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Light-Curing Resins

Introduction

It has passed more than ten years since Three Bond put ultraviolet-curing resins on the market. At present, more than 100 types of resins have been developed, including the Three Bond 3000 and 3100 series' and some prototypes, which have been used in a wide range of fields, including the electrical and electronic markets as well as the automobile, optic, and medical fields.

The present report features "light" curing resins, including not only resins cured by radial rays such as ultraviolet and electron rays, but also resins cured by visible light irradiation.

In the present report, the characteristic products and prototypes of ultraviolet-curing resins and new light-curing resins under study are detailed.

Contents

I. UV-imide

1. Background

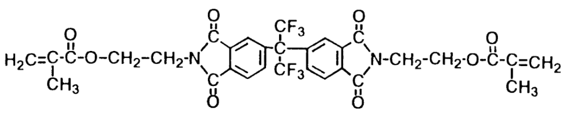
The industrial use of light-curing resins, which are characterized by an increase in molecular weight caused by the chain polymerization of monomers, began around 1960. At present, these resins are used for a wide range of applications, such as in plate-making materials, resists, paints, inks, and electrical and electronic materials.

Light-curing resins are generally acrylic-based, and are thus inferior in heat resistance. Approximately 15 years ago, Mr. Rubner at Siemens presented what might be described as the original version of current light-curing polyimides. Since then, many studies have been conducted showing that light-curing resins have excellent heat resistance. However, most of the resins dissolve in very few organic solvents, and their applications have many limitations.

The following section describes a light-curing imide monomer that has been under study at Three Bond. It has light-functional groups at both terminals of the imide skeleton, and exhibits excellent solubility and heat resistance.

2. Structure of the light-curing imide monomer

Scheme 1-1 shows the structural formula of "6FDAI," a light-curing imide monomer under development. 6FDAI is a bismethacrylate monomer comprising an imide structure having two trifluoromethyl groups in a molecule.



Scheme 1-1

3. Solubility of 6FDAI

6FDAI dissolves in polar organic solvents such as DMF and NMP, and general organic solvents such as chloroform, acetone, and alcohol. In addition, 6FDAI is highly soluble in various light reactive monomers.

4. Light-polymerization and thermal properties of 6FDAI

Fig. 1-1 shows the light-polymerization rate and 5% weight-loss temperature of 6FDAI. The light-polymerization rate was determined through conversion of the methacryloyl group measured using FT-IR spectroscopy, and the 5% weight-loss temperature was determined by measuring the TG under a nitrogen atmosphere. The figure indicates that 6FDAI exhibits excellent thermal stability even when the light-polymerization is inadequate. The low degree of light-polymerization is considered to be due to the solid-phase reaction.

Table 1-1 shows the TG of 6FDAI, the light reactive monomer, and mixtures thereof measured under a nitrogen atmosphere. The 5% weight-loss temperature of HEMA, which is a mono functional light reactive monomer, was 274°C, and that of bi-functional EGDM was 282°C. The thermal stability increased slightly with an increase in the number of functional groups, but the increment in the 5% weight-loss temperature was approximately 10°C. On the other hand, the temperature of bi-functional 6FDAI was 374°C, indicating its excellent thermal stability. The mixtures of 6FDAI and HEMA exhibited higher thermal stability than HEMA alone, suggesting the ability of 6FDAI to improve the heat resistance of light-curing resins.

5. Future prospects

The above provides an outline of 6FDAI. 6FDAI is still under development, and its electrical and optical properties have been studied. 6FDAI is expected to find many applications in the electrical and electronic fields in the future.

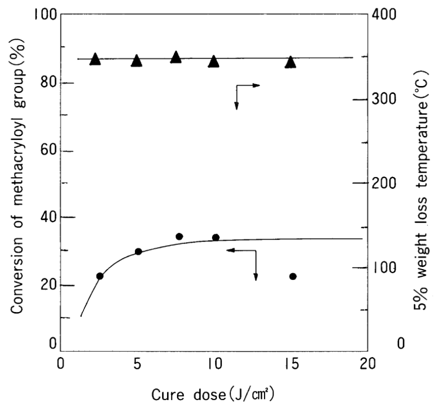


Fig.1-1. Light-polymerization and 5% weight loss temperature of 6FDAI.

Cured with 2mol% 2-Methyl-1- [4- (methylthio) phenil]-2- morpholinopropane-1-one by using one high pressure mercury lamp (4kW).5% weight loss temperature was measured by TG at a heating rate of 10°C/min in nitrogen.
●: Conversion of methacryloyl group, ▲: 5% weight loss temperature.

Table 1-1. Thermal behavior data of cured 6FDAI and UV reactive monomers.[a)]

	T_5 [b)]	T_{10} [c)]
6FDAI	374	408
6FDAI (10mol%)/HEMA [d)]	303	328
6FDAI (20mol%)/HEMA	310	333
HEMA	274	289
EGDM [e)]	282	289

a) Cured with 2mol% 2-Methyl-1- [4- (methylthio) phenil] -2- morpholinopropane-1-one by using one high pressure mercury lamp (4kW). The cure dose was 20J/cm^2.
b) 5%weight loss temperature was measured by TG at a heating rate of 10°C /min in nitrogen.
c) 10% weight loss temperature.
d) 2-Hydoroxyethyl methacrylate.
e) Ethyleneglycol dimethacrylate.

II. Visible-light-curing resins

1. Background

Recently, so-called "ultraviolet-curing resins" have come onto the market. These resins use ultraviolet light as polymerization energy, as it enabled them to be made one-part, solventless, and fast-curing. The properties of the resins have significantly overcome the drawbacks of conventional adhesives, and thus demand for ultraviolet-curing resins is increasing year by year. However, materials that are susceptible or impermeable to ultraviolet light are increasing due to the current remarkable advancements in the material technology. In the adhesion of these materials, outmoded curing resins must be used instead of ultraviolet-curing resins, and therefore technology for causing polymerization using active energy rays other than ultraviolet light is attracting attention. Of the light-curing resins, this section briefly describes the adhesives cured by light in the visible region.

2. Visible-light-curing resins of Three Bond

Unlike conventional ultraviolet-curing resins, the visible light-curing resins of Three-Bond (hereinafter referred to as the "VL Series") are cured by the irradiation of light with an irradiation wavelength of 400 nm or longer. As the effective wavelength is in the visible light region, the visible light-curing resins have the following advantages over conventional ultraviolet-curing resins:

1) Visible light-curing resins enable adhesion between materials susceptible or impermeable to ultraviolet light.
2) The irradiation energy for the resins is visible light that is easy on the human body, unlike ultraviolet light.
3) As the resins can be cured by simple radiator systems such as general-purpose halogen lamps, the cost of radiators can be reduced.
4) As the effective wavelength is long, the resins allow the loading of more fillers than ultraviolet-curing resins.

However, when general purpose light sources are used, visible light-curing resins may take longer to cure than ultraviolet-curing resins, as general purpose light sources have lower power than general radiators used for ultraviolet-curing resins.

3. Properties and performance

The Three Bond VL Series is composed of a VL-001 type for laminated glass, a VL-002 type for ultraviolet impermeable engineering plastics, and a VL-003 type for general purposes. Table 2-1 shows their appearance and basic physical properties. All three types have low viscosity, and their adhesiveness to various materials is nearly equal to that of commercially available ultraviolet-curing resins. The VL-001 type is also characterized by the low refractive index of its cured resin. Fig. 2-1 shows the relationship between the irradiation time and the adhesive strength of the VL-001 type under shear for a glass/glass test piece. According to the result, the adhesive strength under shear became almost constant at a light irradiation time of approximately 90 seconds, in spite of the low intensity of illumination.

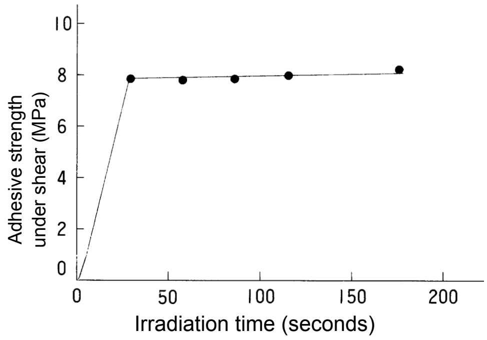


Fig. 2-1. Relationship between the irradiation time and the adhesive strength of the VL-001 type under shear for a glass/glass test piece
(Irradiation conditions)
Intensity of illumination: 5.4 mW/cm^2 (420 nm)
Light source: 300-W halogen lamp
(All of the adherends were fractured.)

Table 2-1. Appearance and basic physical properties of visible-light-curing resins

Grade	VL-001	VL-002	VL-003
Appearance	transparent liquid	transparent liquid	transparent liquid
Viscosity (Pa•s)	1.5	0.7	7
Specific gravity	1.03	1.03	1.05
Hardness (JIS-D)	85	50	50
Water absorption (2 hours of boiling)	1	1.2	0.7
Adhesive strength under shear (MPa)	9.8 (Glass/glass)	95 (PC/PC)	90 (Glass/glass)
Refractive index (25°C)	1.47	1.51	-
Glass transition temperature (°C)	106	65	58

4. Future prospects

The Three Bond VL Series described above is a series of a new type of light-curing resins using visible light. The resins require further development and improvement in order to reduce their curing time.

In the future, it will be necessary to change the light sources for light-curing resins to those with longer wavelengths, in order to increase their sensitivity.

III. Ultraviolet-curing silicon resins

1. Background

At present, silicon resins are very widely used in industrial fields due to their heat resistance, cold resistance, and flexibility. The resins can be broadly divided into molding and liquid resins, and their applications include sealing, coating, molding, and potting materials.

Liquid resins are divided into two-part and one-part curing resins. Heat curing and moisture curing had been the predominant curing methods, but silicon resins cured by a new technique, ultraviolet curing, have been studied for the past ten-odd years.

This section describes the ultraviolet-curing silicon resins that have been newly developed by Three Bond.

2. Ultraviolet light

Ultraviolet light consists of electromagnetic waves with a wavelength of 10 to 400 nm. The light is attracting attention not only for its curing effect but also for its bactericidal effect. It is said that the ultraviolet curing method was first discovered in ancient Egypt, where a resin was cured by sunlight for the preservation of a mummy. At present, visible light-curing resins have been studied, as previously mentioned. Fig. 3-1 shows the classification of electromagnetic waves.

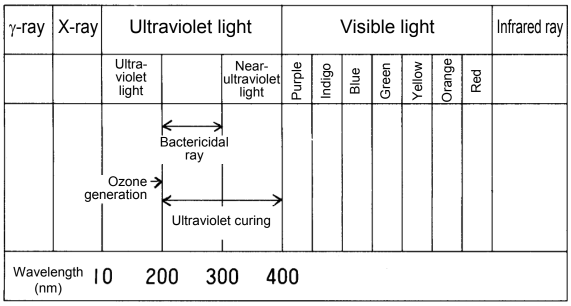


Fig. 3-1. Classification of electromagnetic waves

3. Requirements and problems against conventional resins

Conventional liquid-silicon resins have required a large amount of time, mixing, and/or heating for curing. On the other hand, conventional ultraviolet-curing resins involved the problems of heat and cold resistance and flexibility, and the drawback of the insufficient curing of areas unexposed to ultraviolet light.

The newly developed ultraviolet-curing silicon resins combine ultraviolet-curing and moisture-curing properties, and will solve the problems of conventional ultraviolet-curing resins (see Table 3-1).

Table 3-1. Comparison between the new resins and conventional resins

Properties	UV/RTV silicon	Silicon resin	UV resin
Curing time	Short	Long	Short
Heat-resistance	○	○	△
Cold-resistance	○	○	△
Flexibility	○	○	△
Skin irritation	○	○	△

4. Components and curing mechanism of the ultraviolet-curing silicone resins

The ultraviolet-curing silicon resins are composed of siloxane as the main chain, and alkoxysilane, which is a moisture reactive functional group, and the methacryloyl group, which is an ultraviolet-curing functional group, as the terminals. The formulation is comprised of the oligomer having the structure shown below, a moisture-curing catalyst, a light-initiator, a filler, an adhesion improver, and a stabilizer.

These resins cause radical polymerization when irradiated with ultraviolet light, or cause demethanolization condensation when exposed to moisture in air to form crosslinkage (see Figs. 3-2, 3-3, and 3-4).

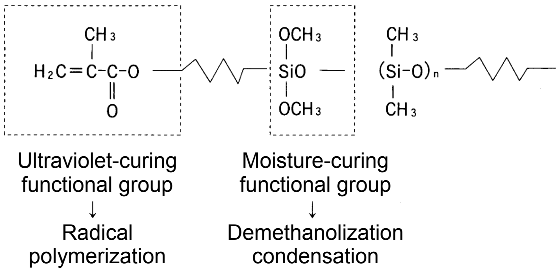


Fig. 3-2. Oligomer structure

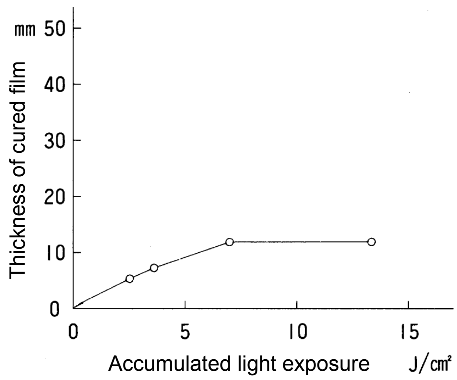


Fig. 3-3. Ultraviolet-curing property of Three Bond 3161

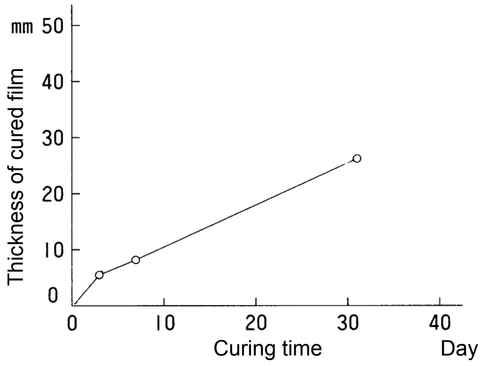


Fig. 3-4. Moisture-curing property of Three Bond 3161

5. Characteristics of Three Bond ultraviolet-curing resins

Recently, Three Bond has put three grades of ultraviolet-curing resins on the market: Three Bond 3161, 3164, and 3165. They have the properties and characteristics specified below.

1) They have excellent ultraviolet-curing properties.
2) As they are one-part and solventless, they cause less skin irritation.
3) Where ultraviolet light cannot be used, they are cured by moisture in air (dealcoholization type).
4) They have excellent cold and heat resistance (-60°C to 200°C).
5) They contain virtually no low-molecular siloxane (0.03% or lower).
6) They have good adhesive properties.

6. Uses

Once the surfaces of the resins have been cured by ultraviolet irradiation, the parts unexposed to ultraviolet light and the deep parts are cured by moisture. Thus, the resins have a very wide range of uses, including the following:

1) Adhesives, sealing, and coating materials for electrical and electronic components
2) Coating materials for electrical circuit boards
3) Adhesives, potting, and sealing materials for various electrical components
4) Other vibration-deadening and vibration absorbing materials

7. Future prospects

In the future, ultraviolet-curing silicon resins will be required to have various characteristics, such as high tensile strength, high degree of elongation, coloring (white, black), low hardness, higher RTV curing speed, flame retardancy, heat radiation property, and electrical conductivity. We hope that these ultraviolet-curing resins are applied and deployed for a wide range of uses.

Table 3-2. Properties

Test item	Unit	ThreeBond 3161	ThreeBond 3164	ThreeBond 3165
Appearance		Translucent liquid	Opaque white liquid	Opaque white paste
Viscosity	Pa•s {P}	4 {40}	50 {500}	---
Specific gravity		0.98	1.00	1.03

Table 3-3. Physical properties of cured resins

Test item	unit	ThreeBond3161	ThreeBond3164	ThreeBond3165
Hardness (JIS-A)		25	25	38
Degree of elongation	%	107	135	157
Tensile strength	Mpa {kgf/cm^2}	0.49 {5.0}	0.85 {8.7}	1.8 {18}
Volume resistivity	Ω•cm	4.0 X 10^{12}	1.3 X 10^{13}	5.3 X 10^{13}
Surface resistivity	Ω	1.7 X 10^{14}	13 X 10^{15}	3.8 X 10^{15}
Electrical breakdown strength	kV/mm	12.3	15.6	15.6
Permittivity 10^5 Hz		3.07	2.98	3.00
Dielectric dissipation factor: 10^5 Hz		0.01	0.0073	0.0061
Cure shrinkage	%	-	0.39	0.24
Heat mass change	%			
80°24h		-0.82	-0.61	-0.73
150°24h		-3	-2.1	-2.2
Adhesive strength under tensile shear	Mpa {kgf/cm^2}			
Acryl/acryl		0.36 {3.7}	1.2 {12}	0.60 {6.1}
Polycarbonate/polycarbonate		0.96 {9.8}	1.4 {14}	1.0 {10}
Glass/glass		4.2 {43}	2.8 {29}	1.6 {16}
Glass/Fe		2.0 {20}	1.3 {13}	1.7 {18}
Glass/Al		0.66 {6.8}	1.1 {11}	0.73 {7.4}
Glass/Cu		1.3 {13}	2.9 {20}	1.8 {19}

Irradiation conditions High-pressure mercury light (HMW 244-11CM type), 4 kW, 80 W/cm
Dominant wavelength: 365 nm Irradiation distance: 15 cm Intensity of illumination: 150 mW/cm^2
Curing conditions Accumulated light exposure 30 kJ/m^2 [3J/cm^2]+25°C 55% RH×7 days

IV. VL/NIR curing technique

1. Summary

What is the VL/NIR curing technique?

The VL/NIR (Visible Light/Near IR) curing technique is a curing system using a wide range of light sources, from visible light to near-infrared rays. Unlike the conventional ultraviolet-curing method, the technique uses light with wavelengths of approximately 400 to 900 nm, which cure resins quickly. One of the other characteristics of the technique is that the light sources used are halogen, xenon, and infrared lamps, which are gently to the human body and are released by relatively inexpensive radiators. This section focuses on the high loadings of fillers, which is a feature of the VL/NIR curing technique, and briefly describes automotive mending putty as one application of the technique.

2. Curing system

Before beginning to discuss the main subject, this section briefly describes the curing system used by the VL/NIR curing technology. The technique uses a combination of a dye (D^+A^-) having an absorption band in the visible/near-infrared region, and a photo-initiator (B^+N^-). As shown in Fig. 4-1, the dye excited by the light in the visible/near-infrared region transfers its energy or electrons to the photo-initiator to generate radicals, and the generated radical species initiate the polymerization.

3. Mending putty

At present, the automobile industry is putting its energies not only into production but also into repair that is referred to as "aftermarket." In many industries, recycling is taken particularly seriously in light of environmental concerns, and the automobile industry is no different. Accordingly, interest in automotive repair materials is increasing. Mending putty is synonymous with automotive repair materials. Most commercially available mending putty is two-part, and the kneading before use requires considerable experience. Most types of putty contain unsaturated polystyrene diluted with styrene, leading users to be exposed to styrene vapors during use. The Three Bond photo-curing putty described herein is a one-part, solventless photo-curing resin. Composed of one fluid, it does not require weighing or kneading, unlike conventional mending putty, and the light-curing property decreases the working time. Table 4-1 shows a comparison between light-curing putty and commercial putty. The light-curing putty is characterized by its almost unlimited pot life. General types of putty are cured with peroxides, and thus the time between kneading and application is limited. In addition, the putty is normally kneaded in an amount larger than that used in actual usage, resulting in wasting of the putty. On the other hand, the light-curing putty has no limitation on its pot life unless exposed to light, and will not cure for up to 24 hours even when exposed to fluorescent lighting. In addition, the curing time can be reduced to approximately one-fifth that of commercial putty, and the curing time will not be increased or decreased by seasonal factors. As photo-curing putty does not use styrene for dilution of the resin, it has a different odor from commercial putty, and emits little foreign odor during use. Light-curing putty has basic physical properties almost identical to those of commercial putty, and has excellent thick film curing properties.

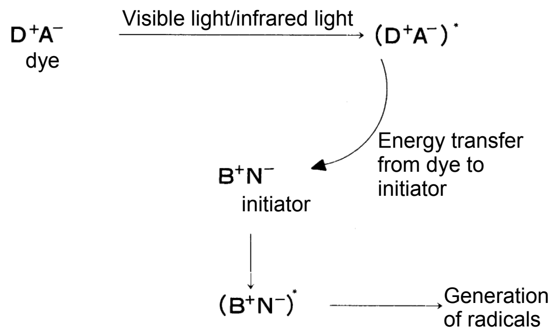


Fig. 4-1

Table 4-1. Comparison between body- repair putty resins

	Commercial putty	light-curing putty
Product form	Two-part	One-part
Appearance	Gray, highly viscous substance	Blue, highly viscous substance
Curing time (minutes)	15 to 30	2 to 5
Pot life (minutes)	5 to 45	No limitations when not exposed to light
Machinability	Good	Good
Hardness (JIS-D)	80	80
Adherence	Good	Good

4. Future prospects

Prior to the coating process, three to five types of mending putty are appropriately used in one mending process. The light-curing putty described herein is assumed to be sheet metal putty when it dries it's like an automobile body. In the future, we will further study the ability of the property using different types of putty.

V. Adhesion between the disk plate and the hub of the optical disk

Optical disks, on which record, play back, and erase by a light beam in a noncontact manner, have advantages such as a large storage capacity, user-friendliness, and resistance to scratches and stains. They are expected to serve as mass storage media for various types of information, such as coded and image information, and have already become a part of our daily lives in the form of music compact disks and video disks.

The optical disk system is composed of a disk plate for storing information and a drive unit for driving the plate. On optical disks such as photomagnetic disks, a disk shaped component, which is referred to as a hub, is attached to the center part of the disk base. The hub magnetically attaches the disk plate to the turntable of the drive unit, and matches the center of rotation to the center of the spindle. The hub is made of various materials selected in accordance with the material and size of the disk plate. For example, 3.5-inch photomagnetic disks have an integrally molded hub made of a magnetic metal plate and a plastic.

At present, two methods are predominantly used to mount the hub on the center part of the disk base: a method using an ultraviolet-curing resin and a method using ultrasonic welding. The former method has the advantages over the latter method of a large adhesion area and sufficient adhesive strength. However, the former method requires a two-step curing process in which a base and a hub sandwiching an ultraviolet-curing resin are cured temporarily and then permanently, and thus the curing speed and adhesive strength during the temporal curing significantly influence the reliability of the optical-disk product.

The temporal curing is carried out with the base pressed against the hub, thus the ultraviolet-curing resin to be used must have fast-curing properties at a low intensity of illumination. Ultraviolet irradiation is conducted under extreme conditions: the intensity of ultraviolet illumination is several dozen mW/cm^2, and the irradiation time is approximately one second. Under such conditions, conventional ultraviolet-curing resins did not provide adhesion or did not achieve sufficient adhesive strength, and thus they tended to become misaligned prior to the main curing.

To solve these problems, we have developed an optical-hub adhesive, 30Y-206-1. Table 5-1 shows the properties of 30Y-206-1 and the cured resin thereof.

Table 5-2 shows the adhesive strength between a disk base and a hub. Under ultraviolet irradiation conditions of 70 mW/cm^2 and one second, the adhesive had both the hardness and strength that were stronger than fracturing the base. Besides, when the ultraviolet irradiation was approximately 500 mJ/cm^2 during the main curing, the adhesive provided sufficient adhesive strength. This will reduce the time required for adhesion of the hub and the cost of operating the equipment. On the other hand, the deterioration in the adhesive strength was very small in the evaluation of durability in an environmental test, which will contribute to improvement of the reliability of optical disks.

As previously mentioned, 30Y-206-1 has fast-curing properties at low intensities of illumination, which had been hardly achieved by conventional ultraviolet-curing resins, and has good adhesiveness and durability that will significantly contribute to an improvement in the productivity of optical disks.

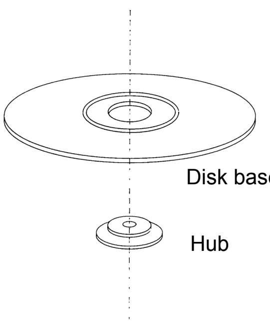


Fig. 5-1. Optical disk structure

Table 5-1. Properties of 30Y-206-1 and the cured resin

	Unit	Measurement	Test method
Appearance		Pale yellow transparent liquid	3TS102
Viscosity	mPa•s {cP}	2800 {2800}	3TS203
Specific gravity		1.03	3TS211
Hardness of cured resin		JIS-D-70	3TS387
Degree of elongation	%	250	3TS311
Tensile strength	Mpa {kgf/cm^2}	29.4 {300}	3TS311
Adhesive strength under shear[1)]	Mpa {kgf/cm^2}	6.9 {70}	3TS310

1) The adhesive strength under shear for polycarbonate/polycarbonate

Table 5-2. Adhesive strength between the polycarbonate base and the hub[1)]

	Adhesive strength N[kgf][2)]	State of fracture
Temporal curing (70 mW/cm^2×1 sec) alone	177 {18.0}	Fracture in the base material
Temporal curing + main curing (500 mJ/cm^2)	552 {56.3}	Fracture in the base material
Temporal curing + main curing (1 J/cm^2)	594 {60.5}	Fracture in the base material
Temporal curing + main curing (2 J/cm^2)	652 {66.5}	Fracture in the base material
Temporal curing + main curing (3 J/cm^2)	677 {69.0}	Fracture in the base material
Following environmental testing [3)]	589 {60.0}	Fracture in the base material

1) After approximately 0.01 g of 30Y-206-1 was applied to the hub, the hub was affixed to the base plate and attached thereto by the irradiation of ultraviolet light.
Temporal curing was conducted using a 500-W spot irradiator equipped with a ring-shaped guide.
Main curing was conducted using a 4-kW high-pressure mercury light (conveyor type).
2) The adhesive strength was the same as the pull-out strength of the base and hub.
3) Environmental test conditions: 85°C×90% RH×250 h
The test was conducted on samples that had been cured using ultraviolet irradiation of 2 J/cm^2.

VI. UV conformal-coating material

1. Protection of populated printed circuit boards

Printed circuit boards for automobiles, aircrafts, construction machinery, and other machinery are used in harsh environments ranging from very low temperature to high temperature and high humidity. Printed circuit boards for household electrical appliances such as washing machines and bath water heaters are also used under high humidity conditions for an extended period. Under any conditions, printed circuit boards are required to have high reliability, and thus protection methods for such printed circuit boards have been studied. One such method is the envelopment of printed circuit boards in synthetic resins. Printed circuit boards are protected from harsh environments by the potting, molding, or conformal coating of various moisture proof and dust proof synthetic resins. Of these, conformal coating in particular is attracting attention, as it protects electronic components with a thin film to provide various advantages such as ease of repair, good heat radiation properties, and a reduction in the weight of the base. At present, the synthetic resins frequently used as conformal coating materials are low-viscosity organic-solvent solutions composed of synthetic resins such as acryl, polyurethane, and epoxy dissolved in organic solvents.

2. New requirements for conformal coating agents

Controls have been implemented for organic solvents over the past few years, which have led to new requirements for conformal coating materials in order to improve the work environment. Conformal coating materials are required to have low viscosity in order to allow thin-film coating. They are also required to have the physical properties necessary to minimize deterioration of the electrical performance of the coated base as a result of environmental stress. The requirements for the materials are as follows:

1) One-part and solventless
2) Low viscosity (100 mPa•s) that allows spray coating and dip coating
3) Excellent electrical insulation properties
4) Excellent chemical resistance
5) Good heat cycle resistance
6) Excellent moisture resistance (low moisture permeability)
7) No foreign ions such as halogen ions
8) Good repairability
9) Ease of handling
10) No influence on the work environment

3. Ultraviolet-curing conformal coating materials

Ultraviolet-curing resins are a means of satisfying the new requirements for conformal coating materials. Ultraviolet-curing resins achieve low viscosity without the use of organic solvents, and are cured in seconds by the irradiation of ultraviolet light. This enables increases in workability and productivity, and significant improvements in the working environment in comparison with conventional organic solvent solutions. Ultraviolet-curing resins having heat-curing and moisture-curing properties can be cured at areas in the shade of components mounted on a printed circuit board (the area unexposed to ultraviolet light). Table 6-1 shows a comparison of various conformal-coating curing processes, and Table 6-2 shows the properties of various synthetic resins. Appropriate resins should be selected in accordance with the use environmental conditions of printed circuit boards.

Table 6-1. Comparison of various conformal-coating curing processes

Item / Curing process	Curing speed	Workability	Productivity	Cost of equipment	Work environment
Moisture-curing	1	1	1	5	3
Heat-curing	3	2	3	2	3
Two-part curing	4	2	3	2	3
Combination with another light-curing process	5	5	2 to 4*	3	4
Solvent-solution vaporizing	4	3	3	4	1

The greater the number of points, the greater the benefit.
* : The point differs depending on the curing mechanism to be combined.

Table 6-2. General properties of various synthetic resins

Item / Resin	Heat resistance	Heat-cycle resistance	Moisture permeability	Water absorption	Chemical-resistance	Safety
Silicon-based resins *1	5	5	1	4	1	5
Urethane-based resins *2	3	3	3	3	3	1
Acryl-based resins *1	3	3	4	3	4	3
Epoxy-based resins *1	4	1	5	5	5	3

*1: Solventless curing type　　*2: Solventless moisture-curing type

4. Coating method and curing techniques

For the protection of electronic components mounted on printed circuit boards from environmental stress, it is of course important to select resins with suitable properties, and it is also important to use the coating and curing techniques in order to enable the most of those properties. The susceptibility of populated printed circuit boards to coating or ultraviolet irradiation varies significantly according to the number, shape, and size of the mounted components. When performing actual coating, it is required to review the system. Table 6-3 shows the review items of the system and processes.

Table 6-3. Review items of application and curing techniques

Application	Method	Spray coating, dip coating, flow coating, brush coating, etc.
	Selection references	Production, work environment, viscosity of resin, size and shape of substrate, thickness of coating film
Curing	Lamp	Number of high-pressure mercury lights and metal halide, electrodeless, xenon, and mercury xenon lamps
	Selection references	Resin curing wavelength The number of lamps is determined by the production, and by the size and shape of the base.

VII. Two-part ultraviolet resins

1. Background

Ultraviolet-curing resins have been widely used in the electric and electrical fields to reduce the amount of time required for production, as they cure in seconds to achieve good productivity. Actual components may have shaded areas unexposed to ultraviolet light, and ultraviolet-curing resins having anaerobic-curing or heat-curing properties are used for such components. However, anaerobic curing is difficult for areas having a large clearance, and heat curing inevitably requires heating and is therefore unsuitable for in-line equipment. To solve these problems, two-part reactive ultraviolet-curing resins have been developed.

2. Reaction mechanism

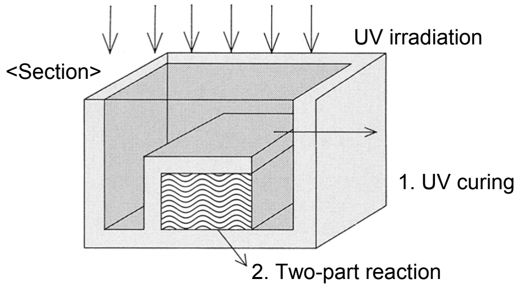
The upper part of the resins is cured by ultraviolet irradiation, and then the shaded part is cured by two-part reaction within several minutes. The two-part reaction is an oxidation-reduction reaction, and the curing is accelerated with the heat of the reaction at the ultraviolet-curing part.

1. Ultraviolet-curing $\quad \underset{\text{Photo-initiator}}{R} \xrightarrow{h\nu} R\cdot$

2. Two-part reaction curing

$$\underset{\text{Peroxide}}{ROOH} + \underset{\text{Metal salt}}{M} \longrightarrow \underset{\text{Initiator radical}}{\boxed{RO\cdot}} + M^{+} + OH^{-}$$

$$\boxed{RO\cdot} + CH_2{=}\overset{H,CH_3}{\overset{|}{C}}-\underset{O}{\underset{\|}{C}}-OR \longrightarrow ROCH_2-\overset{H,CH_3}{\overset{|}{\underset{\cdot}{C}}}-\underset{O}{\underset{\|}{C}}-OR$$



3. Dedicated dispenser

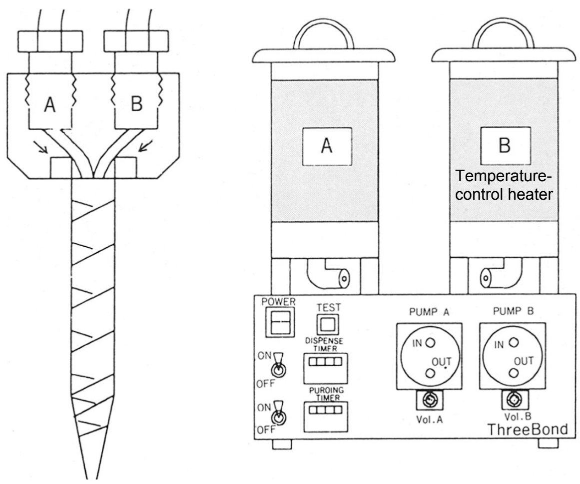
Concurrently with the development of the resin, we also developed a dispenser and established a dedicated application system.

1) Two-fluids mixing method

As the dispenser is of the static type, the two fluids are only mixed at the nozzle attached to the dispenser. Therefore, even if the resin is gelated by a failure occurring during mixing of the resin, production can immediately be resumed only by replacing the nozzle.

2) Anti-gelation function

The gelation initiates within 10 to 15 minutes after mixing of the two fluids. Therefore, the dispenser has an apparatus for purging the resin remaining in the nozzle after the lapse of a certain length of time (purging timer).



4. New product (high-viscosity, low-odor type)

At present, two types of two-part ultraviolet-curing resins, Three Bond 3088 and 3088B, are on the market. In addition, we have developed 30Y-221, which has a higher viscosity. As 30Y-221 emits little odor and causes little irritation, it is a highly safe product.

The table below shows the properties of 30Y-221.

We believe that the new product can be incorporated into in-line equipment. We also aim to expand the applications of the new product.

Name of prototype	30Y-221	
Two fluids	Main agent	Curing agent
Appearance	Purple transparent liquid	Colorless transparent liquid
Viscosity	25Pa•s {250P}	25Pa•s {250P}
Thixotropy	2.45	2.45
Gelation time	15 minutes (25°C)	
Skin irritation	1.0 or lower (PII)	

Conclusion

Light-curing resins have made significant contributions to industry due to their rapid curing properties. On the other hand, the functions of the resins have been advanced and increased in response to the requirements of industry.

One of the major drawbacks of light-curing resins has been the difficulty of curing of dark or deep parts, but this drawback is being eliminated.

We believe that the applicability and marketability of light-curing resins will be expanded if the resins described herein are added to the Three Bond product line. In addition, the functions of light-curing resins will be advanced and increased in response to various requirements from users.

We are working to develop the desired resins.

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