ThreeBond TECHNICAL NEWS

ThreeBond Technical News
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NEW PRODUCTS
ThreeBond 7700 Gold Label series

Introduction

The advent of instant adhesive dates back to 1949, when Goodrich Co. of the US discovered alpha-cyanoacrylate synthesis method. Since 1959, when the world's first instant adhesive "Eastman 910" appeared in the market, practical applications are going on around the world and improvements on cyanoacrylate adhesive are under way night and day seeking for higher functionality.

Instant adhesive means an adhesive which can stick adherends in seconds, as understood by the name. It is one-part non-solvent and can be used at ordinary temperature without any emission of environmental burdens, whose pro-environmental nature is widely supported. However, it has more than a few weak points to overcome as an adhesive and many trials have been made for better cyanoacrylate monomer synthesis method, additive compositions, etc.

ThreeBond started production of instant adhesive in 1969 and placed various products on the market known as "ThreeBond 1700" series with different features. In 2006, we also launched "ThreeBond 7780 Gold Label" series, the ultra-fast curing instant adhesives focusing on "INSTANT", the raison d'etre of the products.

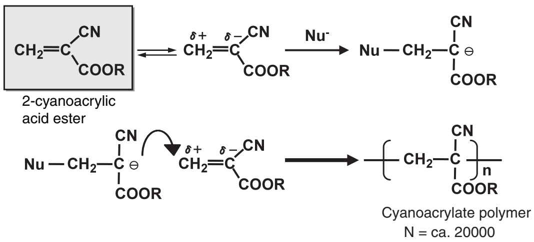
In this issue, we introduce two products of "ThreeBond 7700 Gold Label" series, developed by ThreeBond to realize high peeling- and impact-resistance and greater adhesion capabilities for difficult adherends, which were weak points of conventional instant adhesives.

Contents

1 Reaction mechanism of instant adhesive

The principal component of instant adhesive is alpha-cyanoacrylate, which has strong electrophilic groups such as cyano group, carbonyl group, etc. in its molecules, causing great charge imbalance to keep polarity in the molecules. Therefore base component such as moisture in the air works as nucleophilic agent to proceed to anionic polymerization as shown in Figure-1.

Instant adhesiveness by instant adhesives comes from its extremely sensitive, momentarily progressing reaction to anionic polymerization.



Nu⁻: nucleophilic agent – water on adherend surface, amine compound in hardening accelerator, etc.

Figure-1 Reaction mechanism of instant adhesive (Cyanoacrylate)

Curing mechanism of instant adhesive is controlled almost by this sensitive anionic polymerization and radical polymerization by heat or light is negligibly-small, allowing traces of various acidic substances to be added to improve preservative property. Curing starts when both of the whole surface reached alkalinity by least bit of water (alkaline component) absorbed in adherends having neutralized the acidic substances. Typically, radical polymerization inhibitors are added to avoid the progress of radical polymerization, be it ever so slow, during preserving period.

2 Advantages and disadvantages of instant adhesive

Major advantages of instant adhesive are:

(1) Rapid curing at ordinary temperature
(2) Good workability brought by “one-part and non-solvent”
(3) Shear-resistant adhesion capability
(4) Applicable to a wide variety of adherends
(5) Clear and colorless curing adhesion layer

Typical disadvantages are:

(1) Blooming
(2) Low heat resistance (up to 80°C)
(3) Hard curing with less flexibility and impact resistance
(4) Moisture and water resistance to be improved
(5) Filling adhesion to be improved

Instant adhesive can be used for almost all adherends to give strong adhesion as well as rapid curing. This advantage has found various applications in the market of home consumer, industrials and medical services.

Disadvantages described above are being improved gradually by selecting monomer types and investigating additives, especially for insufficient impact-, peeling-, and thermal cycle-resistance due to hard and brittle curing of instant adhesive.

These disadvantages are gradually improved by selecting monomers and investigating additives.

Some examples:

(1) To improve impact-, and peeling-resistance

Toughening components or additives such as elastomer has been formulated to ThreeBond1730 series for a great improvement.

(2) To improve resistance for humidity, heat and heatcycle

Bridged structure has been introduced into ThreeBond1757 by adding additives to enable heat and heatcycle resistance over 100°C, which conventional instant adhesives could not realize.

Now let us introduce our new products to improve weak points of instant adhesive.

3 Ultrahigh peeling- and impact-resistant instant adhesive “ThreeBond 7737 / 7738”

3-1. Outline

To overcome above mentioned weak points of less impact-, peeling-resistance, ThreeBond 7737 / 7738 have been developed for ultrahigh peeling- and impact-resistance, which has been realized by adding and alloying a special toughening component (elastomer) for ethyl-alpha-cyanoacrylate, the main component of instant adhesive.

These adhesives also have high adhesion under high heat and heatcycle environment. (Hereafter ThreeBond 7737 / 7738 are shown TB7737 / 7738.)

3-2. Properties and features

Basic properties of TB7737 / 7738 are shown in Table-1. “Curing promoter combined” in “Set time” row shows the value got when our promoter TB1796 is applied to one of the two surfaces, and 30 seconds later, the other being stuck with the adhesive applied.

Table-1. Basic properties of TB7737 / 7738

Test items		Adherend	Unit	TB7737	TB7738	Test method
Appearance		−	−	Pale yellow clear	Pale yellow clear	3TS-201-01
Viscosity		−	mPa･s	2000	5000	3TS-210-01
Structural viscosity ratio		−	−	4.8	5.0	3TS-211-02
Specific gravity (25℃)		−	−	1.07	1.08	3TS-213-02
Set time (25℃, 50%RH)	Adhesive only	NBR	sec	90	90	3TS-220-04
		Fe		90	90	
		ABS		25	25	
	Accelerator combined	NBR		25	25	
		Fe		7	7	

Table-2 shows the adhesion strength on various adherends in comparison with our old products. Lap shear strength was tested with sandblasting process for metals, and without it for non-metals. The measurement was carried out at ordinary temperature after 24 hours' curing of adhesion under 25°C and 50%RH.

Table-2. Lap shear strength on various adherends

Adherends	Lap shear strength [MPa]		
	TB7737	TB7738	Our conventional products
Iron	25.7	27.7	16.0
Aluminum	20.4	21.4	15.0
Stainless steel	18.2	17.5	12.9
Brass	24.1	26.1	5.2
Copper	20.3	18.8	13.8
Nickel	26.8	28.6	20.0
Zinc chromate	9.3	8.4	4.8
Rigid PVC	1.5	1.4	1.4
PC (Polycarbonate)	6.2(*)	5.4(*)	2.9
Phenol	9.2(*)	8.5(*)	7.6(*)
6-Nylon	7.8(*)	5.3(*)	2.7
6,6-Nylon	11.9	11.6	3.0
ABS (Acrylonitril-butadiene-styrene resin)	7.2(*)	7.6(*)	5.9(*)
Glass epoxy	16.0	17.5	16.0
PBT (Polybutylene terephthalate)	2.4	2.5	
PET (Polyethylene terephthalate)	8.8(*)	11.5(*)	9.7(*)
PPO (Polyphenylene oxide)	4.0	4.0	3.7
PPS (Polyphenylene sulfide)	3.2	3.7	4.5
HIPS (Impact-resistant polystyrene)	4.0(*)	4.0(*)	4.0(*)
Acrylic	6.6(*)	5.4(*)	4.6(*)
Polyacetal	0.4	0.5	0.5
NR (Natural rubber)	0.4(*)	0.4(*)	0.4(*)
CR (Chloroprene rubber)	0.6(*)	0.6(*)	0.6(*)
NBR (Nitrile rubber)	0.7(*)	0.7(*)	0.8(*)
SBR (Styrene-butadiene rubber)	1.5(*)	1.5(*)	1.7(*)
EPDM (Ethylene-propylene-diene terpolymer)	0.7(*)	0.7(*)	0.8(*)

Note: * in the table indicates material failure of adherends.

Table-2 shows high shearing adhesion strength especially on metals and good adhesion on a wide variety of things regardless of material.

Table-3 shows peeling-, and impact-resistant adhesion strength, Figure-2: heat-resistant adhesion at various temperatures, Figure-3: heatcycle adhesion.

Peeling adhesion strength was tested for 2 L-shaped metal plates stuck by the surface of 25 x 100mm under 25°C, 50%RH. The strength was measured for 25mm width at the speed of 50mm/min, at ordinary temperature after 24 hours' curing of adhesion under the same environment. Iron and aluminum are degreased.

Impact resisting adhesion strength was tested for 2 blocks of iron stuck by the surface of $3cm^2$ under 25°C, 50%RH. The strength was measured by Charpy impact test after 24 hours' curing of adhesion under the same environment.

Table-3. Peeling-, and impact-resisting adhesion strength

Test items	Adherend	Unit	TB7737	TB7738	Our conventional product	Test method
Peeling adhesion strength	Fe/Fe	kN/m	**3.4**	**4.2**	1.0	3TS-304-21
	Al/Al		**3.4**	**2.9**	2.0	
Impact-resisting adhesion strength	Fe/Fe	kJ/m^2	**28**	**34**	13	3TS-324-01

Heat resisting adhesion was tested for two iron plates stuck under 25°C, 50%RH. The strength was measured after 24 hours' curing of adhesion under the same environment for lap shear strength by 2 hours' exposure at various temperatures.

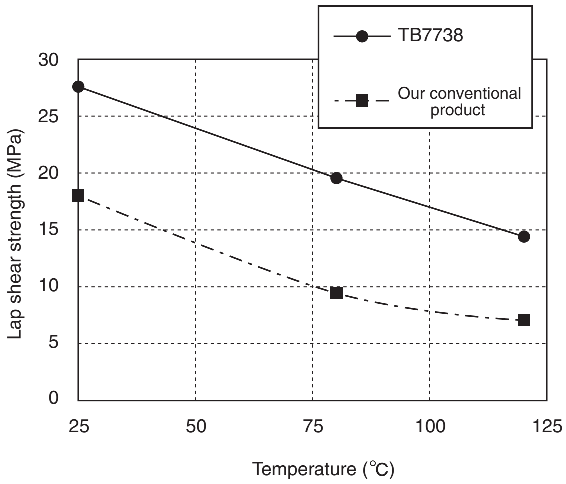


Figure-2. Heat resisting adhesion at various temperatures

Thermal cycle resistance was tested for two iron test specimens stuck under 25°C, 50%RH. The strength was measured after 72 hours' curing of adhesion under the same environment for lap shear strength back in ordinary temperatures from predefined exposure to heat cycles alternating between – 40°C x 1 hour and 120°C x 1 hour.

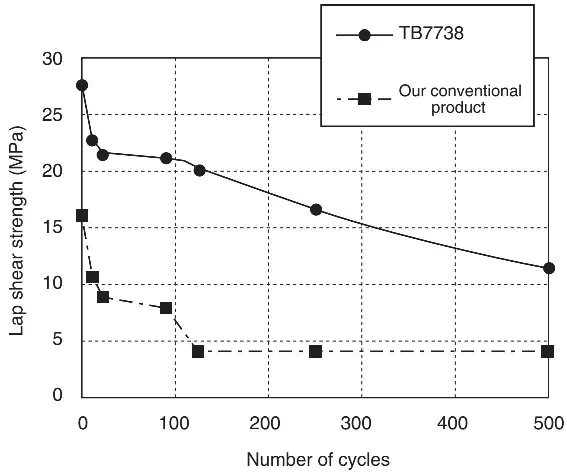


Figure-3. Heatcycle resistance

Table-3 shows that the new products have far more improved peeling and impact adhesion strength compared to old improved ones. Figure-3 and 4 also shows that they keep lap shear strength over 10MPa for 120°C aging and 500 thermal cycles between -40°C and 120°C.

TB7737 / 7738 are so high-functional that keep adhesion strength and impact resistance under these extremely harsh environments.

3-3. Main applications

TB7737 / 7738 series have ultrahigh peeling and impact-resisting strength that could not be realized by conventional products. Therefore, they can be used in more harsh environments where instant adhesives have not been applied. The appearance is in semi-gel state, not drippy but fluid enough to apply to bonding small parts of electronics.

<Main applications>

(1) Bonding general parts requring high strength and impact resistance
(2) Dripping-free sticking such as on vertical surface
(3) Bonding various electronics parts on printed-circuit board such as IC chips, condensers, etc.
(4) Bonding speaker parts such as cone paper and magnets
(5) Bonding weather-strip for cars, etc.

4. Exclusive multi-primer “ThreeBond 7797” for instant adhesives

4-1. About primers

High-polymer materials such as polypropylene, polyethylene, polyacetal, polytetrafluoroethylene (teflon®), silicone rubber are very commonly used for consumer and industrial uses. However these materials are known difficult to adhere generally, which have required very much effort to solve the problem of insufficient adhesion when stuck with usual adhesives.

The main characteristics causing the insufficiency can be interpreted as due to little surface energy of the materials and little wettability of adhesives on the surface of adherends which should contribute to adhesion, that is, little conformity of adhesives with adherends.

Cyanoacrylate, the adhesive material of instant adhesives, is a polar material whereas difficult adherends such as polypropylene are nonpolar, which explains the difference of SP (solubility parameter) value telling the difficult onset of adhesion.

Existing typical solution to this problem has been improving the surface wettability of adherends for adhesion onset by applying and interposing pretreatment material (primer) comprised of components such as amine and solvent. However, it is difficult to get stable onset of adhesion for the wide variety of adherends.

ThreeBond has now developed high-reliability multi-primer which deliver stable onset of adhesion for a wide variety of adherends after its research for primers to solve the problem of adhesion difficulty.

Exclusive multi-primer “ThreeBond 7797” for instant adhesives specialized to be used with instant adhesive has excellent quick drying and workability in addition to good adhesion for difficult adherends. Details are described below.

(Hereafter ThreeBond 7797 is referred to as TB7797.)

4-2. Properties and characteristics

Properties and general characteristics of TB7797 are shown in Table-4. Lap shear strength was tested for difficult adherends, both of whose surfaces to stick were applied with TB7797 by absorbent cotton and left 2 minutes for solvent sublimation, then one of the surfaces was applied with TB7784 (see Table-8 at the end) and stuck, and the strength was measured after 24 hours’ curing of adhesion under 25°C, 50%RH.

Table-4. Properties and general characteristics of TB7797

Test items	Adherend	Unit	Characteristic value	Test method
Appearance	-	-	Clear and colorless	3TS-201-01
Specific gravity (25℃)	-	-	0.67	3TS-213-01
Lap shear strength (25℃, 50%RH×24hrs) TB7784	PE	MPa	5.0(*)	3TS-301-11
	PP		6.6(*)	
	POM		9.0(*)	
	PTFE		2.5 (*: deformed)	
	Silicone rubber		0.3(*)	

Note: * in the table indicates material failure of adherends.

Tables 5, 6 and 7 show lap shear strengths and environmental durabilities (heat resistance, thermal cycle resistance, and chemical resistance) of various adherends when stuck using TB7797 and TB7784.

Lap shear strengths of various adherends are measured at 50mm/min tension rate for gum elastomer, 10mm/min for others.

Table-5. Lap shear strengths of various adherends

Adherends	Lap shear strength [MPa]	
	TB7784 TB7797 combined	TB7784 No primer combined
Iron	8.2	15.3
Aluminum	11.8	16.1
SUS304	8.1	15.4
Brass	7.8	11.5
Copper	9.6	13.3
Nickel	6.3	15.7
Zinc chromate	3.0	8.0
Rigid PVC	6.5(*)	4.4(*)
PC (Polycarbonate)	5.8(*)	6.2(*)
Phenol	6.6(*)	9.2(*)
6-Nylon	6.1(*)	7.8(*)
6,6-Nylon	13.1(*)	11.9
ABS (Acrylonitril-butadiene-styrene resin)	6.7(*)	7.2(*)
Glass epoxy	14.6	18.8
PBT (Polybutylene terephthalate)	11.5(*)	4.5
PET (Polyethylene terephthalate)	9.3(*)	10.6(*)
PPO (Polyphenylene oxide)	2.8	6.8
PPS (Polyphenylene sulfide)	4.6	2.5
HIPS (Impact-resistant polystyrene)	4.5(*)	4.4(*)
Acrylic	4.6(*)	8.7(*)
Liquid crystalline polymer	3.8	2.0
Polyacetal	9.0(*)	1.3
PP (Polypropylene)	5.0(*)	0.3
PE (Polyethylene)	6.6(*)	1.2
PTFE (Polytetrafluoroethylene)	2.5(*: deformed)	0.3
Silicone rubber	0.3(*)	0.3(*)
NR (Natural rubber)	0.4(*)	0.4(*)
CR (Chloroprene rubber)	0.6(*)	0.6(*)
NBR (Nitrile rubber)	0.9(*)	0.8(*)
SBR (Styrene-butadiene rubber)	1.7(*)	1.8(*)
EPDM (Ethylene-propylene-diene terpolymer)	0.7(*)	0.8(*)

Note: * in the table indicates material failure of adherends.

Table-5 shows high lap shear strength onset for plastics hard to bond such as polyethylene.

As for exposure test, lap shear strength was measured back in ordinary temperature after exposing for predetermined time.

Table-6. Lap shear strength after exposure

TB7784		Lap shear strength [MPa]				
Exposure condition		PE	PP	POM	PTFE	Silicone rubber
80℃	250h	4.7(*)	6.2(*)	3.0(*)	2.5 (*: deformed)	0.2(*)
60℃×95%	250h	4.6(*)	6.6(*)	2.6(*)	2.5 (*: deformed)	0.3(*)
60℃×95%RH	250h	4.6(*)	6.6(*)	2.6(*)	2.5 (*: deformed)	0.3(*)
Heat cycle (-40℃×1h to 60℃×1h)	60 cycles	4.9(*)	6.6(*)	7.4(*)	2.5 (*: deformed)	0.2(*)

Note: * in the table indicates material failure of adherends.

As for chemical resistance, lap shear strength was measured back in ordinary temperature after 250 hours' immersion in various chemicals.

Table-7. Lap shear strength after immersion in various chemicals

TB7784		Lap shear strength [MPa]				
Chemicals	Immersion temp.	PE	PP	POM	PTFE	Silicone rubber
Tap water	40℃	4.8(*)	6.3(*)	7.9(*)	2.5 (*: deformed)	0.3(*)
Engine oil	40℃	4.9(*)	6.6(*)	7.9(*)	2.5 (*: deformed)	0.2(*)
Gasoline	25℃	4.2(*)	6.0(*)	8.6(*)	2.5 (*: deformed)	0.2(**)
Heating oil	25℃	4.6(*)	6.2(*)	7.6(*)	2.5 (*: deformed)	0.1(**)
Methanol	25℃	4.6(*)	6.6(*)	7.2(*)	2.5 (*: deformed)	0.3(*)

Note: * in the table indicates material failure of adherends.
** in the table indicates material failure by swelling of silicone rubber itself.

Figure-4 shows the status after lap shear strength test of PE (polyethylene) test specimen, on which TB7797 was applied and stuck with TB7784. The figure tells how adhesion strength for difficult adherends improves with TB7797.

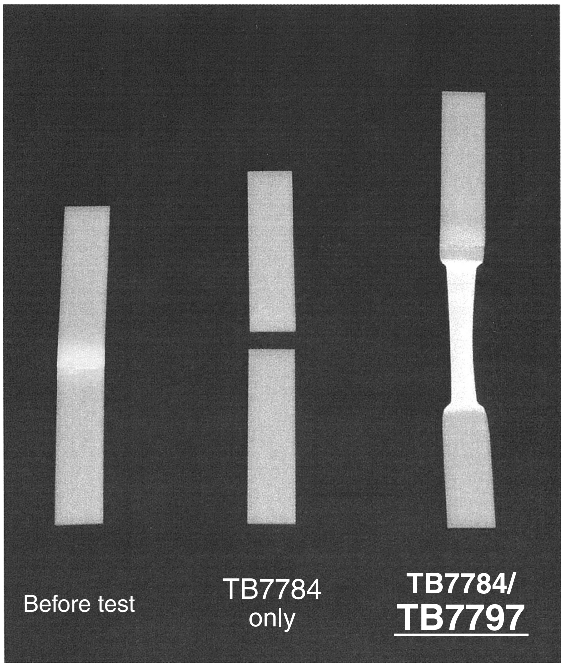


Figure-4. Polyethylene test specimen after lap shear strength test

As seen above, TB7797 is a multi-primer which dramatically improves adhesion for various difficult adherends, and delivers onset of stable adhesion under exposure environment by heat and chemicals.

Main features of TB7797 are:
(1) Far improved adhesion for difficult adherends
(2) Quick drying and good workability
(3) Brush, absorbent cotton, cotton swab, etc. can be used for easy application
(4) Usable for all ThreeBond instant adhesive series (TB1700 and 7700 series)

4-3. Applications

TB7797 is an exclusive primer specialized in instant adhesive. It is recommended to be used as pretreatment material for instant adhesive when bonding parts comprising of various difficult adherends (polypropylene, polyethylene, polyacetal, polytetrafluoroethylene, silicone rubber).

5. Product line of ThreeBond 7700 Gold Label series

We launched "ThreeBond 7780 Gold Label" series, the ultra-fast curing instant adhesives focusing on "INSTANT", the raison d'etre of the products, in the course of development. We are also seeking a way to more multi-potent products by adding higher functionalities in this series. Please see Table-8 below for the product line of ThreeBond 7700 Gold Label series since 2006 launch.

We continue to develop and improve product line of ThreeBond 7700.

Table-8. The product line of ThreeBond 7700 Gold Label series (as of January, 2009)

Category	Application	TB grade	Viscosity [mPa・s]	Features
ThreeBond 7700 Gold Label series	Ultrahigh peeling-, impact-resistance type	7737	2000	- Excellent peeling strength and impact resistance
		7738	5000	- Good heat and humidity resistance
	Standard type	7741	2	- General purpose type for various materials
	Ultra-fast curing type	7781	2	- Good for ultra-fast curing - Good for porous materials and acid paper - Good adhesion for difficult adherends (POM, PPS, etc.)
		7782	15	
		7784	160	
		7785	500	
		7786	1000	
	Multi-primer specialized in instant adhesive	7797	—	- Adhesion brought to the extent of material failure for PP, PE, PTFE, POM, etc.

Note: TB is referred to as ThreeBond

Conclusion

It has been 60 years since the development and penetration of alpha-cyanoacrylate adhesive and a wide variety of products has been delivered until now through repeated improvements by many researchers. They have advantages of one-part and non-solvent, and instant curing, however, they also have disadvantages of blooming, less heat-resistant and less impact-resistant; the latter having been big issues for ages to overcome.

The two products introduced here are supposed to have shown the possibilities of instant adhesives for multifaceted applications by not only overcoming disadvantages of instant adhesives and improving peeling- and impact-resistance, but solving the issues of adhesion of difficult adherends which has been generally thought very difficult for any types of adhesives.

We appreciate your continued support as we strive to meet the needs of customers and develop new products. We are also going to focus on improving preservative quality of instant adhesive itself and developing completely new high functionality never found in existing ones.

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