ThreeBond
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48

New Materials for On-Line-Gasket System (OLGS)

Introduction

Since the company's founding, Three Bond has developed and supplied a variety of sealants, including liquid gaskets, to prevent leaks in industrial products. For almost 20 years, our products have been used in assembly lines operating throughout Japan. During these years, silicon materials have come into wide use in transportation-related equipment and devices such as engines, transmissions, and differential gears, contributing significantly to cost reductions and the streamlining of assembly processes.

This issue of Three Bond Technical News introduces a two-part fluorine-based liquid gasket and an anaerobic-curing liquid gasket -- both newly developed for Three Bond's On-Line-Gasket System (OLGS) -- and explains their technical characteristics.

Contents

I. Two-part fluorine-based liquid gasket (Three Bond 1119)

1. Development background

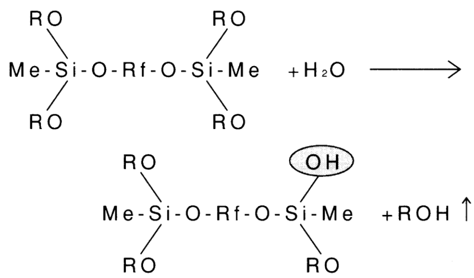
Fluorocarbon rubber is now seen as an essential industrial material due to its outstanding properties and characteristics, such as its high resistance to heat, chemicals, and solvents.

Demand for fluorocarbon rubber in Japan is said to total 1,600 to 1,700 tons in volume, with approximately 60% of this demand attributable to automotive applications. This points to the suitability of fluorocarbon rubber for the various requirements of today's automobile industry -- in terms of safety, environmental friendliness, energy conservation, and comfort. Automotive applications of fluorocarbon rubber can be divided roughly into two groups: those involving fuel systems and those involving engine lubrication systems. Specifically, fluorocarbon rubber is used as a sealing agent in engine parts, fuel hoses, and diaphragms, and also as a vibration insulator in engine mounts. Because of its superb properties, fluorocarbon rubber is used in applications of increasingly harsh conditions demanding higher performance -- automotive applications in particular. In addition, demands for lower cost are emerging, as are those for higher functionality in order to satisfy various regulations. Fluorocarbon rubber manufacturers are working hard to develop higher-quality, better-grade materials to respond to these developing needs.

In an attempt to respond to such expectations, Three Bond has now developed a completely new two-part fluorine based liquid gasket, a room temperature curing product that are different from conventional molded products such as O-rings, sheets, and hoses.

2. Product outline

One-part RTV silicon rubber hardens from the surface as the polymer-terminus hydrolytic group (≡Si-OR) reacts with moisture in the air and changes to a silanol group; the rubber then undergoes condensation reactions as the silanol group comes into contact with other hydrolytic groups. Even if the main polymer component is replaced with perfluoropolyether, curing begins from the surface according to the same reactions seen in RTV silicon, as shown in Fig. 1. However, measurement of the moisture permeability of the hardened layer indicates that perfluoropolyether has a much lower moisture permeability value than silicon, as shown in Table 1; thus, perfluoropolyether prevents the penetration of moisture into deeper layers, and only a thin superficial layer hardens.



-Rf- : Perfluoropolyether polymer unit

Fig. 1 Reaction mechanism of one-part RTV fluorocarbon rubber

Table 1 Problem of moisture permeability

	Moisture permeability (1 mm in thickness) $g/m^2 \bullet 24h$	Deep curing
Silicon	100	○
Perfluoropolyether	4	×

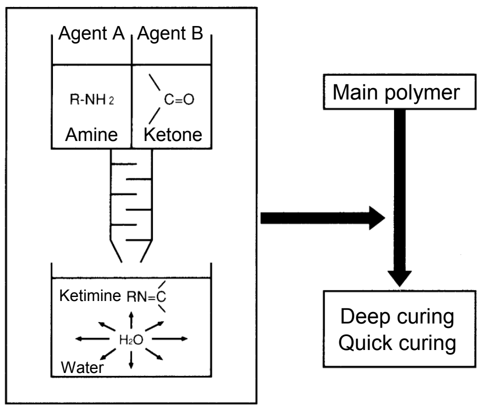


Fig. 2 Improvement of deep curing performance

To address the problem of moisture permeability seen with fluorocarbon rubber (as shown in Table 1), the two-part fluorine-based liquid gasket developed by Three Bond incorporates a reaction mechanism (see Fig. 2) to cause internal water generation at the time two liquids are mixed, thus allowing the surface to harden in the same way as in one-part RTV and also enabling uniform curing at the depth below surface.

Thus, Three Bond 1119 is room temperature curing two-part fluorine based liquid gasket and fluorocarbon rubber can be formed in a short period of time when agent A and agent B are mixed at a ratio of 1 to 1.

3. Features

(1) Excellent resistance against chemicals
(2) Excellent resistance against heat
(3) Excellent low-temperature characteristics
(4) Non-combustibility, water repellency, oil-repellency, low moisture permeability
(5) Hardens into elastic rubber in a short time at room temperature

The following shows physical properties of Three Bond 1119 (Table 2), characteristics in the cured state (Table 3), chemical resistance characteristics (Table 4), heat resistance characteristics (Table 5), fuel-C resistance characteristics (Table 6), engine oil resistance characteristics (Table 7), and low temperature characteristics (Table 8).

Table 2 Physical properties

Three Bond 1119			Measurement	
Item	Test method	Unit	Agent A	Agent B
Appearance	3TS-201-02	-	Black paste	White paste
Viscosity	3TS-210-03	Pa•s (P)	150 (1500)	260 (2600)
Specific gravity	3TS-213-02	-	1.76	1.80
Workable time	-	Minutes	10	
Viscosity after mixing	*1	Pa•s (P)	190 (1900)	

*1 Measurement of viscosity after mixing: Fill 100-ml polyethylene with Three Bond 1119 mixed using a dedicated dispensing system, and start measurement immediately using 3TS-210-03 device. The value measured after 10 minutes is determined as "viscosity after mixing."

Table 3 Characteristics in cured state

Item	Test method	Unit	Measurement
Hardness (JIS-A)	3TS-215-01	-	39
Elongation rate	3TS-320-01	%	97
Tensile strength	3TS-320-01	Mpa (kgf/cm^2)	1.03 (10.5)
Shearing adhesive strength (Fe/Fe)	3TS-301-23	Mpa (kgf/cm^2)	0.54 (5.5) CF100
Shearing adhesive strength (Al/Al)	3TS-301-23	Mpa (kgf/cm^2)	0.59 (6.0) CF100

Curing condition: 25°C × 7 days CF: Coagulation factor

Table 4 Chemical resistance characteristics

Test item	Test method	Immersion temperature	Unit	Characteristic value
Gasoline (unleaded)	JIS K 6820	45 to 50°C	wt%	-3
Kerosene	JIS K 6820	45 to 50°C	wt%	-2
30% Sulfuric acid	JIS K 6820	25°C	wt%	-2
10% Hydrochloric acid	JIS K 6820	25°C	wt%	-2
10% Caustic soda	JIS K 6820	25°C	wt%	-2
Toluene	JIS K 6820	25°C	wt%	-2
Methyl ethylketone	JIS K 6820	25°C	wt%	-2
Methanol	JIS K 6820	25°C	wt%	-2

24-hour immersion

Table 5　Heat Resistance

Item	Unit	120°C × 240 hrs.	120°C × 500 hrs.
Hardness (JIS-A)	-	57	60
Elongation rate	%	70	61
Tensile strength	Mpa (kgf/cm^2)	2.53 (25.8)	2.52 (25.7)
Shearing adhesive strength (Fe/Fe)	Mpa (kgf/cm^2)	1.38 (14.1) CF50	1.61 (16.4) CF100
Shearing adhesive strength (Al/Al)	Mpa (kgf/cm^2)	1.57 (16.0) CF50	1.73 (17.7) CF100

Table 6　Fuel-C resistance characteristics

Item	Unit	25°C × 240 hrs.	25°C × 500 hrs.
Hardness (JIS-A)	-	39	42
Elongation rate	%	86	87
Tensile strength	Mpa (kgf/cm^2)	1.14 (11.6)	1.41 (14.4)
Shearing adhesive strength (Fe/Fe)	Mpa (kgf/cm^2)	0.50 (5.1)	0.35 (3.6)
Shearing adhesive strength (Al/Al)	Mpa (kgf/cm^2)	0.62 (6.3)	0.53 (5.4)

Table 7　Engine oil resistance characteristics

Item	Unit	150°C × 240 hrs.	150°C × 500 hrs.
Hardness (JIS-A)	-	51	52
Elongation rate	%	85	84
Tensile strength	Mpa (kgf/cm^2)	2.74 (28.0)	2.47 (25.2)
Shearing adhesive strength (Fe/Fe)	Mpa (kgf/cm^2)	0.92 (9.4)	0.81 (8.3)
Shearing adhesive strength (Al/Al)	Mpa (kgf/cm^2)	0.84 (8.6)	0.98 (10.0)

Engine oil: Grade 5W-30SH

Table 8　Low-temperature characteristics

Item	Unit	-30°C × 240 hrs.	-30°C × 500 hrs.
Hardness (JIS-A)	-	42	40
Elongation rate	%	90	108
Tensile strength	Mpa (kgf/cm^2)	1.13 (11.5)	1.28 (13.1)
Shearing adhesive strength (Fe/Fe)	Mpa (kgf/cm^2)	0.74 (7.5)	0.69 (7.0)
Shearing adhesive strength (Al/Al)	Mpa (kgf/cm^2)	0.76 (7.8)	0.76 (7.8)

4. Main applications

In automobile production, Three Bond 1119 is used as a sealant for engine parts. It can be used as a sealant for lubricating devices such as oil pumps and oil filters; fuel devices such as fuel tanks, fuel pipes, fuel pumps, fuel filters, and charcoal canisters; fuel injection devices such as sensors; and intake devices such as intake manifolds and surge tanks.

In the chemical industry, the product can be used as a sealant for pumps and piping for chemicals, or as a lining or coating agent for tanks that require chemical resistance.

The product can also be used in office equipment, including parts and components requiring heat resistant rubber in photocopiers.

The product can also find applications in the energy industry, nuclear power industry, and aerospace industry.

5. Key points of development

Perfluoroelastomers presently available on the market are copolymers with tetrafluoroethylene (TFE) and perfluoromethyl vinyl ether $CF_3OCF=CF_2$ (ϕ-MVE) as the main monomers, combined with a small amount of special crosslinked monomers as a third component. The backbone chains of perfluoroelastomers based on TFE/ϕ-MVE are completely fluorinated; they thus offer excellent resistance to chemicals, solvents, and heat. However, their relatively rigid backbone chains make such perfluoroelastomers difficult to process; nor is crosslink processing easy. In addition, these polymers are very expensive. As a result, they are generally sold on the market as molded products.

By constructing a backbone chain with a flexible perfluoropolyether polymer, Three Bond has succeeded in developing an innovative new product: "liquefied fluorocarbon rubber," or Three Bond 1119. In other words, by synthesizing a both end functional perfluoroelastomer and incorporating the crosslink technology used in one-part RTV silicon, we have achieved room-temperature curing. Further, by resolving the issue of moisture permeability discussed above, we have also enabled thick layer curing.

6. Future topics

There is room for improvement in the rubber based properties of Three Bond 1119. Since the product employs one-part RTV silicon crosslink technology in the crosslink group, the heat resistance of the perfluoroelastomer itself is not maximized. Further improvements are possible through the application of advanced polymer physico-chemical engineering techniques. However, current technology in the chemical field does not allow us to take such an approach. This represents the main topic to be addressed in the future.

Needless to say, when it becomes possible to synthesize perfluoroethers for use as raw materials, at low cost, and when it is possible to mold and cure the material easily, perfluoroelastomers will be able to replace certain other elastomers, generating significant market demand in the process. In fact, no currently available elastomer can offer performance superior to that of perfluoroelastomer in terms of the harsh environmental conditions seen in the space industry and semiconductor field. The future of perfluoroelastomers is thus bright, with even higher performance anticipated.

参考文献の訳が抜けています。

II. Anaerobic-curing liquid gasket

Introduction

It has been more than 30 years since anaerobic-curing liquid gaskets first became commercially available. An anaerobic curing liquid gasket does not harden under normal opened air conditions after application. The polymerizing cure process occurs rapidly immediately after the material is formed into a thin layer between metal parts at a joint or fitting where oxygen is absent. Because this characteristic leads to improved workability on production lines, anaerobic-curing liquid gaskets have been used as Formed-In-Place Gaskets (FIPG), mainly in the automobile and construction equipment manufacturing industories.

This issue introduces a new member to of Three Bond's anaerobic-curing liquid gasket lineup, and explains its technical characteristics.

1. Background

It is well known that this type of anaerobic-curing composition is comprised of a radical polymeric monomer with acrylate and/or methacrylate as the main constituent, as well as a polymerization initiator, curing accelerator, polymerization inhibitor, and other elements.

Factors that have promoted the widespread use of anaerobic-curing liquid gaskets in the automobile and construction machinery industries include the following.

(1) Prevents loosening of bolts otherwise seen due to the effect of material fatigue common to solid gaskets
(2) Eliminates the need to provide clearances in equipment design
(3) Offers high adhesive strength for improved rigidity at joints and connections
(4) Excess sections extending from joints/connections after assembly disperse into oil
(5) Surface finishing process has minimal effect on adhesive and sealing performance
(6) Does not harden until assembly is completed
(7) Excellent resistance to chemicals
(8) Does not cause foaming in oil

RTV silicon is the main FIPG material used in Japan today. The reasons for its popularity include its excellent heat resistance and low-temperature characteristics. Additionally, although anaerobic-curing liquid gaskets do not harden quickly when used on pressed steel flanges (such as oil pans and automatic transmission fluid pans) due to the large clearances involved, RTV silicon does harden in such cases, as it is moisture-curing. Finally, efficient application technology is now available, involving the use of a Mohno pump.

Anaerobic-curing liquid gaskets are generally used on flat groove-less flanges made of rigid die-cast aluminum offering a uniform contact surface with no clearance or warpage. However, as parts materials are becoming lighter in order to reduce product weight, demand is growing for new anaerobic-curing liquid gaskets, such as those made of RTV silicon, that are flexible enough to follow the movement of joints. To respond to such emerging needs, Three Bond has introduced a new product developed by adding flexibility to the features of the conventional anaerobic-curing liquid gasket. The company has also resolved the previous drawback relating to heat resistance, and has improved the dispenser application technology.

2. Three Bond 1131F and 1133B

2-1. Outline

Three Bond developed the 1131F and 1133B anaerobic-curing liquid gasket products that are exclusively used on metal flanges. The Three Bond 1131F offers excellent flexibility, similar to that of RTV silicon, at the same time offering improved connection rigidity. Three Bond 1133B is flexible and offers high adhesive strength and heat resistance. The dedicated bead application system also incorporates dramatically improved coating technology.

2-2. Physical properties and characteristics

Three Bond 1131F

External appearance	Blue paste
Viscosity	50 Pa•s (500P)
Thixotropic ratio	3.1
Specific gravity	1.12
Set time	5 min
Shearing adhesive strength (Al)	3.9 Mpa (40kgf/cm^2)
Elongation	150%
Tensile strength	5.3 Mpa (54kgf/cm^2)

Three Bond 1133B

External appearance	Blue paste
Viscosity	100 Pa•s (500P)
Thixotropic ratio	2.9
Specific gravity	1.12
Set time	5 min
Shearing adhesive strength (Al)	6.1 Mpa (62kgf/cm^2)
Elongation	100%
Tensile strength	18.6 Mpa (190kgf/cm^2)

2-3. Features of Three Bond 1131F and 1133B

1) Flexibility: The use of urethane-modified polyester and urethane-modified polyether as the backbone chain of the base polymer (oligomer) has led to unprecedented levels of flexibility as well as of rigidity.
2) Resistance against chemicals: Due to the greater molecular weight of the cured material, resistance against engine oil, automatic transmission fluid, gear oil, etc. is very high.
3) Curing speed: Although conventional products require a long setting time under low-temperature conditions (5°C), the addition of a new curing catalyst has reduced the setting time significantly.
4) Adhesive strength: Since Three Bond 1131F was developed with an emphasis on flexibility, adhesive strength was set to a medium level. With Three Bond 1133B, flexibility is slightly lower, but adhesive strength is higher.
5) Minimum foaming: Because the base polymer is urethane-modified acrylate, the products will not foam after being dispersed in oil.
6) Dispersibility in oil: Because urethane-modified acrylate is used as the base polymer, the products offer high mutual solubility in various types of oil; uncured substances disperse in oil.
7) Maintainability: Since the base polymer is urethane-modified acrylate, spraying the Three Bond PANDO 391D gasket remover swells this type of liquid gasket left on flange surface, thus allowing easy removal with a scraper.

2-4. Characteristics

(1) Temperature and curing speed (Fig. 1)
Anaerobic-curing liquid gaskets reach practical strength (50% of final strength) in approximately one hour with an ambient temperature above 5°C.

(2) Clearance and curing speed (Fig. 2)
Because anaerobic-curing liquid gaskets have polymerization inhibition function against oxygen in radical polymerization, curing performance decreases if the clearance is large. If the clearance is less than 0.1 mm, there will be no problems in practical application.

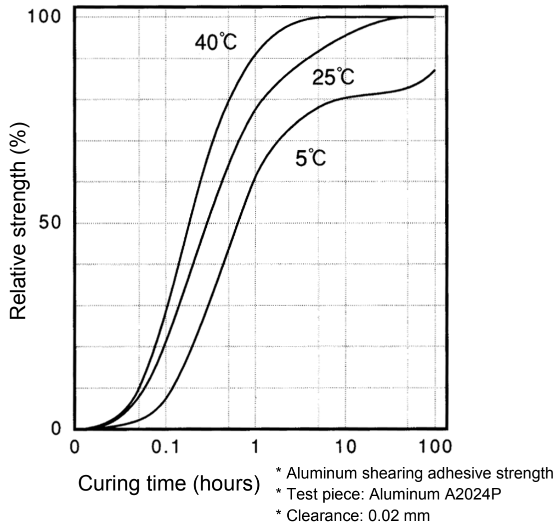


Fig. 1 Relationship between temperature and curing speed

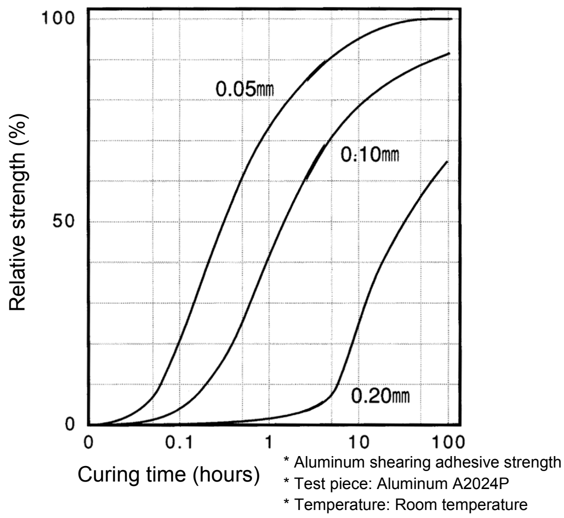


Fig. 2 Relationship between clearance and curing speed

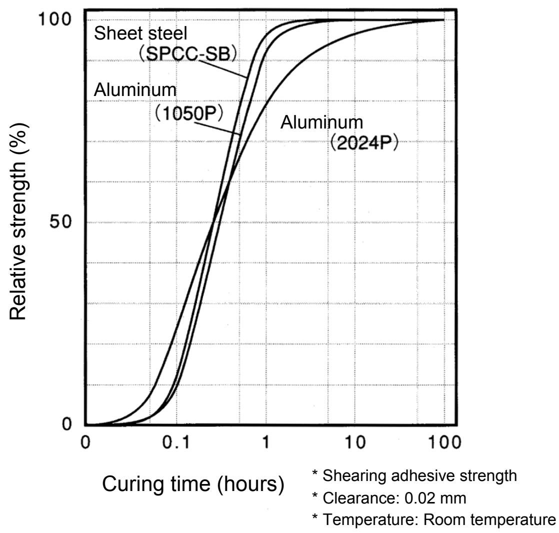


Fig. 3 Relationship between material and curing speed

(3) Material and curing speed (Fig. 3)

Metal surfaces affect the curing performance of anaerobic-curing liquid gaskets. Since ordinary die-cast aluminum (ADC) contains copper, it is high active material. For this reason, aluminum A2024P test pieces, which have components similar to those of die-cast aluminum, were used in the basic property test.

Table 1 Components in test piece materials

Material	Cu	Si	Fe	Al
ADC	4.0 to 10.0	9.6 to 12.0	1.0 or less	Remnant
A2024P	3.8 to 5.0	0.5 or less	0.5 or less	Remnant
A1050P	0.05 or less	0.25 or less	0.4 or less	99.5 or more

(Wt%)

(4) Surface roughness and adhesive strength (Fig. 4)

Finishing precision has almost no effect on adhesive strength.

(For (1), (2), (3), and (4), Three Bond 1131F and 1133B exhibit similar tendencies.)

(5) Thermal strength (Fig. 5)

Since the cured material softens under high temperatures, the resin strength decreases. As a result, the adhesive strength tends to decrease as well. Nonetheless, Three Bond 1133B retains sufficient adhesive strength at temperatures above 120°C.

The following shows the results of various reliability tests.

(6) Three Bond 1131F and 1133B's resistance to automatic transmission fluid (Figs. 6 and 7)

(7) Shearing adhesive strength of Three Bond 1131F and 1133B after thermal aging (Figs. 8 and 9)

(8) Shearing adhesive strength after cold-heat cycles (Fig. 10)

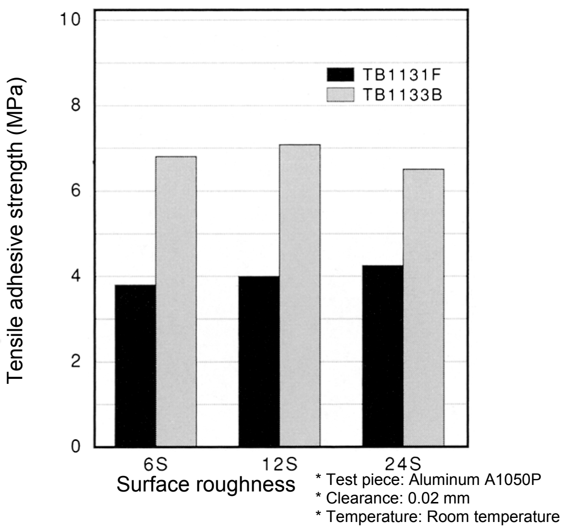


Fig. 4 Surface roughness and tensile adhesive strength

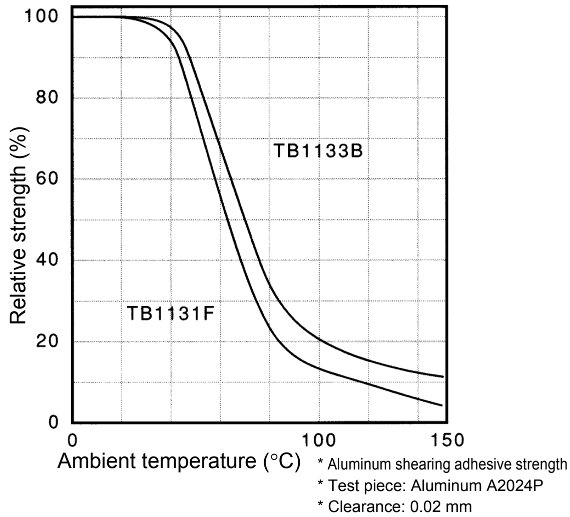


Fig. 5 Thermal shearing adhesive strength

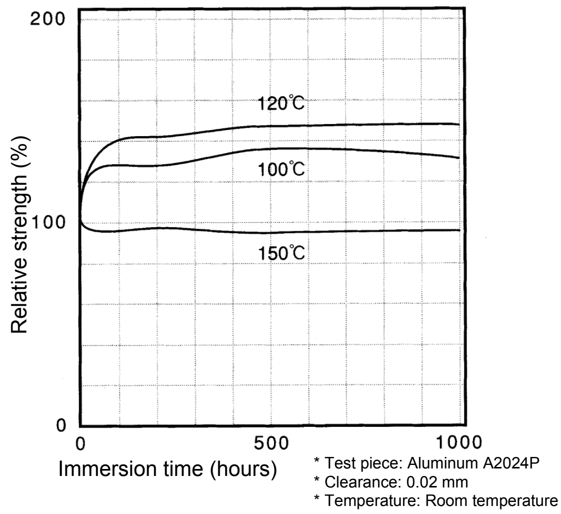


Fig. 6 Shearing adhesive strength of TB 1131F after immersion in automatic transmission fluid

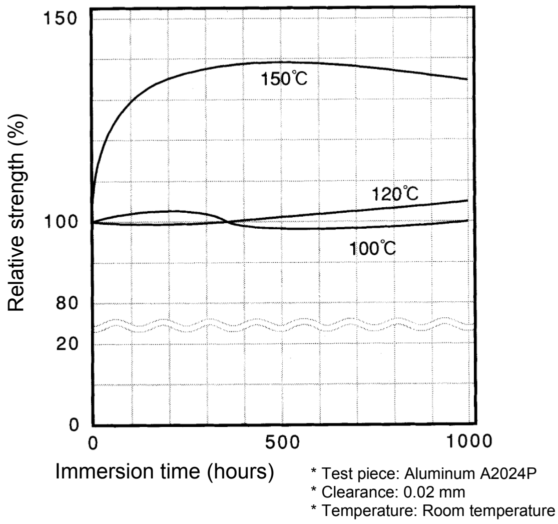
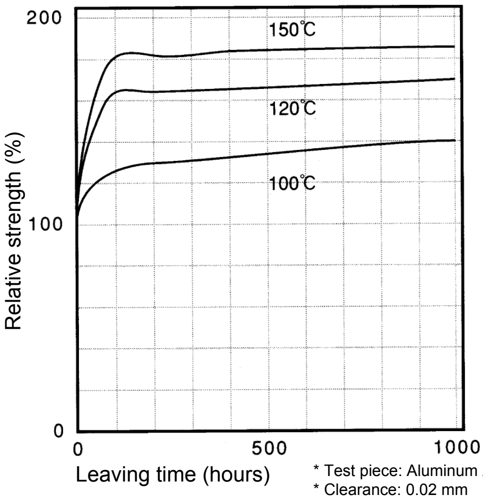
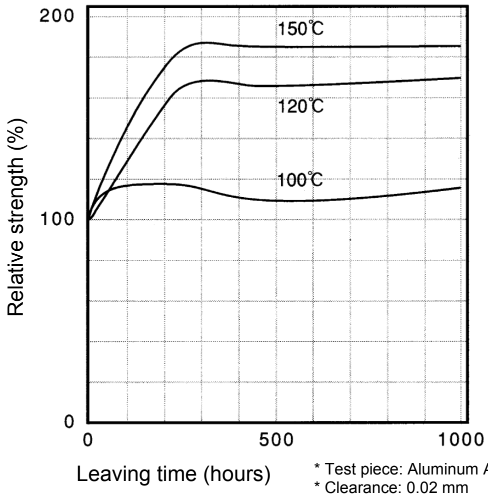


Fig. 7 Shearing adhesive strength of TB 1133B after immersion in automatic transmission fluid



* Test piece: Aluminum A2024P
* Clearance: 0.02 mm
* Temperature: Room temperature

Fig. 8 Shearing adhesive strength of TB 1131F after thermal aging



* Test piece: Aluminum A2024P
* Clearance: 0.02 mm
* Temperature: Room temperature

Fig. 9 Shearing adhesive strength of TB 1133B after thermal aging

3. Bead coating system for anaerobic-curing liquid gasket

3-1. Outline

This bead coating system is a precision machine that coats anaerobic-curing liquid gasket in a thin bead on a flange surface.

3-2. Features

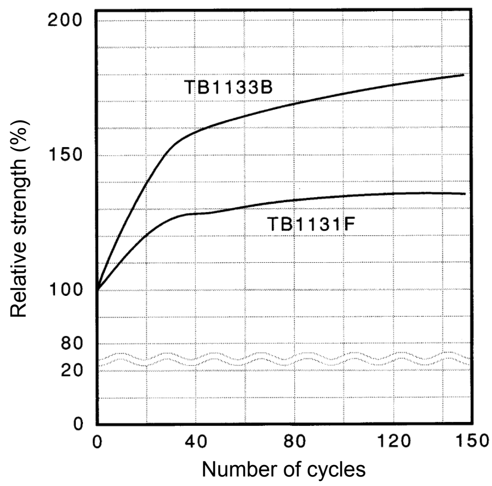
(1) No discontinuity of bead
The system has mechanisms to allow coating with removing air bubbles in the material.

(2) Detection device to check discontinuity
The system certainly finds discontinuity with higher level of image processing than conventional methods.

3-3. Mechanism

(1) Air bubble removal (Photo 1) (Fig. 11)

A screw with pitch decreasing continually toward the tip (in the direction of the nozzle) creates a continuous volumetric change of threads and compresses the anaerobic-curing liquid gasket while transporting the material. Air bubbles escape to a lower-pressure area and are released to the atmosphere from the rear end of the screw. This mechanism separates air bubbles from the material, thus preventing bead discontinuity during dispensing material from the nozzle tip.



* Aluminum shearing adhesive strength
* Test piece: Aluminum A2024P
* Clearance: 0.02 mm
* Cycle condition: -30°C × 1 hr. to +150°C × 1 hr. per cycle
* Temperature: Room temperature

Fig. 10 Shearing adhesive strength after cold-heat cycles

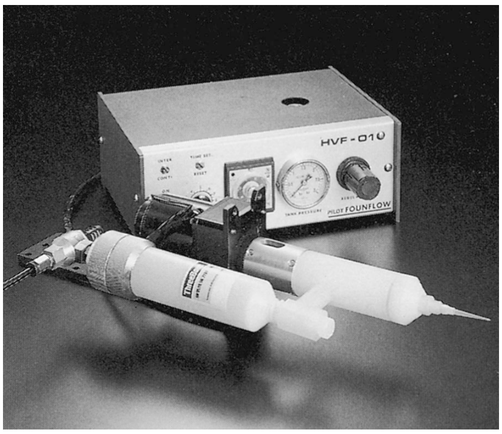


Photo 1

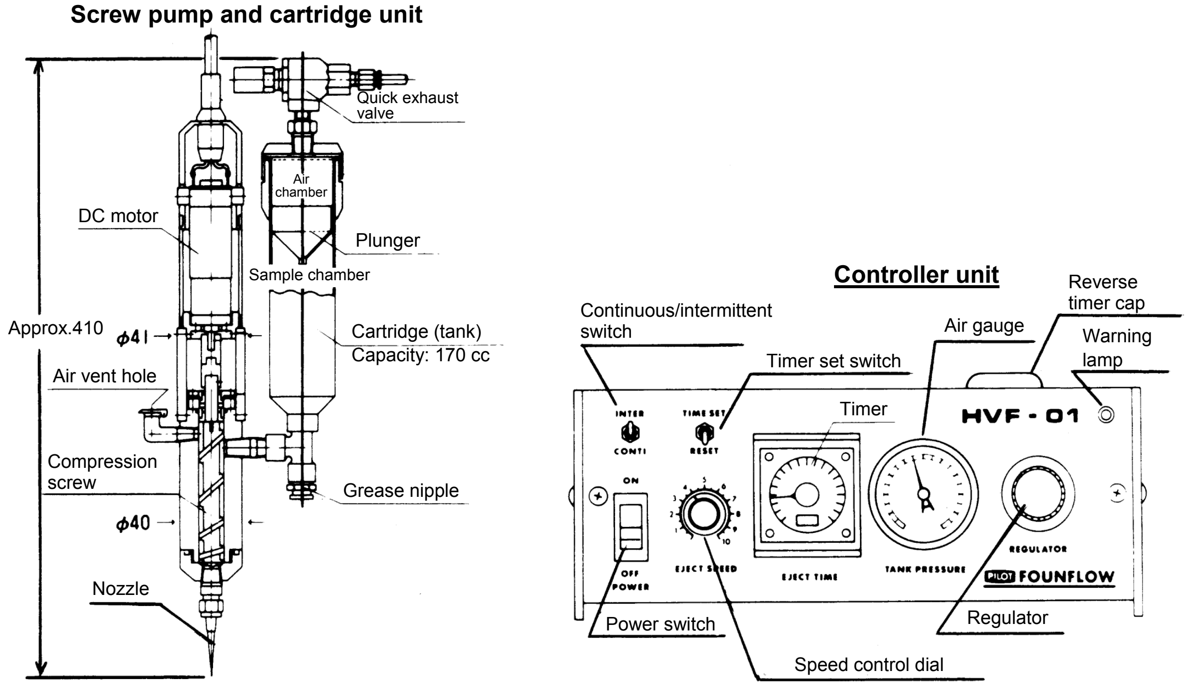


Fig. 11 Anaerobic-curing liquid gasket precision application system

(2) Application detection (Photo 2)

An image processing system with a CCD camera is used to detect discontinuity, width, and positional deviation of coated beads. To prevent influences of intensity changes in ambient light and diffused reflections, contrast image processing system is used for accurate verification. Various conditions such as gap width, deviation amount, and minimum bead width can be set precisely, and teaching operations are performed almost automatically.

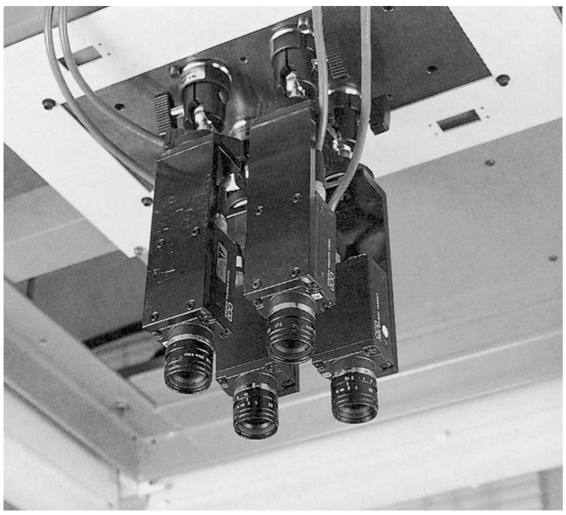


Photo 2

3-4. Equipment

By combining the outstanding mechanisms described above and the coating technology (including robotics) that has cultivated through the development of the OLGS, the equipment performs high-precision bead-form coating of anaerobic-curing liquid gaskets. Three Bond also manufactures and supplies coating systems which satisfy specific customer needs. For more details of the systems, contact Three Bond Engineering Co., Ltd.

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