ThreeBond
TECHNICAL NEWS

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Eco-friendly adhesives

Introduction

Many countries and industries worldwide have set environmental regulations that affect the use of chemical substances. ThreeBond pursues its various activities as a company for whom handling chemical substances is a central mission.

This issue mainly focuses on ThreeBond activities in areas related to topics of substances of environmental concern. It also describes ThreeBond's past activities in this area, how evaluations and analyses are performed, and future plans and other points.

ThreeBond pursues its manufacturing activities based on the keyword of "eco-friendly." It carefully monitors regulations applicable within each country and industry. This issue summarizes some of ThreeBond's ideas as a global enterprise.

We hope this issue will help readers as a reference in their corporative activities.

ThreeBond is abbreviated TB hereafter.

Contents

1. Background

Recent years have seen growing public interest in environmental issues. Protecting the environment is one of several key topics of corporate activity. With the globalization of economic activity, overseas regulations restricting substances of environmental concern are also beginning to affect Japanese companies.

ThreeBond is no exception. It currently strives to develop eco-friendly products and merchandise free of substances of environmental concern.

2. Substances of environmental concern

"Substances of environmental concern" is a generic term for substances that adversely affect the global environment or human health. Hundreds of thousands of chemical substances are currently produced industrially and sold worldwide; some have raised concerns regarding their potential impact on the environment and on health.

Above all, Europe (EU) has traditionally demonstrated high awareness of environmental issues and recycling. Various environmental standards recently established have repercussions not just for the EU, but in other countries around the world, including Japan.

In response to regulations governing substances of environmental concern, many manufacturers in the electrical and electronic industries and the automotive industry have taken various measures, including establishing standards even more rigorous than those imposed under the EU standards or requiring the manufacturers of the materials and components to provide certificates or guarantees demonstrating that their products are entirely free of or contain less than the regulated levels of hazardous substances. These measures are known as "green procurement," "green purchasing," or "green partnering." ThreeBond pursues manufacturing and procurement that minimize environmental impact, including its ThreeBond green procurement activities. With the support of its suppliers, ThreeBond monitors, investigates, and analyzes substances with potential environmental repercussions based on the ThreeBond Group Management Criteria of Environmental Impoacts (Table 1).

The next section describes various regulations that apply to substances of environmental concern. It also addresses ThreeBond's evaluation methods and activities in response to regulations.

Table 1: Regulations on substances of environmental concern and user/self regulations

	Name	Target products	Requirement summary	Restricted substances (ThreeBond monitoring substance) and threshold values		Evaluation method
Regulations on substances of environmental concern	ELV[*1]	Automobile	• Hazardous substances may not be used. • End-of-life vehicle collection • Recycling	(1) Lead (Pb) (2) Mercury (Hg) (3) Hexavalent chromium (Cr)	1,000 ppm or less	XRF
				(4) Cadmium (Cd)	100 ppm or less	
	WEEE[*2]	Electrical and electronic equipment	• Collecting and recycling used products	Restrictions under the RoHS Directive		
	RoHS[*3]	Electrical and electronic equipment	• Hazardous substances may not be used.	(1) Lead (Pb) (2) Mercury (Hg) (3) Hexavalent chromium (Cr) (4) Polybrominated biphenyls (PBB) (5) Polybrominated diphenyl ethers (PBDE)	1,000 ppm or less	XRF ICP-MS
				(6) Cadmium (Cd)	100 ppm or less	
	REACH[*4] (Substances of Very High Concern, SVHC: 46 substances)	Substances manufactured or imported	• Unregistered chemical substances may not be sold (provided) commercially. • Content at or above the threshold value requires the provision of information.	Dibutyl phthalate (DBP) Diisobutyl phthalate (DIBP) Bis (2-ethylhexyl) phthalate (DEHP) n-Butyl benzyl phthalate (BBP)	0.1 wt% or less	GC-MS
	European Commission Decision No. 2009/425/EC	Substances manufactured or imported	• Hazardous substances may not be used.	Dibutyltin compounds (DBT) Di-n-octyltin compounds (DOT)	0.1 wt% or less[*6]	GC-MS
User/self regulations	Halogen regulation	Substances manufactured	User regulations	Chlorine (Cl) Bromine (Br) Chlorine (Cl) + bromine (Br)	0.09 wt% or less 0.09 wt% or less 0.15 wt% or less	Ion chromatography
	VOC[*5] reduction self regulation	Substances manufactured	Self regulation	Organic solvent Toluene Methanol, etc.	Reduction	GC

*1 End of Life Vehicles Directive
*2 Waste Electrical and Electronic Equipment Directive
*3 Restriction of Hazardous Substances Directive
*4 Registration, Evaluation, Authorization and Restriction of Chemicals
*5 Volatile organic compounds
*6 By weight of tin

3. Regulations on substances of environmental concern

3-1 RoHS Directive

■ Overview

Recent regulations in Europe (EU) concerning substances of environmental concern include the following measures:

(1) The ELV Directive (July 2003) promotes the recycling of automobiles and prohibits the use of hazardous substances in automobiles.
(2) The WEEE Directive (August, 2005) requires the collection and recycling of electrical and electronic equipment.
(3) The RoHS Directive (July 2006) prohibits the use of hazardous substances in electrical and electronic equipment.

These directives specify the restricted (hazardous) substances and their threshold values (See Table 1). Above all, the electrical and electronic industries require proof, and analysis results that show that products are entirely free of or contain less than the regulated levels of RoHS-restricted substances.

■ Evaluation methods

The methods for verifying ThreeBond products with respect to RoHS Directive requirements can be classified roughly into two categories. One involves screening analysis based on X-ray fluorescence analysis (XRF)[*7] (Figure 1). XRF enables simple measurements regardless of sample form; ThreeBond uses it mainly for product inspections at plants.

*7 X-ray fluorescence analysis

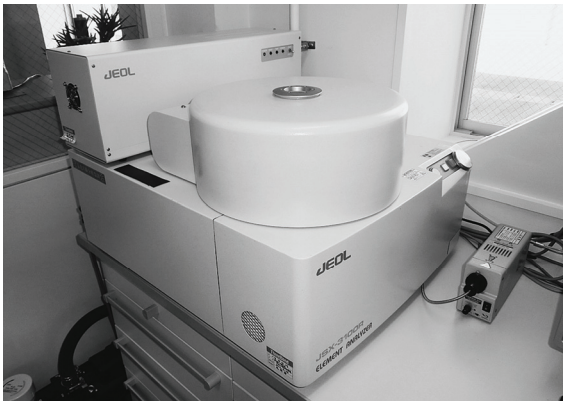


Figure 1: X-ray fluorescence analyzer (XRF)

The other is a precise measurement with an inductively coupled plasma-mass spectrometer (ICP-MS)[*8] or an atomic absorption photometer (AA)[*9] (Figures 2 and 3). Precise quantitative analysis can be performed through elemental analysis of lead, mercury, cadmium, and total chromium in samples thermally decomposed in a strong acid. Here, hexavalent chromium can be verified with a UV-VIS photometer (diphenylcarbazide absorption photometry).

*8 Inductively coupled plasma-mass spectrometer
*9 Atomic absorption

Figure 2: Inductively coupled plasma-mass spectrometer (ICP-MS)

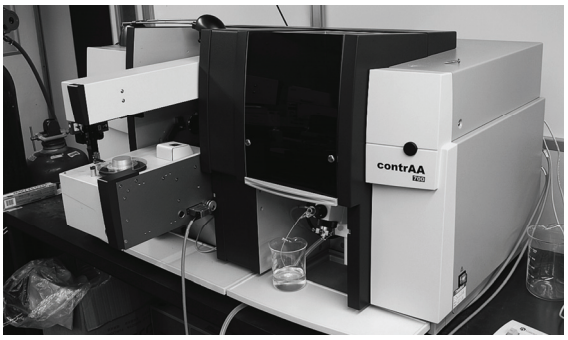


Figure 3: Atomic absorption photometer (AA)

Although polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) can each be verified with a gas chromatography mass spectrometer (GC-MS), the lower limit of detection differs depending on the number of bromine atoms, rendering quantitative analysis difficult. ThreeBond starts by verifying that no other bromine compounds are present, then performs a quantitative analysis of total bromine by XRF or ion chromatography, combined with an automatic sample combustion system (described later) for the judgment.

■ Activities

ThreeBond has specified six RoHS-restricted substances as banned substances and confirms the use or presence of these substances in materials with the cooperation of suppliers. Verified materials are registered in the in-house database, which is then used as a reference when ThreeBond develops products. In addition, from the development stage to post-commercialization, ThreeBond performs in-house and third-party analyses for any required verification.

3-2 REACH Regulation (SVHC)

■ Overview

To protect human health and the environment from the hazards posed by chemical substances, the Regulation concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) went into force in Europe (EU) on June 1, 2007. Toxic substances of very high concern such as carcinogens, mutagens, and reproductive toxicants have serious impact on the environment and human health; 46 are specified in the Substances of Very High Concern (SVHC) candidate list, as of 2010.

Among the SVHC candidates, phthalates—used in various resin products—are regarded to have significant impact on the environment and on health. Phthalates are used mainly as plasticizers in plastics. Significant amounts are used to add flexibility to vinyl chlorides. They are also used in adhesives and sealants to add flexibility to cured materials.

■ Evaluation method

Phthalates can be analyzed with a double-shot pyrolyzer GC-MS (Figure 4).

After the sample is heated to 150°C to 300°C in the pyrolyzer, the gasified sample is introduced into the GC-MS. The mass chromatogram obtained is used for qualitative analysis of phthalates. A standard sample containing 100 ppm to 1,000 ppm is prepared, and quantitative analysis is performed by the calibration curve method.

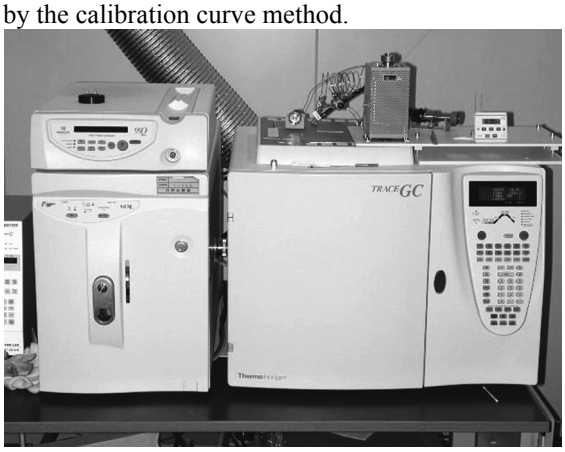
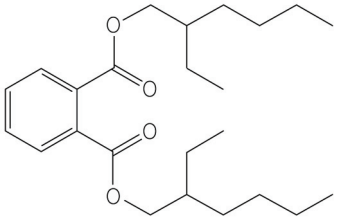


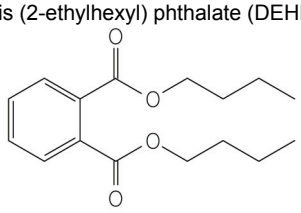
Figure 4: Pyrolyzer GC-MS

■ Activities

As discussed earlier, the list of REACH SVHC candidates has been increased to 46 substances. Of the 15 substances specified in June 2008 when the list was first published, bis (2-ethylhexyl) phthalate (DEHP) and dibutyl phthalate (DBP) are regarded to have reproductive toxicity (Figure 5). Since these two phthalates are also listed among ThreeBond banned substances, ThreeBond is currently making every effort to achieve their complete abolition.



Bis (2-ethylhexyl) phthalate (DEHP)



Dibutyl phthalate (DBP)

Figure 5: Phthalates used in adhesives

Described below are two examples of ThreeBond's countermeasures:

(1) Anaerobic sealants

ThreeBond offers a wide range of anaerobic sealants, from low strength sealants to high strength sealants. However, since the major component of anaerobic sealants is acrylic resin, it is difficult to design a low strength product that allows removal. For this reason, the DEHP plasticizer was added to low-strength anaerobic sealants to adjust the breakdown torque to a low value. As a result of efforts to develop DEHP-free products, we can achieve low strength without DEHP (Table 2).

Table 2: Evaluation and comparison of phthalate countermeasure product

Product name	Countermeasure product TB1342H	Conventional product TB1342
Major component	Acrylate (Methacrylate) resin	
Torque control lubricant	Substance not applicable	DEHP
Viscosity	150 mPa•s	150 mPa•s
2-h breakdown torque	8.7 N•m	8.0N•m
24-h breakdown torque	15.7N•m	14.5N•m

(2) Chassis coating material

Plasticizers are used to soften a cured body. One example involves chassis coating materials. One type of conventional chassis coating material contains bitumen (natural asphalt) as a major component.

This bitumen forms a high-gross coating film when applied to a surface. However, bitumen is extremely hard, and the coating film is fragile and friable. Without treatment, it cannot follow the

deformation of the adherend or exhibit its inherent durable coating performance. Adding a plasticizer here softens the coating film and increases adhesion to the substrate. Conventionally, DEHP has been added. Thanks to efforts to develop DEHP-free products, we can now achieve the same performance with a plasticizer that complies with applicable regulations (Table 3).

Table 3: Evaluation and comparison of DEHP countermeasure product

Product name	Countermeasure product TB6101B	Conventional product TB6101
Plasticizer	Substance not applicable	DEHP
Flexibility	No peeling	No peeling
Shock resistance	No cracking	No cracking

3-3 European Commission Decision No. 2009/425/EC (tin regulation)

■ Overview

"Organotin compounds" is a generic term for compounds containing tin-bonded alkyl or aryl groups. Their reproductive toxicity is an issue of concern.

European Commission regulations ban the use or marketing of dibutyltin (DBT) compounds in member nations after January 1, 2012, whether in mixtures, molded articles, or components to be supplied to the general public, when concentrations exceed 0.1% by weight of tin. One-part moisture-curable adhesives are excluded until January 1, 2015. Similarly, dioctyltin (DOT) compounds cannot be used or marketed in member nations after January 1, 2012, in molded articles and their components, for supply to or use by the general public, in applications intended for contact with skin, of concentrations exceed 0.1% by weight of tin.

■ Evaluation method

Tin content at or greater than 0.01 wt% can be detected by qualitative analysis with XRF screening. Concentrations at or less than 0.01 wt% are analyzed by ICP-MS after acid decomposition pretreatment of the sample. However, quantitative analysis can be extremely difficult, due to problems associated with the stability of tin.

■ Activities

A small amount of DBT is added to one-part moisture-curable adhesives as a curing catalyst. Although TB1530 series products are used for various purposes as one-part moisture-curable adhesives, since they contain DBT, ThreeBond is developing an alternative product that is free of DBT (Table4).

Table 4: Evaluation and comparison of DBT countermeasure product

Prototype/product name	Countermeasure product 15X-200	Conventional product TB1530
Major component	Special polymer containing silyl groups	
External appearance	White	White
Viscosity	100 Pa•s	100 Pa•s
Tack-free	7 min	7 min
Hardness	A49	A44
Tensile strength	5.6 Mpa	5.9 Mpa
Elongation percentage	255%	280%

3-4 Halogen regulations

■ Overview

Customers in the electrical and electronic industries have recently begun to demand halogen-free measures for ThreeBond products. Each customer has a slightly different definition of halogen-free and the corresponding threshold values. However, the target halogens in the halogen-free measures for the electrical and electronic industries are generally two elements: bromine and chlorine. The definition of halogen-free here means that the amount of halogen is at or below the threshold values and is not used deliberately. Although this halogen-free requirement does not set universal test methods or standards, the test methods and threshold values defined in the JPCA-ES01 standard for copper-clad laminates generally apply. The JPCA-ES01 standard specifies the following maximum acceptable concentrations as threshold values:

Chlorine (Cl) content rate: 0.09 wt% (900 ppm) or less

Bromine (Br) content rate: 0.09 wt% (900 ppm) or less

Total chlorine (Cl) and bromine (Br) content rate: 0.15 wt% (1,500 ppm) or less

■ Evaluation method

ThreeBond analyzes the total halogen content based on the JPCA "Test Method for Halogen-Free Materials."

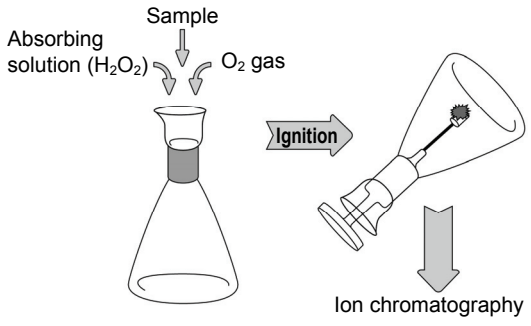


Figure 6: Combustion flask method

This analysis first uses a method known as the combustion flask method (Figure 6) to burn, gasify, and dissolve the sample into the absorbing solution. It then measures the absorbing solution via ion chromatography. Procedures involving a combustion flask require considerable skill. ThreeBond has introduced an automatic sample combustion system and an ion chromatography system (Figure 7) to perform high-precision analysis for halogen-free measures.

Figure 7: Automatic sample combustion/ion chromatography system

■ Activities

(1) Chlorine (Cl) countermeasures

Chlorine is a significant problem for ThreeBond adhesives used in electrical and electronic fields. Chlorine appears in conventional epoxy adhesive without halogen countermeasures and in certain acrylic adhesives.

Epoxy resin uses epichlorohydrin, a chlorine compound, in the monomer manufacturing process. This means the epoxy monomer contains chlorine as an impurity (Figure 8).

Classification	Manufacturing method	Epoxy monomer structure
Glycidyl ether type	Phenol + Epichlorohydrin	
	Alcohol + Epichlorohydrin	
Glycidyl ester type	Carboxylic acid + Epichlorohydrin	
Glycidyl amine type	Amine + Epichlorohydrin	

Figure 8: Manufacturing methods for epoxy monomers

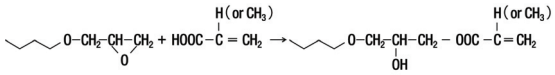
This is an indispensable process in the manufacture of epoxy monomers. To reduce chlorine originating from the monomer, one must use the distilled epoxy monomer, from which impurities including chlorine have been removed. In addition, most powder latent hardeners used in one-part epoxy resins are produced by the reaction of liquid hardener and the epoxy monomer. Some even contain chlorine atoms in their structures. All this means that the selection of the hardener is also a key factor.

Table 5: Evaluation and comparison of halogen (Cl) countermeasure product (TB2200 series)

Product name	Countermeasure product TB2217P	Conventional product TB2217H
Cl content	< 900	700 to 1000 ppm
Br content	ND*	ND
Cl + Br	< 900 ppm	700 to 1000 ppm
Halogen guarantee	○	×
Curing condition	120°C × 10 min	120°C × 10 min
Hardness	D85	D89
Tensile shear bond strength	22.8 MPa	25.7 MPa
Usage	HDD, SMT	SMT

* ND: Detection limit or less

Acrylic monomers are materials used for anaerobic sealants and ultraviolet curable resins. Some also contain chlorine. Generally, this type of monomer is called an epoxy acrylate. Made from the epoxy monomer, it contains chlorine originating from the epoxy monomer (Figure 9).



Epoxy monomer Acrylic (methacrylic) acid Epoxy acrylate

Figure 9: Manufacturing method for epoxy acrylate

In particular, the acrylic adhesives used in the electrical and electronic fields must meet a wide range of requirements. These requirements are often met by combining various types of monomers, including epoxy acrylate in certain cases (Table 6).

Table 6: Evaluation and comparison of halogen (Cl) countermeasure product (TB1300 series)

Product name	Countermeasure product TB1354	Conventional product TB1353
Cl content	< 900 ppm	700 to 1000 ppm
Br content	ND	ND
Cl + Br	< 900 ppm	700 to 1000 ppm
Halogen guarantee	○	×
Viscosity	1000 mPa•s	650 mPa•s
Set time	2 min	1.5 min
2-h strength	36 Mpa	26 MPa
Usage	To fasten HDD motor sleeves	

(2) Bromine (Br) countermeasures

To reduce the risk of fire due to external or spontaneous ignition, automotive parts, building materials, and electric appliances often incorporate inflammable materials.

Traditionally, halogen (bromine or chlorine) flame retardants have been widely used to make organic materials inflammable. However, since they sometimes generate toxic substances during combustion, restrictions on their use are being imposed in accordance with several regulations, including the RoHS Directive.

ThreeBond has developed adhesives certified by the UL94 V-0 flame retardant standard, without using halogen flame retardants. It sells the TB1537 series (Table 7).

Table 7: Features of TB1537 series

Product name		TB1537	TB1537B	TB1537D
Curing mode		One-part moisture curable		
Major component		Special polymer containing silyl groups		
External appearance		White	Black	Gray
Viscosity		55 Pa•s		
Hardness		A72	A74	A71
Tensile strength		5.0 MPa	3.9 MPa	4.3 MPa
Cure shrinkage rate		2.0%	2.2%	2.3%
Volume resistivity rate		1.9×10^{10} Ω•m	2×10^{10} Ω•m	2.7×10^{10} Ω•m
Tensile shear bond strength	Aluminum	4.3 MPa	4.3 MPa	4.3 MPa
	Stainless steel	3.5 MPa	3.3 MPa	3.5 MPa
	Glass epoxy	4.7 MPa	4.5 MPa	4.7 MPa
Flame resistance		UL94 V-0 certified, UL File No. E148575		

3-5 Reducing volatile organic compounds (VOCs)

■ Overview

"Volatile organic compounds (VOCs)" is a generic term for organic compounds that have volatility and gasify in ordinary atmospheres. They include diverse substances such as toluene, xylene, and ethyl acetate. They are widely used in paints, adhesives, solvents, inks, and other materials.

VOCs are considered to generate photochemical oxidants*10 and suspended particulate matter (SPM)*11, which adversely influence respiratory organs.

To suppress the emission of VOCs, the Air Pollution Control Act was amended in May 2004, the Order for Enforcement of the Air Pollution Control Act (government ordinance) was amended in May 2005, the Ordinance for Enforcement of the Air Pollution Control Act (ministerial ordinance) was amended in June 2005, and the VOC emission control started in April 2006.

■ Activities

Many traditional adhesives and coating materials work their cure as organic solvents (VOCs) evaporate. To reduce VOCs, these adhesives are being replaced by non-solvent (reactive) materials and water-based materials, which use water as the dispersion medium. However, in certain applications, they cannot be replaced due to performance or cost, and many VOCs continue to be used. Described below are water-based materials currently being developed by ThreeBond.

(1) Water-based precoat bolts

Precoat bolts are functional parts in which microencapsulated reactive resin or specially blended synthetic resin is applied to the threads of screws, bolts, and plugs to provide the threads themselves with sealing, locking, adjusting, and lubricating qualities.

In the coating process, in which the precoat bolt process solution is applied to the bolts or other materials, the process solution generally contains organic solvent as a diluent solvent. This diluent solvent is released into the atmosphere in the drying process.

ThreeBond has developed water-based process solutions and has sold bolts treated with this solution as water-based precoat bolts to replace conventional solvent-type products. Although it is only at ThreeBond Group plants that process precoat bolts that the VOC has been reduced, Article 17-15 of the Air Pollution Control Act states, "All persons . . . must seek to promote the suppression of emissions or scattering of volatile organic compounds by selecting products that use smaller amounts of volatile organic compounds when purchasing products." Technical News No.64 describes the details of the water-based precoat bolts.

(2) Water-based moisture-proof coating materials

Today, various electric appliances and transport machinery, including automobiles, are equipped with electronic substrates. Depending on the usage environment, the electronic substrates must be protected from moisture and water. Conventional substrate coating materials contain solvent-vaporizing components, which generate VOCs. ThreeBond has developed a water-based moisture-proof coating material to replace them (Table 8).

Table 8: Evaluation and comparison of VOC countermeasure products

Prototype name	15X-168-1	15X-168-2
Major component	Aqueous emulsion	
External appearance	Black	Clear, colorless
Heating residue	42%	
pH	8.1	
Surface resistivity	1.0×10^{11}Ω	
Adhesion test (cross-cut test)	Copper board, no peeling Glass epoxy, no peeling	

*10 Generic term for oxidizing substances (Ox) generated in photochemical reactions involving nitrogen oxides and hydrocarbons. Examples include ozone and peroxyacyl nitrate. Photochemical oxidants cause photochemical smog.

*11 Suspended particulate matter

(3) Easy-peeling water-based pressure sensitive adhesive

Prototype 15X-195 does not contain VOCs, is capable of curing at room temperature, and has better removable adhesion performance than conventional water-based pressure-sensitive adhesives across a wide temperature range, from room temperature to high temperatures. As a low-viscosity product, it can also be sprayed, increasing its range of applications (Table 9).

Table 9: Evaluation results of VOC countermeasure product

Prototype name		15X-195
Major component		Aqueous emulsion
External appearance		White
Viscosity		150 mPa•s
Heating residue		54%
pH		8.4
180° peeling adhesive strength (Al/Al)	25 °C	3.3 kN/m
	80 °C	0.9 kN/m
	100 °C	0.7 kN/m

(4) Water-based chassis coating materials

ThreeBond markets chassis coating materials that prevent rusting in the underbody of automobiles. This category of products includes solvent-based and water-based chassis coating materials, with the latter gradually displacing the former. Once, water-based coating materials contained a small amount of methanol to adjust freezing temperatures. Since methanol content is kept to levels at which it does not fall into the category of organic solvent specified in the Ordinance on the Prevention of Organic Solvent Poisoning, its effects on the work environment are minor. Nevertheless, to help reduce VOCs, users ask for products entirely free of methanol. In addition, the introduction of GHS*[12] now requires GHS indications on labels of products containing methanol exceeding a specified value, a factor promoting the methanol-free movement.

ThreeBond's methanol-free product provides functional properties equivalent to the conventional product (Table 10).

Table 10: Evaluation and comparison of methanol countermeasure product

Product name	Countermeasure product TB6161	Conventional product TB6161
External appearance (undiluted solution)	Black	Black
Viscosity	190mPa•s	200 mPa•s
Heating residue	28%	24%
Tack free time	30 min	30 min
Flex resistance	3 mm passed	3 mm passed
Salt spray test	Rust width: 2 mm or less	Rust width: 2 mm or less

*12 Globally Harmonized System of Classification and Labeling of Chemicals

Summary

With economic growth in emerging countries like China and India, the environmental regulations set by each country are expected to increase the number of target substances of environmental concern, resulting in more rigorous regulatory conditions not just in the EU, but in Asia as well.

To become a company that regards issues related to the global environment even more seriously, ThreeBond will work on product development and ensure product distribution channels while monitoring trends in global environmental legislation related to chemical substances and ThreeBond products and strengthening its information gathering networks.

ThreeBond will continue to strive to provide products that create environments friendly to its customers and to the world.

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