ThreeBond TECHNICAL NEWS

Three Bond Technical News
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46

Instant Adhesives
(Cyanoacrylate Adhesives)
<Part 3>

Introduction

It has passed 38 years since instant adhesives were first introduced to the global market in 1957. Today, instant adhesives are used in a variety of applications for industrial, medical, and general domestic purpose. The main reason that usage fields of instant adhesives have expanded can be found on its ease of use, which is one-part adhesive and bonds any materials strongly and instantaneously at room temperature. As it can be used easily, demands of instant adhesives are high, however, especially in industrial fields it is not adopted in many cases due to the bonding performance and durability. Therefore, it is demanded to develop instant adhesives with higher performances.

Three Bond has developed and marketed ThreeBond 1731 / 1733, and ThreeBond 1737 / 1738 as the products improving peeling strength and shock resistance that are disadvantages of instant adhesives. This issue will introduce the background and history of the development of these products and will describe their characteristics.

Contents

Introduction
1. Polymer properties and strengthening 2
2. Instant adhesive properties and strengthening 3
3. Polymerization-inducing phase-separated structure of cyanoacrylate/rubber alloy 5
4. Second-generation instant adhesives-ThreeBond 1731 and 1733 6
5. Third-generation instant adhesives-ThreeBond 1737 and 1738 7
6. The ThreeBond 1700 Series 8

1. Polymer properties and strengthening

Wu has reported that the properties of thermoplastic polymers can be classified into the following types based on two molecular parameters: entanglement density υ_e (mmole/cc) of the polymer chain and the characteristic ratio C_∞[1).

(1) Brittle polymers (hard and brittle polymers)

$\upsilon_e \leq \sim 0.15$, $C_\infty \geq \sim 7.5$

(2) Pseudo-ductile polymers (soft polymers)

$\upsilon_e \geq \sim 0.15$, $C_\infty \leq \sim 7.5$

(3) Intermediate polymers

$\upsilon_e = \sim 0.15$, $C_\infty = \sim 7.5$

Figure 1 shows how various polymers are grouped according to this classification scheme.

Also, regarding polymers alloyed by adding rubber components, Wu shows optimal dispersion morphology of the rubber components for strengthening polymers, as follow.

(1) Optimal diameter of rubber particle exists for alloys consisting of brittle polymers/rubber component (Figure 2).

(2) Optimal surface-to-surface distance between rubber particles exists for alloys consisting of pseudo-ductile polymer/rubber component (Figure 3).

(3) Special rubber phase morphology is required for alloys consisting of intermediate polymer/rubber component.

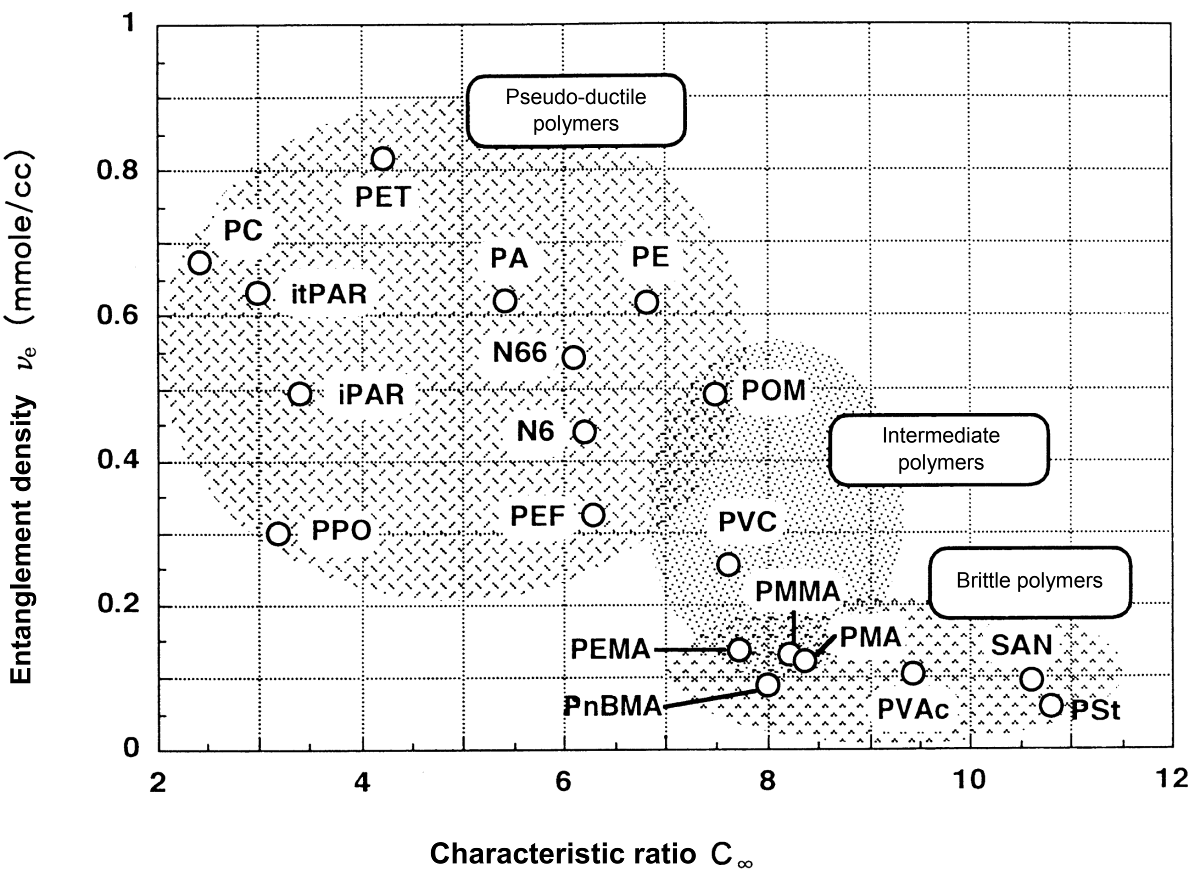


Figure 1: Classification of various thermoplastic polymers

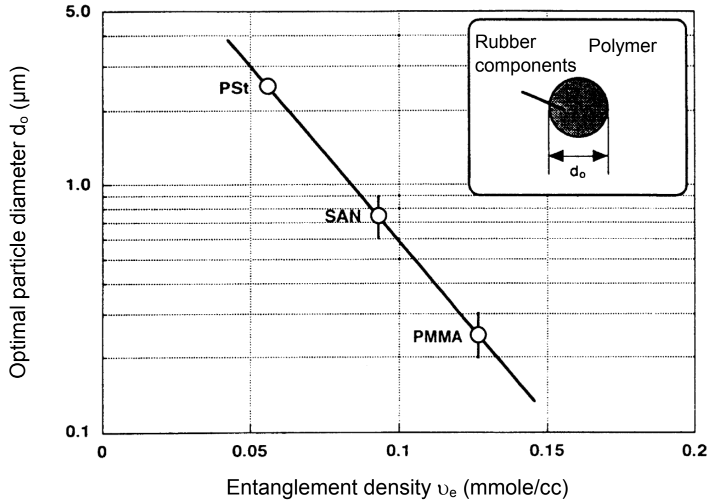


Figure 2: Brittle polymers and optimal particle size

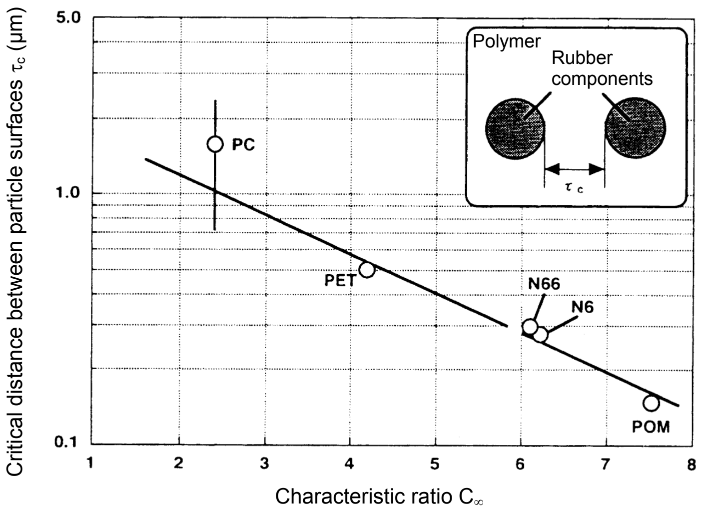


Figure 3: Pseudo-ductile polymers and critical distance between particle surfaces.

2. Instant adhesive properties and strengthening

Cyanoacrylate (cyanoacrylic acid ester), the main constituent of instant adhesives, reacts with trace amounts of moisture on the surface of the materials to be bonded and cures by polymerization to form cyanoacrylate polymers (Figure 4).

Because these polymers are hard and brittle, they feature high shearing strength in the shearing direction, but are weak in strength for peeling and shock. Figure 5 shows the results of calculation according to Wu's method[2)] of two molecular parameters representing polymer properties for ethyl cyanoacrylate, the most popular adhesive on the market today.

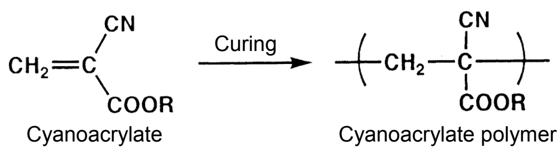
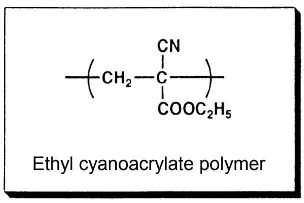


Figure 4: Curing of cyanoacrylate



$\nu_e \approx 0.079 < 0.15$

$C_\infty \approx 9.15 > 7.5$

Figure 5: Ethyl cyanoacrylate polymer and values of molecular parameters

When strengthening poly (ethylcyanoacrylates) (PECA), which is a brittle polymer according to Wu's classification, by adding rubber components, it is concluded that there an optimal rubber particle diameter exists. Figure 6 shows the brittleness of PECA compared to other polymers, and Figure 7 shows the results of calculation for the optimal diameter of rubber particle.

According to Wu's theory, for alloy consisting of PECA/rubber, the optimal particle diameter for strengthening PECA is around 1 μm.

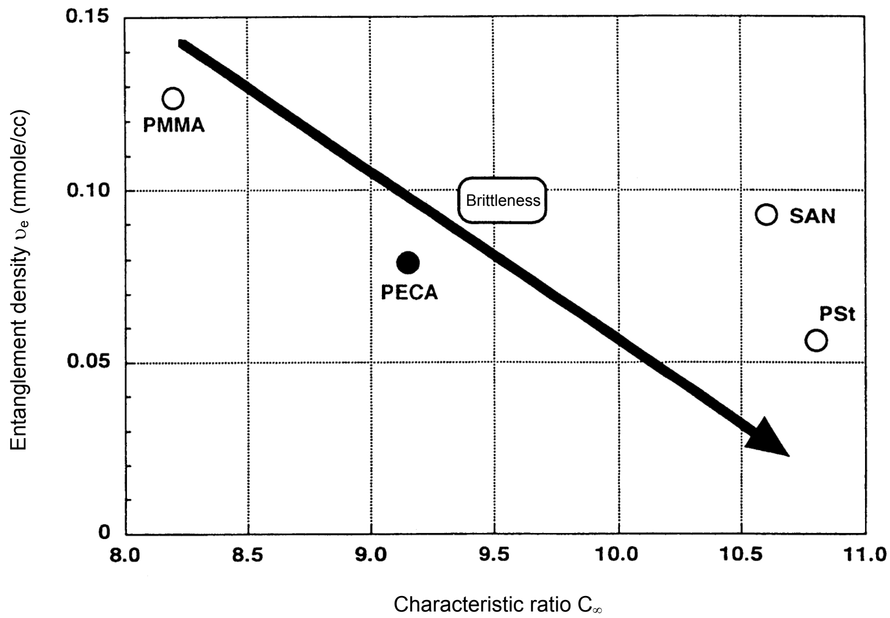


Figure 6: Brittleness of PECA

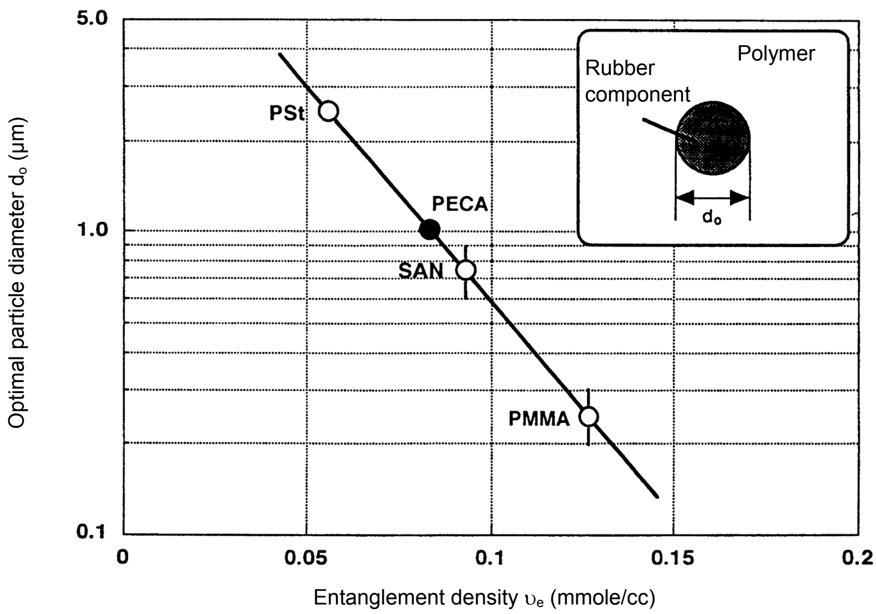


Figure 7: Entanglement density and the optimal particle diameter for PECA

3. Polymerization-inducing phase-separated structure of cyanoacrylate/rubber alloy[3,4)]

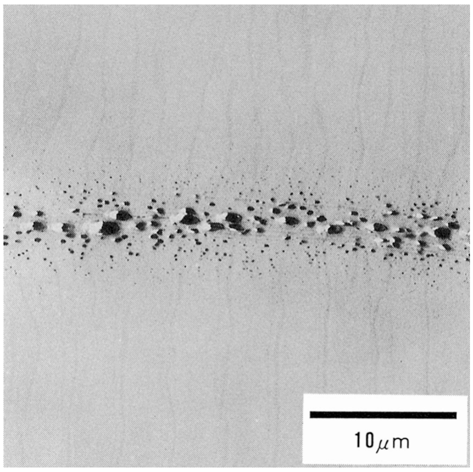


Figure 8: Dispersion of rubber particles within cured adhesive

Figure 8 is a transparence type electron microscope image of the state of rubber component dispersion within the cured cyanoacrylate adhesive to which a rubber component has been added.

The rubber is concentrated in the central portion of the cured adhesive, and it was found that the rubber particles were dispersed in spheres of diameters ranging from the submicron level to around 1 micrometer. This concentrated morphology is understandable in that the curing of cyanoacrylate is initiated by contact with moisture on the surface of the materials to be bonded. As stated above, curing progresses from the bonding surface toward the interior parts of the adhesive. Therefore, the rubber particles are concentrated at the central portions of the adhesive, ultimately leading to phase separation (Figure 9).

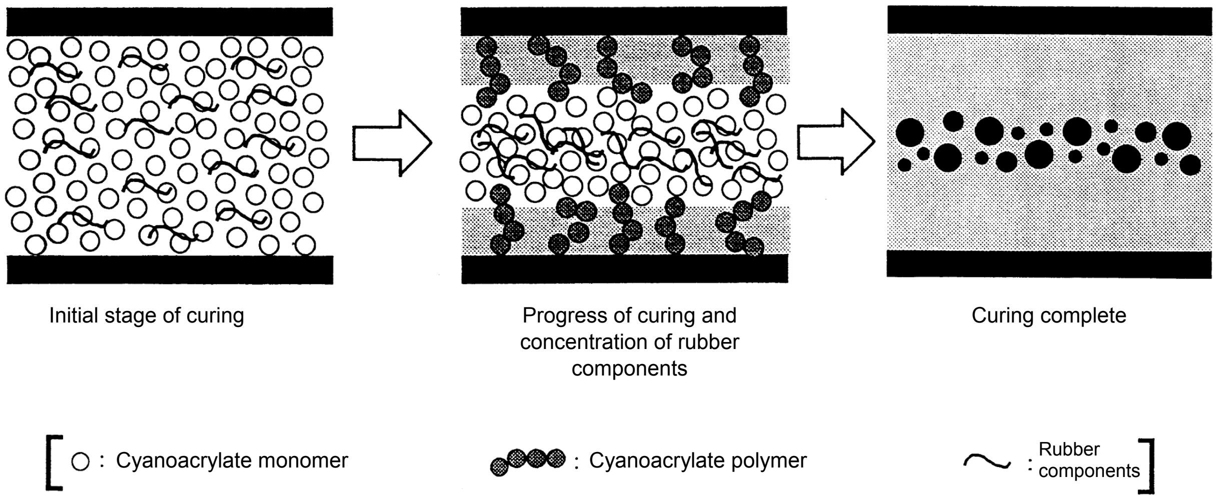


Figure 9: Polymerization of cyanoacrylate and phase separation

We developed instant adhesives with higher peeling strength and excellent shock resistance, applying the examination for strengthening polymers through alloying with rubber, and the results of analysis of the phase separation structure based on the unique polymerization mechanism of cyanoacrylate,

4. Second-generation instant adhesives –ThreeBond 1731 and 1733[5, 6, 7]

ThreeBond 1731 and 1733 are second-generation high-performance instant adhesives with non-conjugated rubber components dissolved in the main constituent, cyanoacrylate; these components undergo phase separation as curing progresses (Figure 10). Table 1 shows the properties and general characteristics of these products.

In addition to the properties shown in Table 1, alloying with rubber improves cold resistance, heat cycle resistance based on reduction of thermal stress, and heat resistance. Furthermore, with the improvements of bonding ability for the bonding resistant materials such as ethylene-propylene-diene terpolymers (EPDM), it became possible to apply these adhesives on semi-structure applications that could not use conventional instant adhesives.

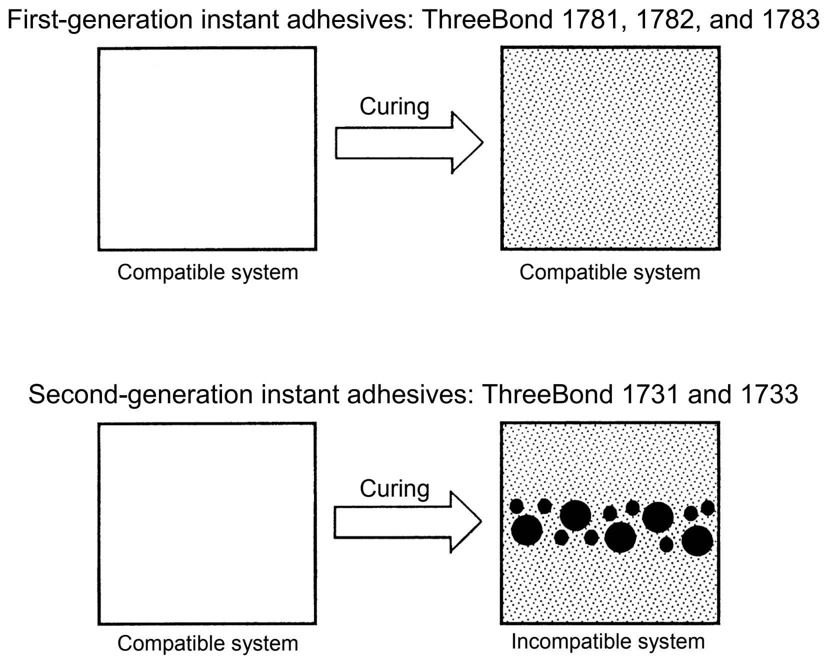


Figure 10: Phase structures of first-generation and second-generation instant adhesives

Table 1: Properties and general characteristics of ThreeBond 1731 and 1733

Items		Units	TB1731	TB1733
Color and appearance		-	Lemon yellow	Lemon yellow
Viscosity		mPa•s {cP}	20 {20}	150 {150}
Set time	Fe/Fe	Seconds	10	20
Shearing adhesive strength	Fe/Fe	Mps {kgf/cm^2}	19 {190}	16 {160}
	Al/Al		10 {100}	11 {110}
Peeling adhesive strength	Fe/Fe	kN/m {kgf/25mm}	3.0 {8.0}	3.0 {8.0}
	Al/Al		2.0 {5.0}	2.0 {5.0}
Impact adhesive strength	Fe/Fe	kJ/m^2 {kgf•cm/cm^2}	34 {35}	34 {35}

(TB: abbreviation for ThreeBond)

5. Third-generation instant adhesives –ThreeBond 1737 and 1738[8)]

ThreeBond 1737 and 1738 are third-generation high-performance instant adhesives in which the conjugated rubber components are dispersed within the main constituent, cyanoacrylate, with a pre-designed phase separation structure regardless curing of the adhesive (Figure 11). The properties and general characteristics of these adhesives are shown in Table 2.

A special feature of these third-generation instant adhesives is the pre-designed dispersion state of the rubber components. Thus, consistent performance is achieved at all times. One example of where this is advantageous is on materials to be bonded with acidic surfaces, such as wood, on which adhesives cure more slowly; as a result, the dispersion of the rubber components in second-generation adhesives is not consistent on such surfaces. In other words, the changes on curing speed result changes of dispersion state, and appeared as changes of performance.

Furthermore, ThreeBond 1737 and 1738 are semi-gel-type and gel-type formulations, respectively, with high thixotropic properties. Thus, these products offer improved workability and are better suited for automated adhesive application. That thixotropic properties are high mean that there exists large difference between adhesive viscosities in stressed conditions (such as when squeezing the adhesive out of the container) and unstressed conditions (such as after coating onto the material to be bonded). Thus, these adhesives are good in fluidity, but also proof against dripping.

Third-generation instant adhesives: ThreeBond 1737 and 1738

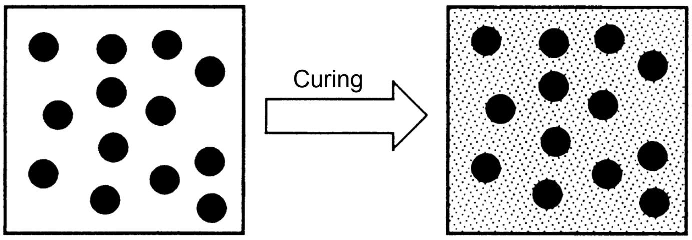


Figure 11: Phase structure of third-generation instant adhesives

Table 2: Properties and general characteristics of ThreeBond 1737 and 1738

Items		Units	TB1737	TB1738
Color and appearance		-	Light blue	Light blue
Form		-	Semi-gel form	Gel form
Specific gravity		-	1.04	1.04
Viscosity		Pa•s {cP}	2 {2000}	5 {5000}
Thixotropic index		-	5.2	5.6
Setting time	NBR/NBR	Seconds	20	30
	Fe/Fe		30	40
Shearing adhesive strength	Fe/Fe	MPa {kgf/cm^2}	16 {160}	16 {160}
	Al/Al		15 {150}	15 {150}
Peeling adhesive strength	Al/Al	kN/m {kgf/25mm}	1.3 {3.3}	2.0 {5.0}
Impact adhesive strength	Fe/Fe	kJ/m^2 {kgf•cm/cm^2}	13 {13}	13 {13}
Dielectric breakdown voltage		MV/m {kV/mm}	26 {26}	48 {48}
Volume resistivity		Ω •m { Ω •cm}	3.53×10^{11} {3.53×10^{13}}	1.59×10^{11} {1.59×10^{13}}
Surface resistivity		Ω	2.51×10^{14}	4.40×10^{14}
Dielectric constant		-	3.287	3.375
Dielectric loss tangent		-	0.033	0.036

(TB: abbreviation for ThreeBond)

6. The ThreeBond 1700 Series

Three Bond instant adhesives and related products are introduced. These include a variety of products with a wide range of properties and functions suited to the workability and usage. Related products include peelers for removing cured adhesives, curing accelerators, and primers to enable adhesion of bonding resitant materials such as polyethylene, polypropylene, and polyacetal.

We also provide automatic coaters, the S-II Coater, which ejects adhesives via pressurized air, and the SMF-02B Coater, which ejects adhesives using a tubing pump mechanism.

Table 3: Three Bond instant adhesives and related products

ThreeBond 1700 Series			Color	Viscosity mPa•s [cP]	Content
Multi - purpose grade	Ethyl type	1741	Colorless	3 {3}	2, 2, 50 g
		1743	Colorless	100 {100}	20 g
		1745	Lemon yellow	500 {500}	20, 500 g
		1747	Lemon yellow	2000 {2000}	20 g
	Methyl type	1701	Colorless	3 {3}	20, 50 g
		1702	Colorless	35 {35}	2, 20, 50 g
Functionality grade	Colored type	1702 B	Blue	35 {35}	50 g
		1741 D	Blue	3 {3}	20 g
		1743 D	Blue	100 {100}	20, 500 g
	Slow curing type	1713	Colorless	100 {100}	20 g
	Low-odor low-blooming type	1721	Colorless	10 {10}	20, 50 g
	High peeling strength and impact resistant type	1731	Lemon yellow	20 {20}	20, 50 g
		1733	Lemon yellow	150 {150}	20, 50, 500 g
		1737	Light blue	2000 {2000}	50 g
		1738	Light blue	5000 {5000}	20 g
	Gel type	1739	Colorless	Gel form	20, 500 g
	Impact-resistant and heat-resistant type	1781	Colorless	3 {3}	20, 50, 500 g
		1782	Colorless	80 {80}	20, 50, 500 g
		1783	Lemon yellow	1000 {1000}	50, 500 g
	Fast curing woodwork type	1785 B	Colorless	3 {3}	20 g
		1786	Colorless	150 {150}	20, 50 g
		1787	Lemon yellow	1100 {1100}	20, 50 g
Peeler		1795	Colorless	1.0 {1.0}	50 g
Curing accelerators		1796	Lemon yellow	0.9 {0.9}	45 g
		1796 B	Lemon yellow	0.9 {0.9}	45 g
		1796 E	Lemon yellow	0.9 {0.9}	500 ml
Adhesive primers for hard-to-bond surfaces		1797	Lemon yellow	0.85 {0.85}	100 ml

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