ThreeBond TECHNICAL NEWS

ThreeBond Technical News
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Pre-Irradiation System: Applications

Introduction

Photosetting resins offer several benefits:

- fast curing
- one-part, solvent-free compositions
- superior workability

These characteristics make them ideal for adhesive, sealant, and coating applications, which contribute significantly to industry. Still, for most applications, the cured products of irradiated photosetting resins are used simply as they are: as paints, printing inks, adhesives, and sealants.

ThreeBond would like to propose a new concept, which it calls a pre-irradiation system. Through photo irradiation, this system seeks to provide resins with new functionality going beyond the mere curing provided by conventional methods.

This paper discusses this new pre-irradiation system and various applications, with a special focus on P-MEC, which has made possible solvent-free compositions by harnessing light; G-II, which increases viscosity with irradiation to produce sealants with superior initial sealing properties; and EPCS, which achieves curing shadow area by activating catalysts.

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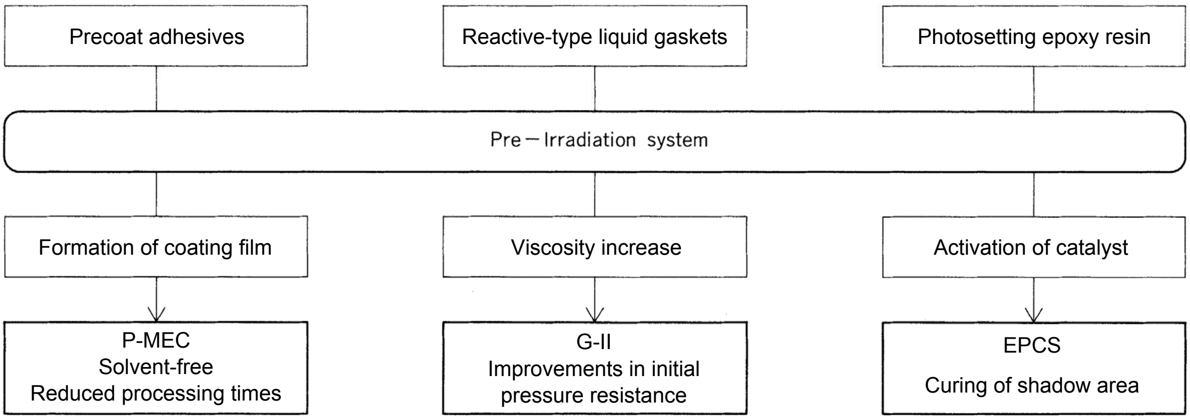


1. Solvent-Free Photosetting Binder-Type MEC Coating (Tentative Name: P-MEC)

1-1. Background

The MicroEnCapsulation bolt pre-coating process (MEC; the acronym used hereafter) refers to a special coating of microencapsulated highly-reactive binder applied to bolts to give the bolts a lock-and-seal function. The coating remains inactive until the bolt is used. When the bolts are fastened with nuts or by other means, the microcapsules are broken and the binder is released, triggering a polymerization reaction that keeps the bolt from coming loose while preventing leaks from the bolted area.

Since its development approximately 20 years ago, MEC coating has enjoyed a long and successful history as an agent used to prevent bolt loosening and leaks. It has become an essential component of sealants and binders for applications that involve significant levels of vibration and impact, including automobiles, vehicles, agricultural machinery, and construction machinery, as well as applications that require light weight, compact design, and high precision, such as electric, electronic, and precision instruments.

The following are the main constituents of a raw MEC coating solution:

(1) microcapsules
(2) catalyst or curing agent
(3) binder
(4) organic solvent

Organic solvents, mainly chlorinated solvents and aromatic solvents, have been widely used to dissolve binders or to adjust viscosity. However, growing environmental awareness in recent years has reduced their use. A complete ban on 1,1,1-tricholoethane usage was imposed by the end of 1995; aromatic solvents such as toluene and xylene are regulated under the Fire Service Act, Labor Safety and Sanitation Law, and Offensive Odor Control Law; and 1,1,1-tricholoethane is listed as an ozone-depleting substance under the U.S. Clean Air Act.

To eliminate the need to use such substances, we applied the concept of the pre-irradiation system to develop a solvent-free MEC coating that uses no organic solvents. We call this system photo-MEC coating (hereafter abbreviated “P-MEC”).

1-2. P-MEC Coating: Overview

As a binder, P-MEC coating uses a substance that cures when exposed to light, rather than conventional solvent-type binders. This reduces drying times and eliminates the need for solvents.

As Table 1 shows, conventional MEC coatings require a drying process for the solvent after application. In the case of M10 bolts, this time-consuming process requires two hours for natural air drying and 30 minutes for forced drying at 50-60°C. The procedure also requires a large area for the bolts to dry before packing and shipping.

In contrast, the steps for coat application → irradiation → complete film formation can be completed in 20-30 seconds. Since the bolts can be shipped as finished products immediately after irradiation, the space required for the coating process is reduced significantly.

Table 1. Comparison of processing times (for M10 bolts)

	Conventional MEC	P-MEC
Processing time	Natural air drying 2-6 hours Forced drying 50-60°C × 30 min.	20-30 sec.

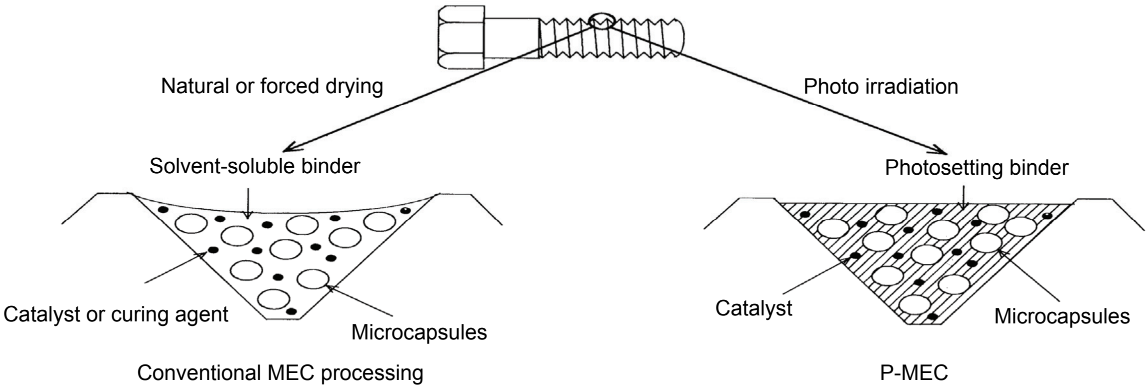


Figure 1. Comparison of Constituents

Table 2 shows the performance of P-MEC when using microcapsules containing epoxy resin. For comparison, we show the results of torque testing under the same testing conditions for ThreeBond 2430 (hereafter abbreviated as TB2430), a conventional epoxy-type coating.

The tests show P-MEC offers equivalent or better performance.

P-MEC provides answers to various questions posed by growing environmental awareness. We believe it will become the mainstream for pre-coated bolt products. Nevertheless, the technology remains in its early stages. We seek to achieve rapid commercialization by incorporating requests and feedback from our customers to produce a product meeting your needs.

Table 2. Comparison of loosening torque

Items	Units/ Conditions	Measured values	
		TB2430	P-MEC
Loosening torque	N•m at 25°C (kgf•cm)	37 ~ 54 (380 ~ 550)	51 ~ 61 (520 ~ 620)
	N•m at 90°C (kgf•cm)	27 ~ 33 (280 ~ 340)	35 ~ 38 (360 ~ 390)

(Measurement Conditions)

- Bolt: M10 × P1.5
- P-MEC coating: Following application of the P-MEC concentrate, we performed photo irradiation to a cumulative light dose of 6,000 mJ/cm^2.
- Method of measurement: Each coated bolt was inserted into two flat washers and fastened to the nut at a torque of 29.4 N·m (300 kgf·cm), then allowed to stand at room temperature for 48 hours before we measured loosening toque.
  For the heat-resistance test, we also measured loosening torque for a completely cured bolt at 90°C.

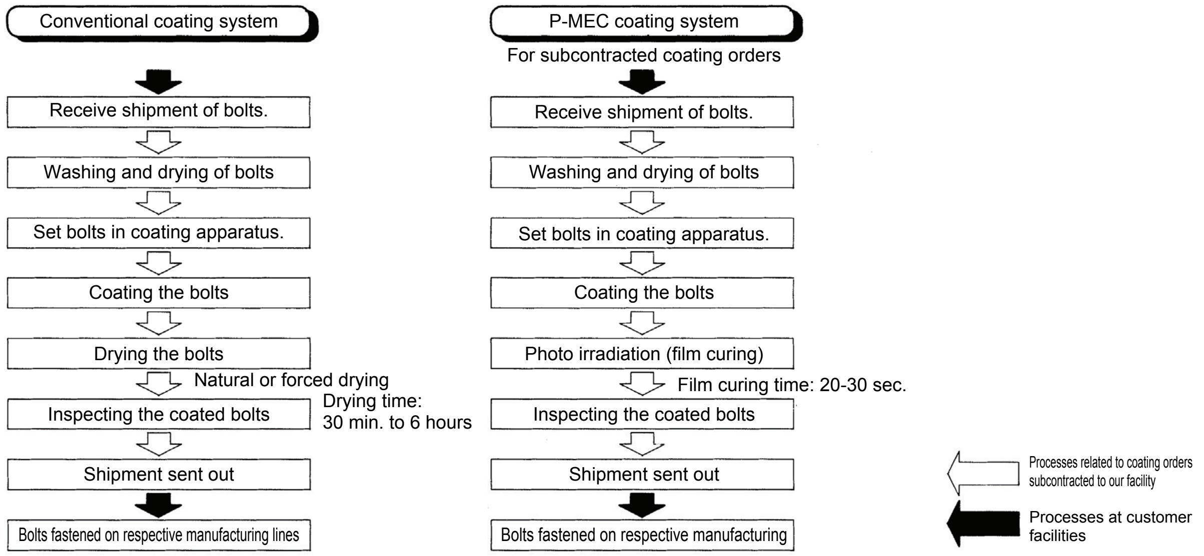


Figure 2. Comparison of the General Scheme of Processing Systems

2. Photothickening Liquid Gasket (Tentative Name: G-II)

2-1. Background

Liquid gaskets include silicone-based, acrylic ester-based, and synthetic rubber-based gasket types. Currently used in a wide range of applications, these liquid gaskets allow adhesive sealing of materials such as asbestos that solid gaskets cannot seal. They eliminate the possibility of leaks due to gasket fatigue and allow coating application and installation to be performed on site. Liquid gaskets are also easily managed. These advantages have made liquid gaskets the preferred choice over solid gaskets and contributed to widespread use. In the automotive industry, the OLGS (On-Line Gasket System), which uses a one-part RTV silicone-based composition, is used for various components, including oil pans, gear boxes, and water pumps.

The one-part RTV silicone-based composition offers excellent thermal resistance, chemical resistance, and elastic properties, making it ideal for applications around the engine unit where the effects of vibrations and heat are significant. However, because atmospheric moisture induces crosslinking reactions in the one-part RTV silicone-based composition, it can take some time before the curing process is complete (standard curing condition: 25°C × 55% RH × 1 week), making it unsuitable for applications that would entail exposure to pressure immediately after installation. In short, the composition has poor initial pressure resistance. Until now, countermeasures for applications requiring initial pressure resistance involved increasing the initial viscosity of the silicone and dramatically accelerating curing rates. Manufacturing high-initial-viscosity silicone is difficult due to the high loads required. Handling high-initial-viscosity silicone requires a large dispensing pump that inevitably slows line speed. An increase in curing speed also has adverse effects, including significantly reduced shelf life, as well as poor sealing properties attributable to the weak sealing power associated with progressive surface curing during the coating and installation process.

To resolve these problems, we applied the pre-irradiation system concept to develop a composite G-II made from a combination of one-part RTV silicone and photosetting resin.

2-2. G-II: Overview

The G-II system is a liquid gasket whose viscosity increases rapidly when irradiated with light, giving the product high initial pressure resistance and adhesive strength immediately after installation. G-II offers the following benefits:

- Low resin viscosity (initial viscosity) for high workability
- High initial pressure resistance achieved by photo irradiation
- Applicability to parts having large gaps
- Excellent adhesive properties

These features allow use of G-II for applications for which conventional liquid gaskets are poorly suited. They also improve productivity by reducing initial leakage (in the uncured state).

As with conventional products, the main constituent of G-II is a condensation-type silicone, to which photosetting components are added. After application, crosslinking reactions in the photosetting resins occur within the silicone component during the photo irradiation process. As shown in Fig. 4, the cured materials are scattered within the gasket and act almost as filler agents, increasing viscosity. Silicone, the main constituent, eventually cures by reacting with atmospheric moisture, as with conventional products.

The key distinction of G-II is that it is merely thickened by pre-irradiation, not cured. This gives G-II an adhesive sealing effect, like conventional OLGS.

Compared below are the physical and mechanical properties of G-II and ThreeBond 1217 (hereafter abbreviated TB1217), a high-viscosity product in our current product lineup.

Table 3. Comparison of G-II and TB1217: Physical and Mechanical Properties

Items	Units and conditions	Measured values	
		G-II	TB1217
Appearance	Visual inspection	Pale white paste	Gray paste
Specific gravity	at 25°C	1.05	1.40
Viscosity (SOD viscometer)	Pa•s at 25°C (P)	25 (250)	180 (1800)
* Hardness	JIS-A	59	57
* Elasticity	%	300	240
* Tensile strength	MPa (kgf/cm^2)	6.0 (61)	2.3 (23)
* Shear bond strength Fe/Fe	MPa (kgf/cm^2)	2.16 (22)	1.67 (17)
* Shear bond strength Al/Al	MPa (kgf/cm^2)	1.47 (15)	1.77 (18)
* Pressure resistance	MPa (kgf/cm^2)	> 2.0 (> 20)	> 2.0 (> 20)

* To measure the properties of the cured G-II, we used a cured product with viscosity increased by standard irradiation of 3,000 mJ/cm^2 (Final setting time: 25°C × 55% RH × 1 week).

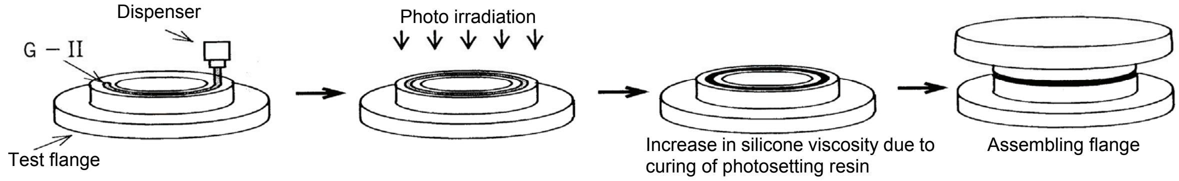
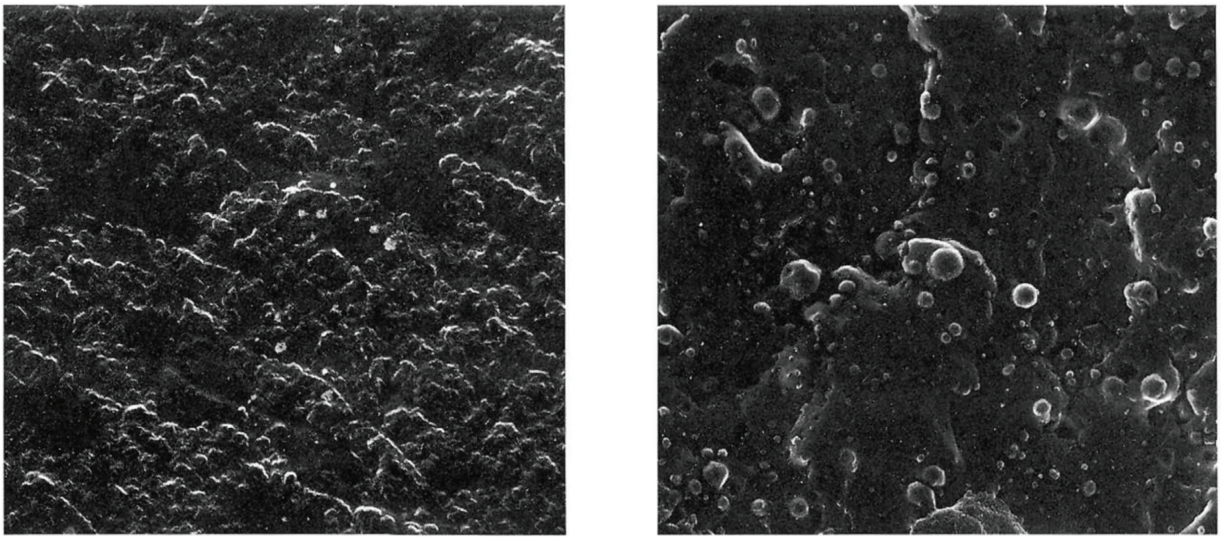


Figure 3. Simplified Process Diagram



Before photo irradiation

After photo irradiation

Figure 4. Microscopic Photograph of Cured G-II Product

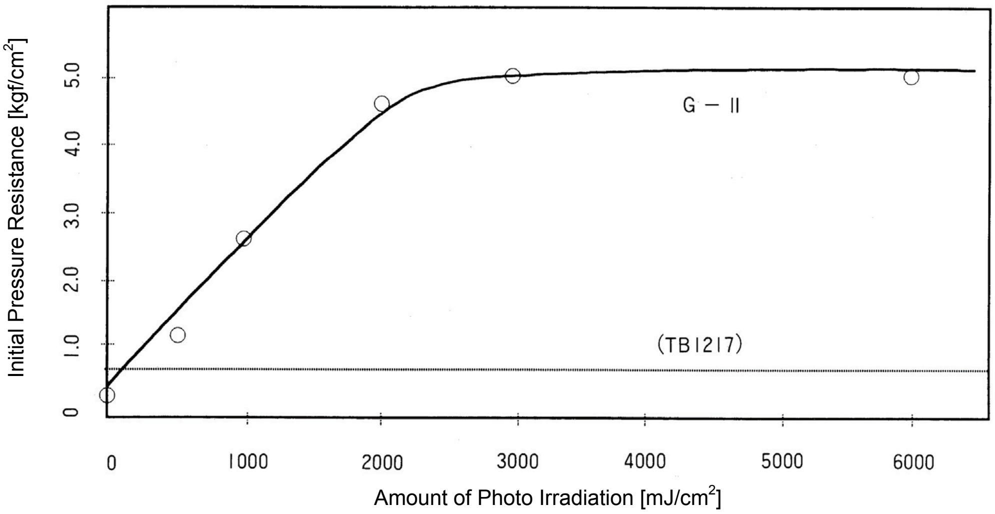


Figure 5. Comparison of Initial Pressure Resistance of G-II and TB1217

As the table shows, G-II has extremely low viscosity, approximately 1/7 that of TB1217. Figure 5 shows how initial pressure resistance changes during the photo irradiation process. When G-II is exposed to light, pressure resistance increases rapidly, reaching a value of 0.5 MPa (= 5.0 kgf/cm^2) following irradiation of 3,000 mJ/cm^2. In contrast, the initial pressure resistance of TB1217 is a mere 0.06 MPa (= 0.6 kgf/cm^2). G-II is clearly superior in terms of initial pressure resistance.

G-II also offers excellent adhesive properties comparable to conventional products, a characteristic achieved by providing the G-II with photothickening properties, rather than photocuring properties, to secure high adhesive strength.

We achieved the high initial pressure resistance of G-II by adding photosetting properties into one-part RTV silicone to give it photothickening properties. Future efforts will target rapid commercialization, focusing on the development of a photo-irradiation system suitable for installation on actual manufacturing lines and on tests involving actual work pieces.

3. One-Part, Solvent-Free, Fast- and Room-Temperature-Curing System (Tentative Name: EPCS)

3-1. Background

The biggest challenge presented by photosetting resins is that areas not reached by light—in other words, the areas that remain un-irradiated—do not cure. For this reason, photosetting resins cannot be used to make parts that have areas in shadow or opaque areas, despite the numerous other advantages offered by photosetting resins. Since actual parts often have such shadow or opaque areas, this issue has limited the scope of applications for photosetting resins.

To make photosetting resins suitable for such applications, we have taken various measures that adopt dual-curing properties. Some examples are given below:

(1) Addition of heat curing properties
(2) Addition of anaerobic curing properties
(3) Addition of primer curing properties
(4) Addition of moisture curing properties
(5) Addition of two-part resin curing properties

However, all of the above apply only to radical-polymerizable acrylic resins. Radical polymerization is susceptible to oxygen inhibition, as well as problems including significant cure shrinkage and outgassing. Cation-polymerizable resins do not present these issues but cannot be used with the above methods for curing un-irradiated parts.

Dark curing, in which reactions continue to advance even after irradiation is halted, is a well-known phenomenon observed with photosetting cation-polymerizable resins. Some studies have suggested that dark curing may allow bond formation in opaque components and potting in un-irradiated areas. In addition, research is underway to develop a coating method and corresponding photo-irradiation unit that will irradiate photosetting resins as they are being ejected in liquid form from the dispenser into a cast for curing.

However, the dark curing experiment assumes a case in which the resin is first applied in a thin coating to a substrate and irradiated, after which another substrate is placed over it to sandwich the resin. This procedure makes it unsuitable for a unit that irradiates resins as they are being ejected.

To overcome this problem, we introduced the concept of pre-irradiation, in which a resin is first irradiated with energy (light), then coated onto the substrate in its as-yet uncured form, and allowed to cure after it is cast in place. We call this newly developed system the Energy Precharge Curing System (hereafter abbreviated as EPCS).

3-2. EPCS: Overview

EPCS is a one-part, solvent-free, fast- and room-temperature-curing system of epoxy resin that uses light as its energy source but also relies on the phenomenon of dark curing of cationic polymerization to cure portions that light cannot reach.

Some features of the epoxy-based (cation-polymerizable) photosetting resin are listed below.

- Superior heat and chemical resistance
- Low skin irritability and reduced odor
- Zero susceptibility to oxygen inhibition during curing
- Significantly less cure shrinkage

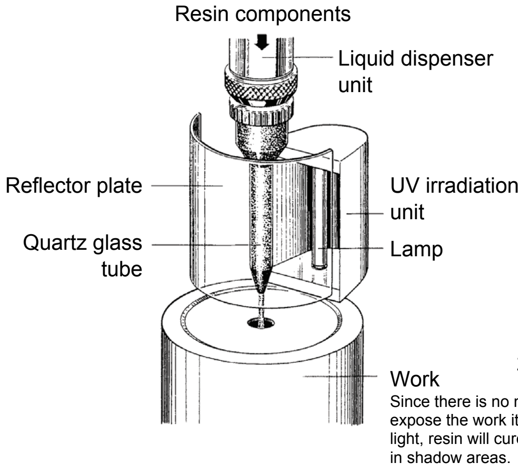
We expect growing demand for this photosetting resin in the coming years.

Figure 6 shows a schematic diagram of EPCS. As the photosetting epoxy resin is ejected from the dispenser and passes through a transparent tube, it is irradiated by light and moved to an area where the resin is allowed to cure. This system cannot be used for acrylic photosetting resins that cure rapidly (radical polymerization).

We used the apparatus shown in Fig. 7 to perform a test. We poured photosetting epoxy resin into a polypropylene disposable mixer while exposing it to light from the sides of the mixer. This irradiation was performed with a 200-W spot-type irradiation unit. Triple fiber optic light guides were used to irradiate the mixer from three directions from a distance of 20 mm. The resin ejection rate was defined as the volume of resin ejected into a measuring cup during a period of 30 seconds while light was irradiated with the apparatus shown in Fig. 7. We measured the time required for resin gelation to complete, from the start of ejection, as well as the hardness of the cured product after being allowed to stand at room temperature for one day. In this test, the resin ejection rate corresponds to the amount of irradiation for normal resin curing systems. Slower ejection rates mean longer irradiation times and greater irradiation. An ejection rate of 0 mg/s corresponds to conditions for conventional irradiation procedures (conveyor belt systems and spot-irradiator curing). The results are shown in Fig. 8.

Figure 8 shows that gelation takes place immediately after resin ejection at an ejection rate of 40 mg/s. The hardness we measured after allowing the resin to stand at room temperature for one day was 87, equal to resin cured by conventional methods (JIS-D). Similarly, the gelation time was approximately 15 minutes for an ejection rate of 100 mg/s; the hardness after one day was 87 (JIS-D). Resin gelation takes longer at higher ejection rates, which are associated with reduced irradiation. When ejection rates exceed 150 mg/s, the resin fails to cure completely. Conversely, at ejection rates below 40 mg/s, the resin cured inside the mixer, preventing ejection. Thus, the range of possible ejection rates for this device is 40 to 150 mg/s. If this condition is met, the EPCS will allow the resin to cure, even in areas light cannot reach.

We believe the EPCS will overcome the disadvantages of photosetting resin and expand its scope of applications. Many issues remain to be resolved, including the determination of a basic resin blend, establishing standard conditions for the resin/system, and compatibility with applications that require various shapes, among others. Nevertheless, we anticipate rapid commercialization of EPCS.



Since there is no need to expose the work itself to light, resin will cure, even in shadow areas.

Figure 6. Schematic Diagram of EPCS

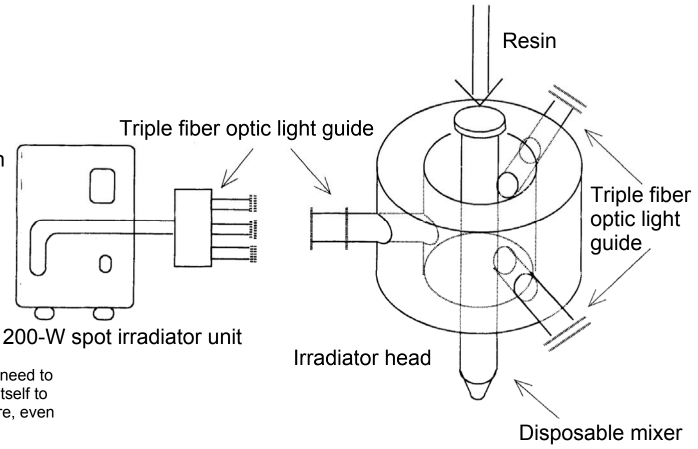


Figure 7. Test Apparatus

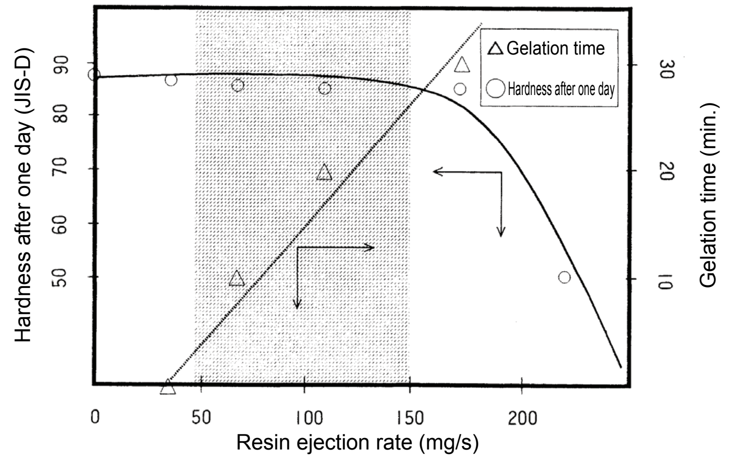


Figure 8. Relationship between Ejection Speed/Hardness/Gelation Time

Concluding Remarks

We hope this paper has clearly described the pre-irradiation system concept proposed by ThreeBond. Although this paper focused on only three systems based on this concept, we believe it can be modified to suit a wide range of applications.

ThreeBond will continue to pursue research and development into new technologies. Our goal is to develop technologies and products that satisfy the needs of our customers.

<References>
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J. Radiat. Curing/Radiat. Curing Spring, Wu. K. and Weigl S (1991)
ThreeBond Technical News No. 41 (1993)

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Opening the Basic Patent for Hy-Molding (System D)

Hy-Molding (System D), a system introduced in ThreeBond Technical News vol. 24, is used to manufacture plastic composite molded components with an integrated (hybrid) gasket unit for the elastic sealant.

The basic patent for our Hy-Molding (System D) was registered on April 8, 1993.

Patent Registration No.: 1748590
Patent Publication No.: Japanese Patent H4-38567
Date of Application: Sept. 1, 1983

Based on the belief that the patent in question will have widespread industrial applications, ThreeBond will license the patent at no cost for applications that use our elastic sealant materials. The patent will be licensed for a fee for applications using sealant materials from other manufacturers.

To license this patent, please contact us at the following address:

Division in charge: Patents Division
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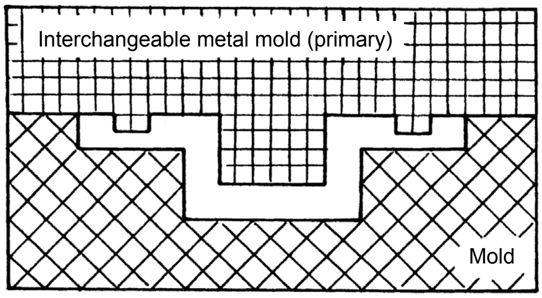
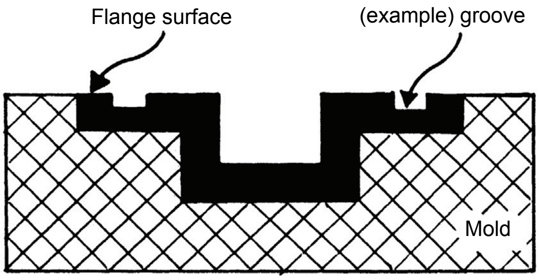
Summary of Patent Rights

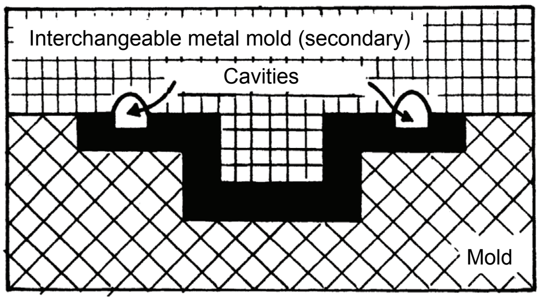
(1) The process uses a forming machine equipped with integrated and interchangeable metal molds (primary and secondary molds).



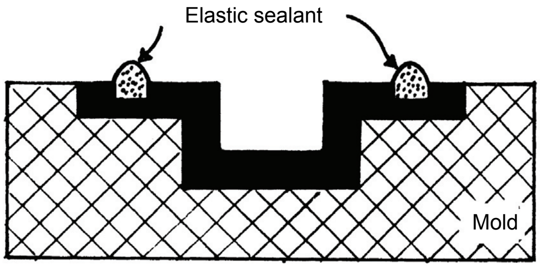
(2) A plastic component has holes, grooves, and indentation patterns formed on the flange surface.



(3) The aforementioned plastic component is not removed from the mold, but covered instead by a separate mold to create cavities for the secondary molding process.



(4) The aforementioned cavities are filled by plastic sealant in the secondary molding process.



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