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## Mini Review

# Current bonding systems for resin-bonded restorations and fixed partial dentures made of silver–palladium–copper–gold alloy

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**Summary** This review article describes about the bonding systems for noble metal alloys, bonding techniques of restorations and fixed partial dentures (FPDs) made of Ag–Pd–Cu–Au alloys, and their clinical performance. Thione monomers, 6-(4-vinylbenzyl-*n*-propyl) amino-1,3,5-triazine-2,4-dithione (VTD), 6-methacryloyloxyhexyl-2-thiouracil-5-carboxylate (MTU-6), and 10-methacryloxydecyl 6,8-dithiooctanoate (MDDT), has been proved effective for bonding noble metal alloys. An acrylic adhesive consists of the tri-*n*-butylborane (TBB) initiator, methyl methacrylate (MMA) monomer liquid with 5% 4-methacryloyloxyethyl trimellitate anhydride (4-META), and poly(methyl methacrylate) (PMMA), is being used for bonding metallic restorations to abutment surfaces. Clinical performance of restorations and FPDs made of Ag–Pd–Cu–Au alloys is overall excellent when they are seated with the currently available noble metal bonding systems.

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## 1. Introduction

Over the last decade, the use of dental adhesives for bonding restorations and fixed partial dentures has increased sub-

stantially. This trend is mainly attributed both to improvement in properties as well as bonding durability of adhesive systems. Current bonding and priming agents contain various functional monomers especially designed for intraoral application, including carboxylic acids, acid anhydrides, phosphates, silanes, and thiones.

Silver–palladium–copper–gold (Ag–Pd–Cu–Au) alloys with 12% gold are extensively used in Japan as cast restorations, fixed partial dentures, and framework of removable dentures. In addition, a number of bonding systems for noble metal alloys have been developed. This paper reports on the

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**Table 1** Priming agents applicable for bonding Ag–Pd–Cu–Au alloys.

Trade name	Manufacturer	Composition	Authors	Year, Ref. No.
V-Primer	Sun Medical Co., Ltd, Moriyama, Japan	VTD, Acetone	Mori et al.	1983 [1]
Alloy Primer	Kuraray Medical Inc., Tokyo, Japan	VTD MDP, Acetone	Mori et al. Omura et al.	1983 [1] 1983 [5]
Metaltite	Tokuyama Dental Corp., Tokyo, Japan	MTU-6, Ethanol	Kimura et al.	1998 [3]
M.L. Primer	Shofu Inc., Kyoto, Japan	MDDT MHPA, Acetone	Fujii et al. Wada et al.	2003 [4] 2001 [6]

VTD; 6-(4-vinylbenzyl-*n*-propyl) amino-1,3,5-triazine-2,4-dithiol, or -2,4-dithione tautomer; MDP; 10-methacryloyloxydecyl dihydrogen phosphate; MTU-6; 6-methacryloyloxyhexyl-2-thiouracil-5-carboxylate; MDDT; 10-methacryloyloxydecyl 6,8-dithiooctanoate; MHPA; 6-methacryloyloxyhexylphosphonoacetate.

bonding systems applicable for noble metal alloys, techniques for seating restorations and fixed partial dentures (FPDs) made of Ag–Pd–Cu–Au alloys, and clinical performance of bonding systems.

## 2. Functional monomers applicable for priming noble metal alloys

Carboxylic acids, acid anhydrides, and phosphates are being used for bonding tooth substrates, base metal alloys, alumina and zirconia ceramic materials. However, they are incapable of bonding noble metal alloys. The use of thione or thiol monomers has been proved effective for bonding noble metal alloys. Mori and Nakamura [1] reported 6-(4-vinylbenzyl-*n*-propyl) amino-1,3,5-triazine-2,4-dithiol (VTD or VBATDT) for use as a priming agent for copper. Using the VTD dithiol-dithione tautomer and tri-*n*-butylborane (TBB)-initiated resin, Kojima et al. [2] reported durable bond of VTD to noble metal alloys. Two sulfur-based functional monomers were thereafter synthesized. One is 6-methacryloyloxyhexyl-2-thiouracil-5-carboxylate (MTU-6) [3], and the other is 10-methacryloyloxydecyl 6,8-dithiooctanoate (MDDT) [4].

Four representative priming agents, all of which consist of single liquid, are currently available (Table 1); V-Primer (VTD), Alloy Primer (VTD), Metaltite (MTU-6), and M.L. Pri-

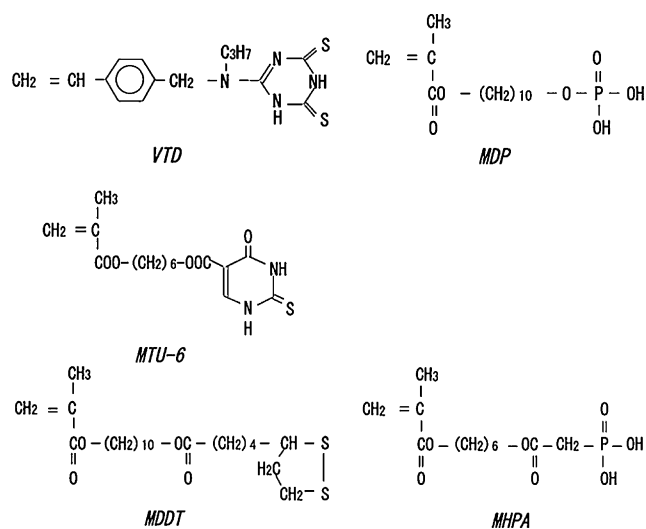
mer (MDDT). Among the functional monomers shown in Table 1, VTD, MTU-6, and MDDT contain sulfur, and considered to be effective for bonding noble metal elements, copper, and noble metal alloys, whereas two acidic monomers, 10-methacryloyloxydecyl dihydrogen phosphate (MDP) [5] and 6-methacryloyloxyhexylphosphonoacetate (MHPA) [6], are considered to be effective for bonding base metal alloys and titanium. Fig. 1 shows the structural formulae of adhesive functional monomers. The single liquid primers eliminated the need for surface modification procedures, and are being successfully used for seating FPDs, cast restorations, and dowel cores made of noble metal alloys.

## 3. Bonding between indirect composites and Ag–Pd–Cu–Au alloys

Before application to seating restoration and FPDs, thiol and thione primers were used for bonding composite veneering materials and cast frameworks made of noble metal alloys. The V-Primer material was effective for bonding between Ag–Pd–Cu–Au alloy and Dentacolor [7], Visio-Gem [8], and Axis [9] composites. An evaluation study comparing the effect of priming agent demonstrated that adhesive performance of the Alloy Primer and Metaltite agents was better than that of the V-Primer material, when the Axis composite was bonded to an Ag–Pd–Cu–Au alloy [9].

## 4. Bonding between luting agents and Ag–Pd–Cu–Au alloys

Single liquid primers were used in combination with resin-based luting agents. An initial evaluation exhibited that durability of bond the Super-Bond C&B resin joined to Co–Cr and Ag–Pd–Au–Cu alloys was comparable [10]. The Super-Bond C&B resin consists of the TBB initiator, methyl methacrylate (MMA) monomer liquid with 5% 4-methacryloyloxyethyl trimellitate anhydride (4-META), and finely pulverized poly(methyl methacrylate) (PMMA) powder (4-META/MMA-TBB resin). According to a 100,000-thermocycling evaluation, bond strength to Ag–Pd–Cu–Au alloy of the Super-Bond resin was 23.0 MPa without application of primer, whereas 38.1 MPa with application of the V-Primer material [11]. Another 100,000-thermocycling evaluation showed that durability of bond to gold and Ag–Pd–Cu–Au alloys using the V-Primer and Super-Bond materials was comparable [12]. Adhesive performance of the Metaltite



**Figure 1** Structural formulae of adhesive functional monomers used for bonding casting alloys.

**Table 2** Technical procedure and clinical performance of resin-bonded restorations and FPDs made of Ag–Pd–Au–Cu alloy.

Castings	Abutments	Pontic, Veneer	Enamel etching	Metal conditioning	Luting agent	Observation period	Authors	Year, Ref. No.
RBFPD	33 35 WA	34 Dentacolor	40% H <sub>3</sub> PO <sub>4</sub>	AAA, V-Primer	Super-Bond C&B Opaque	5.5 years 10 years	Monya et al. This paper	1998 [18] Figs. 2–4
RBFPD	34 36 WA	35 Cast pontic	37% H <sub>3</sub> PO <sub>4</sub>	AAA, Metaltite	C&B Metabond Ivory	6 years	Shimizu et al.	2004 [19]
RBFPD	13 11 21 23 WA	12 22 Axis	65% H <sub>3</sub> PO <sub>4</sub>	AAA, V-Primer	Super-Bond C&B Opaque	4 years	Tanoue et al.	2004 [20]
RBFPD	13 CVR 11 WA	12 Cesead	40% H <sub>3</sub> PO <sub>4</sub>	AAA, V-Primer	Super-Bond C&B Opaque	10 years	Matsumura et al.	2004 [21]
RBFPD	33 35 WA	34 Solidex	37% H <sub>3</sub> PO <sub>4</sub>	AAA, Metaltite	C&B Metabond Ivory	3 years	Shimizu et al.	2006 [22]
RBFPD	13 WA 11 OC	12 Solidex	37% H <sub>3</sub> PO <sub>4</sub>	AAA, Alloy Primer	Super-Bond C&B Ivory	6 years	Shimizu et al.	2006 [23]
RBFPD	23 PR, 25 MR	24 Solidex	37% H <sub>3</sub> PO <sub>4</sub>	AAA, Metaltite	C&B Metabond		Shimizu et al.	2007 [24]
RBFPD	21 23 WA	22 Cesead II	37% H <sub>3</sub> PO <sub>4</sub>	AAA, Metaltite	Super-Bond C&B Ivory	6 years	Shimizu et al.	2007 [25]
RBFPD	34 36 WA	35 Cast pontic	37% H <sub>3</sub> PO <sub>4</sub>	AAA, Metaltite	Super-Bond C&B Ivory		Shimizu et al.	2007 [26]
RBFPD	43 41 WA	42 Composite	40% H <sub>3</sub> PO <sub>4</sub>	AAA, Alloy Primer	Panavia Fluoro Cement	7.5 years	Matsumura et al.	2008 [27]
Rest Seat	43 34	None	37% H <sub>3</sub> PO <sub>4</sub>	AAA, V-Primer	Super-Bond C&B Ivory	11 years	Shimizu et al.	2008 [28]
RBFPD	18 16 WA	17 Cast pontic	40% H <sub>3</sub> PO <sub>4</sub>	AAA, V-Primer	Super-Bond C&B Opaque	6.5 years	Koizumi et al.	2009 [29]
RBFPD	23 WA 25 26 CCR	24 Solidex	37% H <sub>3</sub> PO <sub>4</sub>	AAA, Metaltite	Super-Bond C&B Ivory		Shimizu et al.	2009 [30]
RBFPD	11 22 WA	21 Estenia	65% H <sub>3</sub> PO <sub>4</sub>	AAA, V-Primer	Super-Bond C&B Opaque	9 years	Tanoue et al.	2010 [31]
Fixation	34 36 OC 35 FCR	None	None	AAA, V-Primer	Super-Bond C&B Clear		Shimizu et al.	1999 [32]
Fixation	23 WA, 24 FCR	None	37% H <sub>3</sub> PO <sub>4</sub>	AAA, V-Primer	Super-Bond C&B Ivory	5 years	Shimizu et al.	2002 [33]
Fixation	31 32 33 WA	None	37% H <sub>3</sub> PO <sub>4</sub>	AAA, Alloy Primer	Super-Bond C&B Ivory		Shimizu et al.	2009 [34]
Fixation	45 44 WA	None	37% H <sub>3</sub> PO <sub>4</sub>	AAA, Alloy Primer	Super-Bond C&B Ivory		Shimizu et al.	2009 [34]
Overcasting	17 CCR	16 OC	None	AAA, V-Primer	Super-Bond C&B Ivory	10 years	Shimizu et al.	2008 [35]
Overcasting		14 OC Cesead II	None	AAA, Alloy Primer	Super-Bond C&B Ivory	9 years	Shimizu et al.	2009 [36]

CVR, Composite veneered restoration; CCR, Complete cast restoration; OC, Overcasting; MR, Maryland retainer; PR, Perforated retainer; WA, Wrap-around retainer; AAA, Air-borne particle abrasion with aluminum oxide.

material (MTU-6) was somewhat different from that of the V-Primer. The Metaltite material combined with the Super-Bond resin exhibited greater bond strength to Ag–Pd–Cu–Au alloy than the two alloys for metal-ceramic restorations [13]. Bonding performance of thione primers combined with composite luting agents was also evaluated. The results showed that significant difference in bond strength to Ag–Pd–Cu–Au alloy was not observed between the Alloy Primer–Panavia F system and the Metaltite–Bistite II system [14]. Kajihara et al. [15] examined influence of citric acid–ferric chloride aqueous solution on bonding to dentin or Ag–Pd–Cu–Au alloy. The results showed that bond strength to dentin of the Super-Bond C&B resin was not negatively affected by combined application of thione primers and citric acid–ferric chloride solution. However, application to Ag–Pd–Cu–Au alloy of citric acid–ferric chloride solution negatively affected the usefulness of two thione primers. Koishi et al. [16] compared bond strength of two acrylic resin materials to Ag–Pd–Cu–Au alloy. The results showed that TBB-initiated acrylic resin (Super-Bond) combined with one of the two thione primers showed greater post-thermocycling bond strength than benzoyl peroxide–amine initiated resin (Multi-Bond). The influence of alumina air-abrasion on bonding to Ag–Pd–Cu–Au alloy was evaluated apart from the effect of thione primer. Ishii et al. [17] reported that post-thermocycling bond strengths to Ag–Pd–Cu–Au alloy of the Super-Bond resin were improved by application of high-pressure air-abrasion.

## 5. Clinical reports concerning resin-bonded restorations and FPDs

Table 2 summarizes surface preparations, luting agents, and clinical performance of resin-bonded restorations and FPDs made of Ag–Pd–Cu–Au alloy [18–36]. As shown in the Table 2, V-Primer (VTD) was introduced for the first time as a thione-based primer. In addition, Metaltite (MTU-6) and Alloy Primer (VTD and MDP) are currently used for bonding cast restorations and FPDs. After try-in procedure, the surface to be bonded of resin-bonded FPDs and restorations was air-borne particle abraded with alumina (50–70  $\mu\text{m}$  grain-sized), and then primed with one of the sulfur-based primers. Minimally reduced enamel was etched with 37–40% phosphoric acid, rinsed with water, and air-dried. More than ten clinical reports have been published concerning bonding of Ag–Pd–Cu–Au alloy castings. Except for one case, the castings were bonded with the 4-META/MMA-TBB resins (Super-Bond or C&B Metabond). After observation periods of 3 to 11 years, they are functioning satisfactorily [18–23,25,27–29,31]. Figs. 2–4 show clinical course of a resin-bonded FPD originally reported by Monya et al. [18]. The FPD is functioning for more than 10 years.

The noble metal bonding systems were also applied to seating splinting devices to enamel structure. Similar technique can be applied to fixing mobile teeth using cast retainers [32–34]. Overcasting technique is a unique approach to partially preserve existing long-spanned FPDs. Preparation is applied to either restoration or pontic, in which veneering porcelain or composite material has been broken. Indirect restoration for repairing is laboratory fabricated. After try-in, both the intra- and extra-oral metal surfaces to be bonded

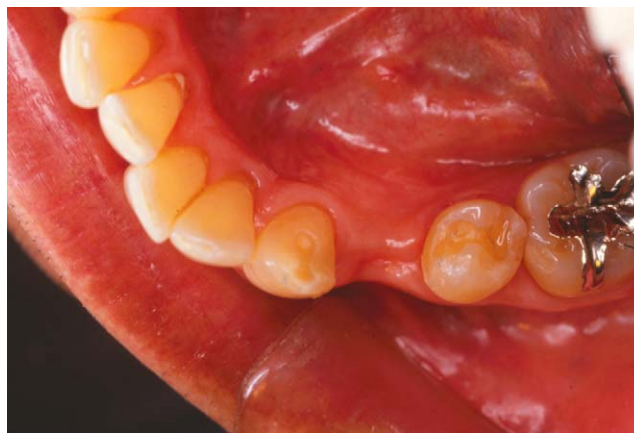


Figure 2 Abutment preparation for a resin-bonded FPD with wrap-around retainers.



Figure 3 A resin-bonded FPD made of Ag–Pd–Cu–Au alloy was seated with the V-Primer and Super-Bond adhesive system [18].

are air-borne-particle abraded with different type abraders, and primed with sulfur-based agent. The surfaces are bonded with TBB-based adhesive. Clinical course of overcasting technique is excellent [23,35,36].



Figure 4 After an observation period of 10 years, the FPD is functioning satisfactorily.

## 6. Clinical performance of resin-bonded FPDs made of Ag–Pd–Cu–Au alloys

Hikage et al. evaluated clinical longevity of resin-bonded FPDs seated with the V-Primer and the Super-Bond adhesive [37]. They reported that ten prostheses had functioned satisfactorily for 8–11 years, although six of the 26 FPDs had become detached. Tanoue et al. [38] assessed clinical performance of resin-bonded FPDs. They reported that five retainers of the 81 resin-bonded FPDs were failed. Also, they reported that the observation duration and corresponding survival ratio for complete survival were 165 months and 43.9%, and those for functional survival were 178 months and 87.7%, respectively.

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