Launch of the BLISTANCE™ blister resistant material series

1. Introduction

O-rings and other elastomer seal materials (hereinafter referred to as "seal materials") are considered to have existed since the second half of the 19th century to the first half of the 20th century. They are one of the components that have supported the development of mankind over the past 100 years by preventing liquids and gases from leaking from joints and other connections of pipes used in a wide range of industries such as automobile, aircraft, chemical and steel.

The development of the aforementioned industries has been extremely rapid, and the environments to which seal materials are exposed are also becoming more severe and complex in the process.

When the elements of environmental complexification that was previously mentioned are broken down, they can be broken down into two, energetic factors and environmental factors[1]. Energetic factors include heat, stress, light, and radiation, while environmental factors include air, water, acids, alkalis, oils, and fluids such as organic solvents.

When seals are used in an environment where such factors are intertwined, their characteristics gradually change and their mechanical strength and chemical properties deteriorate compared to the initial state, or there is a change in appearance. Such phenomena are generally referred to as degradation, and as degradation progresses, seals no longer prevent fluids from leaking and eventually reach the end of their service life.

As mentioned above, degradation is caused by a combination of various factors, and there are many types of degradation. In this paper, we will focus on a type of degradation called blisters, explain its formation mechanism, and introduce our new product line, "BLISTANCE™" series, which is resistant to blisters.

2. Blisters[2]

This section describes the mechanism leading to the occurrence of blisters, a type of degradation in seal materials.

Blisters occur under certain conditions, when seal material such as O-rings in equipment and devices are exposed to sudden pressure fluctuations while in contact with gases and fluids such as volatile liquids under high temperature and high pressure.

Firstly, from a microscopic point of view, elastomers are composed of intertwined molecular chains and are relatively porous materials. Therefore, in high-temperature and high-pressure environments, gases and volatile liquids can easily penetrate the interior of the seal material through the gaps in the molecular chains, and some of which remain inside.

Furthermore, when the pressure is rapidly reduced from the state where the fluid is retained inside the seal material, the gas or volatile liquid expands in volume inside the seal material and tries to escape outside from the surface of the seal material.

When the above phenomenon occurs or reoccurs multiple times, the force of the fluid trying to escape overcomes the mechanical strength of the seal material, causing foaming and cracking inside and on the surface (Figure1).

In industries dealing with elastomers, this type of degradation, where fluids trapped inside physically damage the seal material upon depressurization, is called "blister" (Figure2).

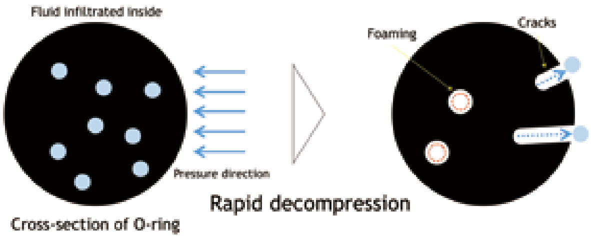

Figure1 Schematic diagram of blister formation mechanism

Figure2 Example of an O-ring where blisters have occurred

When blisters occur, the corresponding area may become a leak path, or fracture due to pressure applied to the fissure, making the seal material unable to perform its function of preventing fluid leakage.
For instance, high-pressure hydrogen gas environments are an area where damage can be caused due to blisters. If a leak occurs due to blister generation of the seal material, the static electricity generated in the surroundings may cause an explosion, which may lead to a severe accident involving human lives.
Moreover, a prime example of volatile fluids are refrigerants (CFC or CFC substitutes), which are also a kind of fluid where the occurrence of blisters is sometimes seen. In recent years, R134a and other CFC alternatives have become the most common refrigerants, and unlike the specified CFCs used in the past, they do not deplete the ozone layer. However, their global warming potential is not significantly different, and their impact on global warming is considered to be significant in case of leakage.
In order to prevent the leakage caused by these blisters, it is important to select the most suitable seal material for that environment. Some of the criteria are described below:

①Select a seal material with high hardness and mechanical strength.
②Select a seal material that has low compatibility with fluids.
③Decrease the cross-sectional diameter of the seal material to reduce the amount of fluid retention inside.

In addition, adjustments to the operating environment, such as lowering the operating temperature and slowing down the decompression rate, are considered to be effective in preventing blister formation.

3. Product overview of the "BLISTANCE™" series

Using ① and ② in the previous section 2 as criteria, we have launched a new series of products called "BLISTANCE™", including both newly developed products as well as previously available blister-resistant seals, to make it easier for customers concerned about or troubled by blisters forming in high-pressure hydrogen gas, high-temperature steam, refrigerant + refrigerant oil, and other environments, to select seal materials.
In this section, we will introduce the features of each of the following four products:

1. "BLISTANCE™- H Series", suitable for use in hydrogen gas environments.
2. "BLISTANCE™- St Series", suitable for use in high-temperature steam environments.
3. "BLISTANCE™- Rf Series", for use in refrigerant + refrigerant oil environments.
4. "BLISTANCE™- Mu Series", for use in a wide range of other environments.

3-1) BLISTANCE™-H series

The BLISTANCE™-H series is a seal material suitable for use in hydrogen gas environments. Currently, BLISTANCE™-HST for low pressure (under 2MPa), BLISTANCE™-HMP for medium pressure (under 35MPa), and BLISTANCE™-HLT series for high pressure (under 95MPa) are available, all three of which are made of EPDM seal material.
The maximum pressure of hydrogen gas used at current hydrogen stations is 82MPa, and its mechanism

is as follows: from a container called a "curdle," through a compressor and a pressure accumulator, cooled by a pre-cooler, and then filled into a vehicle through a dispenser. Since the filling of hydrogen gas from the dispenser into the vehicle is done by using differential pressure, the compression by the compressor affects the filling speed. The higher the pressure to increase the filling speed, the greater the heat generated by adiabatic compression during filling.

Therefore, when hydrogen gas is filled at room temperature, there is a risk of exceeding the heat resistance temperature of the hydrogen tank inside the vehicle (said to be 85℃ for Type IV hydrogen tanks made of CFRP), so it is necessary to cool the hydrogen gas to -40℃ using a pre-cooler (Figure3).

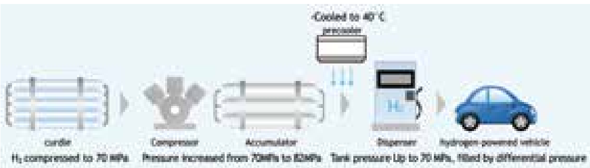

Figure3 Mechanism of a hydrogen station, schematic diagram

In this case, the situation where blisters are most likely to form is when a sudden decompression from 82 MPa to atmospheric pressure occurs while the temperature has risen to around 85℃ and the chances are particularly high with general-purpose seal materials. In addition, the same seal material must be able to seal at a pressure of 82 MPa and temperature of -40℃.

Also, hydrogen gas is handled at pressures of 35 MPa in small hydrogen stations and 2 MPa in hydrogen gas detection sensors, and since these facilities are not equipped with pre-coolers, the presence or absence of low temperature characteristics is not questioned here.

In introducing the BLISTANCE™-H series, we will first introduce the features of BLISTANCE™-HLT, which is most suitable for seals used in areas exposed to high pressure and low temperature[3].

The most remarkable feature of BLISTANCE™-HLT is that even after 11,250 cycles of rapid pressurization and depressurization of hydrogen gas at a pressure of 90 MPa at 90℃, no leakage of hydrogen gas was detected during the cycle test and no trace of blisters was found on the seal material after the test. (The pressure cycle test was conducted at the Hydrogen Energy Products Research and Testing Center (HyTReC)).

We have run a similar test on general-purpose seals and the difference in appearance after the test is apparent (Figure4).

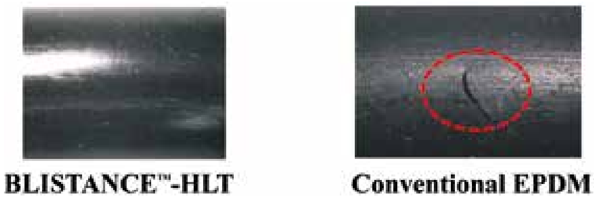

Figure4 Surface condition of O-ring after high-pressure hydrogen cycle test

BLISTANCE™-HLT also has excellent low-temperature properties. The following is a comparison of low-temperature properties between BLISTANCE™-HLT and a general-purpose seal material also made of EPDM. The low-temperature properties were evaluated by conducting a low temperature elastic recovery test (hereinafter referred to as TR test) in accordance with JIS K6261-4. The results are shown below (Figure5, Table1).

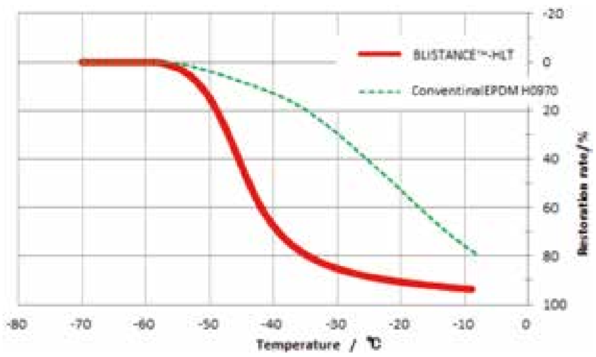

Figure5 Measurement results of BLISTANCE™-HLT TR test (Comparison: General-purpose EPDM)

Table1 Comparison of BLISTANCE™-HLT and H0970 TR values

	BLISTANCE™-HLT	Conventianal EPDM H0970
TR10 (℃)	-51	-43
TR30 (℃)	-47	-30
TR50 (℃)	-44	-21
TR70 (℃)	-39	-13
Shrinkage at minus 40℃(%)	67.4	12.8

The above graph shows that the temperature moves toward room temperature as the horizontal axis moves to the right, and the seal material regains its elasticity as the vertical axis moves downward. From this result, it can be confirmed that general-purpose EPDM regains 10% of its elasticity at around -43℃, whereas BLISTANCE™-HLT regains the same level of elasticity at around -51℃, showing that it has excellent low-temperature properties.

The fact that no leakage of hydrogen gas was detected after 1,000 cycles of 90 MPa pressurization at -40℃ and another 20 cycles of 90 MPa pressurization at -50℃ at HyTReC, indicates that BLISTANCE™-HLT is suitable as a seal material for use in low-temperature and high-pressure hydrogen gas environments.

As mentioned above, BLISTANCE™-HLT is a product that displays its performance in a high-pressure hydrogen gas environment that can be exposed to low temperatures, but it is over-specified for use in a medium-pressure hydrogen gas environment where the temperature is not as low and the pressure is less than 35 MPa or in a low-pressure hydrogen gas environment where the pressure is less than 2 MPa. For these applications, we recommend BLISTANCE™-HMP for medium-pressure hydrogen gas or BLISTANCE™-HST for low-pressure hydrogen gas.

Finally, please refer to VALQUA Technology News No.39 (2020) for the details of BLISTANCE™-HLT characteristics and tests.

3-2) BLISTANCE™-St series

BLISTANCE™-St series is a blister-resistant seal material for high-temperature and high-pressure steam environments, and there is only one type of BLISTANCE™-StHT in the current range.

In general, seal materials made of binary fluororubber (FKM) are used in high temperature environments under air, but it is known that when the environment becomes steam, hydrolysis occurs and the mechanical strength decreases.

In addition, there have been cases where, when used under high pressure, steam penetrated and stayed inside the seal material, which expanded upon depressurization, resulting in blister formation.

Seal materials that are used in food and beverage manufacturing facilities are actually exposed to such conditions, and blister formation can become a problem. The product that we would like to recommend for customers who are facing the above problems is BLISTANCE™-StHT[4]. This product is based on tetrafluoroethylene-propylene rubber (FEPM), and has a different molecular structure from conventional binary FKMs consisting of vinylidene fluoride (VDF) and hexafluoropropylene (HFP) (Table2).

Table2 Molecular structures of FEPM and binary FKM

Type	Molecular Structures
FEPM	$-(CF_2-CF_2)p-(\underset{}{CH}(CH_3)-CH_2)q-$ (TFE, Pr)
FKM (Bipolymer)	$-(CF_2-CH_2)p-(CF(CF_3)-CF_2)q-$ (VDF, HFP)

The most significant feature of BLISTANCE™-StHT, which was developed with our compounding technology using FEPM as base material, is that the value of the compression set rate is lower than that of the conventional FEPM-based seal materials even in a steam environment of 230℃, and that blisters do not occur during decompression due to its improved mechanical strength.

Although EPDM and HNBR-based seal materials have been widely used in the past in steam environments of less than 150℃, BLISTANCE™-StHT seals demonstrate significantly higher capabilities than conventional materials at temperatures above 150℃, where sealing used to be difficult.

The following is a photograph of a compression set test specimen that was actually exposed to a steam environment at 230℃ for 72 hours in a compressed state and then rapidly decompressed, as well as the measured compression set strain rate after exposure to a steam environment at 200℃ for 72 hours (Figure6, Table3).

Figure6 Cross-section of test specimen after 72h of compression in 230℃ steam

Table3 Comparison of compression set rate between BLISTANCE™-StHT and conventional FEPM

	BLISTANCE™-StHT	conventional FEPM
compression set rate (%) 200℃×72h Under steam	18	36

From the above results, it can be seen that BLISTANCE™-StHT does not show blister formation even in environments where it has occurred in conventional FEPM, and furthermore, the compression set rate in steam environment is small and thus favorable.

In addition, as shown in the beginning of this section, FEPM has good acid and alkali resistance. Therefore, BLISTANCE™-StHT can be expected to have a long service life not only in steam but also in acidic and alkaline vapor environments. Thus, customers who have concerns or difficulties about blisters in steam environments or leakage of acidic and alkaline fluids in high-temperature environments are recommended to consider using BLISTANCE™-StHT.

3-3) BLISTANCE™-Rf series

BLISTANCE™-Rf series is a blister-resistant seal material for use in environments where a refrigerant is mixed with refrigerant oil, and there is only one produce, BLISTANCE™RfST, in the current series.

In general, refrigerants (fluorocarbons including CFC alternatives) are used as fluids in areas where heat exchange takes place. Heat exchange is achieved through the process of removing heat from the surrounding environment by vaporization heat as well as its release during liquefaction. The refrigerant changes to a liquid when pressurized, and becomes a gas when the pressure is lowered. Therefore, during heat exchange, the pressure is frequently changed, requiring the refrigerant to change its state each time from liquid to gas and vice versa. Hence, the occurrence of blisters is also seen regarding seal materials in applications where refrigerants are used.

The most important condition for selecting a seal material in a refrigerant environment is that it should have high mechanical strength to withstand blister formation caused by pressure changes, but it is also important that it has low affinity for refrigerants and refrigerant oils used as lubricants, in order to reduce the amount of fluid penetration into the seal material.

BLISTANCE™-RfST, introduced in this section, is a HNBR-based seal material with high mechanical strength and low affinity for refrigerants and refrigerant oils (mineral and synthetic oils).

The following photographs show samples removed from a pressure vessel after depressurization when our conventional HNBR and BLISTANCE™-RfST were placed into a pressure vessel filled with refrigerant and refrigerant oil, and kept at elevated temperature and internal pressure for 72h. (Figure7).

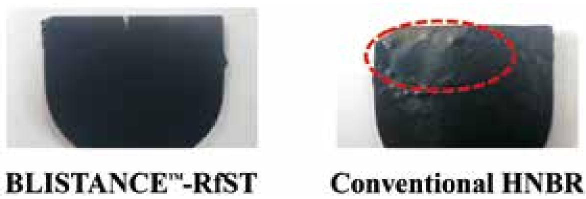

Figure7 Comparison of test specimen surfaces after refrigerant immersion test

Blisters occurred on our conventional HNBR, but were not observed on BLISTANCE™-RfST exposed to a refrigerant environment under the same conditions.

From this example, it can be said that BLISTANCE™-RfST is suitable for use in a refrigerant environment.

In case the main component of the refrigerant oil is a synthetic oil such as polyalkylene glycol, we would also like to recommend the BLISTANCE™-H series, in particular, BLISTANCE™-HMP, as described in 3-1).

3-4) BLISTANCE™-Mu Series

BLISTANCE™-Mu series is not a blister-resistant seal material for specific environments such as high-pressure hydrogen gas, high-temperature steam, and refrigerant environments introduced so far, but all possess high mechanical strength, and therefore, if there is no compatibility problem with the used fluid, they can be considered as products that prevent blister formation.

Currently, we offer three types of products: BLISTANCE™-MuST, a HNBR-based product with hardness 70, BLISTANCE™-MuHP, a HNBR-based product with hardness 95, and BLISTANCE™-MuHT, a FKM-based product with hardness 90.

In order to use the most suitable seal material in any given environment, when blister formation is a concern, please consider the BLISTANCE™-H, St, and Rf series as well.

4. Environmental compatibility and basic physical properties of the BLISTANCE™ series

As a summary, Table4 and 5 show the environmental compatibility and basic physical properties of the BLISTANCE™ series introduced in this paper.

Table4　List of BLISTANCE™ Series Environmental Compatibility

Main Applications	High-pressure hydrogen gas environment			High-pressure steam environment	Refrigerant environment	Other Environments		
Series name	BLISTANCE™ H Series			BLISTANCE™ St Series	BLISTANCE™ Rf Series	BLISTANCE™ Mu Series		
Product name	BLISTANCE™-HST	BLISTANCE™-HMP	BLISTANCE™-HLT	BLISTANCE™-StHT	BLISTANCE™-RfST	BLISTANCE™-MuST	BLISTANCE™-MuHP	BLISTANCE™-MuHT
Material	EPDM	EPDM	EPDM	FEPM	HNBR	HNBR	HNBR	FKM
Nominal Hardness (HA)	70	80	90	90	80/85	70	95	90
Service temperature (℃) *Highest and lowest℃)	-40～120	-40～130	-50～100	0～200	-20～120	-20～120	-15～120	-30～200
Application Suitability / hydrogen / High pressure (～95MPa)	×	×	◎	×	×	×	×	×
Application Suitability / hydrogen / Medium pressure (～35MPa)	○	◎	◎	◎	○	○	◎	◎
Application Suitability / hydrogen / Low pressure (～2MPa)	◎	◎	◎	◎	○	◎	◎	◎
Application Suitability / Steam	○	◎	△	◎	○	○	○	△
Application Suitability / Natural gas	×	×	×	○	◎	○	◎	◎
Application Suitability / Refrigerant※ / Mineral oil as refrigeration machine oil	×	×	×	×	◎	○	◎	×
Application Suitability / Refrigerant※ / Synthetic oil as refrigeration machine oil	◎	◎	◎	×	○	△	○	×

※ R134a, R245fa, R32, R400 series, R1234 series and other refrigerants are applicable

Table5　List of BLISTANCE™ Series Basic Physical Properties

Main Applications			High-pressure hydrogen gas environment			High-pressure steam environment	Refrigerant environment	Other Environments		
Series name			BLISTANCE™ H Series			BLISTANCE™ St Series	BLISTANCE™ Rf Series	BLISTANCE™ Mu Series		
Product name			BLISTANCE™-HST	BLISTANCE™-HMP	BLISTANCE™-HLT	BLISTANCE™-StHT	BLISTANCE™-RfST	BLISTANCE™-MuST	BLISTANCE™-MuHP	BLISTANCE™-MuHT
Material			EPDM	EPDM	EPDM	FEPM	HNBR	HNBR	HNBR	FKM
Normal physical properties JIS K6251 (JIS No.3 dumbbell)	Hardness	–	75	80	93	90	80	73	94	92
	Tensile strength	MPa	17.1	22.4	14.3	26.9	21.9	30.6	28.8	22.7
	Elongation	%	200	180	110	120	185	240	90	110
	100% Tensile Stress	MPa	6.4	9.4	10.4	23.0	10.1	7.9	–	20.0
Heat aging test JIS K 6257 (JIS No.3 dumbbell)	Hardness change	–	±0[※4]	+1[※4]	+2[※4]	±0[※6]	+3[※5]	+3[※5]	+1[※5]	±0[※4]
	Tensile strength change	%	+5[※4]	-4[※4]	+4[※4]	-1[※6]	+8[※5]	+8[※5]	+4[※5]	-3[※4]
	Elongation change	%	+15[※4]	-4[※4]	-9[※4]	±0[※6]	-4[※5]	-11[※5]	-14[※5]	-3[※4]
Compression set test JIS K 6262 (φ29.5×12.5t)	Compression Set Rate	%	12[※5]	7[※5]	16[※4]	20[※6]	14[※]	-13[※5]	19[※5]	9[※4]

※ Both environmental compatibility and basic physical properties are for reference only and are not guaranteed data.

5. Acknowledgments

We would like to express our sincere gratitude to the people at the Development Office of Ihara Science Corporation for their cooperation since the very beginning in the development and evaluation of BLISTANCE™-HLT, in particular, among the BLISTANCE™ series.

6. Conclusion

In this article, we have introduced the BLISTANCE™ series as blister-resistant seal materials, and there is a background that they were seal material with high mechanical strength. Therefore, we hope that the BLISTANCE™ series will be widely used even in environments where blister formation is not expected.

In addition to the expansion of the BLISTANCE™ series, we will continue to work hard on the development of new elastomer materials and the improvement of existing materials so that we can quickly respond to the needs of our customers.

7. References

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