

DENTIN BONDING AGENTS I: COMPLETE CLASSIFICATION  
A REVIEW

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ABSTRACT	KEYWORDS
Traditional mechanical retention methods for restorative materials have largely been replaced by adhesive restorative techniques that prioritize tooth conservation. These bonding techniques facilitate more conservative tooth preparations, reducing the reliance on macromechanical retention and limiting the removal of unsupported enamel. With adhesives advancing rapidly in recent years, it is now an ideal time to evaluate the clinical effectiveness of modern adhesives. This article seeks to provide an updated, clear, and thorough classification of dentin bonding agents, emphasizing current products that aim to improve clinical performance.	Conservative, Dentin bonding agents, Classification, Current products.

Introduction

The principles of adhesive dentistry trace back to 1955 when Buonocore, after observing the industrial application of phosphoric acid to enhance the adhesion of paints and resin coatings to metal surfaces, applied the acid to dental enamel to “render the tooth surface more receptive to adhesion.” Buonocore's pioneering research initiated significant changes in dental practice, ushering in the era of adhesive dentistry. Today, we are in an age where bonding techniques enable more conservative tooth preparation, reducing reliance on macromechanical retention and minimizing the removal of unsupported enamel.

The availability of new scientific knowledge regarding the etiology, diagnosis, and treatment of carious lesions, combined with the introduction of reliable adhesive restorative materials, has further decreased the need for extensive tooth preparation. Initially, the first dental adhesives bonded resins primarily to enamel with little or no adhesion to dentin or sealing of dentinal margins. Subsequent generations of dental adhesives have markedly improved bonding strength to dentin and dentinal margin sealing, while still maintaining a strong bond to enamel. The growing use of dental resins as cements, along with their application in direct and indirect restorations, will likely continue to rise as the use of metals in dentistry declines and patient demand for aesthetic procedures increases.

Classification of Dentin Bonding Agents

Dentin bonding agents can be classified in several ways:

1. **According to Generations**
2. **Based on Mode of Application**
3. **Based on Number of Steps**
4. **Based on Etching Pattern**

## **Classification Based on Generations**

### **First-Generation Adhesives (1960s)**

- The development of surface-active comonomer NPG-GMA was introduced.
- This comonomer was theoretically designed to chelate with calcium on the tooth surface, creating water-resistant chemical bonds between resins and dentinal calcium.
- Bond strength: 2 to 3 MPa.

### **Drawbacks**

- Clinically, it demonstrated poor results.
- **Examples:** Cervident (SS White), Cosmic Bond.

### **Second-Generation Adhesives (Late 1970s)**

- Phosphate ester dentin bonding agents were introduced, containing phenyl P and HEMA in ethanol.
- The mechanism was based on the interaction between the negatively charged phosphate groups in the resin and the positively charged  $\text{Ca}^{++}$  in the smear layer.
- Bond strength: 5 to 6 MPa.

### **Drawbacks**

- The smear layer had poor attachment, and the materials were hydrophobic.
- **Examples:** ScotchBond (3M Dental), Clearfil Bond System.

### **Third-Generation Adhesives (1980s)**

- The third-generation materials were designed to modify, rather than completely remove, the smear layer, allowing penetration of acidic monomers such as phenyl-P and Penta.
- These adhesives introduced acid-etching techniques to significantly alter or remove the smear layer, demineralizing dentin. They also included a separate primer (bifunctional monomer in a volatile solvent), which helped penetrate the dentin through its own monomer and those of the adhesive monomers.
- The adhesive itself is an unfilled or partially filled resin that may contain components of the primer (e.g., HEMA) to promote stronger bond strength.
- Bond strength: 3 to 8 MPa.
- **Examples:** ScotchBond 2, Tenure, Universal Bond 2, Coltene ART.

### **Fourth-Generation Adhesives (Early 1990s)**

- In these systems, both the primer and bonding resin are applied to etched dentin, penetrating the intertubular dentin and forming a resin-dentin interdiffusion zone, or hybrid layer.

- They are capable of bonding to dentin as strongly as to enamel using the total-etch technique.
- These adhesives also introduced the ability to bond to moist dentin (wet bonding) and can bond to multiple substrates, including metal, amalgam, porcelain, and indirect composites.
- Bond strength: 13 to 30 MPa.
- **Examples:** All-Bond 2, OptiBond FL, ScotchBond Multipurpose.

## Fifth-Generation Adhesives

- These adhesives are characterized as "one-step" or "one-bottle" systems. However, this is a misnomer, as they are still applied in two steps (etchant + primer and adhesive) within a single bottle.
- Bond strength: 3 to 25 MPa.

## Drawbacks of Fifth-Generation Adhesives

- These adhesives lack many components needed for effective multisubstrate bonding.
- They require multiple coats for optimal performance.
- **Examples:** Prime and Bond, Single Bond, OptiBond Solo, and OptiBond Solo Plus.

## Sixth-Generation Adhesives (Introduced between late 1990s and early 2005)

1. These adhesives dissolve the smear layer upon application, eliminating the need for rinsing.
2. They minimize postoperative sensitivity by preventing the exposure of dentinal tubules.
3. The bond strength to enamel and superficial dentin is typically higher than that to deep dentin.

<i>Type I</i>	<i>Type II</i>
1. Self-etching primer and adhesive	1. Self-etching adhesives
2. Have components liquid 1-acidic primer liquid-2-adhesive that are separately to the tooth	2. Two bottles or unit dose containing acidic primer and adhesive are first mixed and then applied
3. Are generally compatible with self-cured composite	3. Are not compatible with self-cured composite
4. Example: Clearfil SE bond, adhese	4. Example: Xeno-III Adper Prompt LPOP one-up bond

## Bond Strength of Sixth-Generation Adhesives

- The bond strength to dentin and enamel in sixth-generation adhesives is lower compared to the fourth- and fifth-generation systems.

## Seventh-Generation Adhesives (Introduced Late 2002)

- These adhesives are **self-etching**, eliminating the need for mixing.
- They are **not compatible** with self-cured composite cores or resin cements.
- Typically come in a **single bottle** containing an acidic adhesive.
- Bond strengths and marginal sealing are comparable to those of the sixth-generation system.
- **Examples:** iBond.

## Eighth-Generation Adhesives

- Dual-cured self-etch adhesives suitable for both **direct and indirect restorations**.
- Compatible with self-, light-, and dual-cured resin materials.
- **Examples:** Various dual-cured self-etch adhesives designed for a wide range of applications.

## Classification Based on Mode of Application

Modern dentin adhesive systems can also be classified based on their approach to the smear layer. The primary mechanisms of adhesion include:

### 1. Adhesives That Modify the Smear Layer

- These adhesives incorporate the smear layer into the bonding process, requiring one or two steps.
- **One-step** adhesives use a single adhesive or a combined primer and adhesive.
- **Examples:**
  - One step: Prime and Bond 2.1
  - Two steps: Optec Universal Bond

### 2. Adhesives That Completely Remove the Smear Layer

- These are further subdivided into **two-step** and **three-step** applications:
    - **Two-step process:** Involves dentin conditioning followed by a combined primer and adhesive.
    - **Three-step process:** Involves separate conditioning, priming, and bonding applications.
  - **Multiple bottle systems:**
    - **Examples:** All-Bond 2, ScotchBond Multipurpose
  - **One-bottle systems:**
    - **Examples:** OptiBond SOLO, One Step
- ### 3. Adhesives That Dissolve the Smear Layer
- These adhesives dissolve, rather than remove, the smear layer, and are applied in two steps:
    - A combined conditioner and primer (self-etching primer) is applied first, followed by the application of adhesive resin.
  - **Advantages:**
    - No rinsing required.
    - Quick application.
    - Less postoperative sensitivity than total etch systems.

## CLASSIFICATION BASED ON NUMBER OF STEPS<sup>6</sup>

<i>Generation</i>	<i>Steps</i>	<i>Description</i>
1st	3	Etch enamel, apply adhesive
2nd	3	Etch enamel, apply adhesive
3rd	3	Etch enamel, apply primer
4th	2	Total etch, apply primer
5th	2	Total etch apply adhesive
6th	1 or 2	Apply self-etch adhesive
7th	1	Apply self-etch adhesive

## Classification Based on Etching Pattern

The classification of bonding agents was initially based on generations, as proposed by Dr. Marcos Vargas. However, with the introduction of self-etching primer systems, the generational classification was deemed unnecessary. In fact, this system was officially discontinued by its originator at the 5th Indiana Conference, held at the University Center in June 2000. It was then widely accepted that bonding agents could now be categorized based on their application method as either **total-etch** or **self-etch** systems.

## Total Etching Technique

The total etching technique involves the simultaneous etching of both enamel and dentin. This technique can be performed using either of the following methods:

- **Multibottle systems** (Fourth-generation): These systems require multiple bottles for application.
  - **Examples:** All-Bond 2, ScotchBond Multipurpose.
- **One-bottle systems** (Fifth-generation): These systems use a single bottle for both primer and adhesive.
  - **Examples:** Prime and Bond NT, Single Bond.

## Self-Etch System

In the self-etch system, there is no separate etching or rinsing step. This method offers several advantages:

- It reduces clinical application time.
- It lowers technique sensitivity.
- The residual smear layer remains within the bond.

Self-etch systems can be applied using either a **two-step** or **one-step** procedure and are classified into:

1. **Self-Etching Primers**
2. **Self-Etching Adhesives**

## All-in-One Self-Etching Adhesive Systems

These "all-in-one" systems combine the functions of a conditioner, primer, and adhesive in a single solution. These systems are increasingly used in pediatric dentistry due to their simplicity. The hybridization created by these materials in primary dentin is comparable to that achieved by total-etch dentin adhesives.

- **Examples:** G-Bond (GC America), iBond (Heraeus Kulzer).

## Types of Self-Etch Adhesives Based on Etching Aggressiveness

Self-etch adhesives can be categorized based on their pH, which determines their aggressiveness:

1. **Strong Self-Etch Adhesives**
  - pH: 1 or below.
  - The bonding mechanism is primarily diffusion-based, similar to the etch-and-rinse approach.

- **Drawbacks:** These adhesives tend to have lower bond strengths due to high initial acidity and residual solvent (water) left in the adhesive interface.
- 2. **Mild Self-Etch Adhesives**
  - pH: Around 2.
  - These adhesives demineralize dentin to a depth of only about 1  $\mu\text{m}$ , leaving residual hydroxyapatite attached to the collagen.
  - The weakest property of mild self-etch adhesives is their bonding potential to enamel.
- 3. **Intermediate Strong Self-Etch Adhesives**
  - pH: Around 1.5.
  - These adhesives can be either two-step (e.g., OptiBond Solo Plus) or one-step (e.g., Xeno IV, iBond, G-Bond).
  - **Performance Comparison:** No significant differences were found in bond strength between etch-and-rinse, self-etch primer, and self-etch adhesive categories, except for marginal adaptation, where etch-and-rinse was found to be superior to self-etch adhesives.

## Considerations for Self-Etching Systems

- **Self-etching primers** often contain a significant amount of water as a solvent to promote the ionization of the acidic monomers. Once the solvent evaporates, the adhesive layer tends to be very thin, which may affect mechanical properties.
- A demineralized dentin zone beneath the hybrid layer has been noted in self-etching primer systems. This zone is not fully protected by the adhesive, potentially compromising bond strength.
- **Coating Number Impact:** Increasing the number of consecutive coats of adhesive (up to three coats for total-etch and two for self-etch) may improve bond strength in both systems.

## Conclusion

Adhesive dentistry has significantly transformed restorative dental practice over the past 30 years. The evolution of adhesive materials has made resin-based composite restorations more reliable and long-lasting. As we continue into the new millennium, it is crucial to reflect on past advancements while staying informed about the rapidly progressing trends in adhesive dentistry. These ongoing improvements will continue to shape the future of restorative dental procedures.

## REFERENCES

1. Kenneth J. Anusavice: Phillips science of dental material (2nd ed) Elsevier 2003;p381.
2. Roberson Theodore M. Studervants art and science of operative dentistry (4th ed). Mosby 2002;237-367.
3. Farah John W, Powers John M. The Dental Advisor 2004, 21.
4. Kugel Geroard, Ferrari Marco. The science of bonding from first to sixth generation. JADA 2007;14.
5. Sikri Vimal K. Textbook of Operative Dentistry (2nd ed). 2008;358-83.
6. Dunn James R, iBond. The seventh generation, one-bottle dentine bonding agent. Compendium 2003;24:14-18.

7. Perdigao Jorge. New developments in dental adhesion. Dent Clin N Am 2007;51:333-57.
8. Claus-Peter Ernst, Marcus Holzmeier, et al. In vitro shear bond strength of self-etching adhesives in comparison to 4th and 5<sup>th</sup> generation adhesives. J Adhes Dent 2004;6:293-99.
9. Kanheira Masafumi et al. Relationship between degree of polymerization and enamel bonding strength with self-etching adhesives (all-in-one or 7th-generation). J Adhes Dent 2005;7:300-05.