

DENTINE BONDING AGENTS

PRESENTED BY : DR. SUNITA GARG

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INTRODUCTION

- The development and regular use of adhesive materials has begun to revolutionize many aspects of restorative and preventive dentistry.

Adhesive dentistry began in 1955 by Buonocore on the benefits of acid etching.

- Attitudes towards cavity preparation are altering since, with adhesive materials, it is **no longer necessary to prepare the cavity to provide mechanical retention** through such features as dovetails, grooves, undercuts, sharp internal angles in order to retain the filling .
- These techniques are, therefore, responsible for the **conservation** of large quantities of sound tooth substance

Bonding or adhesion comprise a complex set of physical, chemical and mechanical mechanisms that allow the attachment and binding of one substance to another.

The word adhesion comes from the Latin *adhaerere* ('to stick to')

American Society for Testing and Materials (specification D907) defines adhesion as 'the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking forces or both.'

The substance added to produce the adhesion is known as the **'adhesive'** the material to which it applied is known as the **'adherend'**



Fig. 16.1: Adhesive and the adherend

ADHESION MECHANISM

Mechanical—penetration of resin and formation of resin tags within the tooth surface

II. ***Adsorption***—chemical bonding to the inorganic component (hydroxyapatite) or organic components (mainly type I collagen) of tooth structure. Forces may be primary(ionic and covalent), secondary (hydrogen, dipole interaction),and vanderwaal's valence forces

III. ***Diffusion***—precipitation of substances on the tooth surfaces to which resin monomers can bond mechanically or chemically

COMBINATION

HISTORICAL BACKGROUND

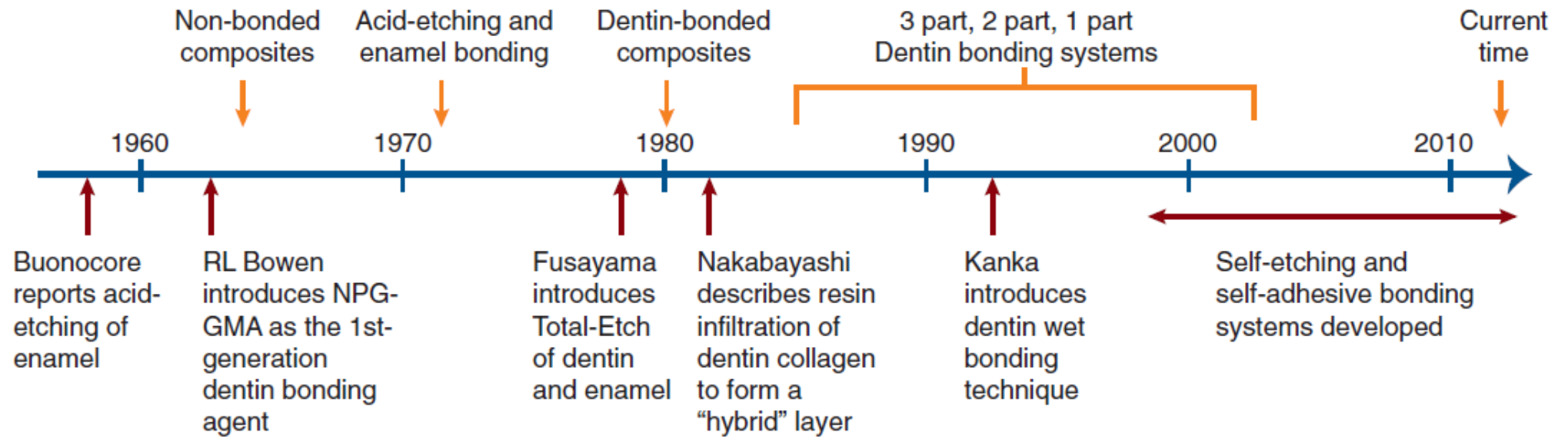
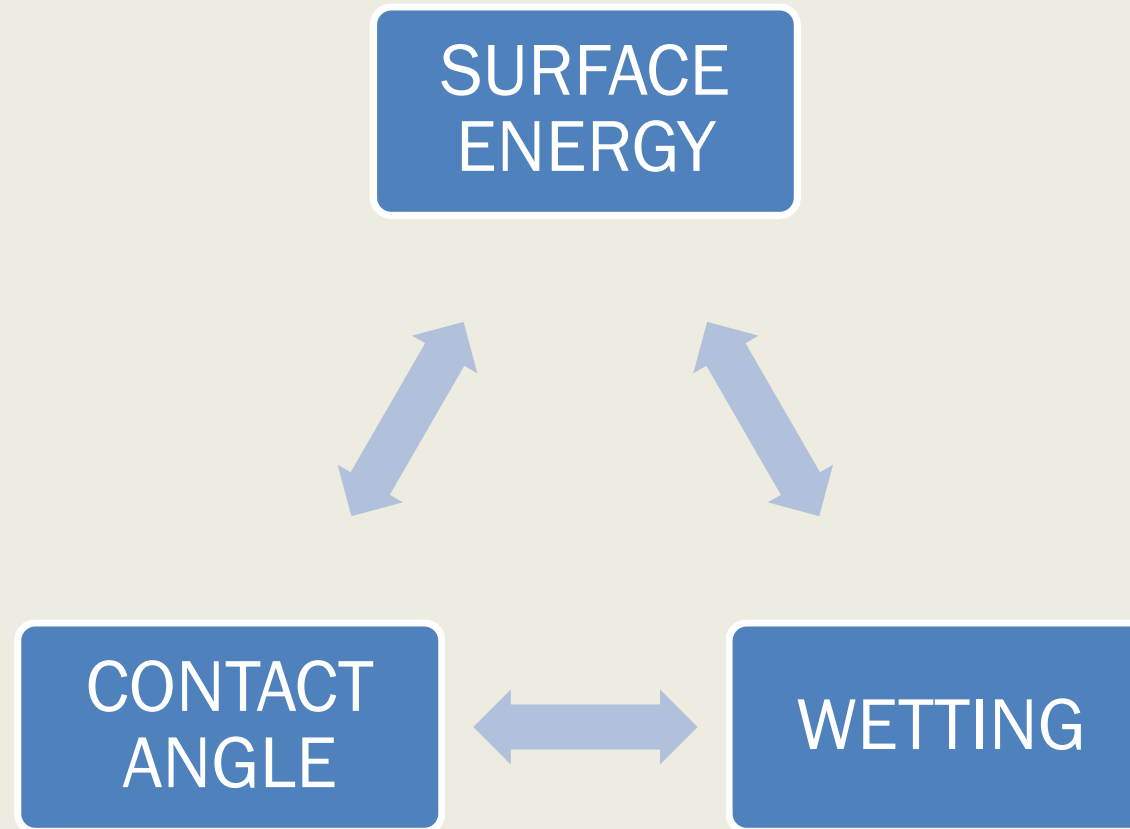


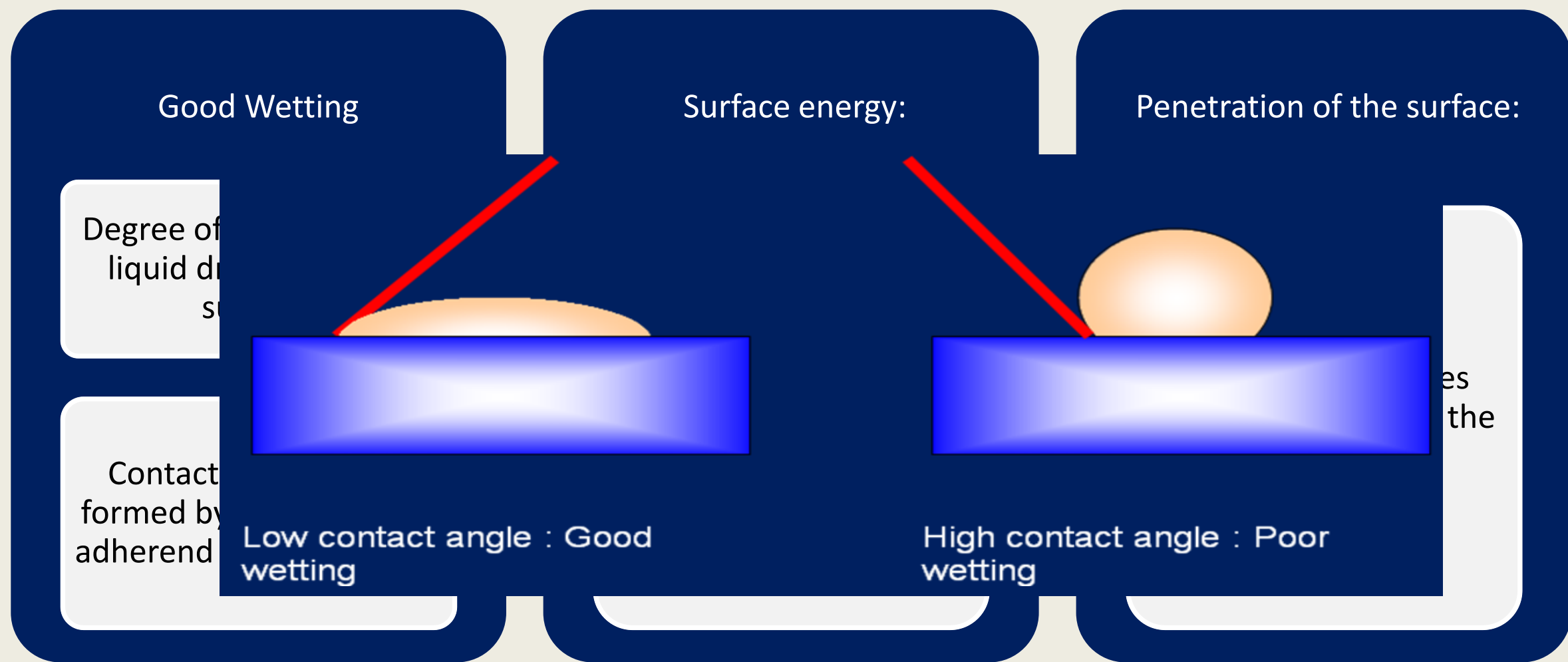
FIGURE 12-1 Major turning points and events in dental bonding technologies.

BASIC CONCEPT OF ADHESION



Not only do they individually control adhesion but are also closely interrelated

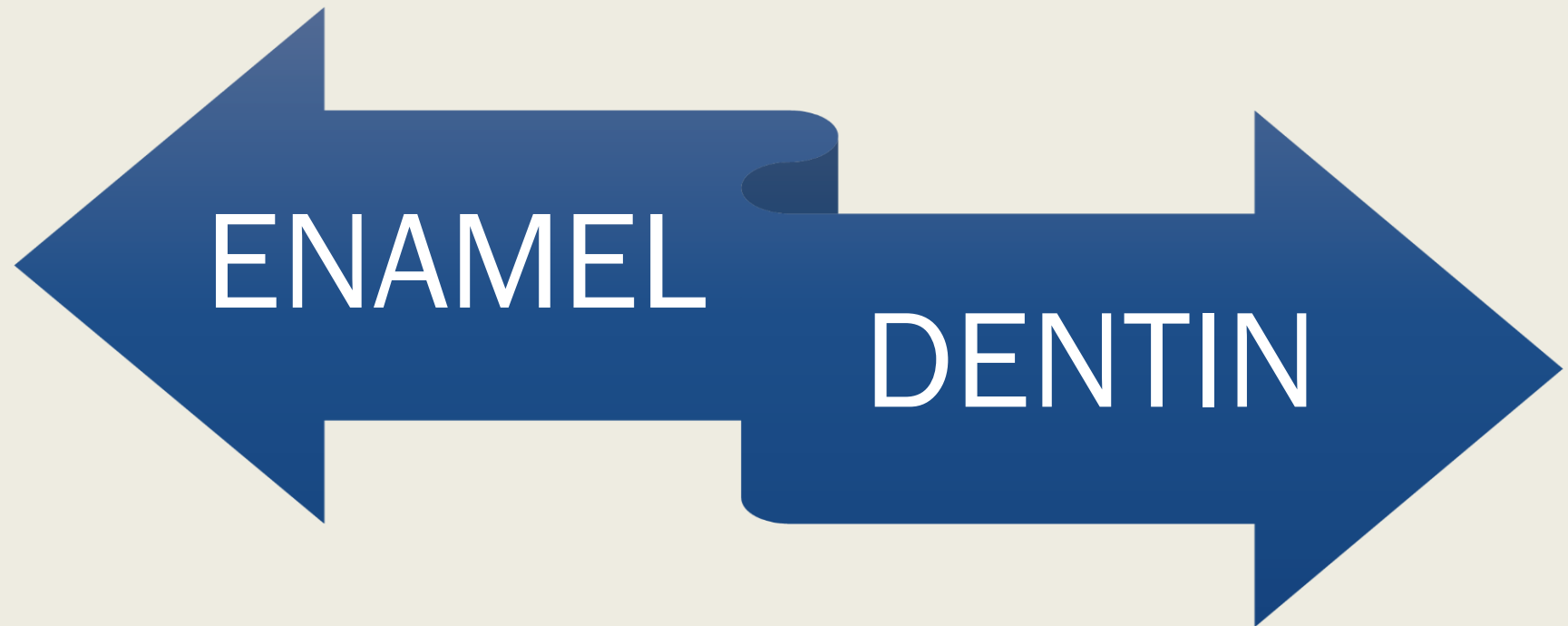
BASIC CONCEPTS OF ADHESION



Therefore an adhesive with low surface tension low contact angle and low viscosity is preferred

TOOTH AS A SUBSTATE FOR BONDING

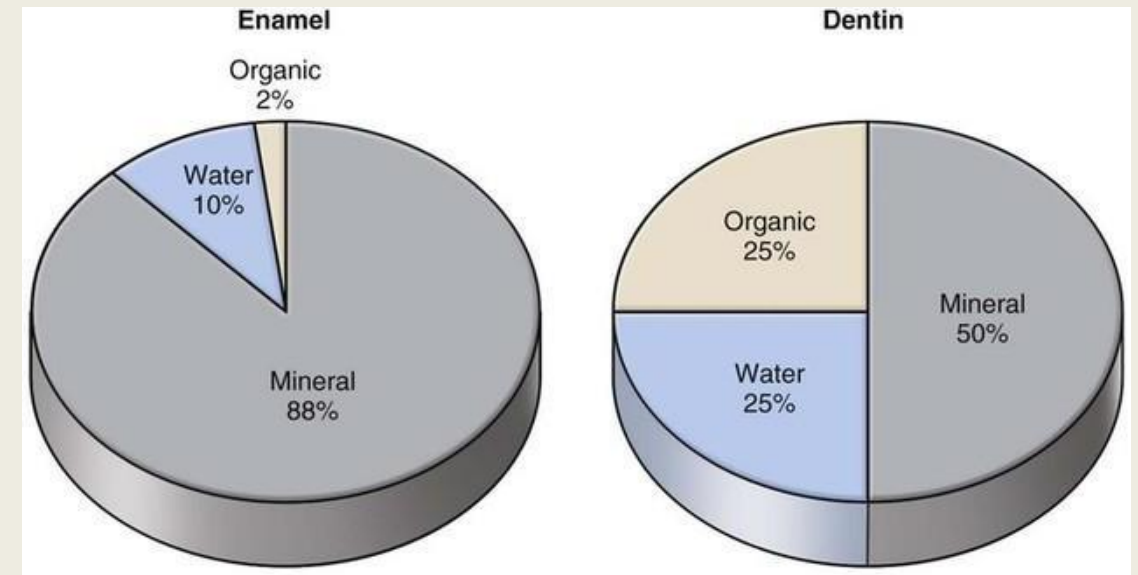
The tooth surface, when used as a substrate for, bonding generally comprises of two components:



ENAMEL

Table 1. Composition of tooth tissues.

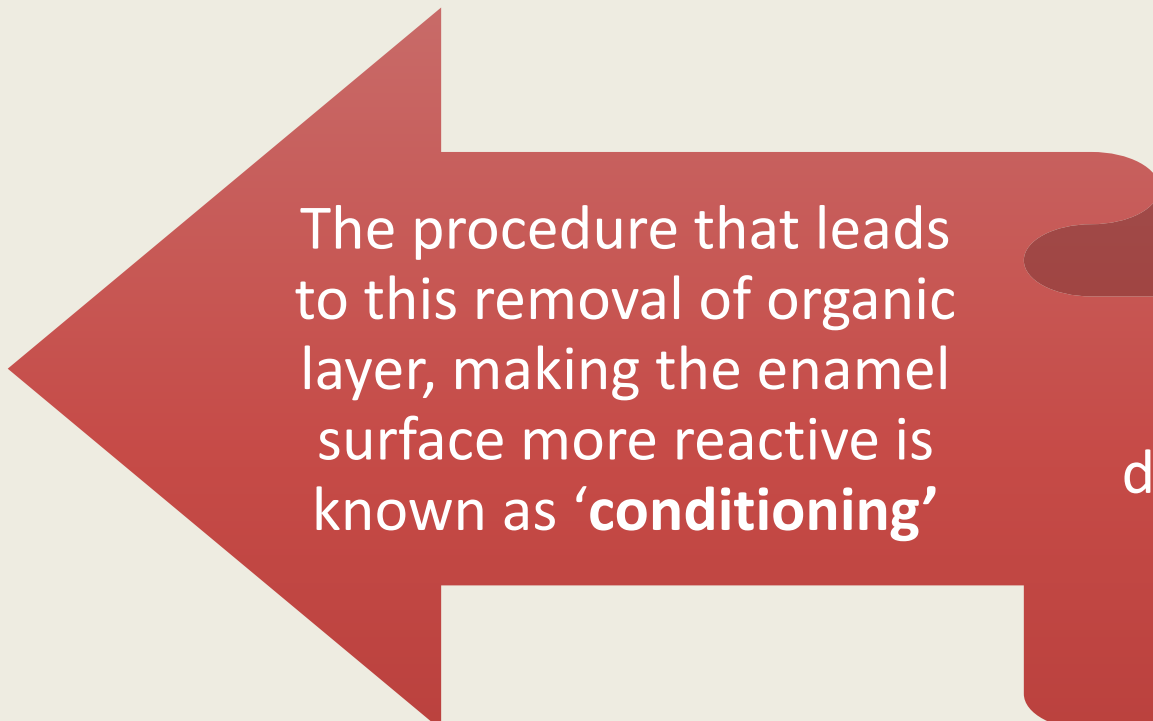
Components	Enamel	Dentine
Inorganic phase (mainly hydroxyapatite) (%)	94-96	50-70
Calcium phosphate ratio	1.64	1.56
Organic phase (mainly collagen) (%)	4-5	20-30
Water (%)	1-4	10-20



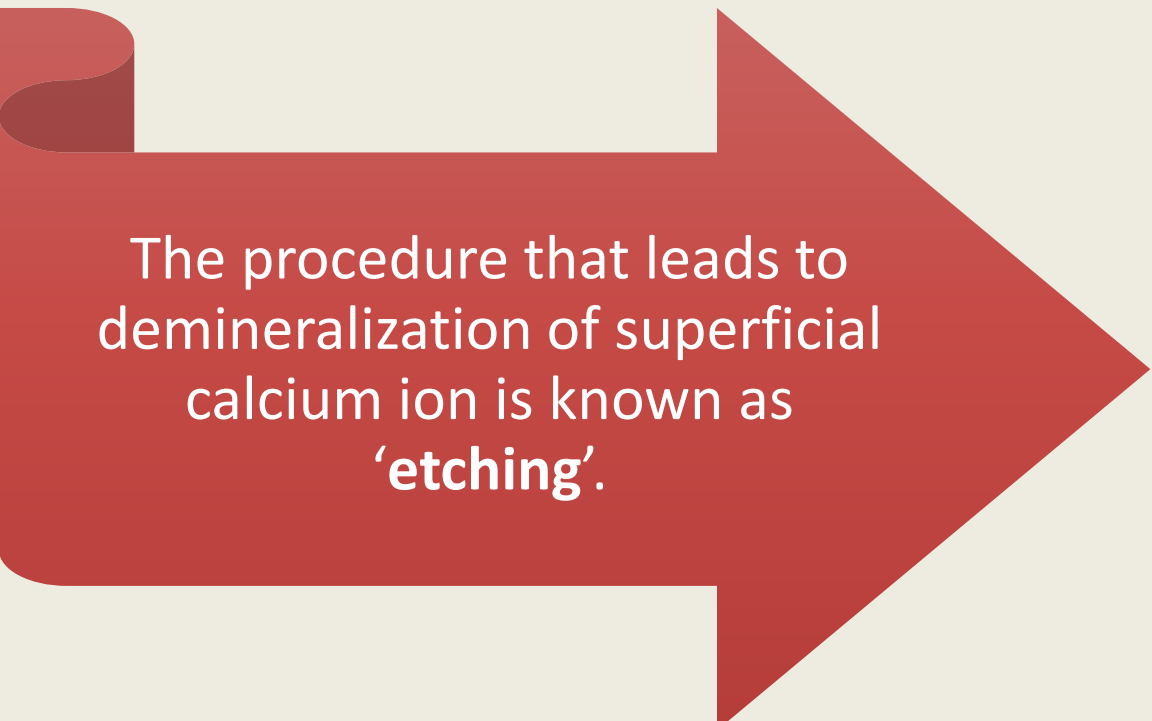
By volume

**Classification review of dental adhesive systems:
from the IV generation to the universal type**

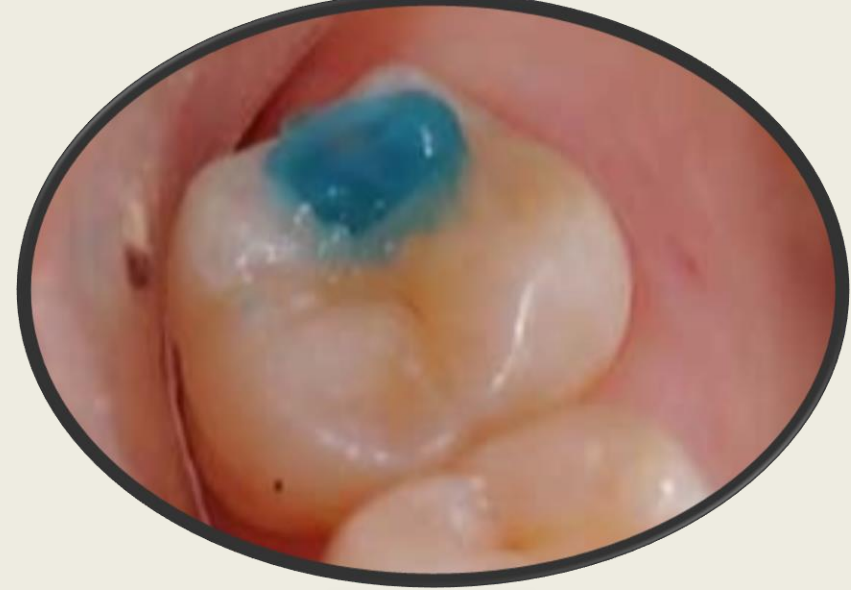
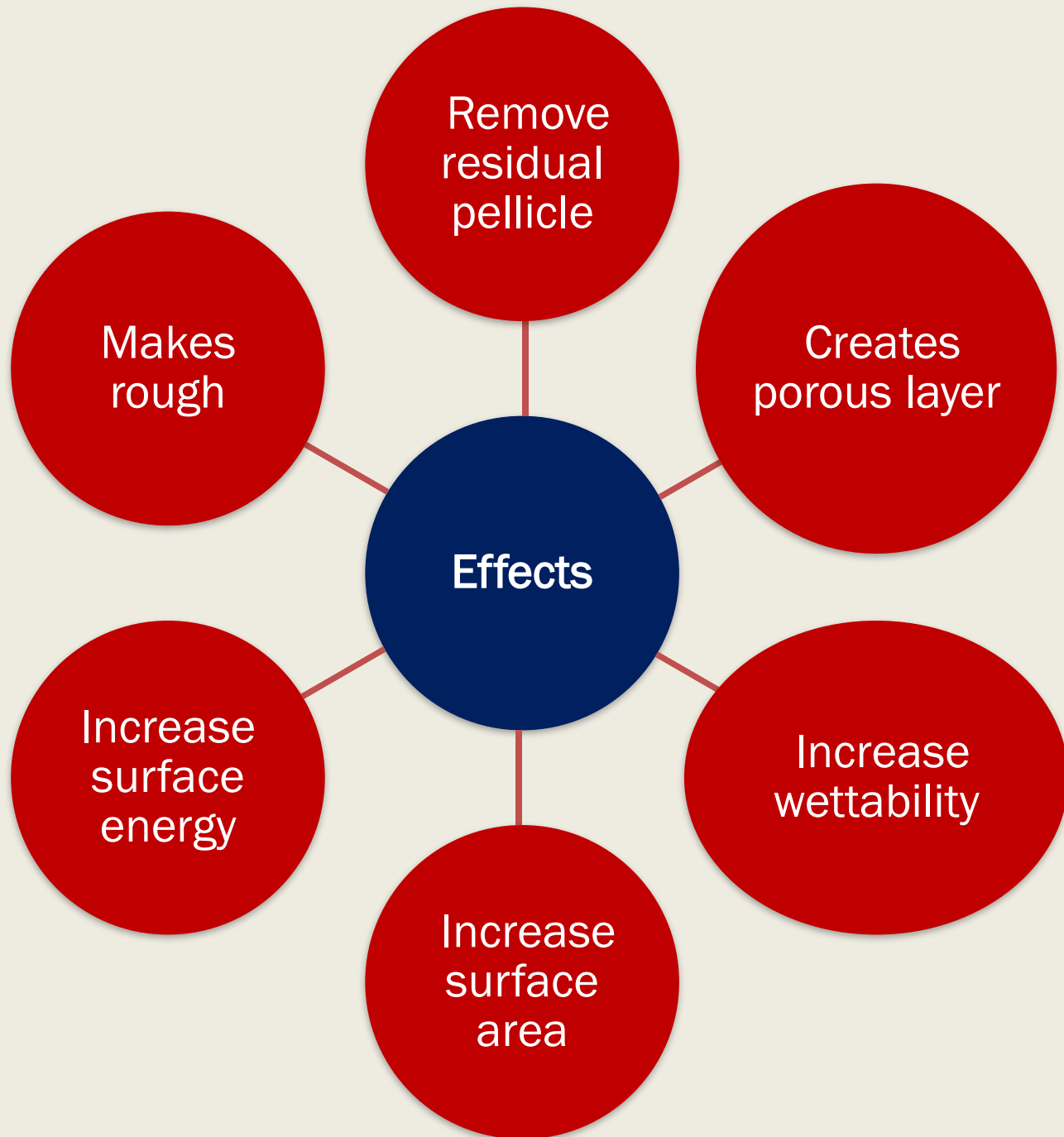
Annali di Stomatologia 2017;VIII (1):1-17



The procedure that leads to this removal of organic layer, making the enamel surface more reactive is known as '**conditioning**'



The procedure that leads to demineralization of superficial calcium ion is known as '**etching**'.



Enamel acid etching – removes **10 micron** of enamel



Creates microporous layer **5 to 50 microns** deep



Smooth surface – irregular surface with high surface energy **72 dynes/cm**



Unfilled liquid acrylic resin (enamel bonding agent)



Wets the surface



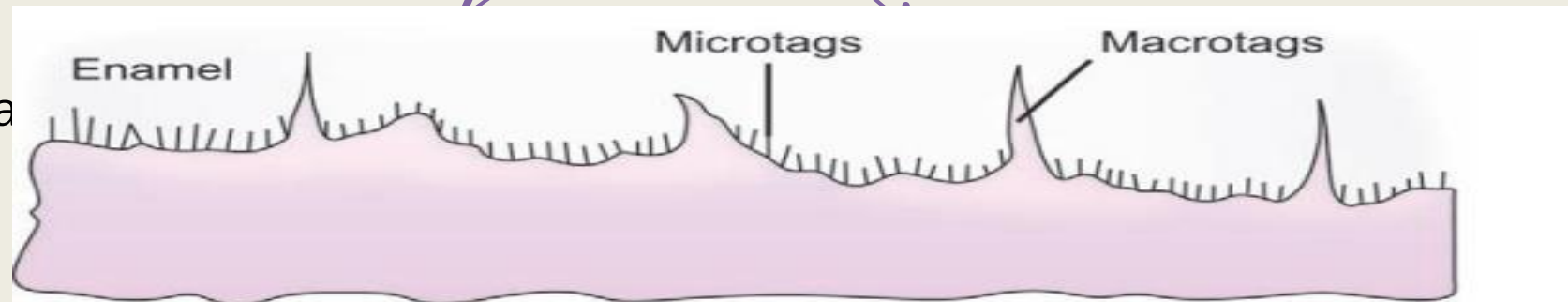
Enters into microporosities by capillary action



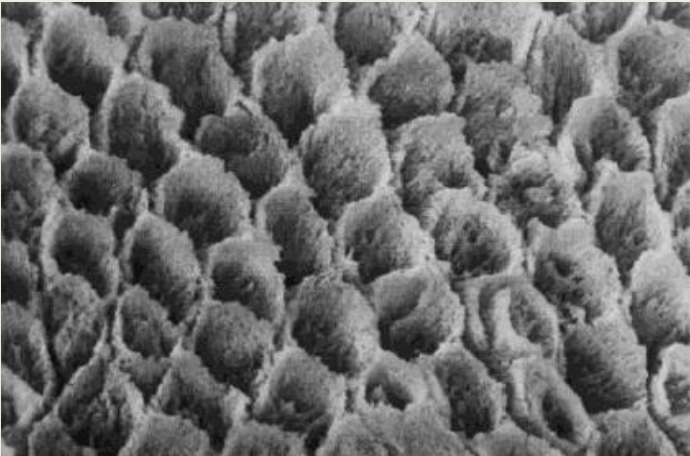
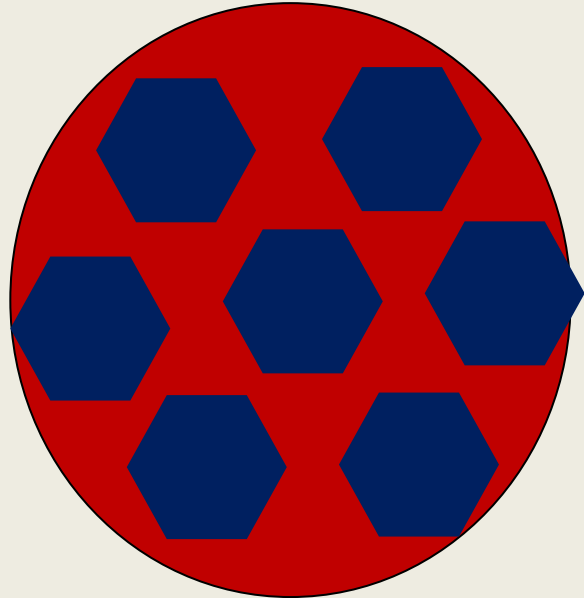
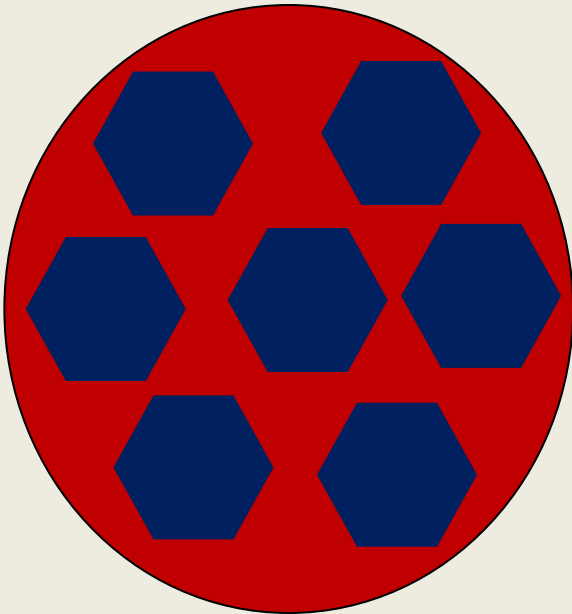
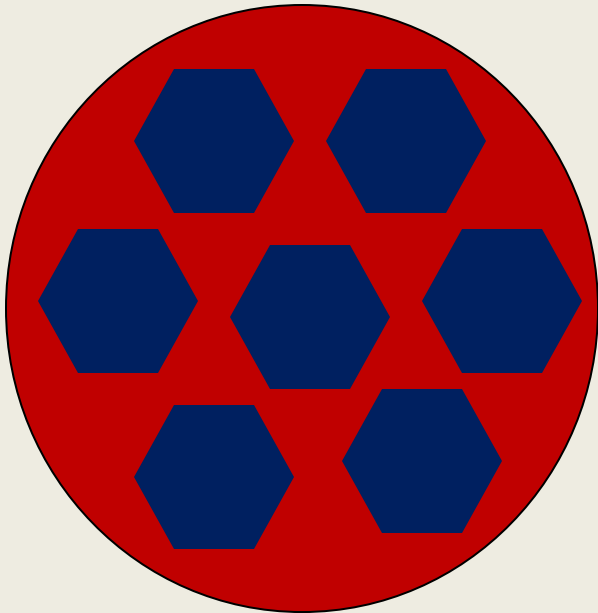
Two types of resin tags are formed

resin tags are approximately $6\ \mu\text{m}$ in diameter and 10 to $20\ \mu\text{m}$ in length and lead to micromechanical interlocking.

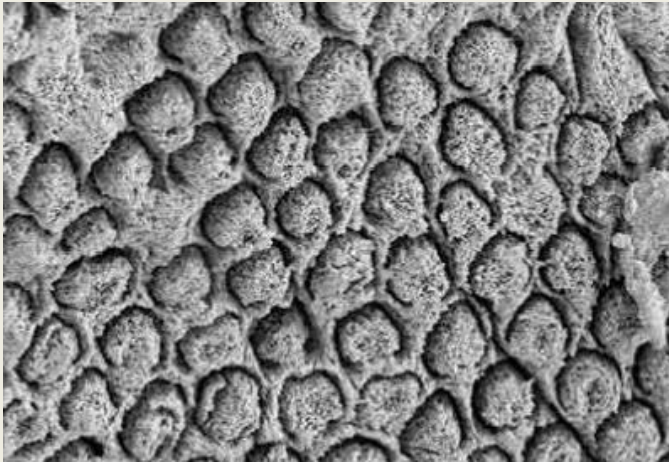
(fill up spaces between prisms)



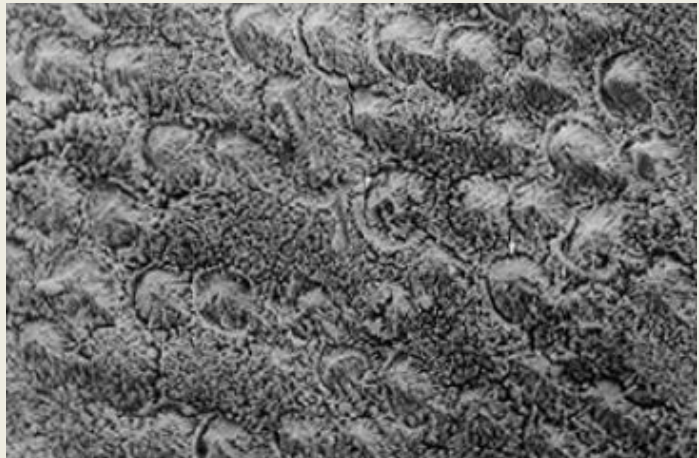
ETCHING PATTERNS OF ENAMEL



PATTERN 1



PATTERN 2



PATTERN 3

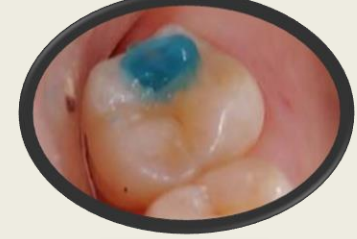
Recently type IV and type V patterns have been added

Type IV pattern displayed only a random distribution of depressions with no preferential destruction of either cores or peripheries. These pitted areas occasionally occurred in **little patches** over the enamel surface. This type of etching pattern is commonly seen in **cervical areas** and rarely on occlusal.

Similarly to type IV pattern, **type V etching** shows no evidence of prism outline. The regions of enamel **are flat and smooth** and lack micro irregularities for penetration of resin. Such type is seen in **high fluoride areas**.

The type of the etching pattern depends in the morphological and mineral content of enamel and the dentist has no control over the pattern.

Phosphoric acid



Concentration 27- 50%
Etching time- not less than 15 sec
Washing times- 5-10 sec

50%

layer of monocalcium
phosphate monohydrate –
PREVENTS FURTHER
DISSOLUTION OF HA

Less than 27%-

Dicalcium phosphate
dihydrate- couldn't easily
removed

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ETCHING TIME

- Time for etching- traditionally, 60 sec
- But SEM studies have shown same surface roughness in 15 sec
- Similar shear bond strengths & marginal leakage values for 15 & 60 sec have been observed
- Current recommendations- permanent teeth, 15 to 20 sec
- Fluoridated enamel, primary teeth- require more time

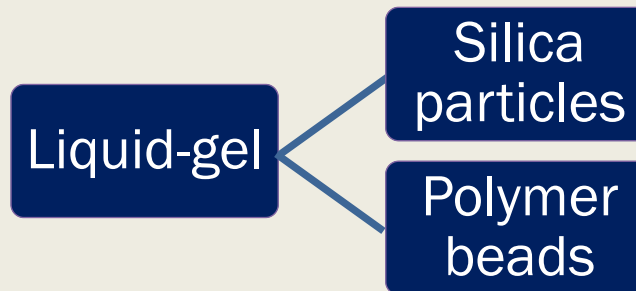
Clinically, the most important measure of a properly etched tooth is the *frosty white appearance* of the surface

ENAMEL ADHESION



LIQUID/GEL

Liquid-gel

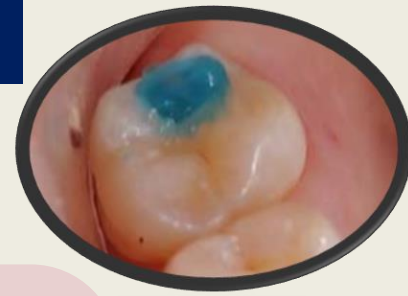


On smooth surfaces, etching liquids and gels result in similar etch patterns.

With deep grooves and fissures, a liquid etch is recommended, because it penetrates the irregularities of the occlusal surface.

ENAMEL ADHESION

NEWER ALTERNATIVES TO ETCHING



Laser etching

Mainly CO₂, Argon, and Nd:YAG Lasers are used. enamel to a depth of 10 to 20 μm .

Laser etching is a process of continuous vaporization and micro explosions.

Air Abrasive Technology

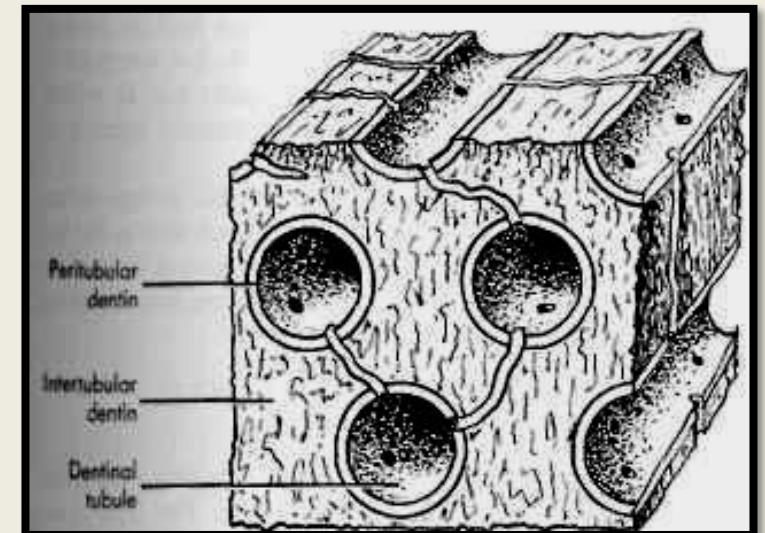
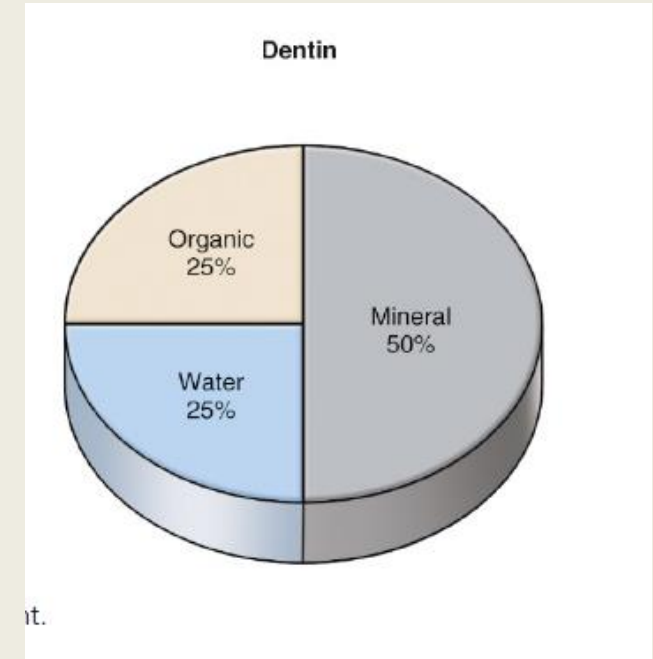
high speed stream of purified Aluminium Oxide particles (0.5 μm) propelled by air-pressure.

It can prepare enamel and dentin for bonding, similar to chemical etching.

DENTIN ADHESION

CHALLENGES IN DENTIN BONDING

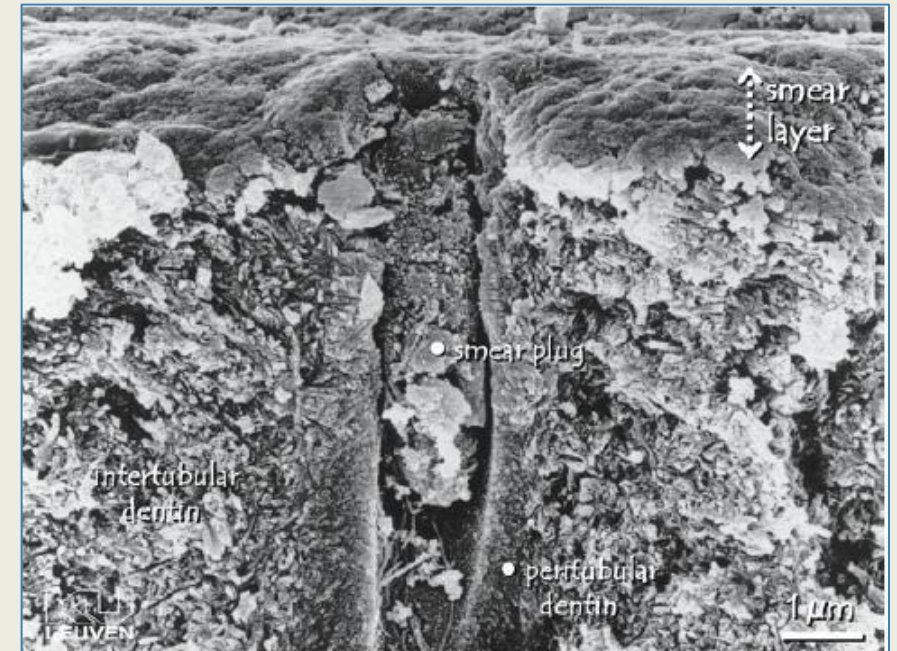
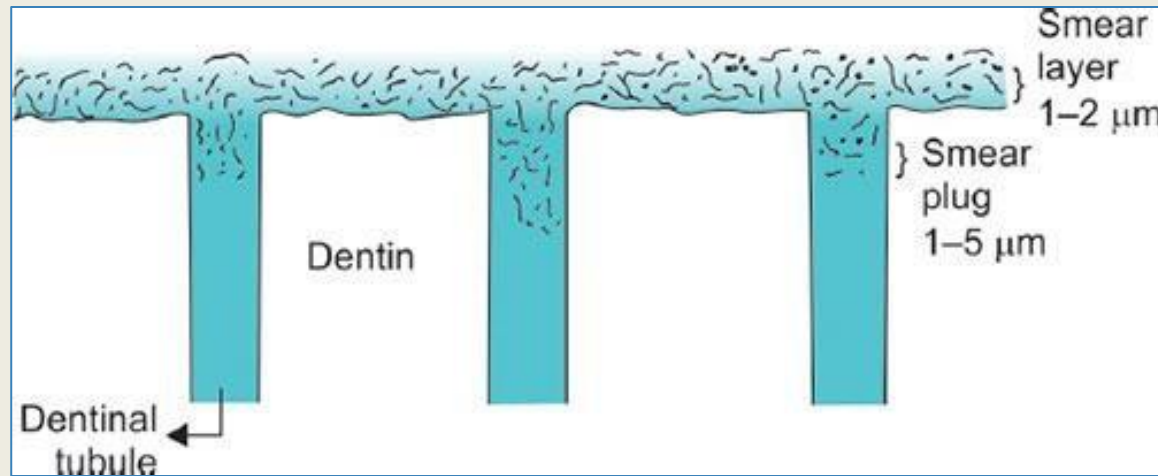
- Higher percentage of organic content(Type 1 collagen) and water
- Dentinal tubules
- Dentinal tubules are permeated with fluid(moist)
- Water content increases by 20 fold from superficial dentine to deep dentin
- HA crystals (smaller + criss cross arrangement)
- Changes due to caries, trauma- sclerotic dentine.
- Smear layer

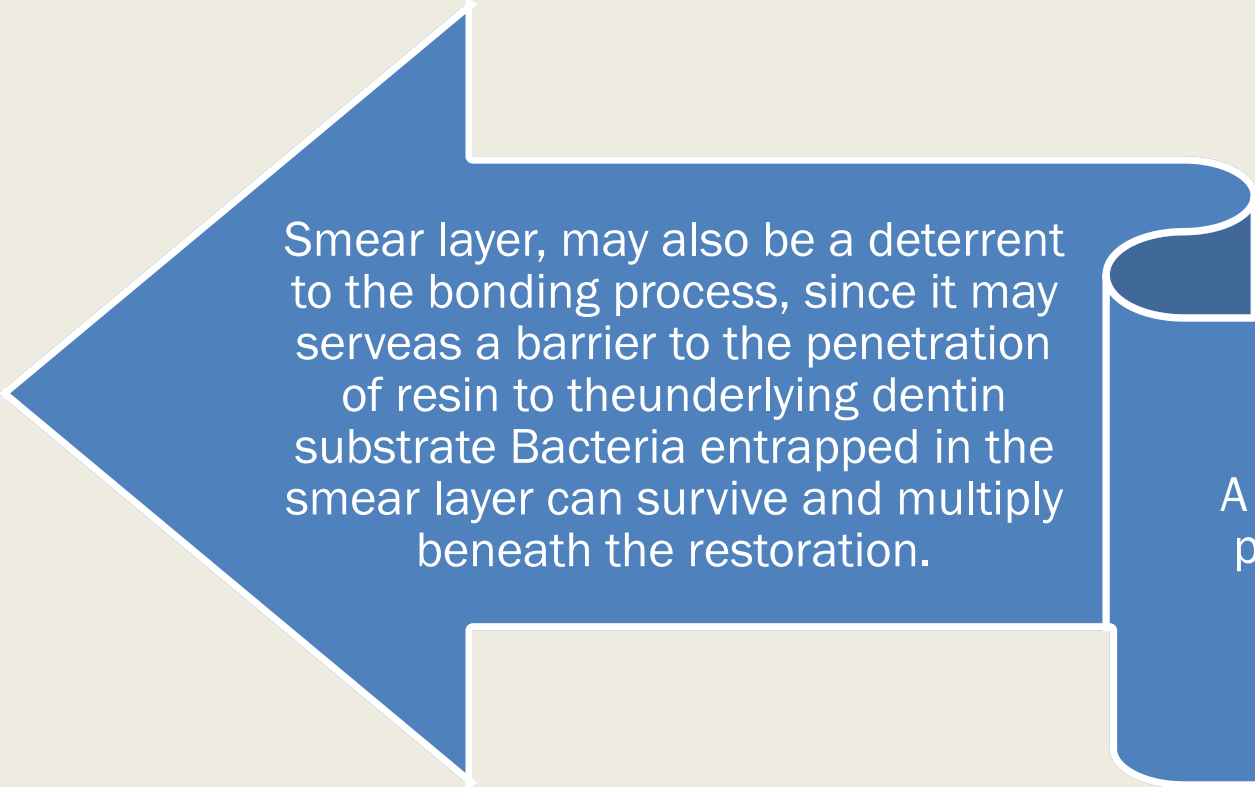


SMEAR LAYER

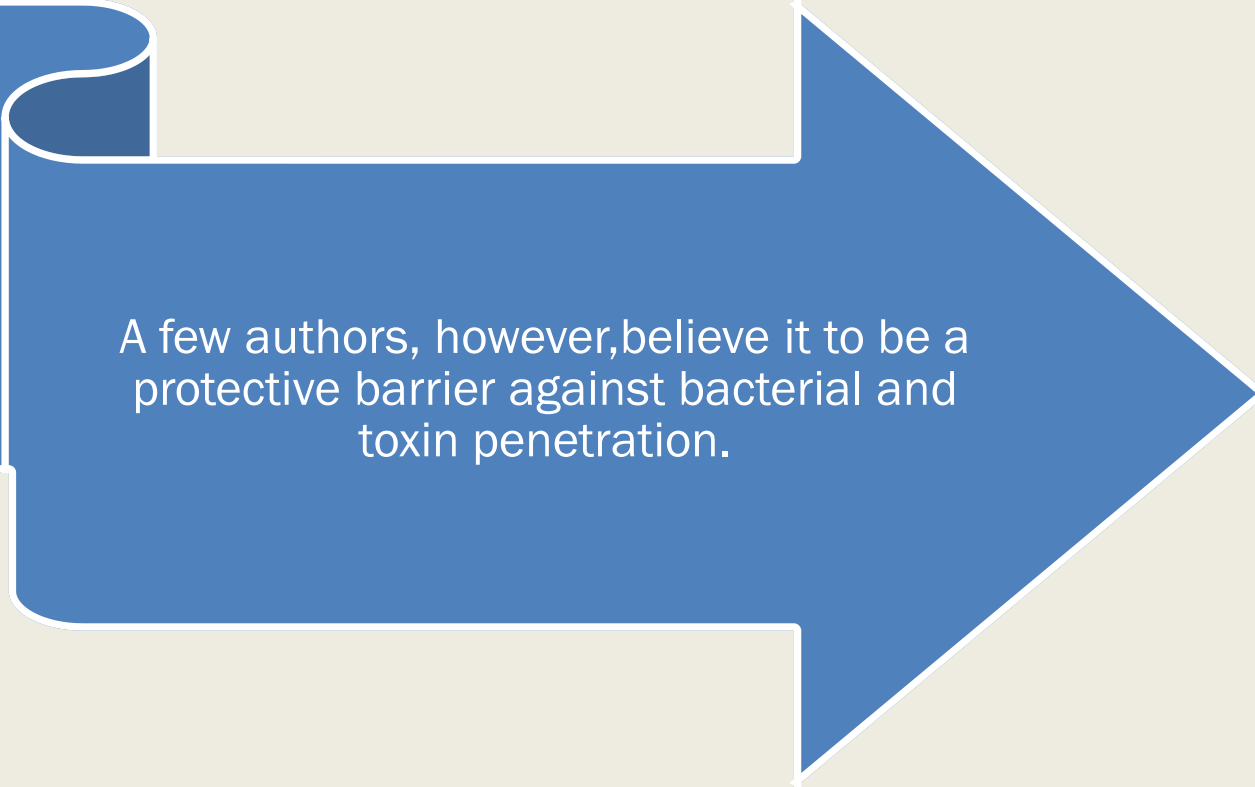
Whenever tooth structure is prepared with a bur or other instrument, residual organic and inorganic components form a 'smear layer' of debris on the surface. The smear layer fills the orifices of dentin tubules, forming 'smear plugs'.

and decreases dentin permeability by nearly 90%





Smear layer, may also be a deterrent to the bonding process, since it may serve as a barrier to the penetration of resin to the underlying dentin substrate. Bacteria entrapped in the smear layer can survive and multiply beneath the restoration.



A few authors, however, believe it to be a protective barrier against bacterial and toxin penetration.

BONDING TO CARIES AFFECTED DENTIN

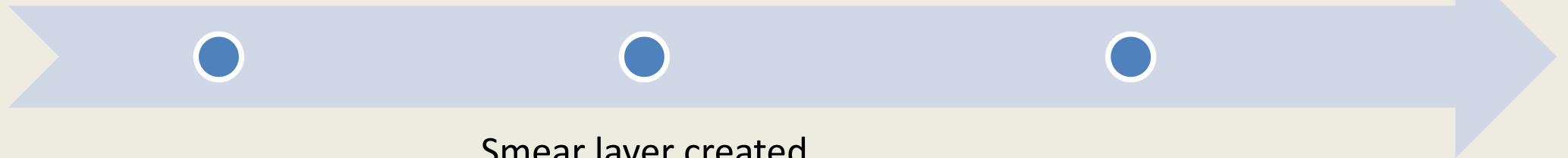
Caries-affected dentin produces lower bond strengths than normal dentin, regardless of the type of adhesive system



reduction in the cohesive strength of caries-affected dentin

chemical and morphological characteristics of caries affected dentine

dentin is **more susceptible to the acid etching** due to partially demineralization, resulting in the formation of a deeper demineralized zone



Smear layer created to caries-affected dentin are **thicker**

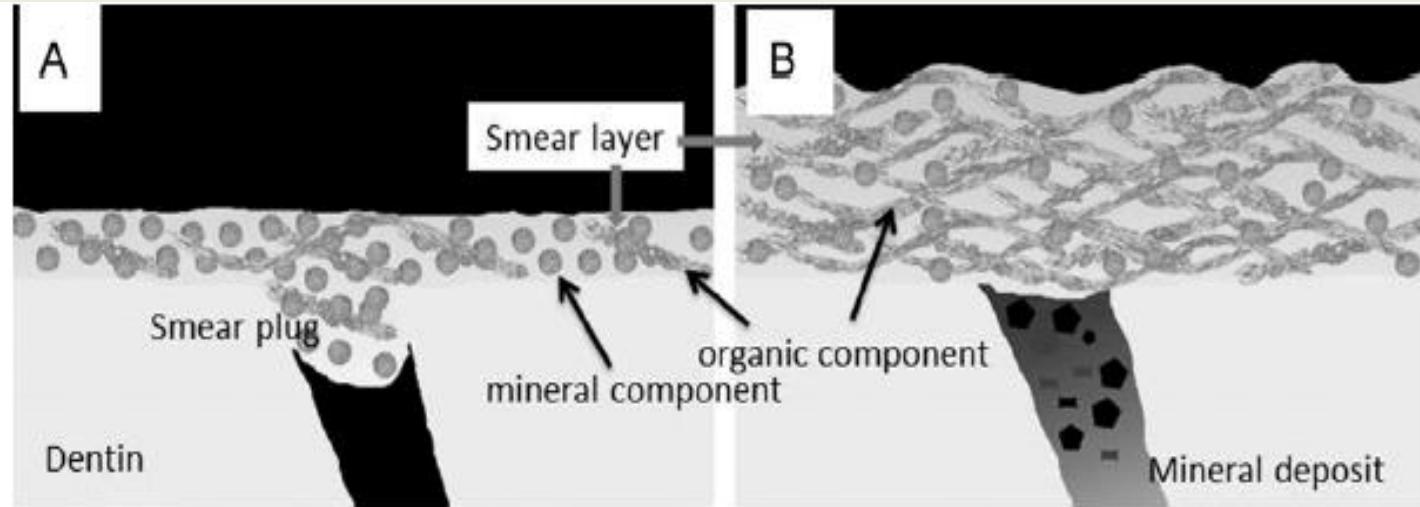


Figure 3 Schematic illustration of smear layers of normal and caries-affected dentin. Caries-affected dentin smear layer is thick with enriched organic components compared with normal dentin smear layer.

Bonding to caries-affected dentin

Masatoshi Nakajima*, Sitthikorn Kunawarote, Taweesak Prasansuttiporn,
Junji Tagami

The smear layer of caries-affected dentin is thick and irregular, and appears to be enriched with organic components compared with that of normal . The disorganized collagen and/or the mineral trapped within the gelatinized collagen cannot be easily removed even when etched with phosphoric acid.

et al. [36] demonstrated that NaOCl treatment of smear layer-covered caries-affected dentin eroded and thinned the smear layer due to dissolution of superficial organic components of smear layer (Fig. 8). Furthermore, they reported that pretreatment with 6% NaOCl for 15 s could significantly improve the bond strengths of 1-step and 2-step self-etch system to caries-affected dentin, while NaOCl-30 s pretreatment did not affect them [36]. On the other hand, for normal dentin, NaOCl-15 s pretreatment did not alter the bond strengths, but NaOCl-30 s pretreatment reduced them [36]. It has been speculated that applying NaOCl for 30 s or longer results in reactive

DENTINE BONDING AGENTS

IDEAL REQUIREMENTS

Criteria for an "ideal" dentin bonding system were enumerated in 1961 at a workshop held at the University of Indiana Dental School (Phillips and Ryge, 1961).

- Provide **high bond strength** to dentin that should be present immediately after placement and that should be permanent,
- provide bond strength to dentin similar to that to enamel,
- show **good biocompatibility** to dental tissue, including the pulp,
- **minimize microleakage** at the margins of restorations,
- prevent recurrent caries and marginal staining,
- be **easy to use** and minimally technique-sensitive,
- possess a **good shelf life**
- **compatible** with a wide range of resins.

Review Article

Dentin Bonding Agents: An Overview

Swati Gupta, Gurkiran kaur¹, Swati Swagatika Biswal², Shubhra Vikas Kaushik³, Shahram Karami⁴, Sandeep Goyal⁵, Simranjit singh⁶

CLASSIFICATION

CLASSIFICATION OF DENTIN BONDING AGENTS

*According to
generations*

*Classification by
mechanism of
adhesion/clinical
steps*

Classification of Modern Adhesives

Generations

1. First
2. Second
3. Third
4. Fourth
5. Fifth
6. Sixth
7. Seventh
8. Eighth

Clinical Steps

1. 3 step
2. 2steps 1 Bottle
3. 2steps 2 Bottle
4. 1 step

Modern Adhesive Strategies

1. etch and rinse
2. self etch
3. Selective etch

FIRST GENERATION

By Bowen in 1965

Agents used: NPG-GMA

Strength: 2-3 Mpa.

Mechanism of adhesion:

co monomer chelates calcium on tooth surface → generating chemical bonds on resin to calcium

➤ **Disadvantages:**

- *The bond strength of these adhesives was poor (about 3 MPa).*
- *Poor mechanical retention.*

Eg: Cervident(S.S White, Lake wood, NJ) First commercially available bonding agent.

- *Cosmic bond(Amalgamated Dental Company)*

SECOND GENERATION-1970s

COMPOSITION-based on phosphate-ester material(phenyl-P) and hydroxyethylmethacrylate(HEMA)

- ❑ **Mechanism of adhesion: Ionic interaction between phosphate groups(resin) and dentinal calcium. (smear layer)**
- ❑ Disadvantages:
 - ❑ Low bond strength **(1-5MPa)**
 - ❑ Hydrolysis of phosphate – Ca⁺⁺ bond.
 - ❑ Bonding obtained to the smear layer, not to the dentin itself.
- ❑ • *Example:* ScotchBond (3M dental), Clearfil bond system

THIRD GENERATION(LATE 1970S TO EARLY 1980S)

not to remove the entire smear layer but rather to modify it

Mild acids- 10%citirc acid, 10% phosphoric acid, 2% nitric acid, 3%ferric chloride

▶ The result was preservation of a modified smear layer with slight demineralization of the underlying intertubular dentin surface.

Clinical results. BOND STRENGTH - **8-15Mpa**

- Drawbacks
 - ▶ Decrease in bond strength with time
 - ▶ More chair side time
 - ▶ Technique sensitive
1. CLEARFIL NEW BOND(KURARAY)
 2. SCOTCHBOND 2(3M ESPE)






Shift to

No Etch

Total Etch
(4th and 5th
generation)

Self Etch
(6th, 7th and
8th
generation)

Classification of dental adhesives by adhesion strategy.

<p>Etch-and-rinse (ER)</p> 	<p>3-step ER Ac + Pr + BR</p>		
	<p>2-step ER Ac + (Pr/BR)</p>		<p>Universal adhesives used as ER adhesives</p>
<p>Self-etch (SE) <i>No separate etchant</i></p>	<p>2-step SE (Ac/Pr) + BR</p>		
	<p>1-step SE (Ac/Pr/BR)</p>		<p>Universal adhesives used as SE adhesives</p>

Three s
and
adhesive
(4th generation)

5th generation

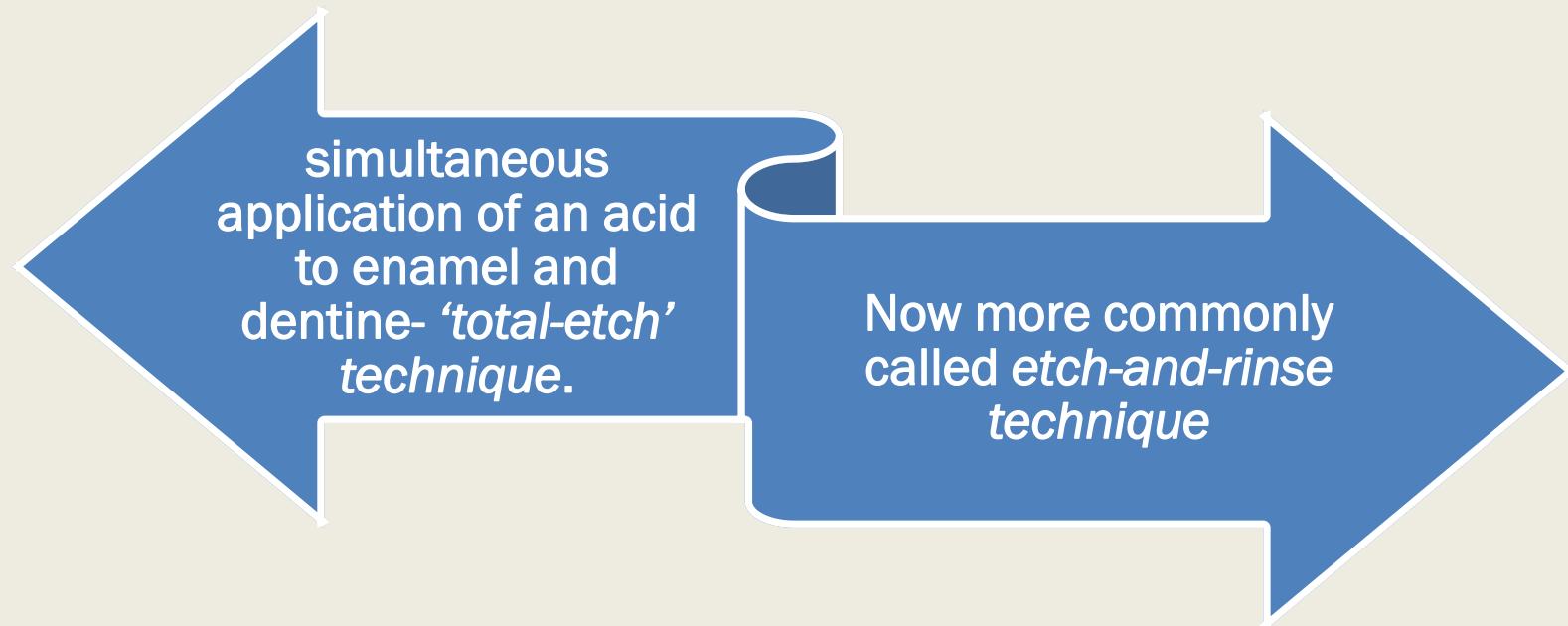
6th generation

7th generation

component
adhesive

3 STEP ETCH AND RINSE (ER) ADHESIVE (4TH GENERATION)

Concept. The smear layer acts as a 'diffusion barrier' that reduces the permeability of dentin, it may be considered an obstacle that must be removed to permit resin bonding to the underlying dentin substrate



I. phosphoric acid-etching gel that is rinsed off;



II. primer containing reactive hydrophilic monomers in ethanol, acetone or water and



III. nonsolvated unfilled or filled resin bonding agent.

Bond strength

20 MPa

Box 15.2 Mechanism of action of three-step etch-and-rinse adhesives

Application of acid to dentin results in partial or total removal of the smear layer and demineralization of the underlying dentin¹⁵⁶



Acids demineralize intertubular and peritubular dentin, open the dentin tubules and expose the collagen fibres (Fig. 15.6), increasing the microporosity of the intertubular dentin (Fig. 15.13)



Dentin is demineralized by up to approximately 7.5 μm , depending on the type of acid, application time and concentration¹⁵⁶



The *primer* in the system is designed to increase the critical surface tension of dentin, which gets decreased after the acid etching step



Bonding mechanism

- I. When primer and bonding resin are applied to etched dentin, they penetrate the intertubular dentin, forming a resin-dentin interdiffusion zone or *hybrid layer*
- II. They also penetrate and polymerize in the open dentinal tubules, forming *resin tags*

etched enamel must be completely dry to form a strong bond with hydrophobic adhesive resins,

KANCA

Etched dentin must be moist (**WET BONDING**) to form a hybrid layer.

The amount of water left in etched dentin is critical

If insufficient water is present, the collagen network will collapse and produce a relatively impermeable layer that prevents resin infiltration and subsequent hybridization. (HYBRIDOID ZONE)

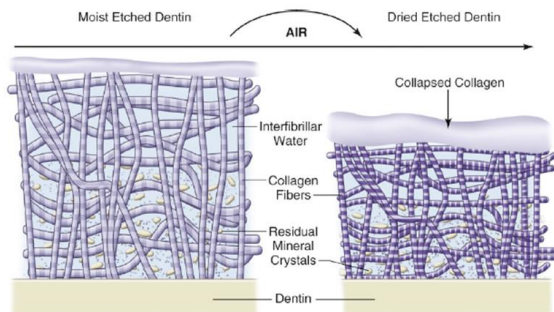


Figure 15.20 Collapse of etched dentin by air-drying.

If too much water remains, resin infiltration cannot fully replace the water in the collagen network (BLISTER & GLOBULE TYPE VOIDS) and, consequently, sets the condition for later leakage into those locations – INCOMPLETE MONOMER POLYMERIZATION

Therefore, a priming step is required to maintain a hydrated collagen network while removing excess water

PRIMER

FUNCTION OF THE PRIMER- expanded collagen network while removing residual water to allow for the infiltration of the hydrophobic adhesive monomer

MONOMER

HYDROPHILIC PROPERTIES
through
phosphate, carboxylic acid,
alcohol, or ester functional
groups.- AFFINITY FOR EXPOSED
COLLAGEN FIBRES

MOST COMMONLY-HEMA , 4-META



SOLVENT

Water ,acetone or alcohol

primer promotes resin diffusion into the moist demineralized dentine with the aim of achieving complete resin penetration

ETHANOL WET BONDING

Gwinnett et al. - *acetone/alcohol-based primers* are applied to demineralized dentine which were used to reconstitute the broken down collagen fibres and remove the excess water.

Resins show better miscibility with ethanol and acetone and remove water easily



WATER CHASING EFFECT

ACETONE HAS A HIGHER VAPOUR PRESSURE THAN ETHANOL WHICH MAY NOT ALLOW THE RESIN TO COMPLETELY INFILTRATE

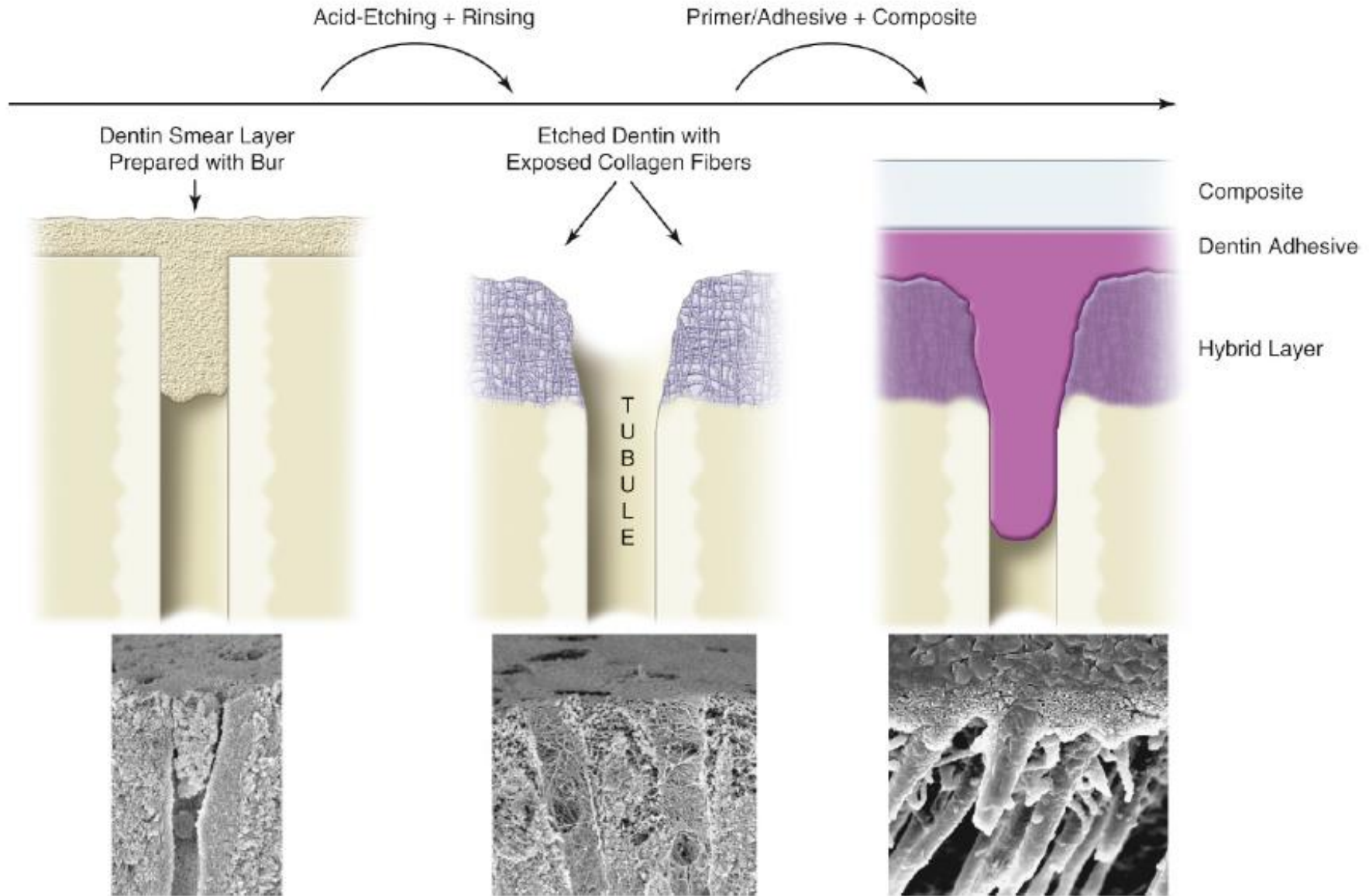


Figure 15.12 Bonding of resin to dentin using an etch-and-rinse technique.

HYBRID LAYER

Infiltration of the demineralized collagen fibres with resin results in the formation of hybrid layer
resin-dentine interdiffusion zone

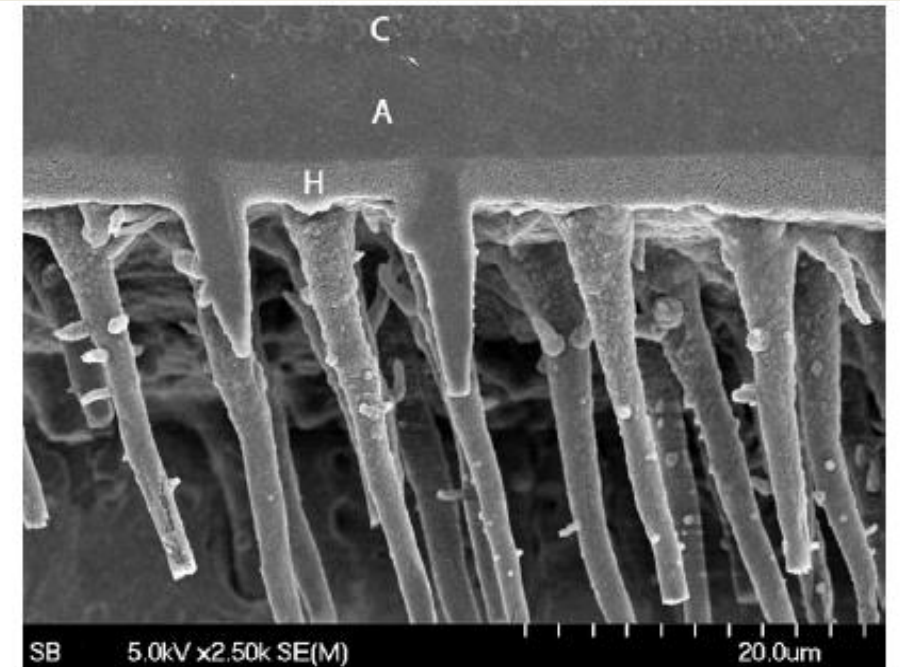
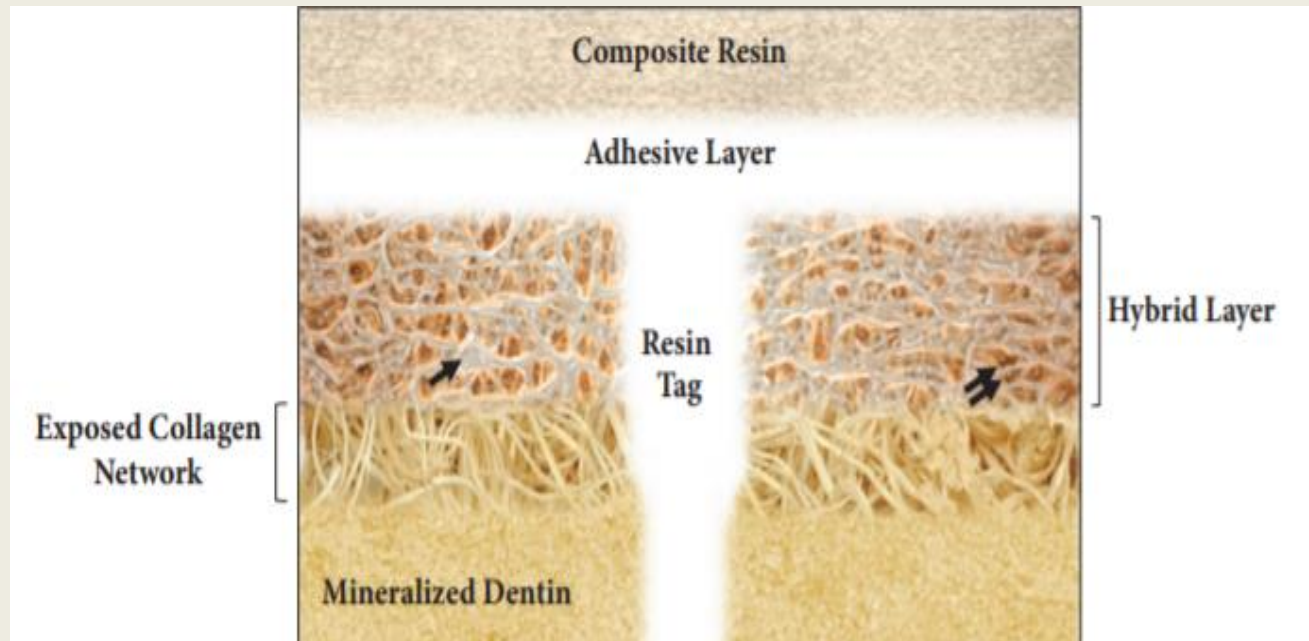


Figure 15.14 Scanning electron micrograph of the transition between composite resin (C)–adhesive (A), adhesive–hybrid layer (H), and hybrid layer–dentin.

The goal of hybridization is to give high bond strengths and a dentine seal

1. **Top zone:**It consists of loosely arranged collagen fibrils with inter-fibrillary spaces filled with the adhesive resin

2. **Mid-zone:**This consists of collagen fibrils infiltrated with resin with residual hydroxyapatite crystals between collagen

3. **Bottom zone:**It shows an abrupt transition to the underlying unaltered dentin with partially demineralized dentin containing hydroxyapatite crystals enveloped by adhesive resin.

The concept of hybridization of dentin is the benchmark of good bonding

The quality of Hybrid layer formed decides the strength of resin dentin interface. The **thicker and more uniform** the Hybrid layer, better is the bond strength.

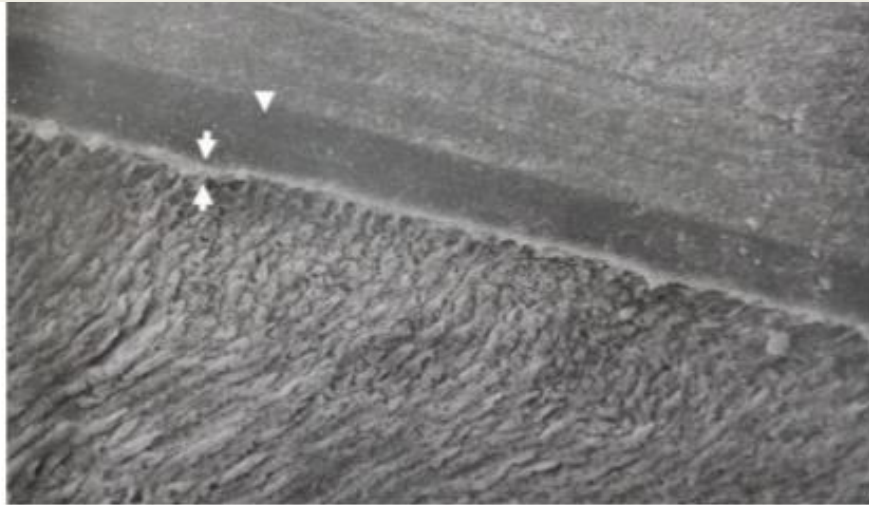


Fig. 1 Hybrid Layer as seen in Total-etch adhesives. Hybrid layer is observed to be uniformly thick.

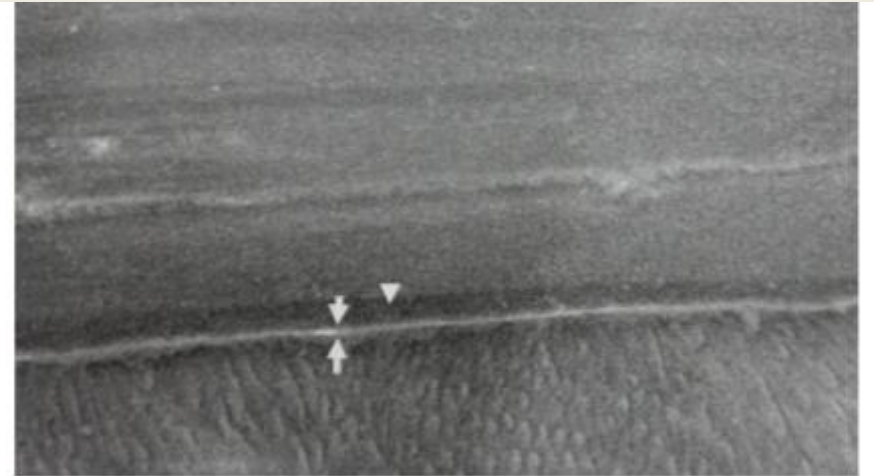


Fig. 2: Hybrid Layer as seen in self-etch adhesives. Hybrid layer is seen to be thin and discontinuous.

Resin tags formed with total-etch adhesives are much longer than those found in self-etch

Resin tags formed by total etch revealed numerous small lateral extensions of micro tags(lateral branches) branching off at right angles from the main resin tags which is a clear sign of proper adaptation and sealing.

Whereas the resin tags formation in self etch adhesive system are smaller and inconsistent

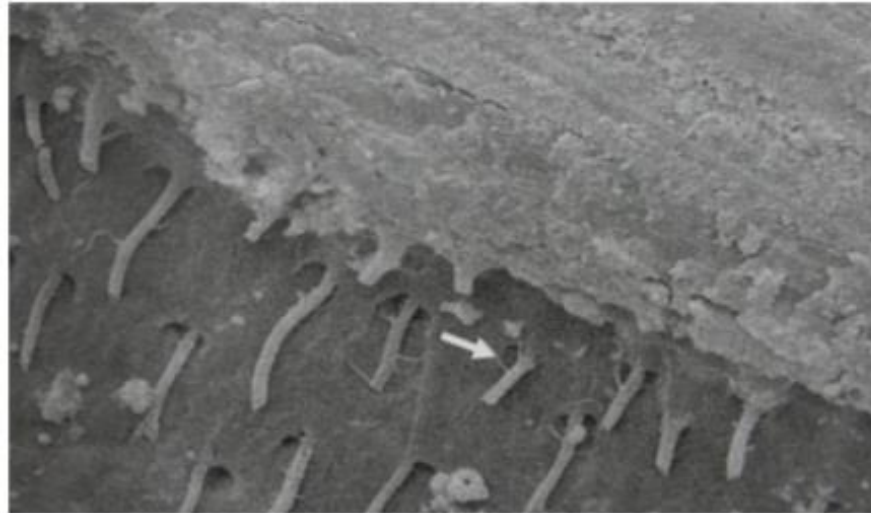


Fig 3: Resin tag formation with lateral branches as seen in total-etch adhesive system

Reverse Hybrid layer:

- Acid etched surface of dentin, when subjected to treatment with NaOCl, , dissolution of exposed collagen fibrils occurs.
- Further the use of self etching primers results in superficial etching of the surface. Here the hybrid **layer is surrounded by more of inorganic material**

Ghost hybrid layer:

- Formed due to incorporation of air bubbles at the substrate adhesive interface.

The hybrid layer degrades coincidentally with decreasing bond strength which contributes to the ageing of dentin bond integrity.



Review Article

Contemporary Dentin Bonding Agents-A Review

Nandini Pugal¹, Praveen rajesh², Dhanavel chakravarthy³, Padmaraj S.N⁴, Vijayaraja⁵

Recent Advances in Adhesive Bonding - The Role of Biomolecules, Nanocompounds, and Bonding Strategies in Enhancing Resin Bonding to Dental Substrates

Eliseu A. Münchow¹ and Marco C. Bottino^{2,*}

¹Department of Dentistry, Health Science Institute, Federal University of Juiz de Fora, Governador Valadares, MG 35010, Brazil.

²Department of Biomedical and Applied Sciences, Division of Dental Biomaterials, Indiana

major strategies available to overcome resin-dentin bond degradation:

- (i) use of collagen crosslinking agents-stable covalent bonds with collagen fibrils, thus strengthening the hybrid layer;
- (ii) (ii) use of antioxidants, which may allow further polymerization reactions over time;
- (iii) (iii) use of protease inhibitors, which may inhibit or inactivate metalloproteinases;
- (iv) (iv) modification of the bonding procedure, which may be performed by using the ethanol wet-bonding technique or by applying an additional adhesive (hydrophobic) coating, thereby strengthening the hybrid layer;
- (v) laser treatment of the substrate prior to bonding- specific topographic changes in the surface of dental substrates, increasing bonding efficacy; and
- (vi) reinforcement of the resin matrix with inorganic fillers or remineralizing agents(PHYSICOMECHANICAL PROPERTIES)

2 STEP ETCH AND RINSE TECHNIQUE (5TH GENERATION)

CONCEPT- to simplify clinical procedure

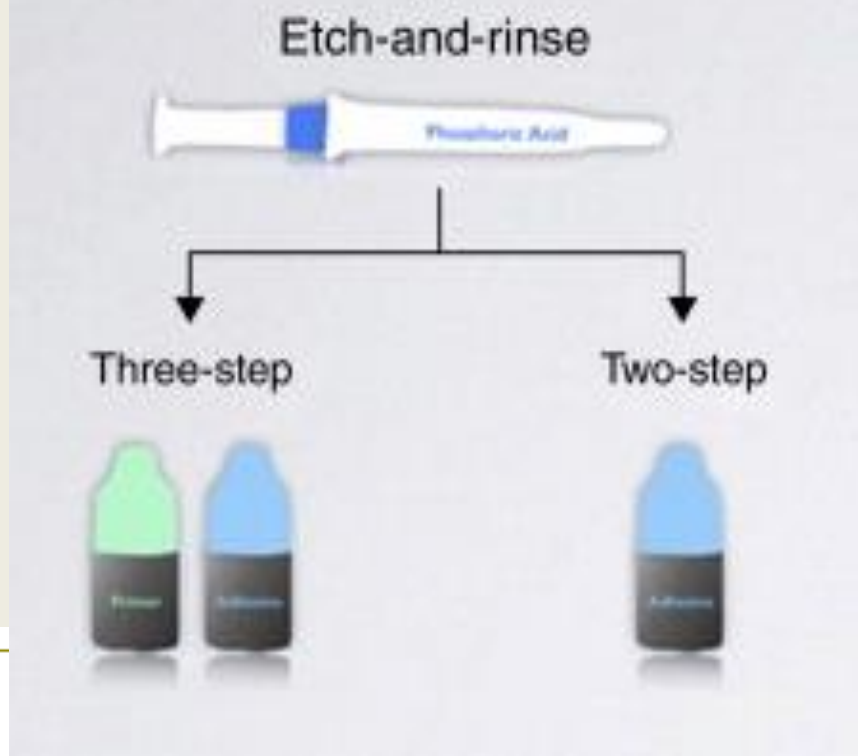
ETCHANT



PRIMER & BONDING AGENT

Mechanism of action- THE SINGLE BOTTLE: solvents and hydrophilic components from the primer that are mixed with the hydrophobic monomers from the bonding agent.

HYDROLYTIC
DEGRADATION



Type	Brand names (manufacturer)	1	2	3
Three-step etch-and-rinse	Adper Scotchbond Multi-Purpose (3M Oral Care) All-Bond 2 (Bisco, Inc.) All-Bond 3 (Bisco, Inc.) OptiBond FL (Kerr Corporation) Solobond Plus (Voco) Syntac (Ivoclar Vivadent)	Phosphoric acid	Hydrophilic primer	Bonding resin
Two-step etch-and-rinse	Admira Bond (Voco) Adper Single Bond Plus (3M Oral Care) ExcITE F (Ivoclar Vivadent) One-Step Plus (Bisco, Inc.) OptiBond SOLO Plus (Kerr Corporation) Prime & Bond NT (DENTSPLY Sirona) Prime & Bond XP (DENTSPLY Sirona)	Phosphoric acid	Combined (hydrophilic primer + bonding resin)	

3 STEP ETCH AND RINSE VS 2 STEP ETCH AND RINSE

- 5TH generation is more susceptible to water degradation because of the presence of hydrophilic primer which makes them more prone to water sorption
- The solvent present in these primers is more difficult to evaporate, often remains entrapped within the adhesive layer after polymerization
- Long term durability of the bond strength was found to be more in 3 step E&R as compared to 2 step

The change of bond strength over time is a very useful indication of relative clinical lifetime and can be evaluated by accelerated aging tests in vitro. Several investigations have found that the bond strength of three-step adhesive systems show little or no decrease in contrast to two-step adhesive systems that decrease significantly during a 4- to 5-year span. Research has also shown that peripheral bonding to etched enamel.

TWO-STEP SELF-ETCH ADHESIVES (6TH GENERATION)

Concept., two-step SEAs contain an **acidic monomer** that functions as a **self-etching primer** and a **hydrophobic bonding resin**.

The acidic primers include a phosphonated and/or carboxylated resin molecule

Mechanism of action

simultaneous etching and priming of enamel and dentin, forming a continuum in the substrate and

II. incorporating smear plugs into the resin tags

CLASSIFICATION OF SELF ETCHING ADHESIVES BASED ON THEIR pH:

ultra-mild (pH \geq 2.5),
Few nm

mild (pH \approx 2),
1microm

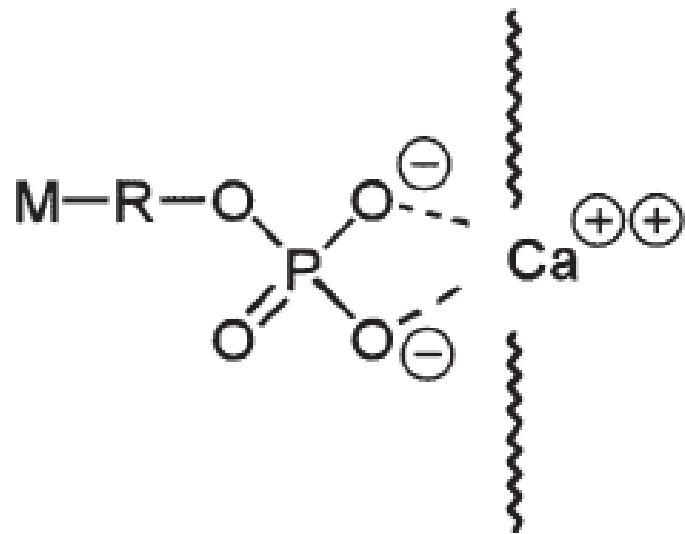
Intermediately
strong (pH
between 1 and 2)
1-2 micom

strong (pH $<$ 1)
Few micrometres

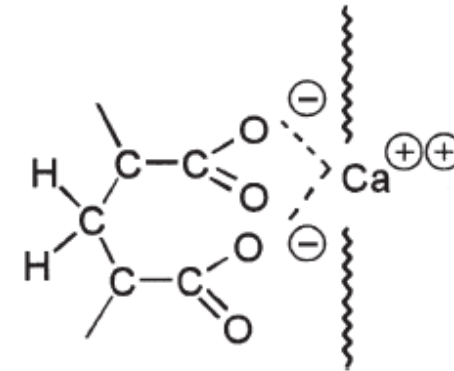
The adhesion mechanism in this case is two-fold:

Micromechanical entanglement of the adhesive with the partially decalcified dentin to form a sub-micrometric hybrid layer;

(B) Chemical/ionic inter-action of functional monomers, such as phosphate or carboxylate, with calcium in hydroxyapatite.



Phosphate based bonding agent



Carboxylate-based bonding agent
(PAA)

FIGURE 12-6 Chemical bonding mechanisms to hard tooth tissues through calcium salt formation with monomers having adhesive functional groups. (Courtesy of K-J. Söderholm.)

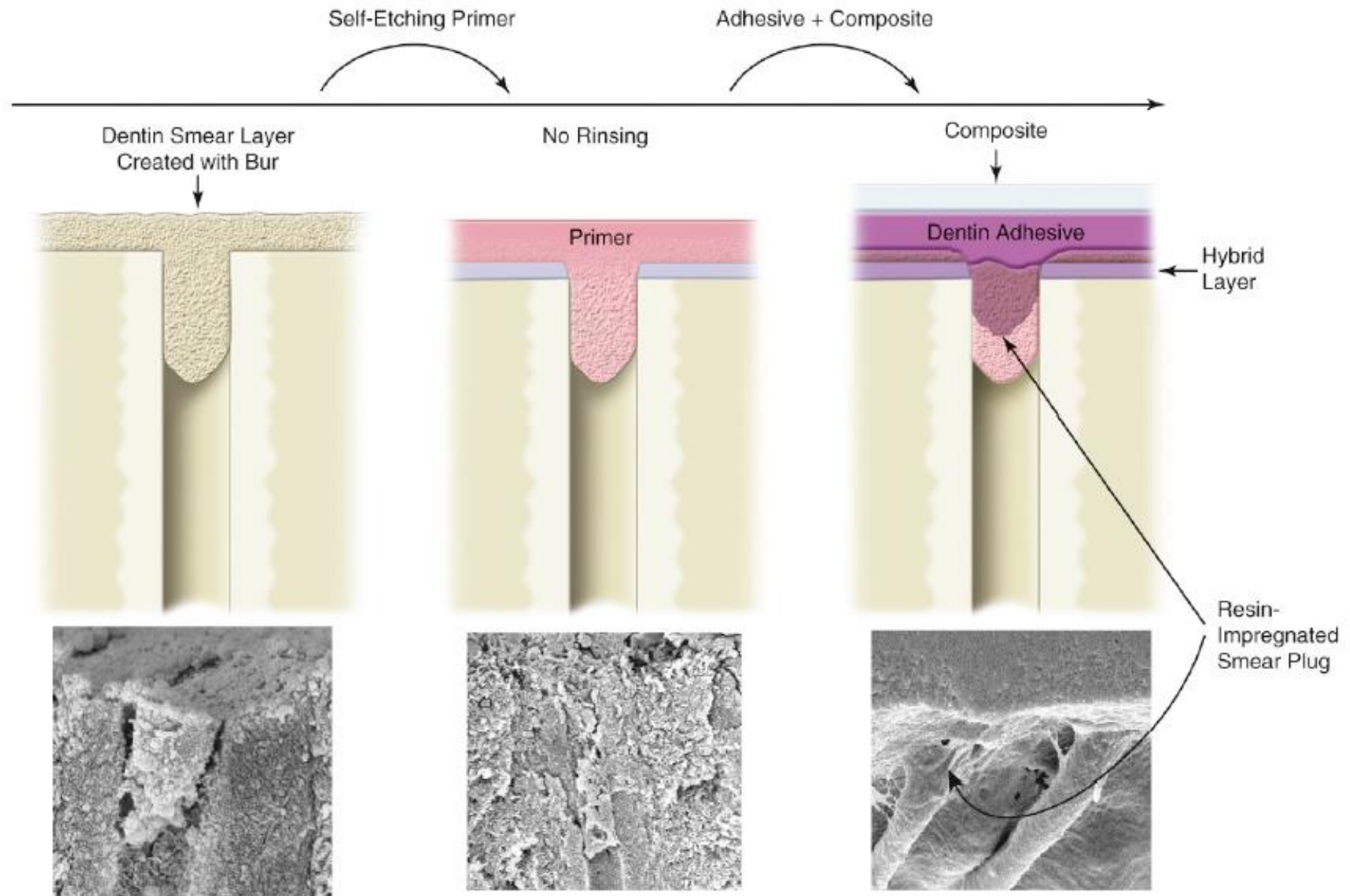


Figure 15.17 Bonding to dentin using a self-etch primer.

Classification review of dental adhesive systems: from the IV generation to the universal type

“over-etch” situation where the demineralization zone is too deep for subsequently placed primers to completely penetrate (33). While data indicates that 6th generation adhesives will adhere well to dentin (41 MPa at 24 hours), the bond to enamel is at least 25% weak to enamel than both the 4th and 5th generation adhesives in pooled data studies. Several respected clinicians have utilized 6th generation adhesives for bonding to dentin after selectively etching the enamel.

Mild SEAs tend to provide excellent dentin bond strengths and poorer enamel bonds, whereas more aggressive self etch systems provide the reverse.

Selective enamel etching

Improved marginal adaptation and marginal discoloration compared to the self-etch strategy



ONE STEP SELF ETCH ADHESIVE (7TH GENERATION)

ALL IN ONE BOTTLE

They have a significant amount of water in their composition which makes them prone to hydrolysis and chemical breakdown

Once polymerized they are more hydrophilic than the 2-step self etch adhesives; this makes them more prone to water sorption and limits the depth of resin infiltration thereby creating voids.

Long term bond stability may be low

ADVANTAGES

The *elimination of rinsing and drying steps* has the following advantages:

- Simplifies the bonding technique; less technique sensitive as etch and rinse
- Reduces the possibility of overwetting or overdrying dentin
- water is always a component of the acidic primer because it is needed for the monomers to ionize and trigger demineralization of hard dental tissues; this **makes SEAs less susceptible to variations in the degree of substrate moisture**
- SEAs are less likely to result in a discrepancy between the depth of demineralization and the depth of resin infiltration because SEAs demineralize and infiltrate dentin simultaneously

DISADVANTAGES

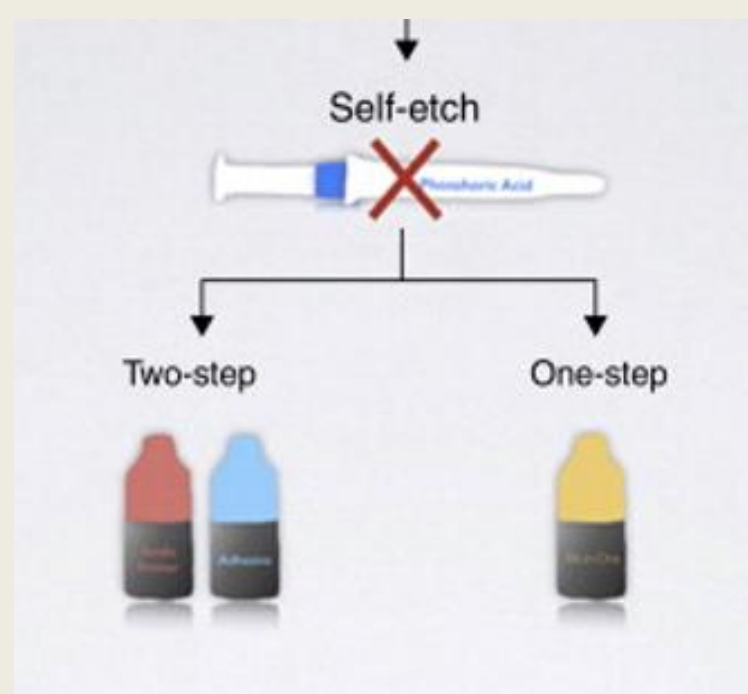
- SEAs *do not etch enamel as well as phosphoric acid*, seam of enamel margin might be compromised
- • SEA more likely to undergo bond deterioration as compared to etch and rinse
- The presence of a hybrid layer that is not completely infiltrated by the adhesive may increase the stresses in resin–dentin interfaces

Influence of multi-step etch-and-rinse versus self-etch adhesive systems on the post-operative sensitivity in medium-depth carious lesions: An in vivo study

**NICOLA SCOTTI, DDS, EMANUELE BERGANTIN, DDS, ROBERTA GIOVANNINI, DDS, LAURA DELBOSCO, DDS,
LORENZO BRESCHI, DDS, GIUSEPPE MIGLIARETTI, PHD, DAMIANO PASQUALINI, DDS & ELIO BERUTTI, MD, DDS**

bonded with multi-step etch-and-rinse versus self-etch systems, showing contradictory results. An in vivo study¹⁷ showed that a two-step self-etch adhesive induced significantly lower post-operative sensitivity than a three-step etch-and-rinse adhesive. Conversely, other in vivo studies^{18,19} did not show differences in post-operative sensitivity when comparing etch-and-rinse and self-etch adhesives.

Thus, this in vitro study evaluated the effect of a three-step



One-step self-etch	Clearfil S ³ Bond Plus (Kuraray Noritake Dental Inc.) Futurabond M (Voco) iBond (Heraeus Kulzer) OptiBond All-in-One (Kerr Corporation) Xeno IV (DENTSPLY Sirona) Xeno V ⁺ (DENTSPLY Sirona)	All-in-one Self-etch hydrophilic primer/bonding resin	
Two-step etch-and-rinse or One-step self-etch	Adhese Universal (Ivoclar Vivadent) All-Bond Universal (Bisco, Inc.) Clearfil Universal Bond (Kuraray Noritake Dental Inc.) Futurabond U (Voco) One Coat 7 Universal (Coltene) Prime & Bond Elect (DENTSPLY Sirona) Scotchbond Universal Adhesive (3M Oral Care) Prime & Bond Active (DENTSPLY Sirona)	Phosphoric acid	Hydrophilic bonding resin
		Self-etch hydrophilic primer/bonding resin	

Table 15.1 Current strategies for adhesion of resins to dentin

	Etchant (E)	Primer (P)	Bonding agent (B)
Three-step etch-and-rinse ^a E + P + B	Removes the smear layer Exposes intertubular and peritubular collagen Opens tubules in a funnel configuration Decreases surface-free energy	Includes bifunctional molecules (simultaneously hydrophilic and hydrophobic) Envelops the external surface of collagen fibrils Re-establishes surface-free energy to levels compatible with a more hydrophobic restorative material	Includes monomers that are mostly hydrophobic such as Bis-GMA; however, can contain a small percentage of hydrophilic monomers such as HEMA Copolymerizes with the primer molecules Penetrates and polymerizes into the interfibrillar spaces to serve as a structural backbone to the hybrid layer
Two-step etch-and-rinse E + [PB]	Removes the smear layer Exposes intertubular and peritubular collagen Opens tubules in a funnel configuration Decreases surface-free energy	Penetrates into the dentin tubules to form resin tags The first coat applied on etched dentin works as a primer—it increases the surface-free energy of dentin The second coat (and third, fourth etc.) acts as the bonding agent used in three-step systems—it fills the spaces between the dense network of	
	Two-step self-etch [EP] + B	Enamel etch is typically shallow The SEP does not remove the smear layer, but fixes it and exposes about 0.5–1 μm of intertubular collagen because of its acidity (pH = 1.2–2) The smear plug is impregnated with acidic monomers, but it is not removed; some SEP monomers bond chemically to dentin When it impregnates the smear plug, the SEP prepares the pathway for the penetration of the subsequently placed fluid resin into the microchannels that permeate the smear plug	Uses the same type of bonding agent included in the three-step etch-and-rinse systems The resin tags form on resin penetration into the microchannels of the primer-impregnated smear plug
	One-step self-etch [EPB]	Etches enamel, but etch pattern is typically shallow Incorporates the smear layer into interface Being an aqueous solution of a phosphonated monomer, it demineralizes and penetrates dentin simultaneously, leaving a precipitate on the hybrid layer Forms a thin layer of adhesive, leading to low bond strengths; a multicoat approach is recommended; an extra layer of a hydrophobic bonding resin improves bond strengths and clinical performance Incompatible with self-cure composite resins unless coated with an hydrophobic bonding resin	

SEP, Self-etching primer; Bis-GMA, bisphenol-glycidyl methacrylate; HEMA, 2-hydroxyethyl methacrylate.

^aAlthough the meaning of the two terms is the same, the term 'etch-and-rinse' is preferred over 'total-etch.'

ETCH-AND-RINSE

SELF-ETCH

Three-Step (Fourth generation)	Two-Step (Fifth generation)	Two-Step (Sixth generation)	One-Step (Seventh generation)
<p>1. Etch Apply for 15 seconds, rinse 15 seconds gently air dry, while keeping dentin moist.</p>	<p>1. Etch Apply for 15 seconds, rinse 15 seconds, gently air dry while keeping dentin moist.</p>	<p>1. Etch and Prime One application without rinsing, gently air-dry.</p>	<p>1. Etch, Prime, and Bond Apply 1 to 5 layers without rinsing, gently air-dry, light-cure.</p>
<p>2. Prime Apply 1 to 5 layers, gently air-dry.</p>	<p>2. Prime and Bond Apply 1 to 5 layers, gently air-dry, light-cure.</p>	<p>2. Bond Apply one layer, gently air-dry, light-cure.</p>	
<p>3. Bond Apply one layer, gently air-dry, light-cure.</p>			

REPRESENTATIVE PRODUCTS CURRENTLY MARKETED FOR CLINICAL USE

Adper Scotchbond Multi-Purpose (3M ESPE)	DenTASTIC UNO (Pulpdent)	Adper Prompt (3M SPE)	AdheSE One (Ivoclar Vivadent)
All Bond 3 (Bisco)	Excite (Vivadent)	AdheSE (Ivoclar Vivadent)	Adper Easy Bond Self Etch (3M ESPE)
DenTASTIC All-Purpose (Pulpdent)	Gluma Comfort Bond (Heraeus Kulzer)	All-Bond SE (Bisco)	Adper Prompt L-Pop (3M ESPE)
Gluma Solid Bond (Heraeus Kulzer)	One-Step Plus (Bisco)	Clearfil Protect Bond (Kuraray)	Clearfil S3 Bond (Kuraray)
Optibond FL (Kerr)	PQI (Ultradent)	Nano-Bond (Pentron)	Futurabond DC (VOCO)
Syntac (Ivoclar Vivadent)	Prime & Bond NT (Dentsply)	One-Step P/TYRIAN (Bisco)	G-Bond (GC), XENO V (Dentsply)
	Single Bond (3M ESPE)	Peak (Ultradent)	I-Bond (Heraeus Kulzer)

8TH GENERATION

2010, voco America introduced voco futurabond DC as 8th generation bonding agent, which contains nanosized fillers (12NM)



Nano-bonding agents are solutions of nano-filler which produce better enamel and dentin bond strength, stress absorption, and longer shelf life

NANO FILLERS >15-20nm or
a content more than 1% - -
can increase the viscosity of
the adhesives

May cause accumulation of
fillers over the top of the
moistened surface

**These clusters may induce cracks and cause
a decrease in bond strength**

To summarize....

Table 2. Classification of dental bonding systems by generations.

Generation	Number of steps	Surface pre-treatment	Components	Shear bond strength (MPa)
1 st	2	Enamel etch	2	2
2 nd	2	Enamel etch	2	5
3 rd	3	Dentine conditioning	2-3	12-15
4 th	3	Total etch	3	25
5 th	2	Total etch	2	25
6 th	1	Self-etch adhesive	2	20
7 th	1	Self-etch adhesive	1	25
8 th	1	Self-etch adhesive	1	Over 30

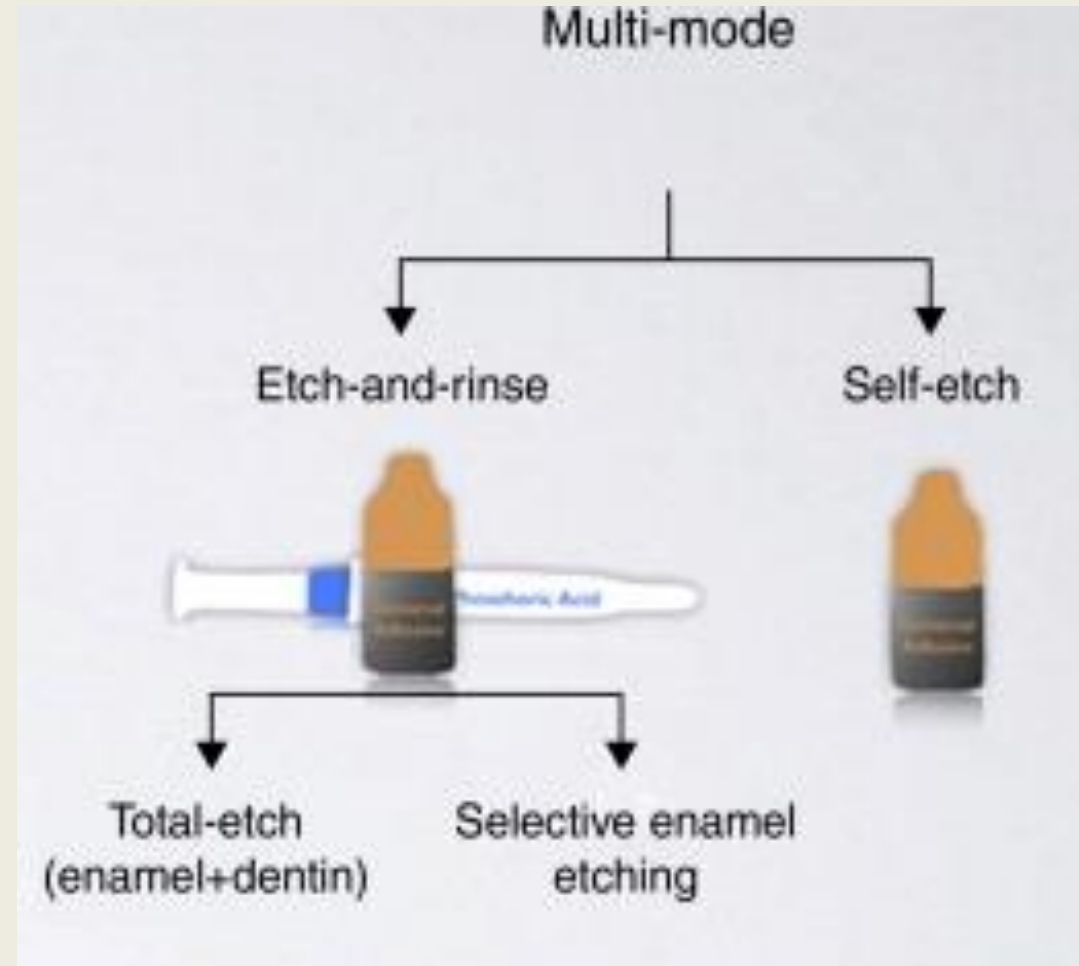
A Comparative Evaluation of Shear Bond Strength of Seventh- and Eighth-Generation Self-etch Dentin Bonding Agents in Primary Teeth: An *In Vitro* Study

Ankur Mishra¹, Monika Koul², Vinod K Upadhyay³, Ahsan Abdullah⁴

CONCLUSION

Shear bond strength of eighth-generation dentin bonding agent, that is, Futurabond DC, was better than seventh-generation dentin bonding agent, that is, Adper Single Bond Universal. And for achieving a definitive conclusion, more *in vitro* and clinical trials with large sample size and longer follow-ups should be conducted to correlate the factors contributing to their bonding efficacy.

UNIVERSAL ADHESIVES



Because of their multistrategy approach, this new generation of one-bottle dental adhesives has become very popular in dentistry.

- The major difference between traditional one-step SEAs and universal adhesives is that *most universal adhesives contain 10-MDP*

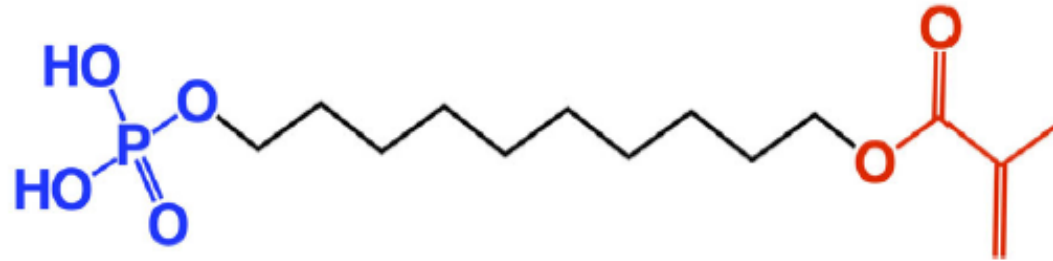


FIGURE 6 The 10-MDP molecule. The methacrylate polymerizable end is shown in red. The short hydrophilic phosphate component is shown in blue; long hydrophobic 10-carbon chain or spacer is depicted in black

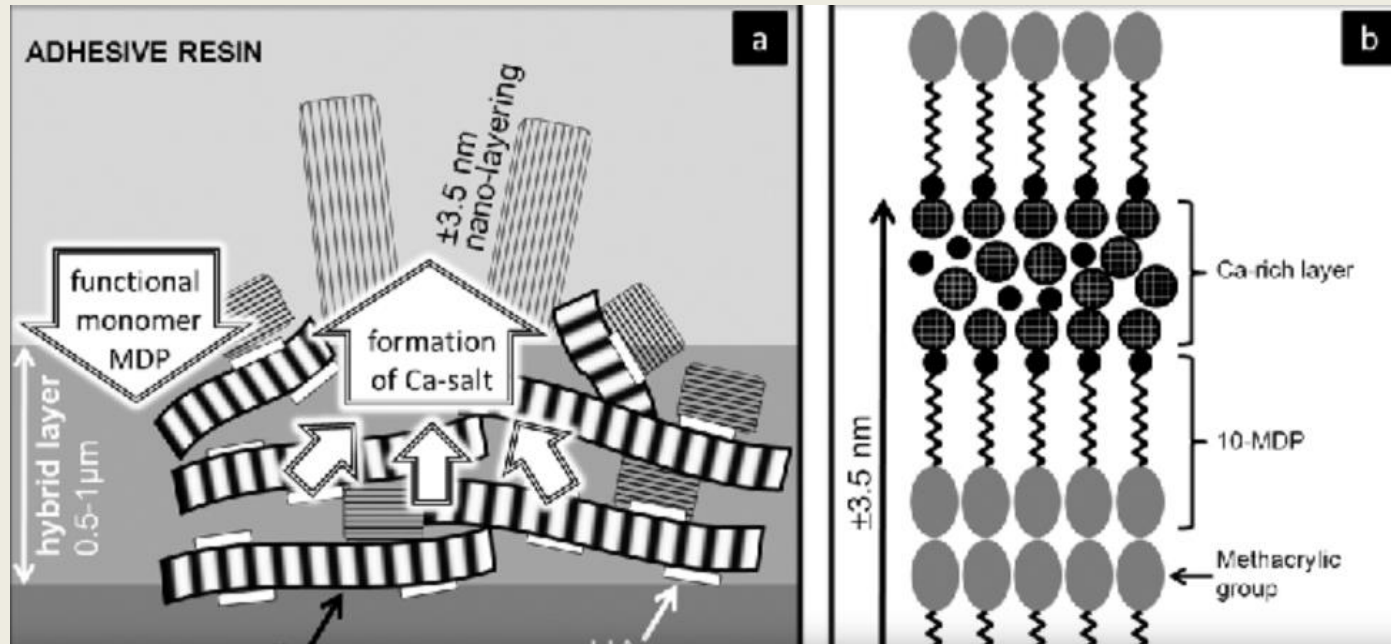
10-METHACRYLOXYDECYL DIHYDROGENPHOSPHATE

The chemical bonding formed by 10-MDP is more stable in water than that of other monomers used in the composition of SEAs, such as 4-META and phenyl-P

This is a hydrophilic monomer with mild-etching properties.

MDP is one of the monomers that enable a universal adhesive to be used with any etching techniques.

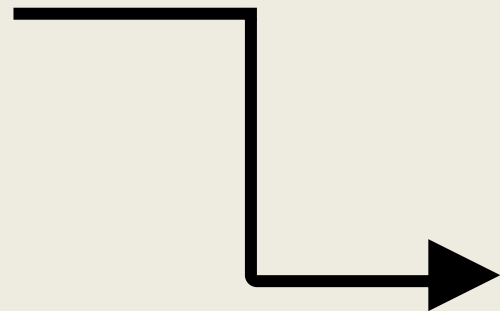
Stable MDP-calcium salts are formed during this reaction and deposited **in self-assembled nano-layers**



Additionally, the matrix of universal is based on a combination of monomers of hydrophilic (hydroxyethylmethacrylate /HEMA) hydrophobic (decandiol dimethacrylate /D3MA,bis-GMA) nature.

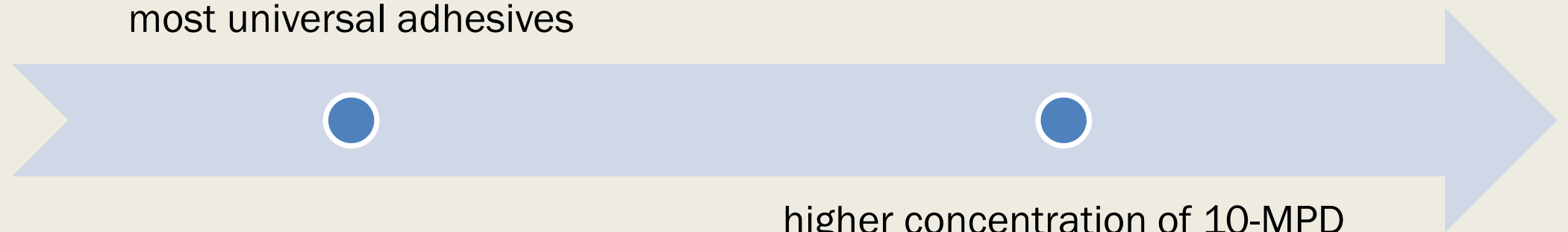
may contain silane in their formulation, potentially eliminating the silanization step when bonding to glass ceramics or resin composites

dentin more receptive to the chemical interaction between 10-MDP and hydroxyapatite



The lesser amount and smaller hydroxyapatite crystals in dentin and their criss-cross orientation compared to a more parallel orientation in enamel.

Active **application** results in higher **bond** strengths to intact enamel for most universal adhesives



higher concentration of 10-MPD molecules in intimate contact with the hydroxyapatite crystals

Name of Material	Scotchbond Universal (3M)	Clearfil Universal (Kuraray)	Futurabond U (VOCO)	All Bond Universal (Bisco)	Premio Bond (GC)	Adhese Universal (Ivoclar)	One Coat 7 Universal (Coltene)
Components	BisGMA, 10-MDP, Vitrebond Copolymer, HEMA, Ethanol, Water, Filler, Silane, Initiators	10-MDP, BisGMA, 2-HEMA, Hydrophilic aliphatic dimethacrylate, Colloidal silica, Silane, Camphorquinone, Ethanol, Water	Liquid 1: BisGMA, HDDMA, UDMA, HEMA, fumed silica, CQ, 10-MDP Liquid 2: Ethanol, water, catalyst	10-MDP, Phosphate monomer, HEMA, BisGMA, Ethanol, Water, Initiators	4-META, 10-MDP, 10-Methacroyldecyl dihydrogen thiophospate, Methacrylate ester, Acetone, Distilled water, Photoinitiators, Silica fine powder	10-MDP, Methacrylated carboxylic acid polymer, HEMA, BisGMA, D3MA,	10-MDP, Methacrylated polyacid, HEMA, Urethane di-methacrylate, Photoinitiators, Filler, Ethanol, Water

Table 1. Components of some Universal Bonding Agents.



Review

Bond strength of universal adhesives: A systematic review and meta-analysis



Wellington Luiz de Oliveira da Rosa, Evandro Piva,
Adriana Fernandes da Silva*

Department of Restorative Dentistry, School of Dentistry, Federal University of Pelotas, Pelotas, RS, Brazil

Clinical studies pointed out that enamel pre-etching resulted in a more durable marginal integrity of restorations bonded with self-etch adhesives.^{21,73} Nevertheless, it is a challenge in clinical situations to use phosphoric acid only on enamel margins, as accidental dentin etching might occur, especially if a low-viscosity etchant is used.^{29,47} For dentin, considering that there is not an improvement in the bond strength with prior acid etching in mild universal adhesives, a self-etch approach might reduce the risk of post-operative sensitivity.^{7,32,36,37} Therefore, based on this meta-analysis, selective enamel etching prior to the application of a mild universal adhesive is an advisable strategy for optimizing bonding.

CEMENTUM BONDING

- clinical problems associated with class-II and class-V cavities in adhesive resin restorations is the weak link of restorative material to root dental structures, when the cervical margin is located below the cemento-enamel junction.
- **Ferrari et al.** reported that cementum treated with dentin bonding systems is infiltrated by the resin, but the predictability of the bond is unclear.
- shear bond strength of a resin composite to EDTA conditioned sound cementum, after treatment with an aqueous primer composed of 5% glutaraldehyde and 35% hydroxyethyl methacrylate, was estimated as 6MPa.
- It seems that after demineralization the increased intrinsic fibrous content of intact cementum surface creates an organic network that lacks the cohesive strength of demineralized dentin collagen, and although it is reinforced by resin infiltration, results in low bond strength.
- Modification of intact cementum surfaces to improve adhesion may include a deproteinization step, prior to any adhesive treatment, in order to remove the high organic content and expose the inorganic substrate, like conditioning with aqueous solutions of sodium hypochlorite (NaOCl)

RECENT ADVANCES

Futurabond DC- 8th Generation

- It is dual-cured and works with all light, self or dual- cured resins .
- Nanosized cross linking agents with fused silica particles
- It works in a self-cured mode without any light great for endo
- It takes only 35 sec. from start to finish.
- It needs only one coat.



Surpass: A Universal Eighth Generation Bonding System

Has the best attributes of the fourth generation and the ease of the sixth-generation bonding systems

Consists of three bottles: **an etchant/conditioner, a primer, and a separate hydrophobic bonding resin**

Etchant/conditioner is **not rinsed** from the tooth.

Bond Strength: **50 MPa**



Eshrak Sofan, Afrah Sofan and Guido Migliau. Classification review of dental adhesive systems: from the IV generation to the universal type. Ann Stomatol (Roma). 2017 Jan-Mar; 8(1): 1-17.

Fluoride releasing bonding agents



Anti-cariogenic

Increases dentin bond strength

Increase the local concentration of **fluoro-apatite** in the mineralized dentin just beneath the hybrid layer

Prevent the release of hydrolytic enzymes from the matrix.

Reduce the solubility of intrinsic calcium phosphate within the hybrid layer.

Examples:

CLEARFIL SE BOND PLUS

ONE UP BOND F

G BOND

FL BOND

Shinohara MS1, Yamauti M, Inoue G, Nikaido T, Tagami J, Giannini M, de Goes MF. Evaluation of antibacterial and fluoride-releasing adhesive system on dentin--microtensile bond strength and acid-base challenge. Dent Mater J. 2006 Sep;25(3):545-52.

DESENSITIZATION

Precipitation of proteins in the tubule
Penetrates the tubule as far as 200um.
Forms series of bridges across the tubule.
Impermeable to odontoblastic fluids.
Examples : GLUMA SYSTEM(5%
GLUTARALDEHYDE+35% HEMA), ALL BOND2



G BOND

new, revolutionary 7th Generation (single component) adhesive that takes the guesswork out of bonding. The unique ***combination of Phosphoric Acid Ester Monomer and 4-MET Adhesive Technology.***

Nano-interaction technology:

Non-conventional interface with the dentin – a “Nano Interaction Zone” (NIZ) with minimal decalcification and almost no exposure to collagen fibers. Ionic bond with hydroxyapatite of tooth structure.



Antibacterial Agents

Clearfil SE Protect, an antibacterial self-etching adhesive.

SE Protect contains an antibacterial monomer, **MDPB (methacryloyloxy-dodecyl pyridinium bromide)** which disinfects the tooth's surface during its application



Shinohara MS1, Yamauti M, Inoue G, Nikaido T, Tagami J, Giannini M, de Goes MF. Evaluation of antibacterial and fluoride-releasing adhesive system on dentin--microtensile bond strength and acid-base challenge. Dent Mater J. 2006 Sep;25(3):545-52.

Evaluation of Antibacterial and Fluoride-releasing Adhesive System on Dentin – Microtensile Bond Strength and Acid-base Challenge

Mirela Sanae SHINOHARA^{1,2}, Monica YAMAUTI³, Go INOUE³, Toru NIKAIIDO³, Junji TAGAMI^{3,4},
Marcelo GIANNINI¹ and Mario Fernando DE GOES¹

¹Dental Materials Division, Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas, Piracicaba, SP, Brazil

²Dental Materials Division, State University of Amazon, Manaus, AM, Brazil

³Cariology and Operative Dentistry, Department of Restorative Sciences, Graduate School, Tokyo Medical and Dental University, Tokyo, Japan

⁴Center of Excellence Program, FRMDRTB at Tokyo Medical and Dental University, Tokyo, Japan

Corresponding author, Toru Nikaïdo E-mail:nikaido.ope@tmd.ac.jp

there were no statistically significant differences among the groups^{7,22)}. These results corroborated those of Imazato *et al.*^{23,24)}, whereby it was found that the incorporation of MDPB into dentin primer did not demonstrate any adverse effect on the bond strength or curing behavior²⁵⁾ of the adhesive system. Regarding the presence of a fluoride-releasing component in the adhesive resin, several studies^{6,24,26–29)} have established the ability of fluoride ions to inhibit secondary caries by the remineralization of dentin around the restoration. According to Han *et al.*⁸⁾, although the mechanism of fluoride action on caries

Go! One Component Self-Etching Light-Cure Adhesive

- low film thickness;
- requires no etching, rubbing, or agitating;
- no HEMA.
- Its specially treated hydrophilic and hydrophobic fillers change from a water-loving to a water-repelling state after polymerization; this provides a surface with no water residue for enhanced bonding
- **Quick color change**
Initially, Go! is a dark yellow color, but upon curing, it changes to clear.



CONCLUSION

Dentine adhesive systems have created a new era in the field of dentistry. Owing to its property of adherence to the tooth structure by both micromechanical and chemical means, it finds a wide range of application in various fields. It has lead to the most desired form of treatment needs, i.e. the conservation of tooth structure, which is the ultimate goal of conservative dentistry

- ✓ Sturdevant C.M, Theodore M. Roberson, Herald O.Heymann, Edward J. Swift; the art science of operative dentistry. Fundamental concepts of enamel and dental adhesion 235-268.
- ✓ James B Summitt . Fundamentals of operative dentistry. 2nd edition... Karl F.Leinfelder. Dentin adhesives for the twenty-first century.
- ✓ Nakabayashi . Hybridization of dental hard tissues by. Quintessence Publication
- ✓ Kenneth.J.Anusavice –philips science of dental materials 11th edition