ThreeBond
TECHNICAL NEWS

Three Bond Technical News
Issued Jun. 1, 2005

64

Precoat Bolt
— Water-based MEC process and water-based threelock process —

Introduction

Precoat bolt is a functional part that can provide screws themselves with the features such as sealing, locking, adjusting, and lubricating by coating microencapsulated reactive resin or special blended synthetic resin on the thread part of screws, bolts, plugs, and pipes in advance. Although there were disadvantages such as working time, environmental pollution, spotty coating, inadequate coating, eruption, and delayed hardening expression for liquid-type sealing agents and locking agents previously used at work places to mount screws, in order to resolve these problems precoat bolt was developed with the precoating technology that coats thread part directly in advance.

Precoat bolts have product groups such as sealock process, MEC process, and threelock process from their characteristics, and they have been field-proven in the automotive industry and electronic/electric industry for many years (see figure 3 on page 3).

These precoat bolts are typically coated in the process shown at figure 1. In this process, organic solvent is typically used as a diluent solvent for precoat resin, and it is the current situation that this solvent is vaporized in the air during the dry process. It is expected that regulations will be severe by part revision of Air Pollution Control Law promulgated recently including experimental regulations (for example, VOC regulation), and the use of de-organic solvents is anticipated through the all manufacturing processes. (Note: ThreeBond is referred to as TB.)

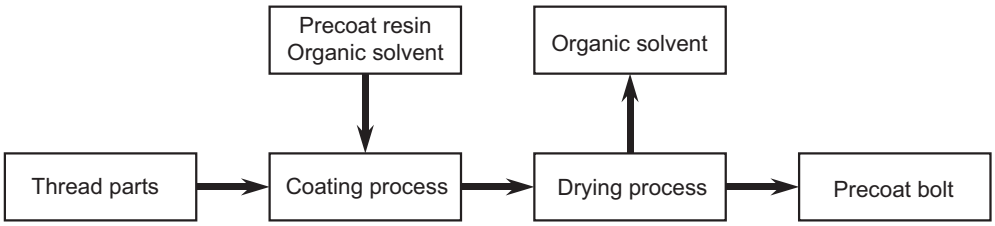


Figure 1, Process to Manufacture Precoat Bolts

Contents

1, About VOC Regulation

A partial amendment of the Air Pollution Control Law was promulgated on May 26th, 2004. This overview is that volatile organic compound (VOC) is concerned as causative agent to generate suspended particulate matter (SPM) and photochemical oxidant (OX) that may affect human bodies, and discharge of them should be suppressed. The mechanism to generate these toxic substances is shown as figure 2.

The government ordinance will determine the details about VOC regulation guideline in this law in future. Therefore, use of all organic solvents will not be inhibited immediately, but it is easily expected that more severe conditions will be imposed in near future for their usage.

This law also includes provisions that customers to use them should select low VOC products, and it seems that some restrictions are applied to both manufacturer and user.

1-1, Action Plans for VOC

To limit VOC discharged from the locations for use when using paints, adhesives, and processing precoat resins, there may be some methods: to collect organic solvents by using condensers (1), to change to alternative solvents such as water (2), and to make a non-solvent system such as powder coating (3). Among these selections, it is an effective action as a short-term solution to install solvent recovery equipments to collect organic solvents, but it is not a permanent countermeasure because the West and the neighboring countries like Korea and Taiwan are taking their own more severe regulations. Solvent-free solution has a high technical hurdle due to the characteristics of the precoat process and it is not realistic in this time. In such a situation, we at ThreeBond have discussed mainly to change the solvent into water as an action plan for VOC for precoat resins.

1-2, Problem to Develop Water-based Solvents

It has many advantages such as compliance to environment, safety, handling ability to change precoat resins solvent from organic solvent to water, but on the other hand, many restrictions or problems are left in the blending and processing operations: drying property, temperature dependency of compounded resins, dissolubility of high polymer resins. For example, as problems in blending, some issues are left: same adhesive component as before cannot be used because there are some differences about dissolubility between water and organic solvents or solvents are sagged after coated because drying is slow. To solve these problems, we have discussed on developing the dispersion technology to newly microencapsulated components in resins and water-based adhesive components. It was also decided to manage a viscosity for resins in the coating process operation, ambient temperature and humidity in drying operation carefully. These endeavors enabled us to manufacture the same level products as conventional organic solvents and to introduce them to the market.

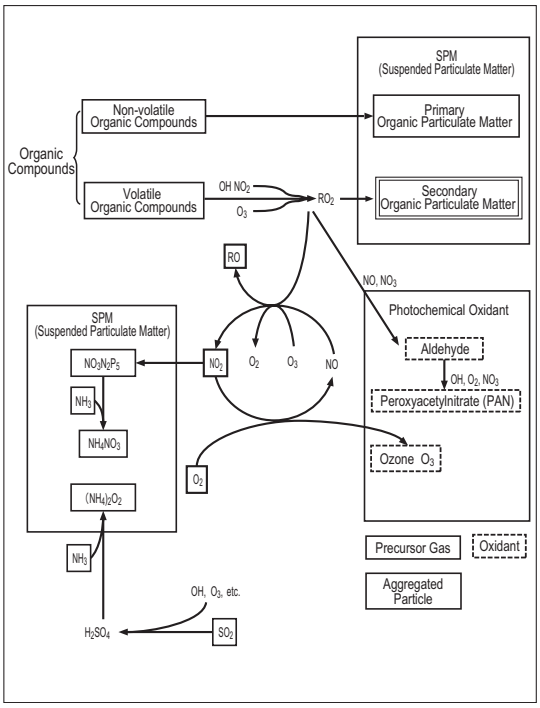


Figure 2, Mechanism such as atmospheric VOC

2, MEC Process

Our precoat bolts are classified according to their characteristics as shown in figure 3. MEC process is one of them, that adhesive component is coated in the dry film on the surface of the thread parts such as bolts. Its appearance is shown in photo 1. Since it is required to make coated component into the dry film, or to coat reactive resin and curing agent separately on the same thread surface, the technology that partial or multiple components are microencapsulated is applied on these precoated thread parts. Thus it is stable unless screws are tightened, however, tightening the screws, i.e. the shearing force enables to break the microcapsules, core substances are bled, and curing agents are mixed. Then the polymerization reaction occurs and prevents the thread joints from loosening and leaking. Also using microencapsulation technology can handle the liquid materials as powder, and it gives us a great advantage to eliminate the problems such as stickiness and dermatitis.

2-1, Solvent-based Acrylic MEC

Solvent-based acrylic MEC consists of microcapsules that contain acrylic monomer as a main component, binders, and filler. Microcapsule is not stayed in the thread joints because it is a powder. Thus binders are used as a component to adhere it on the thread part. Bolts are coated on after dilution in the organic solvent, and precoat film can be acquired that is adjusted to a given film thickness. When bolts are tightened, microcapsules are broken and curing agents are mixed so that reaction has initiated and then adhesive power and sealing performance are exerted. MEC process is classified into low-strength (detachable) to high-strength (permanent adhesive) depending on adhesive strength. TB2411 is classified into low-strength, TB2403 is classified into medium-strength, and TB2471 is classified into high-strength respectively.

2-2, Water-based Acrylic MEC

If diluent solvent is changed into water from organic solvent, problems are left: binder dissolution property to water and stability of microcapsules. For this reason, water-based acrylic MEC is developed by applying a technology that acrylic monomer as its main component is dispersed into water in a special form and by applying a new microcapsule.

Photo 1, Water-based MEC-processed bolts

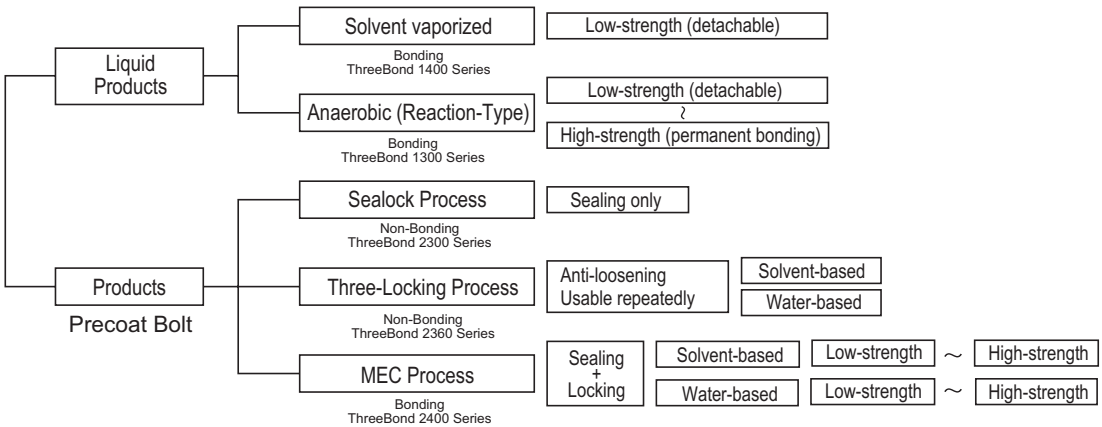


Figure 3, Three Bond Product Series about Screw Tightening

We have experimented to dilute the solvant with water and coat the belts. As results, it is possible to obtain equivalent precoat films with organic solvent. Although it is an water-based product, it is hard to be dissolved into water after drying, and superior films with humidity resistance are provided. There are currently 2 grades according to the strength, TB2457 is classified into the low-strength, and TB2475 is classified into the high-strength.

2-3, Acrylic MEC - Comparison between water-based and solvent-based products

Drying process after coating takes a long time because water is used as solvent. Water-based solvent uses a special blend technology compared to conventional solvents, but reaction mechanism and resin compound after reactive curing remain nearly unchanged.

2-4, Solvent-based Epoxy MEC

Solvent-based Epoxy MEC contains epoxy resin in microcapsules, and it consists of the microcapsules, amine curing agents, binders, filler agents and so on. Both TB2430 and TB2440B as a Solvent-based Epoxy MEC are classified into the high-strength type.

2-5, Water-based Epoxy MEC

Water-based epoxy MEC TB2446 uses the same microcapsule that solvent-based product uses. Water-based Epoxy MEC consists of the microcapsules, amine curing agents, binders, filler and so on. The problems on solubility same as acrylic MEC are left as mentioned above, but this could be developed with a new method. TB2446 is classified into the high-strength type.

2-6, Epoxy MEC - Comparison between water-based and solvent-based products

TB2446 has the following advantages compared with TB2430 and TB2440B:

- ❏ High strength on applying small screws
- ❏ Low dregs on tightening screws
- ❏ Low stickiness of processing bolts in high temperature / high humidity condition
- ❏ No whitening.

Therefore, it is increasing to be used as fixing screws of chassis and PCB (Print Circuit Board) for PCs and cellular phones.

2-7, Curing speed

As a characteristic of acrylic MEC, it has an advantage of fast curing (adsorbing) speed because curing reaction is radical polymerization. For acrylic MEC, it will normally be cured in 24 hours at 25 °C. For epoxy MEC, standard curing time should be in 48 to 72 hours at 25 °C, depending on curing agents used. Figure 4 and figure 5 show curing speeds of acrylic MEC and epoxy MEC. Water-based agents indicates same or highet performance in curing speed compared with solvent-based agents.

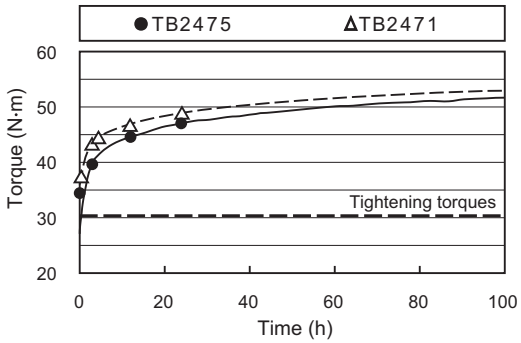


Figure 4, Acrylic MEC - curing speed

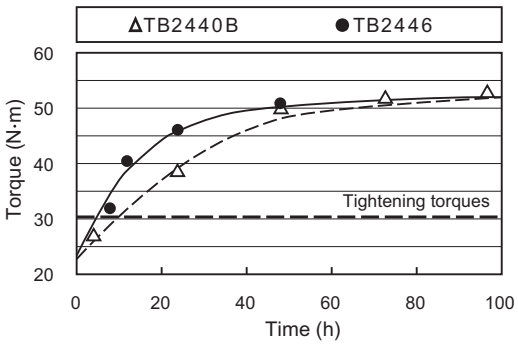


Figure 5, Epoxy MEC - curing speed

- Curing conditions: Loosening torque was measured after bolts were tightened at 30N•m and they were cured for the specified time under 25 °C ambient atmosphere
- Testing Material: Bolts and nuts that are processed with JIS 2nd grade M10 zinc chaomate-plated are used

2-8, Thermal Resistance

Figure of adhesive strength vs temperature is shown below. As shown in the figure, if temperature is getting higher, adhesive strength is getting lower than the tightening torques. This point is referred to as a limit temperature of lock heat resistance. Limit temperature of lock heat resistance for water-based types is 120 °C for TB2457, 150 °C for TB2446 and TB2475.

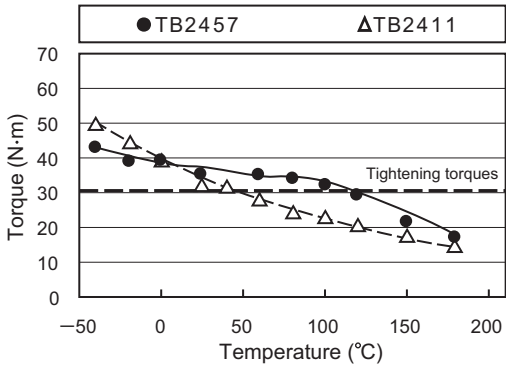


Figure 6, Adhesive strength of low-strength acrylic MEC vs temperature

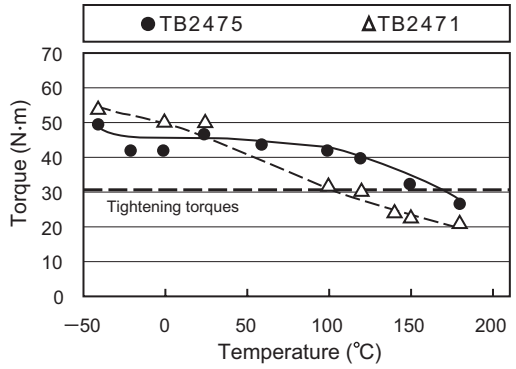


Figure 7, Adhesive strength of high-strength acrylic MEC vs temperature

2-9, Chemical Resistance

Epoxy has an advantage on heat resistance, heat-cycle resistance, and chemical resistance (figure 9).

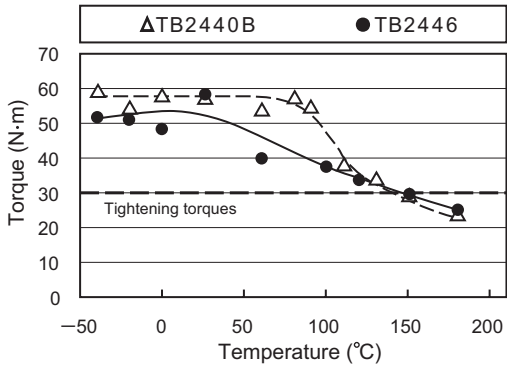


Figure 8, Epoxy MEC strength vs temperature

- Curing condition: Bolts are tightened at 30N•m, and are cured at 25 °C in 24 hours (48 hours, or 72 hours)
- Testing Material: Bolts and nuts that are processed with JIS 2nd grade M10 zinc chromate-plated are used

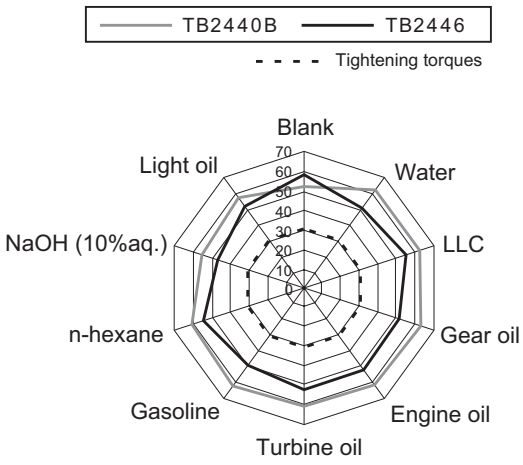


Figure 9, Epoxy MEC - Chemical resistance

- Curing condition: Bolts are tightened at 30N•m, and are cured at 25 °C in 48 hours (or 72 hours)
- Testing Material: Bolts and nuts that are processed with JIS 2nd grade M10 zinc chromate-plated are used

2-10, Sealing Property

MEC process has an excellent pressure resistance not only under room temperature but only in more severe temperature conditions. Method of sealing test is as follows. MEC processed bolts are mounted into sealing test blocks and these blocks are mounted into a hydraulic sealing tester. After cured, they are pressurized and existing of leakage is checked visually (figure 10). Temperature resisting to 8MPa of hydraulic pressure is the sealing limit temperature of heat resistance. The results are shown in the table 1.

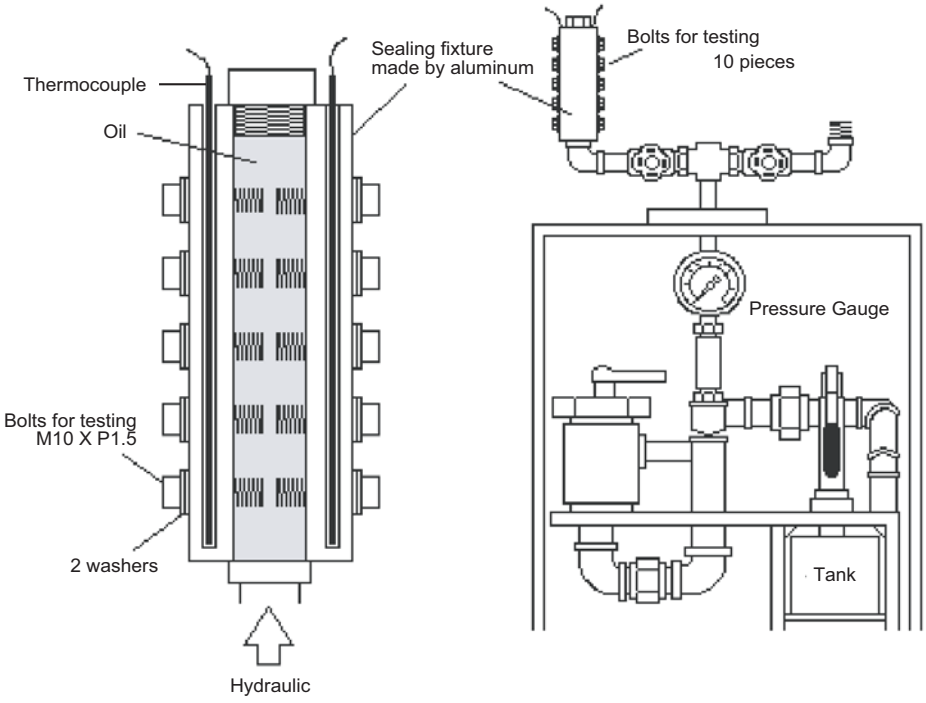


Figure 10, Sealing Tester

Table 1, Sealing property

	Testing Temperature °C	Pressure (MPa)				
		2	4	6	8	10
TB2446	25	0/10	0/10	0/10	0/10	0/10
	150	0/10	0/10	0/10	0/10	0/10
TB2457	25	0/10	0/10	0/10	0/10	0/10
	150	0/10	0/10	0/10	0/10	0/10
TB2475	25	0/10	0/10	0/10	0/10	0/10
	150	0/10	0/10	0/10	0/10	0/10

- Curing conditions: Bolts are tightened at 30N•m, and are cured at 25 °C in 24 hours (or 48 hours)
- Testing Material: Bolts and aluminum blocks (A5052P) that are processed with JIS 2nd grade M10 zinc chromate-plated are used
- Pressurized Conditions: Pressurize up to 10MPa per 1MPa/min

3, ThreeLock Process

ThreeLock process is a self-locking coating process that nylon is a main component (Photo 2). Resistive elasticity of nylon has self-locking effect on the screws to prevent from falling off, and it provides a function to adjust screws. It also has an excellent recycling characteristics, and it conforms to the test according to the JASO standard (Japanese Automobile Standards Organization standard, JASO F 106-96: Prevailing Torque Type Self-Locking Hexagon Nut). Conventional product TB2361 is processed by using solvents as dilution agents.

Photo 2, ThreeLock Process

3-1, Water-based ThreeLock Process

When changing solvent-based ThreeLock TB2361 to water-soluble, most significant was the problem that water-based solvent was easy dropped off in the coating process. Because thickness of coated film affects the performance, it is very important to control thickness of the film. Change on film thickness due to the dropping-off is concerned since vaporization speed of water-based agents is slow compared with solvent-based agents. Therefore, in the water-based TB2365 to solve this problem, some agents are blended to prevent the dropping off that are not available in the solvent-based agents. Also, recycling characteristics are improved by lowering the resin hardness than solvent-based agents (figure 11).

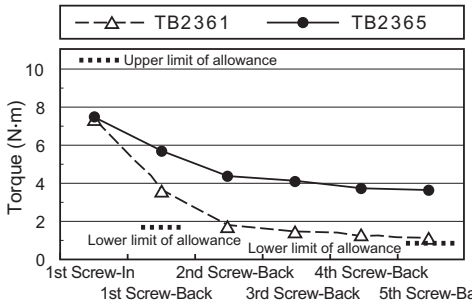
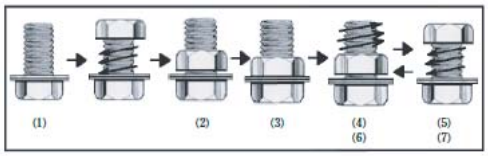


Figure 11, M10 Bolt recycling characteristics

- Testing Material: Bolts and nuts that are processed with JIS 2nd grade M10 zinc chromate-plated are used
- Testing Method

1) Set a spacer to coating processed bolts as shown in the figure.
2) Screw a nut in about 0.8mm to the spacer surface, and measure the maximum value (screw-in torque) during screwing-in.
3) Screw the nut in deeply, and tighten by the specified tightening torque.
4) Then screw the nut back to measure the torque (loosening torque).
5) Screw the nut back until it falls off, and measure the maximum torque (1st screw-back torque) during screwing-back.
6) Screw the nut in about 0.8mm to the spacer surface.
7) Screw back the nut until it falls off and measure the maximum torque (2nd screw-back torque) during screwing-back.
8) Repeat the steps 6) to 7) five times (3rd to 5th screw-back torque).



3-2, Water-based ThreeLock Process for Small Screw Only

ThreeLock was initially developed for standard bolt (M10) as a standard part. However, recently coating on small fixing screws (M1 to M3) for chassis and PCB of PC has been increasing. Using conventional ThreeLock to these small screws caused the problem that dispersion of recycling property is larger. Therefore, we have developed the water-based product TB2364 that can be applied in narrow clearance of small screws. Figure 12 and figure 13 show the comparison of changes on torque between TB2364 used specially for small screws and TB2365 used for normal screws when applying on M3 screws. By implementing blending to suppress the dispersion of film thickness, dispersion of resistive torque during screwing is decreased, and stable repetitive characteristics could be acquired.

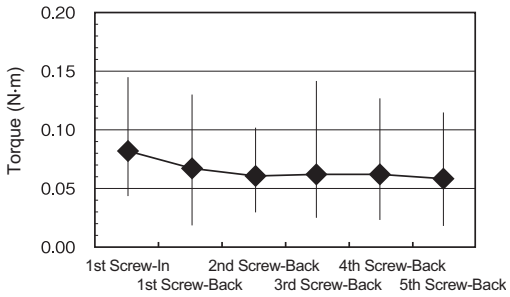


Figure 12, TB2365 M3 Screw Recycling Characteristics

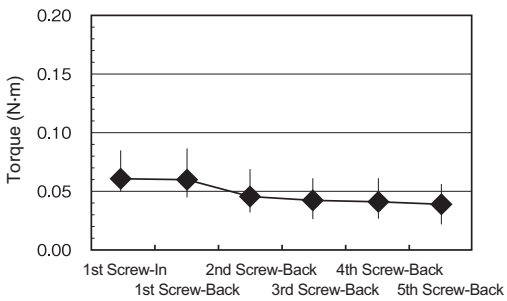


Figure 13, TB2364 M3 Screw Recycling Characteristics

- Testing Material:
  Small round-head screw with cross recess M3
  Nickel plated brass insert nut M3
- Testing Number of testing screws: n=10

4, Conclusion

Making precoat bolts water-soluble has started to spread steadily, although it is not fast. We at ThreeBond believe that migration to solubility will contribute to environmental preservation.

It is expected in the industrial world surrounding us, that chemical material is required to be more environment-friendly on the earth for future. ThreeBond keeps challenge to respond to these needs continuously, not only for the development of precoat bolts with water-soluble resins but also for other products.

<Reference Documents>

1) "Chemical Basic Information Research about Carbon Hydride", Mitsubishi Chemical Safety Institute Ltd.

Yasuo Maeda
Hideki Kanazawa
Material Development Section
Development Department
Research Laboratory
ThreeBond Co., Ltd.

ThreeBond TECHNICAL NEWS
THREE BOND CO., LTD.
1456 Hazama-cho, Hachioji-shi, Tokyo 193-8533, Japan
Tel: 81-426-61-1333