ThreeBond
TECHNICAL NEWS

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Initiatives for Environmentally Friendly Products (HFO-1234yf, New Refrigerant for Automotive Air Conditioning)

Introduction

Automotive air conditioning draws power from the engine of the vehicle. This means that increases in efficiency can lead to improved fuel economy and a reduction in fossil fuel consumption.

ThreeBond released ThreeBond 6905 High Performance Lubricant Agent For Car Air Conditioner to improve the efficiency of automotive air conditioning systems. This product has been well received by a large number of customers.

ThreeBond 6905 contains HFC-134a as a substitute for chlorofluorocarbons (CFCs), the use of which was regulated by the Montreal Protocol in order to protect the ozone layer. However, while the ozone depletion potential (ODP) of hydrofluorocarbons (HFCs) is low, the 2016 Kigali Amendment states that they have a high global warming potential (GWP). As a result, a phased reduction of the production and consumption of HFCs was imposed as of 2019.

In 2019, ThreeBond released ThreeBond 6905B Solstice® yf Refrigerant for Car Air Conditioner. This canned refrigerant for automotive air conditioning contains HFO-1234yf, an environmentally-friendly refrigerant gas with a low global warming potential.

In addition, ThreeBond 6905C, in which the refrigerant gas used in ThreeBond 6905 has been replaced with HFO-1234yf, is scheduled for release in 2021.

This article explains the operation of automotive air conditioning, global efforts to protect the environment, and the necessity of lubricants.

Hereafter, ThreeBond is abbreviated as TB.

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1. Automotive Air Conditioning

The flow of refrigerant gas through an automotive air conditioning system is shown in Figure 1.

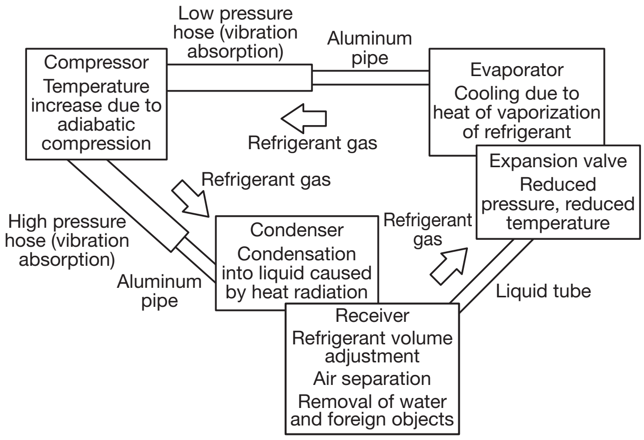


Fig. 1 Flow of Refrigerant Gas

The main components of an automotive air conditioning system are:

(1) Compressor: Suction compressor for refrigerant gas

(2) Condenser: Heat exchanger that uses air (or water) in the surrounding area to cool, condensing the high pressure refrigerant gas

(3) Evaporator: Heat exchanger that evaporates the low temperature liquid refrigerant, cooling the air sent into the vehicle interior

(4) Expansion valve: Controls the flow of refrigerant

(5) Pipes connecting the above parts

Cooling is achieved by exchanging heat with the surrounding area through changes in the state of matter. A theoretical example of cooling is shown in Figure 2.

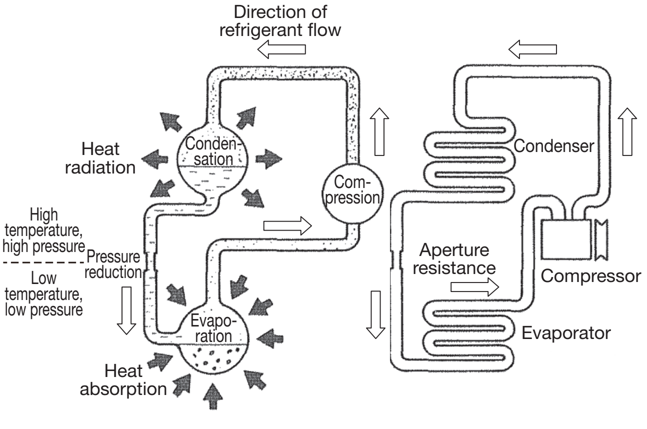


Fig. 2 Theoretical Example of Cooling [1)]

According to the first law of thermodynamics $\Delta U = Q + W$, where ΔU is the change in the internal energy of the system, Q is the quantity of energy supplied to the system from outside as heat, and W is the amount of thermodynamic work done from outside the system. When adiabatic compression occurs, $Q = 0$, and consequentially $\Delta U = W$.

The internal energy of n moles of an ideal monoatomic gas is given by $U = 3/2nRT$ (R: universal gas constant). Therefore, when $\Delta U = W$, the work done from outside the system is converted into the thermal energy of the gas. This means that work done from outside the system with a piston (the compressor) while the system is in an adiabatic state causes the temperature of the gas to increase. Figure 3 uses PV curves to show the increase in pressure due to adiabatic compression.

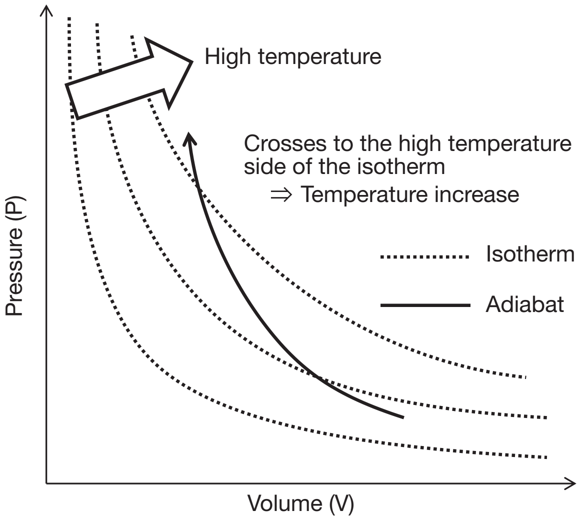


Fig. 3 Isotherm and Adiabat

When the heated gas (refrigerant) is cooled from outside the system by air or water, it condenses into a liquid (in the condenser). The condensed refrigerant is decompressed by the aperture resistance and becomes low temperature, low pressure liquid refrigerant. This liquid is then continuously returned, enabling cooling. At the aperture, the temperature reduction causes part of the high temperature liquid refrigerant to vaporize, cooling part of the refrigerant itself. It is then sent as cold liquid to the evaporator, where cooled air is supplied to the vehicle interior.

2. Refrigerant Gas

Table 1 shows the characteristics of some of the main refrigerants used for automotive air conditioning.

Refrigerant gas must have a low boiling point in order to draw heat from the surrounding area by vaporizing rapidly in the evaporator after passing through the expansion valve, thereby cooling the air in the vehicle interior. In addition, when replacing the refrigerant gas, greater similarity in the temperature characteristics in relation to pressure of the previous and subsequent gases means that fewer changes are needed to the existing mechanisms. This facilitates mechanical design.

In this way, the fact that refrigerant gases are substances that form the basis of the cooling functions of automotive air conditioning places a number limitations on the physiochemical properties that they can exhibit. They are also extremely important substances in terms of protecting the environment. The following aspects are important requirements to be considered when selecting a refrigerant.

Table 1 Characteristics of Main Refrigerants for Automotive Air Conditioning

Refrigerant	Boiling point at 1 atm (°C)	Pressure at 0°C (MPa)	Heat of vaporization at 0°C (kJ/kg)	Remark(s)
CFC-12	-29.7	0.31	151.4	Causes damage to the ozone layer
HFC-134a	-26.1	0.29	198.7	Greenhouse gas
HFO-1234yf	-29.0	0.29	145.2	Environmentally-friendly refrigerant
Water	100.0	0.0006	2502.8	Reference

(1) Safety
Air conditioning is now an integral part of everyday life. Refrigerants must have low toxicity and flammability based on the assumption that there is a risk of leaks in the case of an accident or natural disaster.

(2) Environmental impact
Refrigerants must have a low ozone depletion potential (ODP) and global warming potential (GWP), two values that measure the direct environmental impact of a substance. Ease of collection after use and recycling are also important considerations.

(3) Energy efficiency
Related to environmental impact, the production of the refrigerant gas must not consume large quantities of energy, require the use of a large amount of fossil fuels or generate large quantities of carbon dioxide, which is a greenhouse gas. The ideal refrigerant gas can be produced at low energy cost and has high energy efficiency during use.

(4) Economy
The refrigerant must be low cost, be readily available all over the world, be easy to perform maintenance on, not require the implementation of excessive safety measures, and be recyclable at low cost.

3. Regulation of Fluorocarbons (CFCs)

In 1974, Dr. Frank Sherwood Rowland and Dr. Mario José Molina Henríquez of the University of California published a paper in the journal *Nature* highlighting the ozone layer destruction caused by chlorofluorocarbons (CFCs). This paper sparked a large national debate in the USA, eventually resulting in the regulation of fluorocarbon gases. An overview of initiatives, tightening of regulation, and legislation relating to the use of fluorocarbon gases in Japan and around the world is shown in Table 2.

Table 2 History of Fluorocarbon Gas Regulation 1), 2), 3)

Year	Major developments
1974	Dr. Frank Sherwood Rowland and Dr. Mario José Molina Henríquez of the University of California, USA identify ozone depletion caused by fluorocarbons as a cause for concern.
1977	The United Nations Environment Program (UNEP) decides to examine the issue of fluorocarbon regulation.
1978	The manufacture of aerosol products that use fluorocarbons as propellants is prohibited in the USA.
1979	Aerosol products containing fluorocarbons are prohibited in Canada and northern Europe.
1980	The European Community (EC) recommends the freezing of CFC-11 and CFC-12 production, and that efforts be to reduce the use of fluorocarbons in aerosol products. Japan follows suit.
1985	The UNEP Vienna Convention for the Protection of the Ozone Layer is signed.
1987	The Montreal Protocol on Substances that Deplete the Ozone Layer is adopted and enters into effect in January 1989.
1988	In Japan, the Ozone Layer Protection Law is passed and enters into effect. The total abolition of halon from 1994, the total abolition of CFCs, 1,1,1-trichloroethane and HBFCs from 1996, the total abolition of bromochloromethane from 2002, the total abolition of methyl bromide (with some exceptions for specific uses) from 2005, the phased reduction in the use of HCFCs up to 2020, and the total abolition of HCFCs from 2020 are agreed.
1989	The Japanese Ministry of the Environment and Ministry of International Trade and Industry publish Guidelines for Reducing Emissions from and Rationalizing the Use of CFCs.
1990	The Cabinet Order Regarding Exceptions to Fluorocarbon Refrigerant Collection, Purification and Recycling Equipment is revised and a notification is issued.
1992	The Fourth Meeting of the Parties to the Montreal Protocol is held in Copenhagen. It is agreed to move the deadline for the discontinuation of CFC production forward to the end of 1995, and the regulation of HCFC production and the discontinuation of HCFC production by 2020 are agreed in principle. The United Nations Framework Convention on Climate Change enters into effect in 1994.
1996	The production of CFCs is abolished in developed countries.
1997	The Kyoto Protocol is adopted. Regulations on alternative chlorofluorocarbons with a high global warming potential are adopted. Legally-binding numerical targets are established.
From 1998	Japan: The Act on Recycling of Specified Home Appliances, the Act on Promotion of Global Warming Countermeasures, the Fluorocarbons Recovery and Destruction Act, and the End-of-Life Vehicle Recycling Law are established. The Kyoto Protocol is ratified.
2000	The Japanese Green Purchase Act is established.
2006	The Japanese Fluorocarbons Recovery and Destruction Act is revised.
2013	The Japanese Fluorocarbons Recovery and Destruction Act is revised (the revised Fluorocarbons Act is published). It enters into effect in April 2015.
2015	The Paris Agreement is adopted. Global efforts are made by all signatory countries.
2016	The Kigali Amendment to the Montreal Protocol is agreed. Gradual reductions through the regulation of alternative chlorofluorocarbons are decided.
2020	The revised Fluorocarbon Emissions Control Act enters into effect.

As a result of these tightening regulations, it was established that fluorocarbon consumption as of January 1994 must not exceed 25% of 1986 levels. The production of CFCs was then completely abolished in developed countries in 1996.

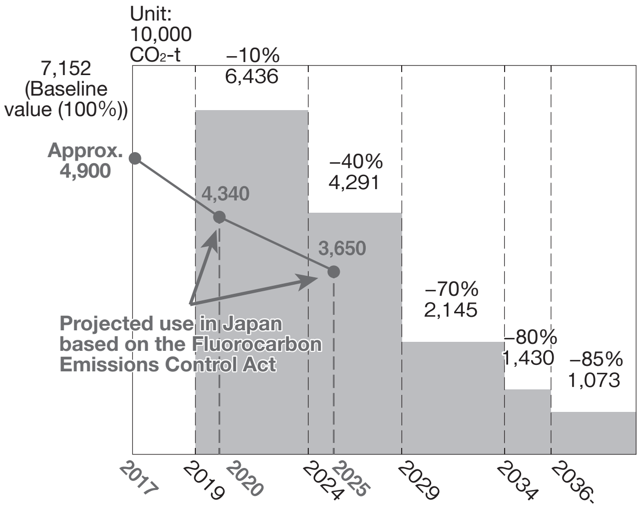
Major CFCs, alternative chlorofluorocarbons and environmentally-friendly refrigerants are shown in Table 3. It has been pointed out that alternative chlorofluorocarbons such as HFC-134a, which is currently the main refrigerant used in automotive air conditioning, have a low ODP but an extremely high GWP. In response to this, the shift to the use of HFO-1234yf as a refrigerant for automotive air conditioning has been accelerating worldwide since the early 21st century. Domestically-produced Japanese automobiles have been gradually transitioning in line with model changes since around 2018, and replacement had been complete in about 10% to 40% of vehicles produced by each automobile manufacturer as of the end of September 2020. The schedule for the phased reduction of alternative chlorofluorocarbons set by the Japanese Ministry of Economy, Trade and Industry and Ministry of the Environment is shown in Figure 4. The target is a 10% reduction from 2019 levels in FY2020 and a 40% reduction from 2019 levels in FY2025.

Table 3 ODP and GWP of Major CFCs, Alternative Chlorofluorocarbons and Environmentally-Friendly Refrigerants [3]

Classification	Name	ODP	GWP (IPCC Fourth Assessment Report)
CFCs	CFC-11	1	4,750
	CFC-12	1	10,900
	CFC-113	0.8	6,130
	CFC-114	1	10,000
	CFC-115	0.5	7,370
Alternative Chloro-fluorocarbons	HCFC-22	0.055	1,810
	HCFC-141b	0.11	725
	HCFC-142b	0.065	2,310
	HFC-23	0	14,800
	HFC-32	0	675
	HFC-125	0	3,500
	HFC-134a	0	1,430
	HFC-143a	0	4,470
	PFC-14	0	7,390
	PFC-116	0	12,200
	SF6	0	22,800
Environmentally-friendly refrigerant	HFO-1234yf	0	1
	HFO-1234ze(E)	0	1

4. HFO-1234yf

HFO-1234yf (hydrofluoroolefin-1234yf, $CF_3CF=CH_2$), also known as 2,3,3,3-tetrafluoro-1-propene, is a colorless, transparent liquefied gas with a molar mass of 114 g/mol. It is a mildly flammable gas with a low boiling point of -29.0°C. Its basic structure is shown in Figure 5.



* Baseline value: Calculated from the average value of 2011-2013 results

Fig. 4 Schedule for the Reduction of Alternative Chlorofluorocarbons in Japan [4]

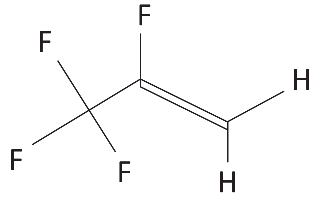


Fig. 5 Structural Formula of 2,3,3,3-Tetrafluoro-1-propene

HFO-1234yf is mainly used as a refrigerant for automotive air conditioning and has the following characteristics [1].

- Low toxicity
- Good thermal stability
- ODP = 0, GWP = 1 (there are some reports that GWP = 4, however, this is still approximately the same as that of CO_2)
- Similar in nature to HFC-134a, with a difference in cooling performance and energy efficiency of less than 5%
- Supports direct expansion systems, no secondary refrigerant required
- Compatible with configurations and materials used as standard in conventional automotive air conditioning systems

A comparison of the physical properties of HFC-134a and HFO-1234yf is shown in Table 4. In general there are no major differences, however, HFO-1234yf has a significantly lower GWP.

PT curves for HFO-1234yf and HFC-134a are shown in Figure 6. The values for pressure response to temperature show similar values for each temperature range, indicating high mutual compatibility with equipment.

Table 4 Physical Property Comparison of HFC-134a and HFO-1234yf 5)

Item	Unit	HFC-134a	HFO-1234yf
Molecular structure	—	CF_3CH_2F	$CF_3CF=CH_2$
Molar mass	g/mol	102.0	114.0
Critical temperature	°C	101.1	94.7
Critical pressure	MPa	4.1	3.4
Freezing point	°C	-101.0	N.D.
Normal boiling point	°C	-26.1	-29.0
Vapor pressure (at 25°C)	kPa	665.0	685.0
Vapor density (at 25°C)	kg/m^3	32.4	38.1
Liquid density (at 25°C)	kg/m^3	1207.0	1091.0
Heat of vaporization (at 25°C)	kJ/kg	177.8	145.2
Heat capacity ratio (at 25°C, 1 atm)	—	1.1	1.1
Water solubility (at 25°C)	ppm	0.1	N.D.
Flammability range (High Pressure Gas Safety Act - Class A)	vol%	No flame propagation	6.3-14.0
Burning velocity	cm/s	No flame propagation	1.5
ODP	—	0.0	0.0
GWP (IPCC AR5)	—	1430.0	1.0
Atmospheric lifespan	Days	14.6	11.0
ASHRAE classification	—	A1	A2L

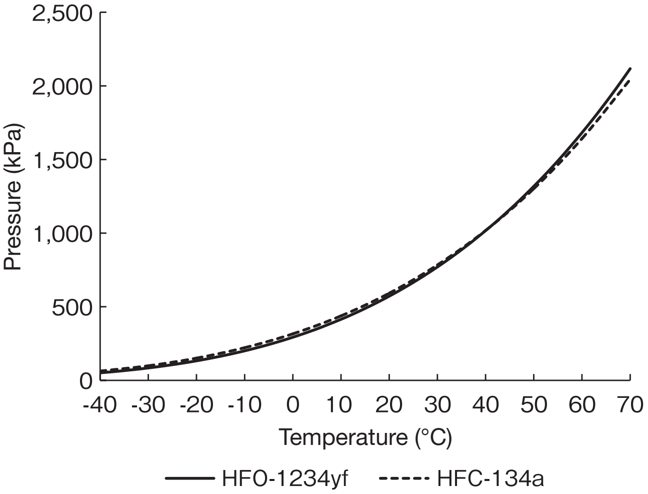


Fig. 6 PT Curves of HFC-134a and HFO-1234yf 5)

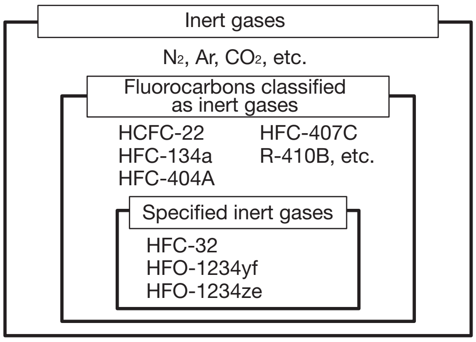


Fig. 7 Overview of Inert Gases, Fluorocarbons Classified as Inert Gases and Specified Inert Gases

While HFO-1234yf has similar physical properties to HFC-134a, it is flammable and therefore presents problems in terms of safety during handling. In consideration of substances such as HFO-1234yf, the USA-based American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) established a new classification of mildly flammable gases (Class 2L) for flammable gases with a lower flammability limit of greater than 0.1 kg/m^3, a heat of combustion of less than 19,000 kJ/kg and a maximum burning velocity of 10 cm/s or less. ISO 817:2014 refrigerant flammability classifications with representative examples of refrigerants are shown in Table 5.

In Japan, flammability risk is mainly evaluated by organizations such as the Japan Society of Refrigerating and Air Conditioning Engineers (JSRAE), the Japan Refrigeration and Air Conditioning Industry Association (JRAIA), and the New Energy and Industrial Technology Development Organization (NEDO). While there was not originally a definition of mild flammability given by the Japanese High Pressure Gas Safety Act, the handling of mildly flammable refrigerants has been clarified following requests from the JRAIA. Since the revision of the law in 2016, HFO-123 4yf has been classified as a specified inert gas, meaning that it is flammable but extremely low risk. An overview of inert gases, fluorocarbons classified as inert gases and specified inert gases is shown in Figure 7.

Following the restriction of the use of HFC-134a in accordance with the Mobile Air Conditioning (MAC) Directive issued by the EU in 2006, which states that the global warming potential of refrigerants used in air-conditioning systems for passenger cars and light commercial vehicles must not exceed 150, HFO-1234yf was developed and put into

Table 5 ISO817:2014 Refrigerant Flammability Classifications with Representative Examples 6)

Flammability class	Definition	Representative refrigerant
Class 3 (highly flammable)	LFL ≤ 3.5 vol% or $H_c \leq 19$ MJ/kg	R-290, R-600a4.5
Class 2 (flammable)	LFL > 3.5 vol% and $H_c < 19$ MJ/kg	R-152a
Class 2L (mildly flammable)	In Class 2, $S_{u,max} \leq 10$ cm/s	R-717, R-32, R-143a, R-1234yf, R-1234ze (E)
Class 1 (no flame propagation)	No flame propagation	R-134a, R-410A, R-22

*R-: refrigerant

practical use by Honeywell and DuPont. AGC established a manufacturing method in 2014 and started supplying HFO-1234yf to Honeywell.

In Europe, HFC-134a has been phased out in all new models since January 2011, and its use in all new vehicles has been banned since January 2017.

Similarly, a bill regulating the use of HFC-134a was submitted in the USA, and reductions in use for automotive air conditioning and general industrial applications have begun. The US Environmental Protection Agency (EPA) allows automobile manufacturers to earn credits for greenhouse gas reduction by adopting HFO-1234yf. (CAFE: Corporate Average Fuel Economy)

This issue is also being considered by the Global Warming Prevention Measures Subcommittee of the Industrial Structure Council Biochemical Policy Committee in Japan, and HFO-1234yf has been put into practical use since around 2018.

5. Lubricant

The flow of refrigerant through automotive air conditioning systems includes sliding parts such as those in the compressor. Lubricating oil is therefore used along the flow path to improve mechanical efficiency. The oil not only lubricates sliding parts, but also serves as a seal for gaps in the operating chamber and connections between parts such as pipes. The compression diagram of a reciprocating compressor is shown in Figure 8.

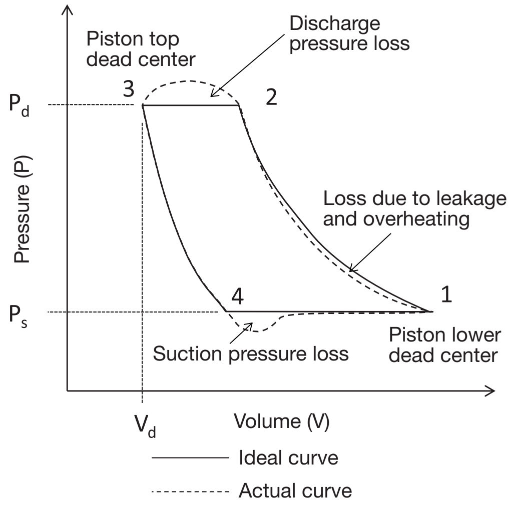


Fig. 8 Pressure Inside Compressor

1→2 shows a gas with suction pressure of P_s being compressed to a discharge pressure of P_d.

2→3 shows this gas reaches the top dead center of the piston while being discharged to the high pressure side, remaining at a pressure of P_d.

3→4 shows the process of the gas with a volume of V_d remaining at the top dead center of the piston (3) expanding to a suction pressure of P_s (4). (Re-expansion stroke)

4→1 shows the process by which the inside of the operating chamber reaches the suction pressure, and new refrigerant gas pushes the suction valve open and is sucked into the operating chamber.

While the solid line shows an ideal cycle, the actual process is as indicated by the dotted line. This difference is due to pressure loss, refrigerant gas leakage, friction, and heat loss. Lubricants are used to reduce losses of efficiency due to friction on these sliding parts.

In addition, while the parts of the refrigerant flow path are generally connected by aluminum piping, hosing is used to connect parts where different vibration systems are used, such as the piping of the compressor and the condenser. Although each connection is sealed with an O-ring or similar part, minute gaps are unavoidable. By permeating these gaps, lubricating oil also prevents the outflow of gas.

While more oil provides better lubrication, oil that circulates with the refrigerant has a negative effect on cooling performance. For this reason, the oil in circulation must be of an appropriate type and volume. In general, oil used in automotive air conditioning requires the following basic qualities.

(1) Appropriate viscosity
(2) High flash point
(3) Low pour point
(4) Excellent oxidative stability
(5) Little effect on organic materials such as O-rings and rubber hoses
(6) High oil film strength
(7) Low water content
(8) Does not cause a chemical reaction with the refrigerant
(9) Excellent compatibility with the refrigerant
(10) Excellent defoaming properties

The basic performance characteristics of TB6905C are shown in Table 6. As TB6905C is in the proper viscosity range, it can reduce resistance due to friction while remaining on sliding parts. This restores the mechanical efficiency of the compressor to a state similar to that of a new vehicle. The base oils polyalkylene glycol (PAG) and polyol ester (POE) have a flash point of approximately 220 to 300°C. TB6905C has a flash point equal to or greater than these oils. This means that there is no increased risk of accidents even when the compressor causes the temperature to rise. In addition, the low pour point of TB6905C ensures that there are no concerns about freezing or crystallization in cold regions.

The insulation stability of TB6905C when mixed with water is shown in Table 7. TB6905C maintains a high dielectric breakdown voltage and volume resistivity even when mixed with a small quantity of water.

Table 8 shows the hydrolysis stability (change in acid value) of TB6905C over time when mixed with water. It was confirmed that TB6905C exhibits excellent hydrolysis resistance, and no change in acid value was observed compared to the initial value.

* The values in Tables 7 and 8 show the stability of the product when mixed with a small quantity of water and do not guarantee the prevention of abnormalities when the product is mixed with water.

Figure 9 shows the results of an SRV (Schwingung, Reibung und Verschleiss) vibration, friction and abrasion test under ASTM D6425 conditions. It was confirmed that by adding TB6905C to POE oil provided a low, stable coefficient of friction in each temperature range.

Table 9 shows the abrasion prevention properties exhibited through the results of a Falex test (the abrasion tester is operated while bubbling the liquid with HFO-1234yf). It was confirmed that adding TB6905C to POE oil improves load resistance and reduces wear.

Table 6 Basic TB6905C Performance Characteristics

Item	Unit	General requirement	TB6905C
Kinematic viscosity (at 40°C)	mm^2/s	90~110	95.38
Kinematic viscosity (at 100°C)	mm^2/s	—	10.53
Flash point	°C	180 or more	276
Pour point	°C	-10.0 or less	-30
Acid value	mgKOH/g	—	0.01
Chemical stability with refrigerant	Color scale (ASTM)	5.0 or less	1
Dielectric breakdown voltage (at 2.5 mm)	kV	24 or more	70
Volume resistivity (at 80°C)	Ω•m	—	45×10^{12}

Table 7 Insulation Stability of TB6905C when Mixed with Water

Item	Unit	No water added	When mixed with 500 ppm of water	When mixed with 1,000 ppm of water
Dielectric breakdown voltage (at 2.5 mm)	kV	70	68	65
Volume resistivity (at 80°C)	Ω•m	45×10^{12}	34×10^{12}	23×10^{12}

Table 8 Hydrolysis Stability (Change in Acid Value) of TB6905C

Days after addition of water	Unit	PB6905C	POE oil
0 days	mgKOH/g	0.01	0.02
7 days	mgKOH/g	0.01	0.04
14 days	mgKOH/g	0.01	0.17
30 days	mgKOH/g	0.01	4.5

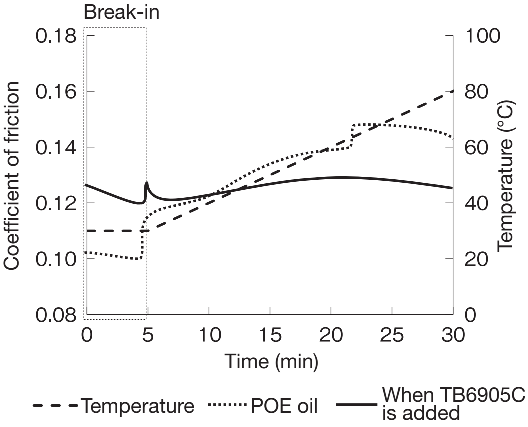
Test conditions: In accordance with the JIS K 2211 refrigerating machine oils testing method for chemical stability to refrigerant (sealed tube test)
Test solution: Base oil (7 mg) + HFO-1234yf (3 mg)
Temperature: 175°C
Water: 1,000 ppm
Catalyst: Fe, Al, Cu

Table 9 Abrasion Prevention Test Results

Item	Unit	POE oil	When TB6905C is added
Load resistance[*1]	Lbf	1010	1260
Abrasion[*2]	mg	5.8	4

*1 Test conditions
Temperature: 60°C
Rotational speed: 300 rpm
Gas injection rate: 70 mL/min

*2 Test conditions
Temperature: 40°C
Rotational speed: 300 rpm
Gas injection rate: 70 mL/min



Weight: 200 N (break-in: 50 N)
Amplitude: 1.5 mm
Frequency: 50 Hz
Temperature: 10°C/5 min (break-in: 30°C)
Time: 30 min (break-in: 5 min)
Test pieces: Cylinder, plate

Fig. 9 SRV Test Results Before and After Addition of TB6905C

Closing

In this article, we covered ThreeBond's environmental protection efforts with regards to automobiles and related products. In addition, ThreeBond is also developing products in a wide range of fields, including cleaning solvents with improved safety and low GWP, and coating agents that use these cleaning solvents. These products are scheduled to be released in the near future.

ThreeBond will contribute to technological innovation in global industry and environmental conservation by focusing on product and technology development in line with market trends. The company will also continue to ensure that it provides safety and peace of mind to all concerned parties through its business activities.

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ThreeBond Co., Ltd. R&D Headquarters
Development Division 3 Automotive Aftermarket Development Section
Toshifumi Kuboyama
Manabu Kirino

ThreeBond TECHNICAL NEWS

ThreeBond Co., Ltd.
4-3-3 Minamiosawa, Hachioji,
Tokyo 192-0398
Tel: +81-42-670-5333