示す。既存冷媒 R1234yf と冷凍機油 POE VG68 の混合体積抵抗率に比べ R474A、R474B とも良好な結果を示しており、この組み合わせであれば電気絶縁性については問題ないことが確認できた。

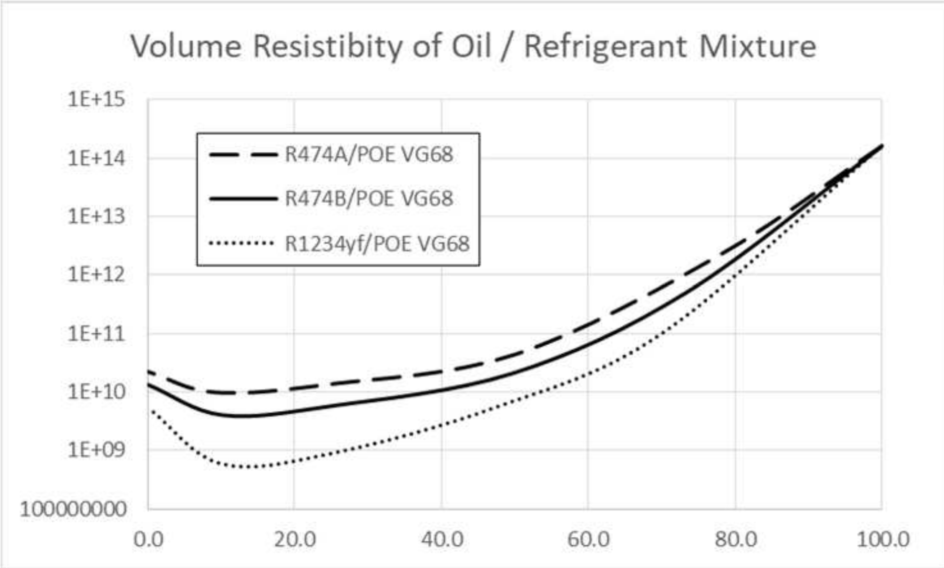

Fig. 1 Volume Resistivity of Refrigeration Oil and Refrigerants

４．おわりに

本研究では油戻りに関するひとつのアプローチとして、圧縮機に戻る部分の冷凍機油の粘性から、油分率 20%の二相分離温度だけでは油戻り性を評価することはできない可能性を示した。

もちろん用途や装置によって冷凍サイクルの条件は異なり、圧力や温度以外の要因も大きくなることは容易に想定できる。しかし、あまり配管の長くない用途や冷房専用の空調用途などでの冷凍機油の選定の幅を増やし、敢えて冷媒と冷凍機油の相溶性が低い組み合わせを選択することで、冷媒の燃焼性によるリスクの低減や、冷凍機油への冷媒の過剰な溶け込みによる冷凍性能の低下などを抑制できる可能性を示したと考える。

また今回、最新冷媒である R-1132(E)を含む HFO 系混合冷媒について、既存の HFC 用冷凍機油との適合性を示し、こうした冷媒への冷凍機油の適用方針の基礎を示すことができた。

冷凍機器の黎明期から冷凍機油を通してこの業界に関わってきた企業グループの一員として、これからも冷凍機油の視点から冷凍空調業界の発展に貢献していきたい。

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