● UFO Polymers for Sealants

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1. Introduction

We have developed new acrylic polymers using the Uniform Functional Oligomer (UFO) technology. The UFO technology is an advancement of the Solid Grade Oligomer (SGO, high-temperature continuous bulk polymerization) process originally licensed from Johnson Polymer in the U.S. Since it uses almost no polymerization solvents, polymerization initiators, chain transfer agents, or similar reagents, it efficiently produces impurity-free polymers that are useful for addressing environmental and resource concerns. This makes it ideal for applications requiring weather resistance, yellowing resistance, and low odor. Specifically, applications in paints that require high weather resistance, dispersants that require low odor and low viscosity, binders for inks, and OPVs are being explored[1].

We use this UFO technology to produce a variety of acrylic polymers and market them under the trade name "ARUFON."

In this article, we focus on sealants, which are one of the applications of solvent-free liquid polymers, and describe the characteristics of ARUFON polymers produced with UFO technology. Sealants using ARUFON exhibit excellent performance in terms of weather resistance, prevention of plasticizer bleeding, and prevention of paint contamination.

2. Sealants

2.1 What is a sealant?

Sealants have been used since the late 1950s for the purpose of filling gaps between concrete, sizing materials, and metal curtain walls to make them watertight and airtight, as well as to maintain aesthetic appeal. While oil-based caulking materials were initially used, elastic sealants were developed in the late 1960s to mid-1970s alongside the spread of high-rise buildings and prefabricated construction. Today, a wide variety of sealants are used, each chosen for its suitability to the application.

Figure 1 shows typical types of building sealants. They can be roughly classified into the two-component type, which is used by mixing the main agent and the curing agent on site, and the one-component type, which cures by reacting with moisture or oxygen in the air when extruded from a caulking gun.

In terms of the reaction mechanism, they can be classified into the reaction-curing type, which solidifies through chemical reaction, and the dry-curing type, which solidifies as water or organic solvents evaporate. At present, the most commonly used sealants are reaction-curing sealants. In particular, polyurethane sealants (polyether containing a hydroxyl or isocyanate group at the terminal), modified silicone sealants (polyether containing a silyl group at the terminal), and silicone sealants (reactive dimethylsiloxane) are widely used. **Figure 2** shows the reaction mechanism.

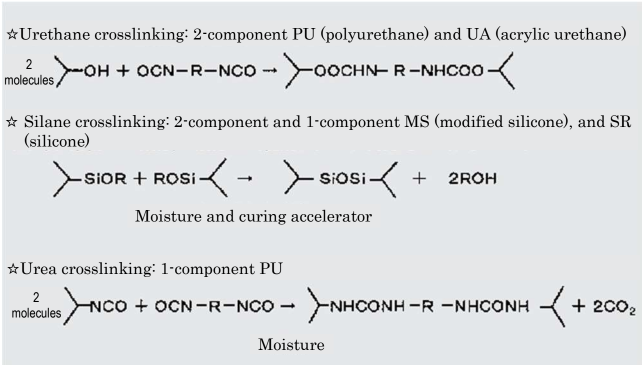


Figure 2: Reaction mechanism of a sealant

2.2 Recent situation

In recent years, there has been a need to improve the durability of various materials from the viewpoints of resource and energy conservation, as well as environmental considerations. In the building industry, efforts are being made to improve housing quality and performance through revisions to the Building Standards Act, the Act on the Promotion of Housing Quality Assurance, and the Construction Material Recycling Act. In particular, the Act on the Promotion of Housing Quality Assurance, which took effect in April of this year, clarifies the seller's warranty liability for defects, with the aim of ensuring that consumers can purchase quality housing with confidence. For example, builders are required to provide a 10-year warranty against defects such as water leakage in waterproof areas (exterior walls, roofs, etc.) caused by construction faults.

Against this backdrop, there is a growing demand for improved weather resistance and other functional improvements in sealants, and various manufacturers are bringing weather-resistant polymers, and sealants made from them, to market. Examples include acrylic urethane sealants[2], fluoropolymer sealants[3], and polyisobutylene sealants[4]. We have also been researching polymers for sealants with good weather resistance, and developed ARUFON, a line of new acrylic polymers using the UFO technology.

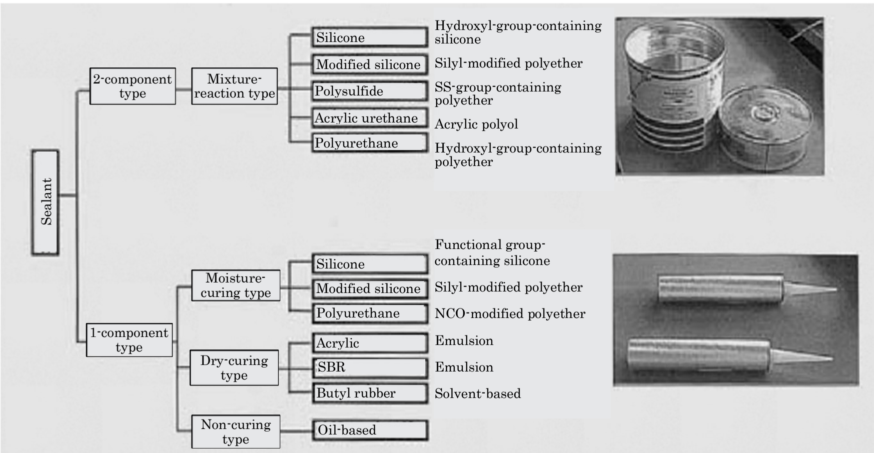


Figure 1: Classification of building sealants (excluding gaskets)

3. UFO polymer "ARUFON"

We have developed various ARUFON grades, ranging from non-functional types to types containing functional groups. As shown in **Table 1**, the grades suitable for sealants are all liquid polymers with low glass transition temperatures. The ARUFON UH-2000 Series contains a hydroxyl group as the functional group and is generally classified as an acrylic polyol. It is suitable as a base polymer for acrylic urethane sealants. The ARUFON UP-1000 Series is a low-viscosity, non-functional acrylic polymer ideal for use as a plasticizer.

Table 1: Typical ARUFON grades for sealants

ARUFON Grade	UP-1000	UH-2000	UH-2030
Application	Plasticizer	Base polymer	Modulus modifier
Type	Acrylic polymer	Acrylic polyol	Acrylic polyol
Appearance	Liquid	Liquid	Liquid
Molecular weight (Mw)	3,000	13,000	3,000
TG (°C)	-60	-55	-63
OHV (mgKOH/g-polymer)	0	20	120
NV (%)	≥ 98	≥ 98	≥ 97
Odor	Almost none	Almost none	Almost none

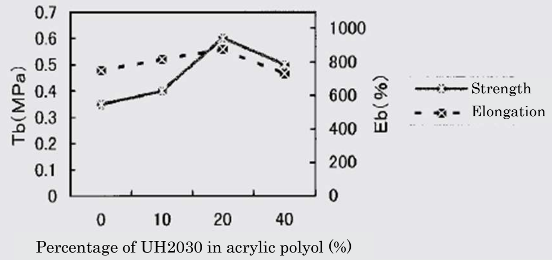
3.1 Evaluation as a base polymer for sealants

Table 2 shows an example of sealant formulations using ARUFON UH-2000 as the base polymer. The formulation uses a main agent containing filler (calcium carbonate), pigment (titanium dioxide), plasticizer, antioxidants (UV absorber, HALS, heat stabilizer), and a curing catalyst, isocyanate-terminated polyoxyalkylene as the curing agent.

Table 2: Example sealant formulation

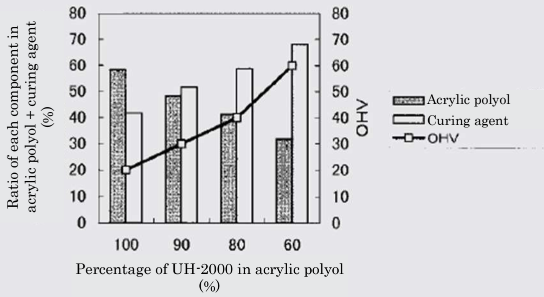
Component	Parts by weight
Main agent	
ARUFON UH-2000	100 to 50
ARUFON UH-2030	0 to 50
Calcium carbonate (light)	110
Calcium carbonate (heavy)	40
Titanium dioxide	10
Plasticizer	25 to 50
Antioxidant	1
Anti-tack agent	(1 to 10)
Curing catalyst (tin-based)	0.1 to 0.3
Curing agent	
Isocyanate-modified polyoxyalkylene	NCO/OH = 1/1

When the two components are mixed and cured immediately before use, the resulting sealant exhibits sufficient elongation and strength. If the modulus needs to be adjusted, ARUFON UH-2030 can be used as a modulus modifier. **Figure 3** shows the relationship between ratio and tensile properties when ARUFON UH-2000 and UH-2030 are blended. The figure shows that the breaking strength (Tb) and elongation at break (Eb) increase as the percentage of UH-2030 increases, then decrease beyond a certain point. This is because, as shown in **Figure 4**, blending the high-hydroxyl-value UH-2030 into the low-hydroxyl-value UH-2000 increases crosslink density and thus strength; however, the proportion of isocyanate-modified polyoxyalkylene curing agent also rises, increasing softness contributed by the polyoxyalkylene chains. Incidentally, when the hydroxyl groups of the polymer and the isocyanate groups of the curing agent are set in equivalent amounts, the ratio of UH-2000 to the curing agent (molecular weight 4,000) is 60/40 by weight, while the ratio of UH-2030 to the curing agent is 20/80 by weight, making the curing agent rich.



Acrylic polyol: ARUFON UH-2000, UH-2030
Curing agent: TDI-modified polyoxypropylene (bifunctional type)
Formulation: See Table 2; Curing conditions: 2 weeks at room temperature
Sample: Cut with a No. 1 dumbbell die, film thickness 1 mm
Tensile speed: 5 cm/min

Figure 3: UH-2000/UH-2030 blending ratio and tensile properties



Acrylic polyol: ARUFON UH-2000, UH-2030
Curing agent: TDI-modified polyoxypropylene (bifunctional)

Figure 4: Ratio of hydroxyl value (OHV) to curing agent when UH-2000 and UH-2030 are blended

Table 3 shows the tensile properties of acrylic urethane sealants using ARUFON. While ARUFON UH-2000 has a low modulus, the UH-2000/UH-2030 combination system achieves a higher modulus.

Table 3: Tensile properties of ARUFON sealants and commercially available sealants

Sealant	50% modulus (MPa)	Breaking strength (MPa)	Elongation at break (%)
ARUFON UH-2000	0.05	0.39	700
ARUFON UH-2000/UH-2030	0.08	0.51	800
Commercial acrylic urethane (Company A)	0.09	0.64	1200
Commercial acrylic urethane (Company B)	0.12	0.87	840
Commercial silicone	0.13	0.69	770
Commercial modified silicone	0.11	0.44	650
Commercial polyurethane	0.19	0.95	1100
Commercial polysulfide	0.15	0.35	450

Curing agent: TDI-modified polyoxypropylene (bifunctional type) for ARUFON, and the dedicated curing agent for each commercial product
Formulation: See Table 2 for ARUFON; commercial products were cured without modification. Curing conditions: 2 weeks at room temperature
Sample: Cut with a No. 1 dumbbell die, film thickness 1 mm
Tensile speed: 5 cm/min

Both show elongation-at-break values comparable to those of commercially available sealants. For reference, **Figure 5** shows the states of the dumbbell before the test and at 600% elongation. It is clear that it delivers sufficient elongation.

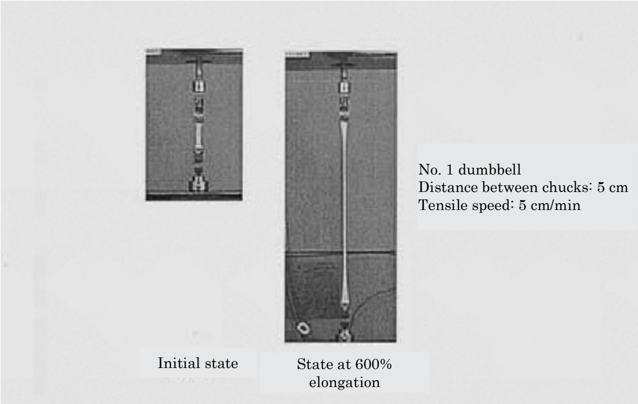


Figure 5: Sealant under tensile test

We conducted QUV (ultraviolet fluorescent lamp) accelerated weathering tests on ARUFON UH-2000-based sealants made with the formulation in **Table 2** and commercially available sealants, and measured the retention of strength and elongation. **Figure 6** shows the results. It has weather resistance (retention of strength and elongation) equivalent to or better than silicone sealants, which are recognized as having high weather resistance. It is assumed that the high weather resistance of the UFO polymer was achieved because of its acrylic polymer skeleton, which has excellent light and thermal stability.

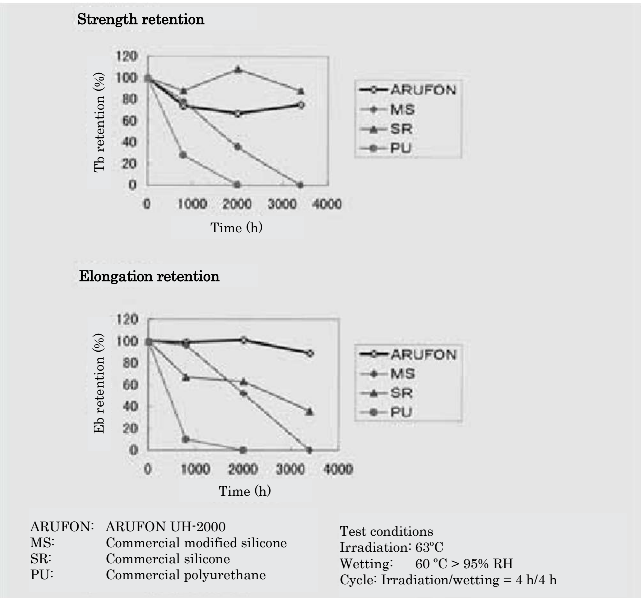


Figure 6: QUV (ultraviolet fluorescent lamp) accelerated weathering test

Furthermore, since UFO polymers do not use polymerization initiators or chain transfer agents, they are free of impurities and unstable polymer terminal groups that may reduce weather resistance, and are considered to exhibit higher weather resistance than acrylic polyols synthesized through normal batch polymerization.

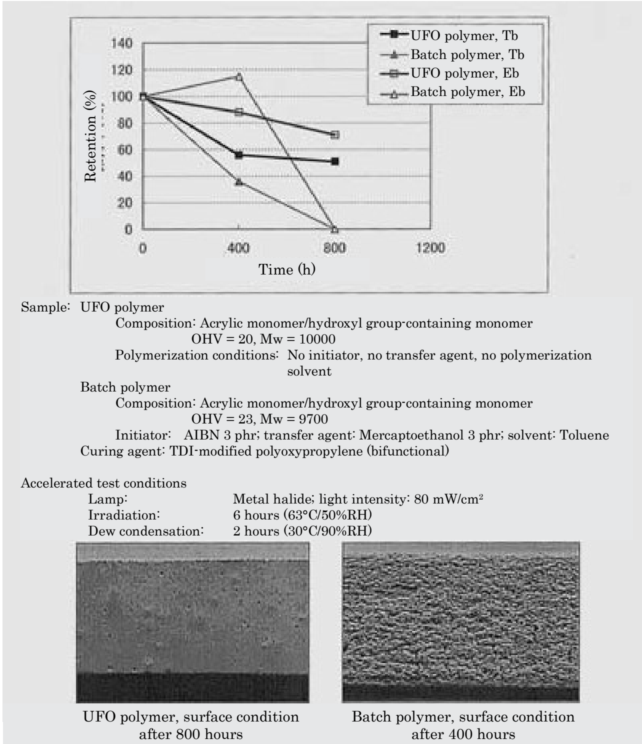


Figure 7: SUV accelerated weathering test on UFO polymer and batch polymer

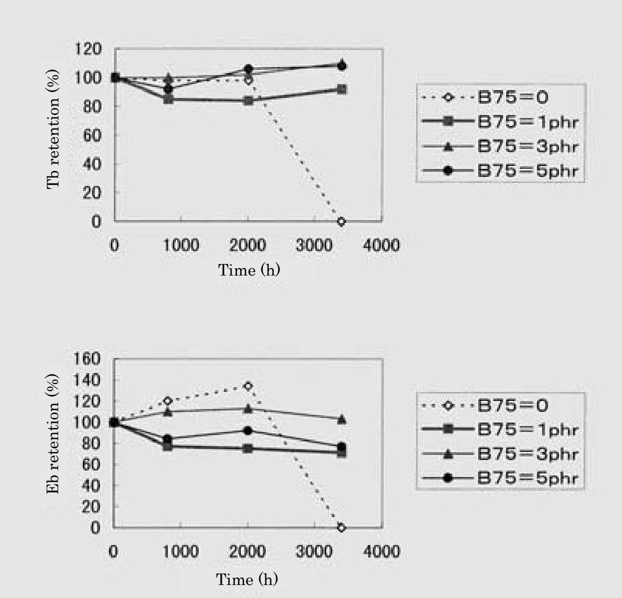
Figure 7 shows the super UV (metal halide lamp) accelerated weather resistance of sealants prepared with the formulation in **Table 2**, using an acrylic polyol made by conventional batch polymerization and an acrylic polyol of the same composition synthesized using UFO technology. The high weather resistance of UFO polymers is clearly shown.

The key to maintaining high weather resistance in the formulation of sealants is the selection of antioxidants. **Table 4** shows the compatibility of ARUFON UH-2000 with antioxidants, and **Figure 8** shows the results of a QUV accelerated weathering test using Tinuvin B75 manufactured by Ciba Specialty Chemicals as an antioxidant. While a decrease in retention can be observed from 2,000 hours when no antioxidant is added, favorable retention is shown when 1 phr or more of the antioxidant is added. Antioxidants are usually an essential component of highly weather-resistant sealants, and the same is true for ARUFON.

Table 4: Compatibility of ARUFON UH-2000 with various antioxidants

Antioxidant	Type	State	Remarks	Compatibility
T. B75	Mixture of three types	Liquid	UVA/HALS/heat stabilizer	○
T. 292	HALS	Liquid	N-Me type	○
T. 144	HALS	Solid	Contains UVA structure within the molecule	○
T. 123	HALS	Liquid	N-OR type	○
S. 770	HALS	Solid	N-H type	Precipitation
T. 571	UVA	Liquid		○
T. 1130	UVA	Liquid		○
T. 327	UVA	Solid		Precipitation
I. 1135	Heat stabilizer	Liquid		○

1 part of each antioxidant was blended per 100 parts of ARUFON UH-2000 polymer; compatibility was assessed based on the degree of turbidity.
T. Tinuvin (Ciba Specialty Chemicals), S. Sanol (Sankyo), I. Irganox (Ciba Specialty Chemicals)



B75: Tinuvin B75, see Table 2 for sealant formulation
See Figure 6 for weathering test conditions.

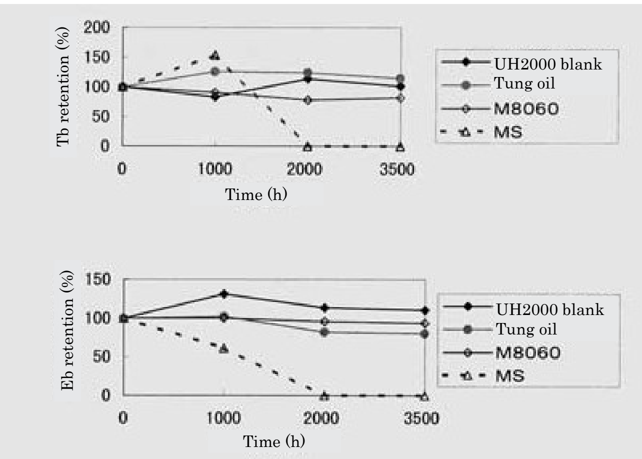
Figure 8: Relationship between the amount of antioxidant added and QUV accelerated weather resistance

If tack is a concern with ARUFON UH-2000-based sealants, we recommend adding an anti-tack agent. As shown in **Table 5**, tung oil, as well as ARONIX, which we manufacture, are effective as anti-tack agents, and the resulting sealants have good weather resistance as shown in **Figure 9**.

Table 5: Types and effects of anti-tack agents

No.	Anti-tack agent	Amount added	Photoinitiator	Comment	Tack
1	-			Blank	×
2	M-8030	5 phr	Irg907	ARONIX (Toagosei)	△
3	M-8060	5 phr	Irg907	ARONIX (Toagosei)	○
4	M-8060	5 phr	Irg1173	Initiator comparison vs. No. 3	×
5	M-8060	2.5 phr	Irg907	Amount comparison vs. No. 3	○△
6	M-8100	5 phr	Irg907	ARONIX (Toagosei)	○
7	Tung oil	5 phr			⊙
8	Tung oil	2.5 phr		Amount comparison vs. No. 7	○
9	Linseed oil	5 phr			△×
10	R15HT	5 phr		Idemitsu Petrochemical, mixture of 1,4-PB and 1,2-PB	×
11	PBB3000	5 phr		Nippon Soda, 1,2-PB	△×
12	Gohselac 500B	5 phr		Nippon Synthetic Chemical Industry, unsaturated polyester	××
13	500B+M-8060	2.5 phr each	Irg907		○

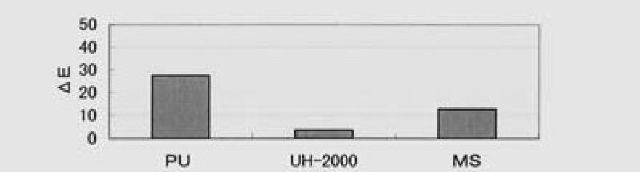
Irg: Irgacure (Ciba Specialty Chemicals), 5 phr added to ARONIX



Addition of 5 phr anti-tack agent, see Table 2 for other formulations
See Figure 6 for weathering test conditions.

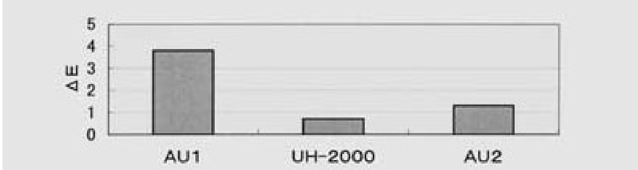
Figure 9: QUV accelerated weathering test on sealant with the addition of anti-tack agents

Another feature of ARUFON UH-2000-based sealants is their excellent compatibility with paint overcoating. Sealants are often coated with an overcoating of paint after installation, but low-molecular-weight compounds may migrate from the underlying sealant to the paint layer over time and cause discoloration of the paint film. Because UFO technology does not contain low-molecular-weight compounds such as polymerization initiators, chain transfer agents, and polymerization solvents, the resulting polymers are expected to bleed less. In fact, as shown in **Figure 10**, ARUFON shows the lowest coating-film contamination among the various base polymers tested. In addition, as shown in **Figure 11**, ARUFON also shows lower coating-film contamination than other acrylic urethane sealants.



PU: Commercial polyurethane sealant (2-component type)
MS: Commercial modified silicone sealant (2-component type)
Outdoor exposure: Funamicho, Minato-ku, Nagoya-shi, Japan; exposure angle: 30° (south-facing); exposure period: 1 year

Figure 10: Comparison of overcoating paint contamination between ARUFON and commercially available sealants

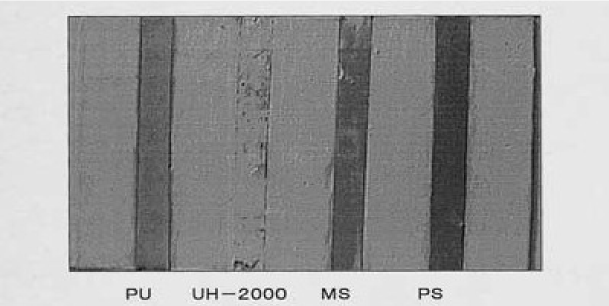


AU1: Commercial acrylic urethane sealant (Company A)
AU2: Commercial acrylic urethane sealant (Company B)
Outdoor exposure: Funamicho, Minato-ku, Nagoya-shi, Japan; exposure angle: 30° (south-facing); exposure period: 4 months

Figure 11: Comparison of overcoating paint contamination between ARUFON and commercially available acrylic urethane sealants

For reference, **Figure 12** shows the state after one year of exposure.

ARUFON UH-2000 can be blended with base polymers of polyurethane sealants to enhance the weather resistance of polyurethane sealants. **Table 6** shows the relationship between blend ratio and QUV accelerated weather resistance when polyoxypropylene with a terminal hydroxyl group (PPG), which is a base polymer, was blended with ARUFON UH-2000. A blend of only 20% ARUFON UH-2000 can noticeably improve weather resistance. It also shows that the weather resistance becomes higher as the percentage of UH-2000 increases.



PU: Polyurethane sealant
MS: Modified silicone sealant
PS: Polysulfide sealant

Figure 12: Contamination test on overcoating paints due to outdoor exposure

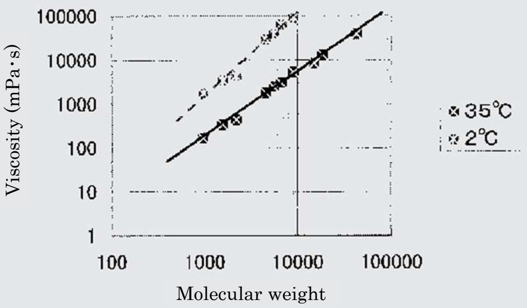
Table 6: Tensile properties and weather resistance of ARUFON/PPG blended systems

Blending ratio (by weight)		Initial strength	Initial elongation	After accelerated weathering test (%)	
UH-2000	PPG	MPa	%	Tb retention	Eb retention
100	0	0.33	700	93	97
80	20	0.29	700	74	94
60	40	0.31	800	62	78
40	60	0.30	750	55	63
20	80	0.31	900	43	61
0	100	0.22	900	Dissolved	←

PPG: Polyoxypropylene containing a terminal hydroxyl group with molecular weight = 4,000
Curing agent: TDI-modified polyoxypropylene (bifunctional)
Sealant formulation: See Table 2
Curing conditions: 2 weeks at room temperature; film thickness: 1 mm
Tensile condition: 5 cm/min
Accelerated weathering resistance test: QUV tester, after 1,000 hours

3.2 Evaluation as a plasticizer

Acrylic polymers with long-chain alkyl groups have a low glass transition temperature and stay in liquid form at room temperature, making them suitable for use as plasticizers. **Figure 13** shows the relationship between molecular weight and viscosity of common acrylic polymers. Two sets of measurement data are shown: 35°C, simulating summer, and 2°C, simulating winter. When used as a plasticizer, it is important that adequate viscosity is maintained from low to high temperatures. Considering the viscosity that allows pipe transport even in winter, a molecular weight (Mw) of 6,000 or less is preferable.



Molecular weight: Mw (weight average)
Viscosity: Measured with a B-type viscometer

Figure 13: Relationship between molecular weight and viscosity of UP-1000-based polymers

The ARUFON UP-1000 Series is a non-functional acrylic polymer with a molecular weight and viscosity optimal for a plasticizer. It is free of so-called endocrine disruptors and can enhance the weather resistance of sealants.

Currently, three grades have been developed, each of which is used for different purposes. **Table 7** shows the compatibility of the UP-1000 Series with the sealant base polymers. UP-1000 and the low-viscosity-type UP-1020 are suitable for sealant applications, while UP-1010 is recommended as a plasticizer for plastics.

Table 7: UP-1000 Series properties and compatibility with base polymers

		UP1000	UP1010	UP1020	DOP
Physical properties	State	Liquid	Liquid	Liquid	Liquid
	NV (%)	≥ 98	≥ 98	≥ 94	≥ 99
	Molecular weight (Mw)	3,000	1,500	1,500	390
	Viscosity (mPa･s)	1,000	4,000	400	60
	SP value	11.7	15.1	12.7	14.3
	Tg (°C)	-60	-32	-66	-
Compatibility	PPG *1	○	×	○	○
	PEG *2	×	×	×	×
	Modified silicone	○	×	○	○
	Acrylic polyol	○	×	○	○
	MDI-modified PPG *3	△	-	△○	○
	TDI-modified PPG *3	○	-	○	○

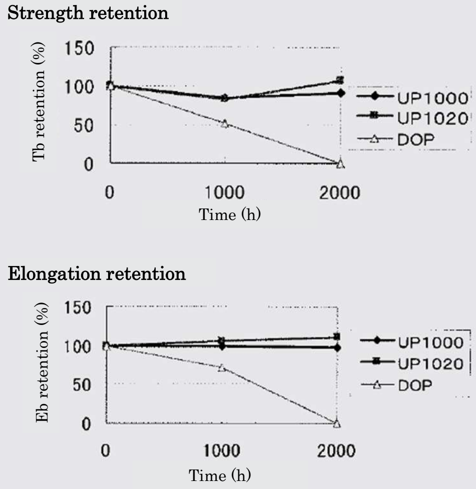
*1: Hydroxyl-terminated polyoxypropylene with a molecular weight of 4,000
*2: Hydroxyl-terminated polyoxyethylene with a molecular weight of 1,000
*3: Isocyanate-terminated polyoxypropylene
Base polymer/plasticizer = 1/1 (by weight)
SP values were calculated from the solubility tolerance with acetone and water
Tg was measured by DSC (inflection point)
Compatibility was visually observed by casting on a glass plate

Table 8 shows the results of tensile properties and weather resistance when the UP-1000 Series is used as a plasticizer for various sealants. Compared to dioctyl phthalate (DOP), which has been conventionally used as a plasticizer, the compatibility with the base polymer and physical properties are at a comparable level. Furthermore, it shows sufficient weather resistance that cannot be achieved with DOP. For reference, **Figure 14** shows the tensile properties (retention) of modified silicone sealants prepared with the formulation in **Table 9** after 2,000 hours of QUV accelerated weathering test, and **Figure 15** shows photographs of the surfaces. These figures show that the sealant using DOP deteriorated, while the sealants using ARUFON UP-1000 and UP-1020 showed no abnormalities.

Table 8: Performance as a plasticizer and weather resistance

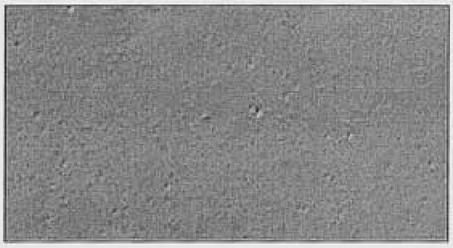
Base polymer	Plasticizer	Bleeding	Initial value			After 1,000 hours of QUV	
			50% modulus	Breaking strength	Elongation at break	Retention (%)	
			(MPa)	(MPa)	(%)	Breaking strength	Elongation at break
PPG *1	UP-1000	None	-	0.3	860	58	131
	DOP	Present	-	0.2	800	Dissolved	←
Modified silicone *2	UP-1000	None	0.2	0.7	410	95	122
	DOP	Present	0.3	0.7	390	52	71
Acrylic polyol *3	UP-1000	None	0.1	0.3	440	96	104
	DOP	Present	0.2	0.4	390	90	95

*1 PPG: Hydroxyl-terminated polyoxypropylene; see Table 2 for sealant formulation; TDI-modified polyoxypropylene (bifunctional/trifunctional) used as the curing agent
*2 Modified silicone: Manufactured by Kaneka Corporation; see Table 9 for sealant formulation
*3 Acrylic polyol: ARUFON UH-2000; see Table 2 for sealant formulation; TDI-modified polyoxypropylene (bifunctional) used as the curing agent
Curing conditions: 2 weeks at room temperature
Tensile condition: 5 cm/min

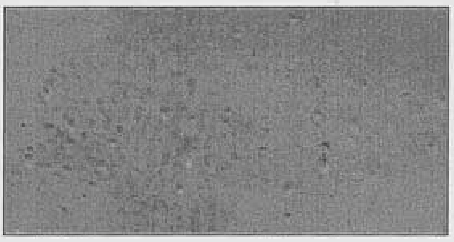


See Table 9 for formulation
See Figure 6 for weathering test conditions.

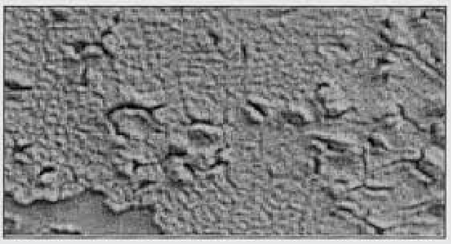
Figure 14: Relationship between plasticizer type and QUV accelerated weather resistance



UP-1000 used as the plasticizer (see formulation in Table 9)



UP-1020 used as the plasticizer (see formulation in Table 9)



DOP used as the plasticizer (see formulation in Table 9)

Figure 15: Surface condition of modified silicone after 2,000 hours of QUV

Table 9: An example of modified silicone formulations

Component	Parts by weight
Modified silicone	100
Plasticizer	50
Calcium carbonate	120
Titanium dioxide	20
Antioxidant	8
Curing accelerator	1

4. Conclusion

We continue to investigate new acrylic polymers using UFO technology, and are currently developing polymers for paints, plastic additives, and various emulsions. In the area of base polymers for sealants, we continue to investigate ways to further improve weather resistance. We hope to continue to launch new grades and improve existing grades while listening to the opinions and requests of our customers.

Reference

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