Aurobindo College of Dentistry

Indore, Madhya Pradesh

INDIA

Module plan

- Topic : Dentin Bonding Systems
- Subject: Endodontics
- Target Group: Undergraduate Dentistry
- Mode: Powerpoint – Webinar
- Platform: Institutional LMS
- Presenter: DR. PRADEEP JAIN

Dentin Bonding or adhesion

Micromechanical coupling or union of restorative materials to dentin, particularly composites, via an intermediary adhesive resin layer. Eick et al.

.

Allow more conservative cavity preparation since reliance on traditional retentive features is reduced.

Dentin bonding agents

Difunctional or multifunctional organic molecules that contain reactive group which interacts with dentin and the monomer of the restorative resin.

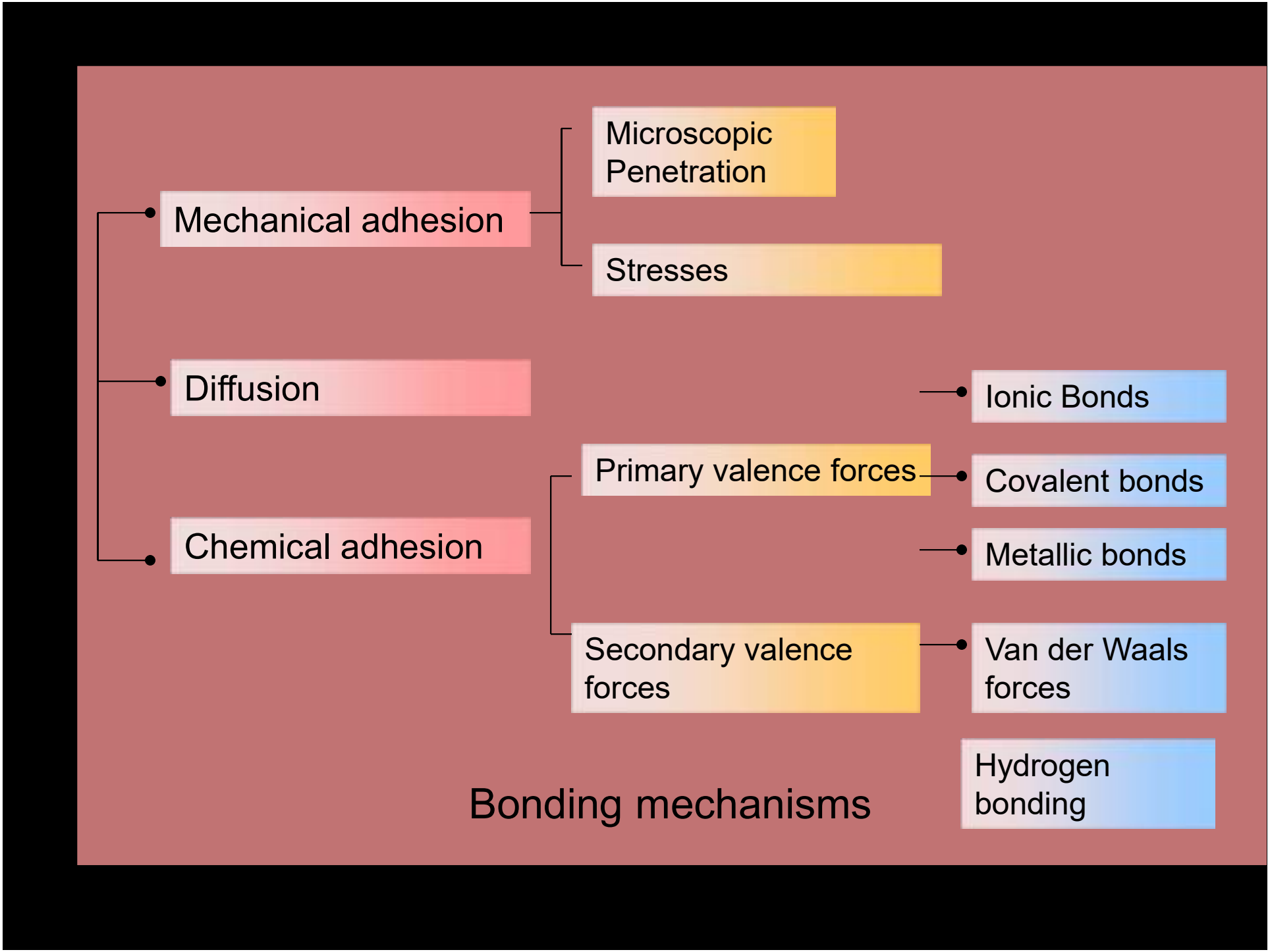
Basic Concepts

The American Society for Testing and Materials(ASTM) Sp no D 907.

Adhesion " the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking forces or both."

Adhesive

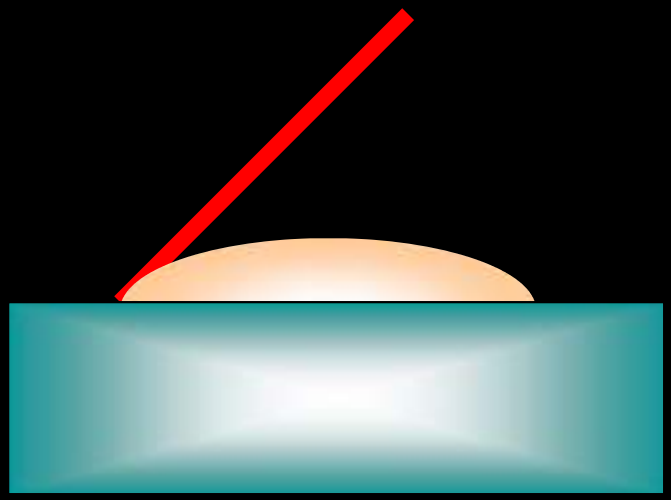
Adherend


Mechanical adhesion
Microscopic Penetration
Stresses
Diffusion
Chemical adhesion
Primary valence forces
Ionic Bonds
Covalent bonds
Metallic bonds
Secondary valence forces
Van der Waals forces
Hydrogen bonding
Bonding mechanisms

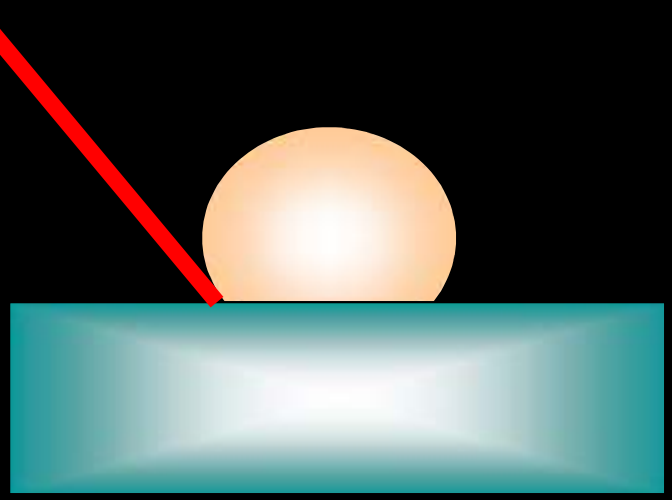
Requirements of good bonding:

(Dental materials and their selection: William J O' Brien Third edition.Sturdevant.)

1.Good Wetting; degree of spreading of a liquid drop on a solid surface



Low contact angle : Good wetting



High contact angle : Poor wetting

2. Surface energy:

Adhesive: Low surface energy

Adherend: High surface energy

.

500-5000 erg/cm2 :Hard Solids

Hydroxyapatite and glass ionomer cement :High surface energy

Collagen and composite :low energy surfaces

3. Surfaces joined should be clean

4.Good penetration

Liquid with low viscosity, low surface tension, low contact angle

Clinical uses of dentin bonding systems:

- Bonding of directly placed resin based restorative materials.
- Bonding of indirectly placed restorative materials.
- Bonding of ceramic restorations.
- Bonding of amalgam restorations.
- Bonding of prefabricated and cast posts.
- Bonding orthodontic brackets.
- Bonding periodontal splints
- Repair existing restorations.
- Sealing of pits and fissures of posterior teeth.
- Treatment of cervical sensitive dentine.
- Reattachment of fractured tooth fragments.
- Pulp capping.
- Reinforce fragile roots internally.
- Seal apical restorations placed during endodontic surgery.

History of dentinal bonding:

Oscar Hagger(1951): GPADMA.
Buonocore: (1955): Acid etching technique

Bowen (1957) : Development of BISGMA.
Schmidt and Purrmann(1958) P Cadurit.
Causton(1965) how primers work.

- **Knight et al(1971) Urethane Dimethacrylate**.(ICI Dental).

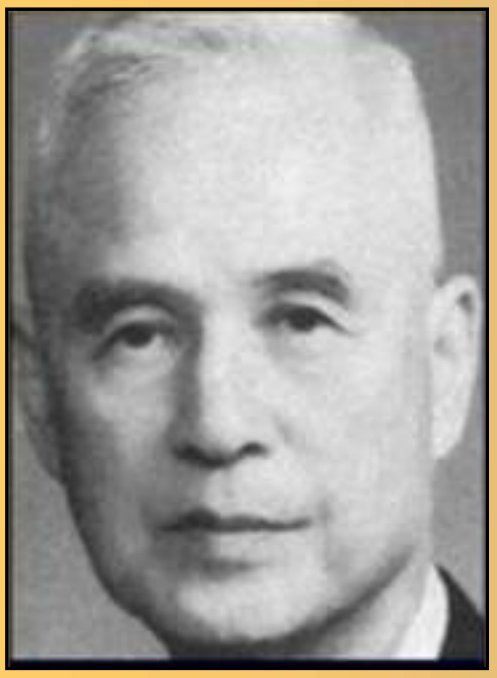
- **Forster and Walker(** Amalgamated Dental Company)**1975)** Urethane dimethacrylate resin for use in resin composite dental materials.

  - Higher molecular weight,
  - Lower viscosity
  - Toughness
  - Less staining than Bis GMA.

- **Gwinnet and Silverstone(1975)** described three patterns of etching of enamel.

Nakabayashi et al(1982) Hybrid layer

.



Fusayama (1987)
Concept of total etching and bonding.

John Kanca (1990s)

Wet bonding technique

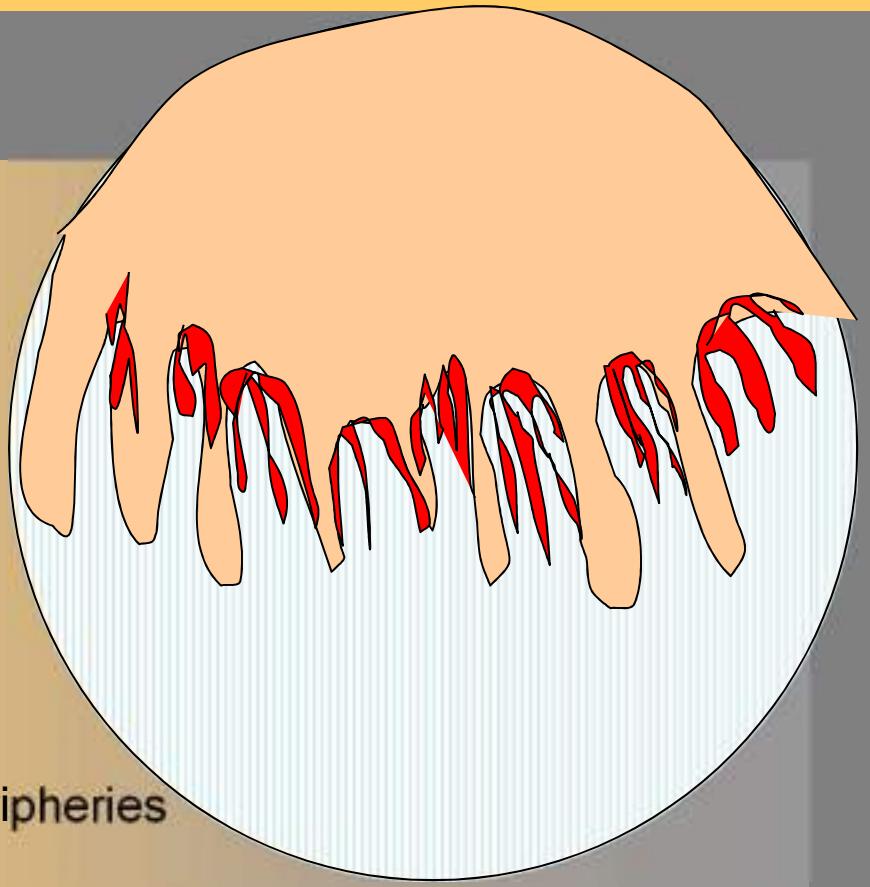
Ferrari et al(1997- 2003) Development of one bottle bonding systems. Sixth and Seventh generation bonding systems.

Ideal requirements of dentin bonding agents:

1961 Phillips and Ryge:

- High bond strength to dentin .
- Provide bond strength to dentin similar to that of enamel.
- Biocompatibility to dental tissue including the pulp.
- Minimize microleakage at the margins of the restorations.
- Prevent recurrent caries and marginal staining.
- Easy to use and minimally technique sensitive.
- Good shelf life.
- Be compatible with a wide range of resins.
- Non toxic and non sensitizing to the operators or patients.
- Bonding agents should seal the tooth surfaces from oral fluids.

Dentin Bonding Systems



Enamel adhesion:

micromechanical retention.

Resin tags

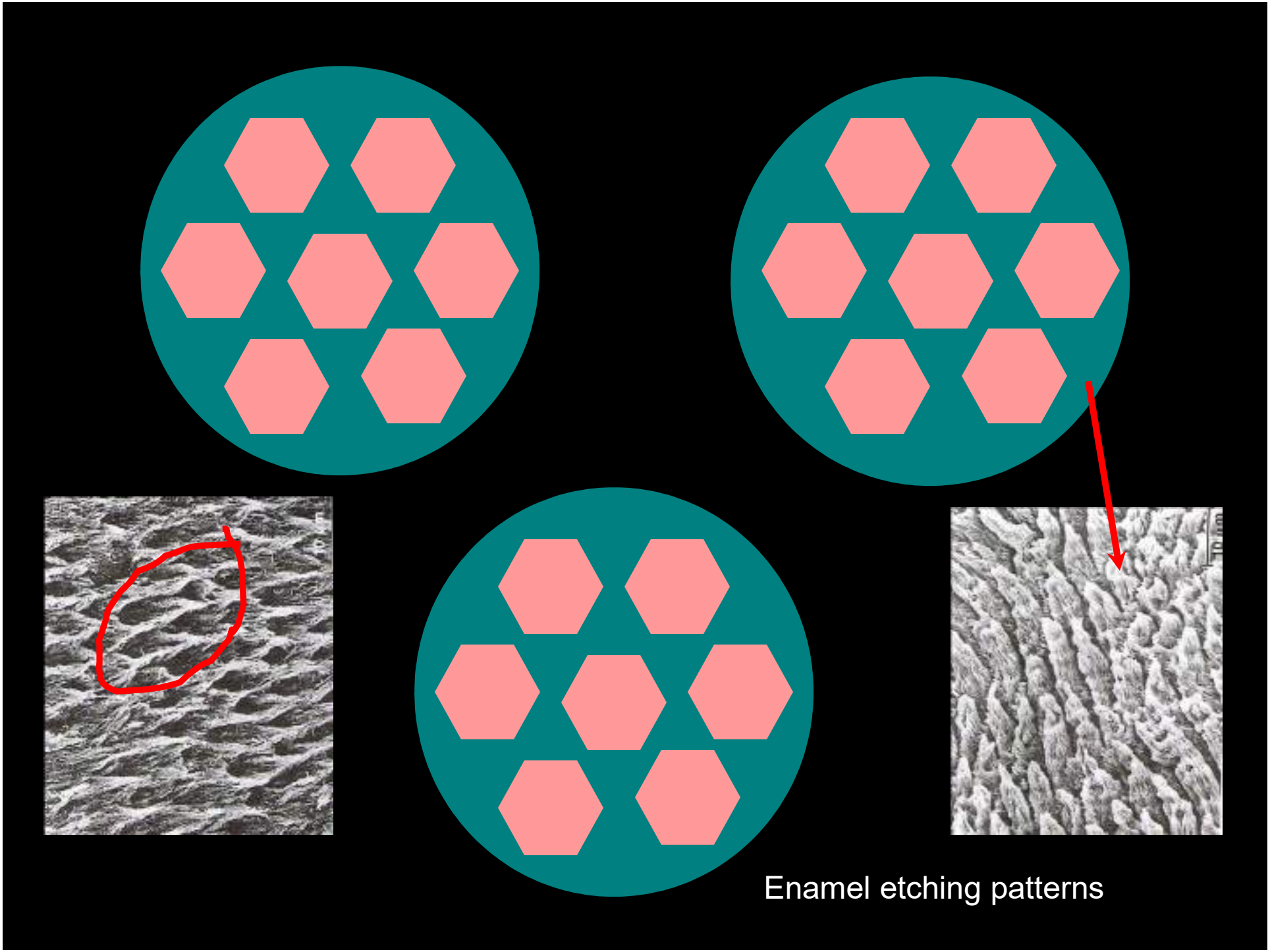
Macrotags:

•Form between the enamel rod peripheries

•2-5 Micrometers

Microtags

•Across the end of each rod where hydroxyapatite crystals have been dissolved


Enamel etching patterns

Phosphoric acid as an etchant:

- **Buonocore :**acid etching with 85% phosphoric acid for 30 sec
- **50 % phosphoric acid for 60 seconds**

monocalcium phosphate monohydrate precipitate

- **Concentrations below 25%**

dicalcium phosphate monohydrate precipitate

- **Concentrations above 40%**

Dissolve less calcium and etch patterns with poorer definitions

- **37% for 15 sec is considered appropriate.**

Benefits of enamel bonding

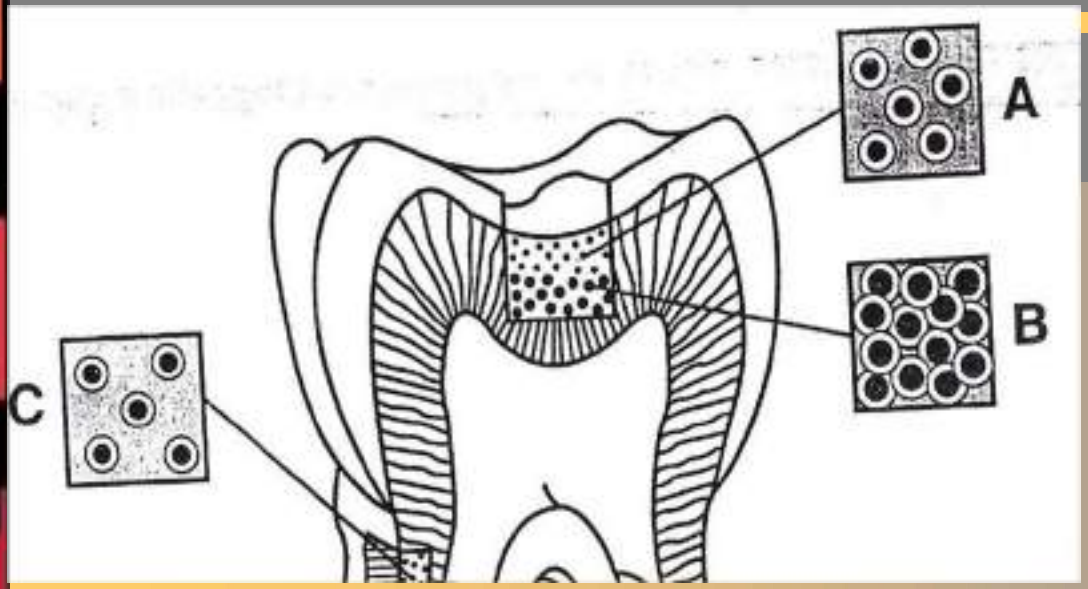
- **Shear bond strengths** in the range of 20 Mpa
- Resisting contraction forces during polymerization
- **Substantial cuspal reinforcement**

Problems to bonding to dentin:

1. Complex histological structure of dentin:

- 45% inorganic.
- Random arrangement of hydroxyapatite crystals
- Tubular nature of dentin that permit fluid flow
- The relative area of dentin occupied by the tubules
  - 45000 per mm2 at the pulp
  - 22-28% at the cross sectional area near the pulp
  - 20000 per mm2 at DEJ in coronal dentin
  - 1-4% near the enamel
- Plasma like fluid in the dentinal tubules is under a slight but constant outward pressure from the pulp

25- 30 mm Hg(30-40 cm H20)



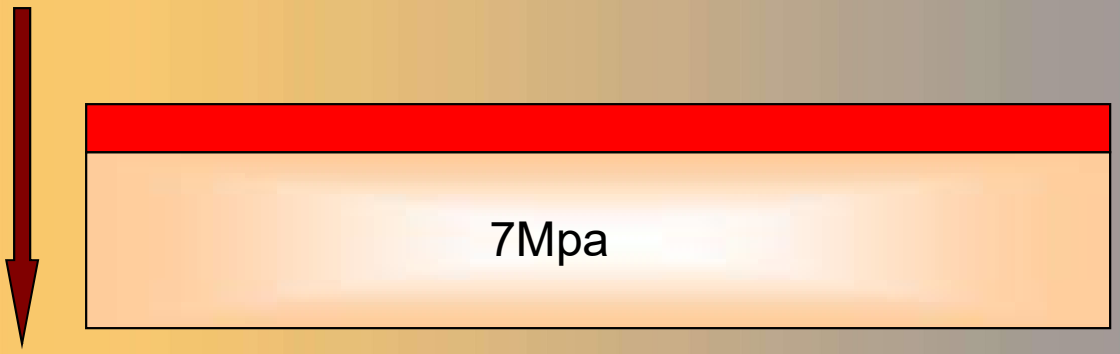
2.Regional variation in the permeability characteristics of dentin:

- Pulp horns >centre of the occlusal surface.
- Proximal dentin >occlusal dentin
- Coronal dentin >root dentin

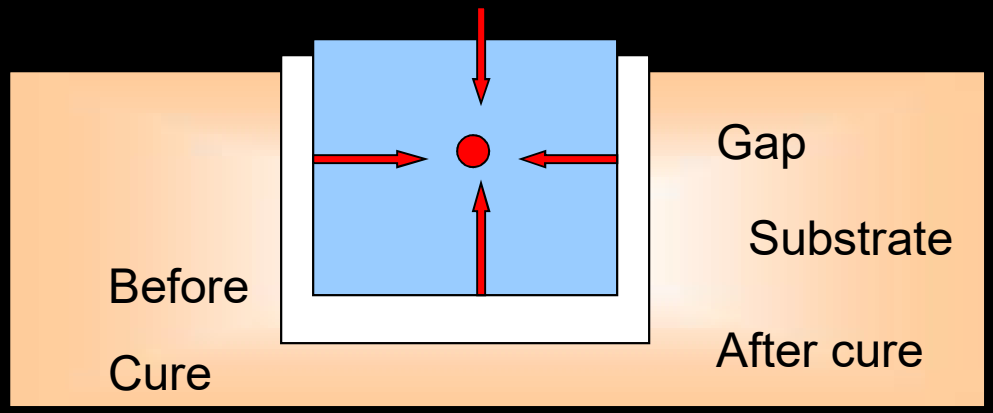
3.Presence of smear layer

4.Alterations in the mineral content and structure of dentin

5. Stresses at the resin dentin interface



Configuration factor



Occlusal class I preparation: C factor of 5.
Proximoocclusal Class II preparation: C factor of 4.
Mesioocclusodistal Class II preparation: C factor of 3.

Classification of dentin bonding agents:

- According to generation.
- According to adhesion strategy(No of clinical applications).
- According to chemical composition. 90
- According to treatment of smear layer. 91
- According to Ph. 89
- According to bond strength 92
- According to mode of curing
- According to type of solvent.

Dentin Bonding Systems

According to generations:

Evolution of bonding agents from

Setco and Reitif 1989.

No etch to total etch

and **self etch.**

I Generation Bonding agents

1970s

- **Buonocore** :GPA-DMA could bond to HCl etched dentin surfaces .(Hydrophilic phosphate group and hydrophobic methacrylate group)
- **Bowen 1965** :N- Phenylglycine glycidyl methacrylate(NPG- GMA)
- water resistant bonds of resin to dentinal calcium.

Agents used in this generation:

- NPG-GMA.
- Glycerophosphoric acid dimethacrylate.(GPA-DMA).
- Cyanoacrylates
- Polyurethanes.

- **Bonding mechanism:**

- Chelation with calcium on the tooth surface to generate water resistant chemical bonds of resin to dentinal calcium.

- **Bond Strength: 2-3 Mpa**

Eg:

- **Cervident(S.S White, Lake wood, NJ)** First commercially available bonding agent.
- Cosmic bond(Amalgamated Dental Company)
- Palakav(Kulzer, USA).

Advantages:

- NPG-GMA acts as a primer and adhesion promoter between enamel/ dentin and resin material by chelation with calcium ions of dentin.

Disadvantages:

- Poor clinical result, when used to restore cervical erosion lesions without mechanical retention.
- Low bond strengths of only 2-3 MPa.
- Carbon 13 NMR analysis, shows that no ionic bonding actually occurs.
- Hydrolysis of GPA-DMA in oral environment.
- Difficulty in bulk polymerization of cyanoacrylates.
- Instability of NPG-GMA in solution.

II generation bonding agents:

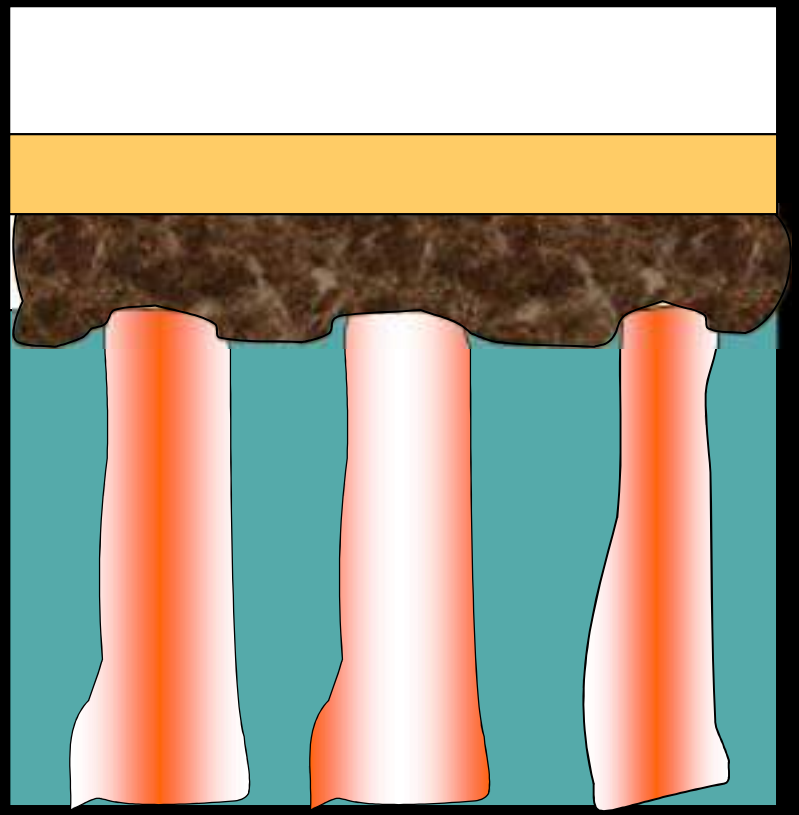
- **1978, the Clearfil Bond System F(Kuraray, Osaka, Japan)**
- Halophosphorous esters of unfilled resins such as BisGMA or HEMA.
- **Systems**
  - Clearfil bond system F.
  - Scotch bond dual cure(3M ESPE).
  - Bondlite (Kerr).
  - Prisma Universal Bond(Johnson and Johnson).
- **Mechanism of action:**
- Surface wetting phenomenon and ionic interaction between negatively charged phosphate groups in the resin and positively charged calcium in the smear layer.
- **Bond strength:** 1- 5 Mpa

Advantages of second generation adhesives:

- The bond strength 3 times more.(Some 30-50% of acid etched enamel)

Disadvantages:

- Low bond strength of 1-10 Mpa
- Hydrolysis of the bonds between phosphonate esters and dentin
- **Poor clinical performance:**
  - Bond achieved limited by cohesive failure in smear layer or break at the smear layer dentin surface.
  - Resins were devoid of hydrophilic groups, large contact angles on intrinsically moist surfaces, did not wet the dentin well.



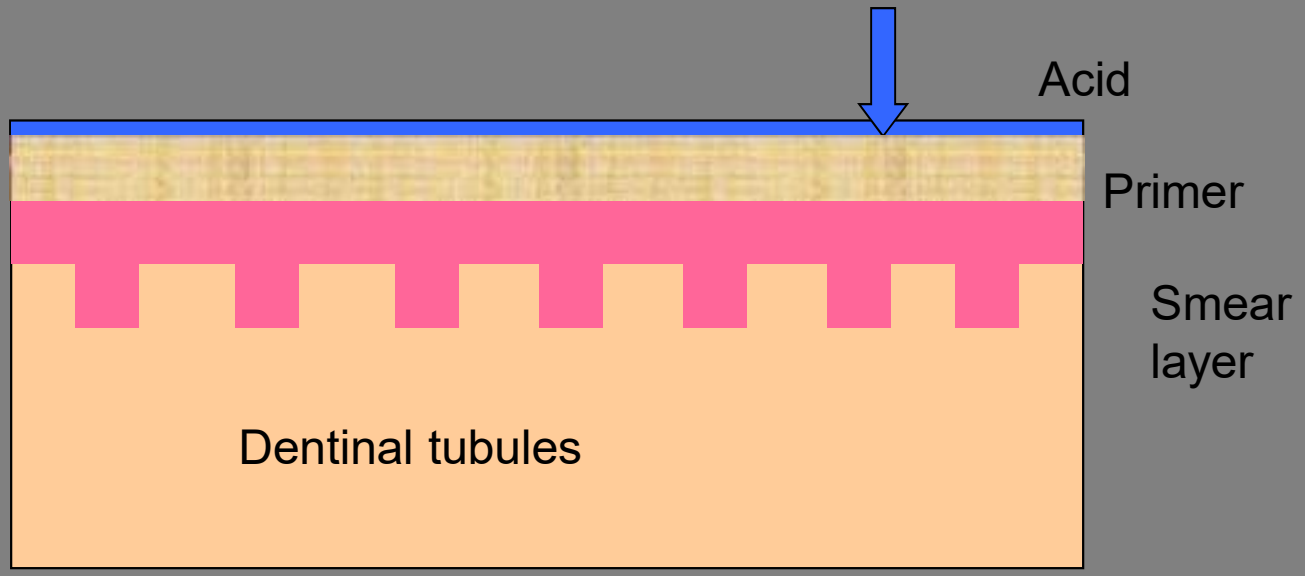
Smear layer not removed in second generation adhesives

Third Generation Dentin Adhesives

mid to late 1980s

Two approaches :

- Modification of smear layer to improve its properties
- Removal of smear layer partially without disturbing the plugs that occluded the dentinal tubules



The phosphate primers modifies the smear layer by softening it; after penetration it cures forming a hard surface.

The dentin primers in third generation adhesives:

- Hydroxyethyl trimellitate anhydride or 4, META

Bisphenyle dimethacrylate or BPDM

- 6% phosphate pentaacrylate, or PENTA
- 30% HEMA
- 64 % ethanol.

Acids used were weak acids such as EDTA or 2.5%Nitric acid)

Bond strength: 9-15 Mpa.

Advantages:

- Bond strengths
- Reduced microleakage relied on mechanical means of bonding as opposed to the less reliable chemical adhesion.
- Better clinical performance.

Disadvantages

- Complex requiring 2-3 applications.

Fusion of concepts of the Europe and Japan.

Dentin Bonding Systems

The agents used were:

- Scotch bond2 (3M Dental)
- Gluma(Bayer/ Miles)
- Tenure(Den- Mat)
- Prisma Universal Bond 3(Caulk/ Dentsply),
- Syntac(Ivoclar Vivadent)
- XR Bond(Kerr)
- Clearfil New Bond(Kuraray)

	System	Conditioner	Primer	Adhesive
1.	Scotch bond 2		**2.5%** maleic acid, 55% HEMA, and a trace of methacrylic acid	Bis GMA(62.5%) HEMA(32.5%) Photoinitiator
2.	Tenure (15 Mpa) Oxalate bonding system	Acidic ferric oxalate which cause staining hence replaced by aluminium oxalate	**5% NTG GMA** PMDM	Bis GMA TEG- DMA
3.	Miragebond (10.9+1.2M)		**NPG(** N phenyl glycine) 2.5% Nitric acid PMDM	
4.	Gluma (15 Mpa)	**17%**EDTA to remove smear layer and free collagen	**35%HEMA** 5% glutaraldehyde	55% Bis GMA TEGDMA.
5.	Prisma universal bond 3		**30%**HEMA 6% PENTA	**50%**UDMA 25%TEGDMA 4.5% PENTA 0.5%GA

Fourth Generation Bonding agents:

Total etch concept :1980s by Bertolotti and Kanca

Hybrid layer Nakabayashi 1982

Impregnation of resin into partially decalcified dentin followed by polymerization created a resin reinforced

Universal Bonding systems

Acid:

7.5 Micrometers Demineralization

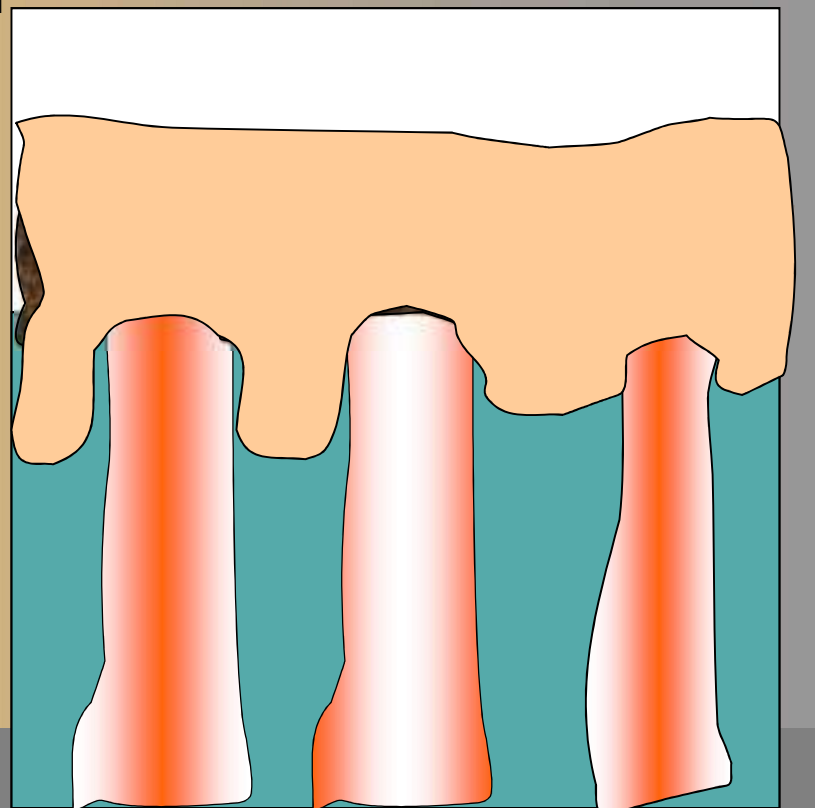
Primer:

Increases the surface energy of the

substrate.(NPG GMA, BPDM)

Unfilled resins

40%BisGMA, 30%UDMA,30%HEMA)



Advantages:

- Bond strength: 18 Mpa.
- No reduction in bond strength when applied to moist surface.
- Can bond to mineralized tissue as well as metal, amalgam, composite and porcelain.

Disadvantages:

- Multiple steps: Technique sensitive.
- Unless the primer and adhesive are applied consecutively, the overlying composite resin will not bond to the surface.

Option of converting the dentin bonding agents from a light curing one to a dual curing oneby incorporation of sulfinic acid derivative(self activating agent).

Agents used in this generation

- All bond 2(Bisco Dental)
- Amalgam- bond(Parkell)
- Clearfil Liner Bond(Kuraray)
- Imperva Bond(Shofu Dental)
- Optibond(Kerr)
- Scotch bond multipurpose(3M Dental)

Name	Bond Strength	Conditoner	Primer	Unfilled resin
All bond 2	21.2+7.8Mpa	37% phosphoric	2%NTG- GMA 16%BPDM	BisGMA 40% 30%UDMA 30%HEMA
Scotch bond multipurpose	21.8 MPa to wet dentin 17.8 Mpa to dry dentin	10% maliec acid 3Mic M depth	Aqueous solution of HEMA Polyalkenoate polymers	Bis GMA containing HEMA
Amalgam Bond		10% Citric acid 19% Ferric Chloride	HEMA with water	4- META MMA-TBB.
Panavia 21 Kuraray	21+_1.5 Mpa	MDP HEMA 5 NMSA		Phosphoric acid ester of MDP

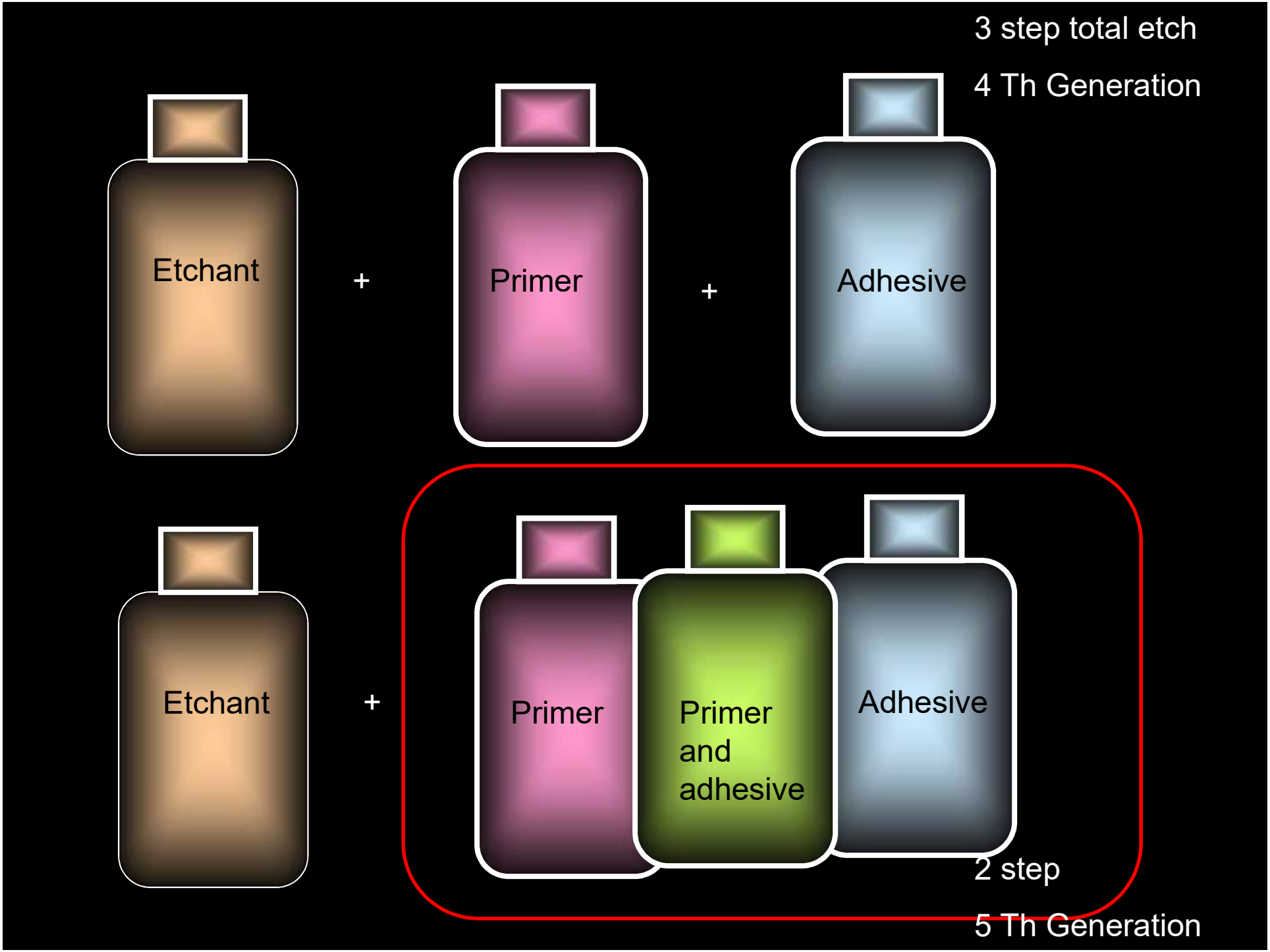
Fourth Generation Adhesives

Scotch bond multipurpose:

The moisture resistance
:formation of bonds between dentinal calcium and the polyalkenoic acid component of the primer.

Panavia 21(Kuraray)

Advantage
Long term Bond strength to metal and silanated porcelain
Disadvantage:
strongly oxygen inhibiting , gel to prevent oxygen from coming in contact with it.


3 step total etch
4 Th Generation
Etchant
+
Primer
+
Adhesive
Etchant
+
Primer
Primer and adhesive
Adhesive
2 step
5 Th Generation

Fifth generation Bonding Agents:

Mechanism of action :
micromechanical retention by

- Penetration into partially opened tubules
- Hybrid layer
- Chemical interactions using first and second order bonding

Moist bonding technique

Moist or wet bonding

Acetone or ethanol solvent displaces water and carries the resins into the collagen.

Rewetting agents

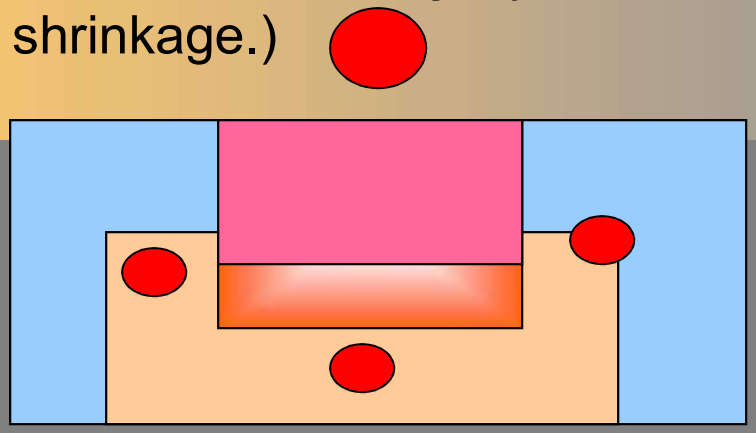
- **Water**
- **Aqueous solutions of HEMA**
  - Aqua Prep(Bisco, Inc) or
  - Gluma Desensitizer(Heraeus Kulzer). glutaraldehyde

Advantages:

- Good bond strength.
- Time saving and relatively simpler to use.
- Some agents have incorporated fluoride and elastomeric components to improve marginal integrity.

Disadvantages:

Post operative sensitivity
(most common in situations that magnify effects of composite polymerization shrinkage.)



C factor of 5

Dentin Bonding Systems

Fifth Generation adhesives

- Prime and Bond
- Prime and Bond 2.1
- Prime and Bond NT(Dentsply Caulk, Milford, Delaware.
- Prime and Bond 2.0(Dentsply De Trey, Konstanz, Germany)
- Single Bond(3M ESPE)
- Optibond Solo
- Optibond Solo plus(Kerr Corporation, Orange California)
- Pq1(Ultradent products, South Jordan)
- Excite(Ivoclar Vivadent.
- Bond 1(Jeneric/Pentron)
- One Coat Bond(Coltene Whaledent)
- Gluma One bond

Dentin Bonding Systems

TABLE 5-3 Composition of Several Fifth-Generation Adhesive Materials

ADHESIVE SYSTEM	ETCHANT	COATS RECOMMENDED	MANUFACTURER	COMPOSITION OF ADHESIVE
Dentastic Uno	38% H_3PO_4 for 15 seconds	2	Pulpdent	PMGDM, proprietary monomers, acetone
EasyBond	10% citric acid / 3% ferric chl for 10 second on dentin an 30 seconds o enamel			4-META, HEMA, dimethacrylate monomer, acetone
Excite	37% H_3PO_4 for 15 seconds			r, HEMA, fumed
Gluma Comfort Bond	20% H_3PO_4 for 20 seconds			crylic glutaral-
One Coat Bond	15 % H_3PO_4 for 30 seconds			ypropyl- ol kenoate phous
One-Step	32% H_3PO_4 with BAC for 15 seconds			, acetone
OptiBond Solo	37.5% H_3PO_4 for 15 seconds			, silica, barium glass, sodium hexa-fluorosilicate, ethanol

Dipentaerythritol pentaacrylate monophosphate

Acetone as solvent

Dentin Bonding Systems

Table 5-3 Composition of Several Fifth-Generation Adhesive Materials—cont'd

	ETCHANT	COATS RECOMMENDED	MANUFACTURER	COMPOSITION OF ADHESIVE
	35% H_3PO_4 for 15 seconds	1	Ultradent Products	TEGDMA, Canadian balsam (tree sap), 15% HEMA, 40% filler with fluoride, ethanol
	34% H_3PO_4 (United States) for 15 seconds 36% H_3PO_4 (Europe) for 15 seconds	1	Dentsply	PENTA, UDMA + T-resin (cross-linking agent) + D-resin (small hydrophilic molecule), butylated hydroxitoluene, 4-ethyl dimethyl aminobenzoate, cetilamine hydrofluoride, acetone, silica nanofiller
	35% H_3PO_4 for 15 seconds	2	3M ESPE	Bis-GMA, HEMA, dimethacrylates, polyalkenoic acid copolymer, initiator, water, ethanol
Tenure Quik with Fluoride	37% H_3PO_4 for 15 seconds	2	Den-Mat Corp.	Dimethacrylate resins, HEMA, PMDM, fluoride, initiator, acetone

Prime and Bond NT

- Is the successor of Prime bond 2.1.
- Contains nanofillers of diameter of 7 micrometers.
- Stabilises the hybrid layer
- Additional crosslinker by penetrating the channels between collagen fibrils to provide **nanoretention**

Second Generation adhesives- 2-4 MPa

Third Generation adhesives- 3-8 MPa

Fourth Generation adhesives-13- 30Mpa

Fifth Generation adhesives- 3-25 Mpa

Sixth Generation Bonding agents:

late 1990s

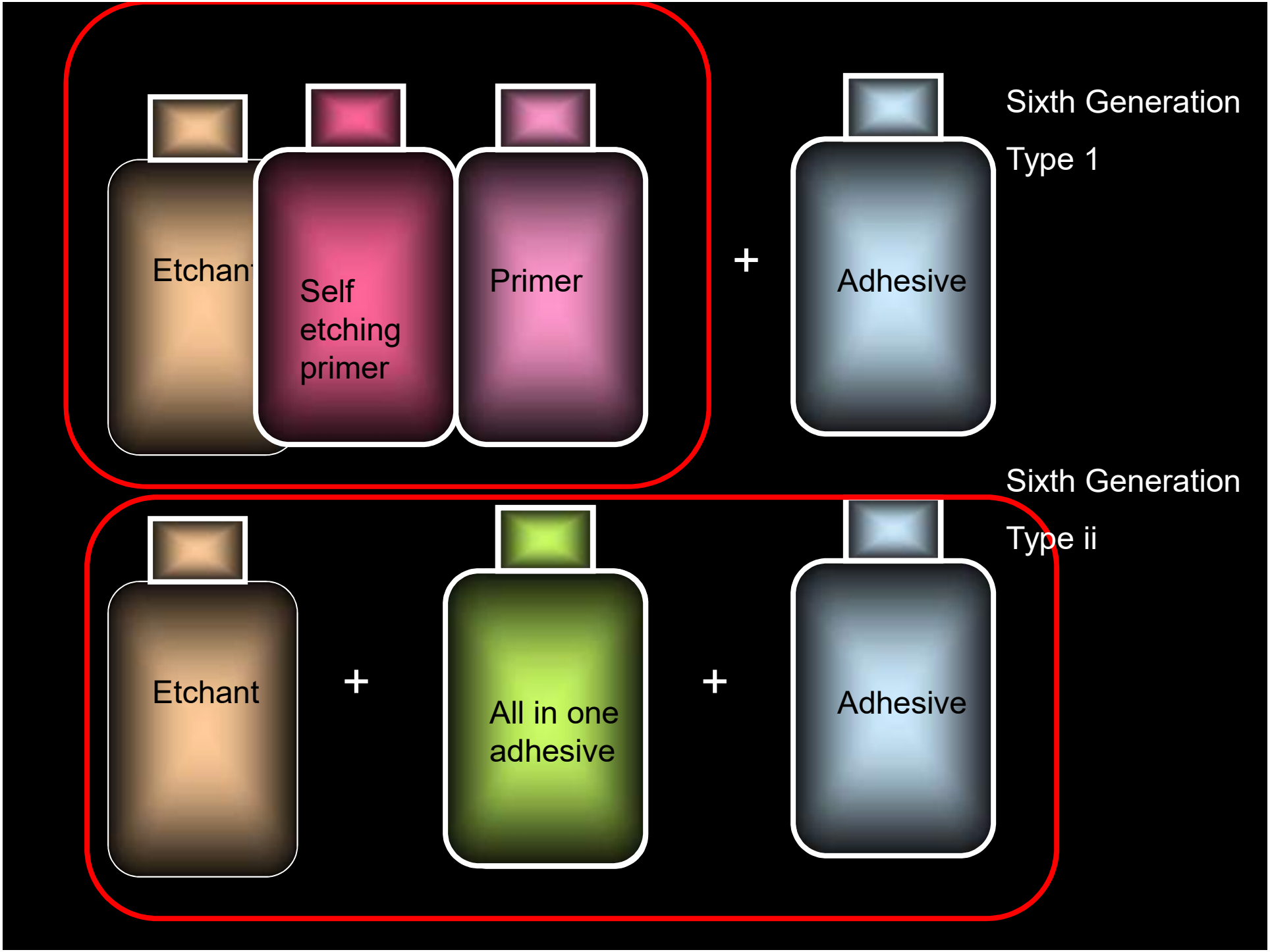
primer and etchant are combined in one step.(**Self etching primers)**

- Type I Two step/ Non rinsing conditioner/ Self etch primer systems
- Type II One step/ Self etching adhesives/ All in one systems

The Dental Advisor: 2003 issue, Vol. 20, No. 8.

Dental update 2004:31:580-89

Journ Esthet Rest Dent 2004;16:57-69.


Etchant
Self etching primer
Primer
+
Adhesive
Sixth Generation
Type 1
Sixth Generation
Type ii
Etchant
+
All in one adhesive
+
Adhesive

Dentin Bonding Systems

Type I Two step/ Non rinsing conditioner/ Self etch primer systems:

- NRC Non Rinse Conditioner(Dentsply De Trey, Konstanz, Germany) followed by Prime and Bond NT(Dentsply)
- Clearfil SE Bond
- Clearfil Liner Bond IIV.
- Tryian(BISCO, Inc, Schaumburg,)
- Simplicity(Apex Dental Materials, Inc, Sandwich, IL)
- UniFil Bond(GC America, Alsip, IL)
- OneCoat Self-Etching Bond(Coltene Whaledent, Cuyahoga Falls)
- AdheSE(Ivoclar Vivadent).

Clearfil SE bond:

- Comes close to the ideal bonding agent.
- Film thickness is slightly high .
- Questions about its ability to stick to some self cured resins.

Simplicity:

- Introduced by Dr. John Kanca.
- Ability to stick to all methacrylate resins light cured, dual cured or self cured.
- Film thickness is sufficiently thin, so can be used to bond posts to endodontically treated teeth and to bond indirect resin inlays.

AdheSE

- Two hydrolytically stable monomers which remain stable in acidic environment.(Phosphonic acid ether acrylate- MA154. and Bis- acrylamide V392).

- The methacrylate based monomers degrade by hydrolysis in a matter of weeks to 20-85% reducing the bond strengths.

- Provide stable consistent long term bond strengths.

- These monomers eliminate the need for refrigeration.

Type II 6 th Generation Bonding agent :One step/ Self etching adhesives/ All in one systems

- Attempt to incorporate all the primary components into a single container.
- Incorporating all components and having it remain stable is a significant challenge.
- In reality, many of these are not all in- one systems at all but require premixing of chemical components (Prompt-L-Popb) or the use of chemically activating pellets or brushes that come with the kit (Touch & Bond, Brush & Bond).

6th Generation Type II.

- Prompt L Pop(3M)
- Touch and Bond (Parkell)
- Brush and Bond(Parkell)
- Xeno III(Dentsply Caulk)
- One up Bond F(J Morita, Kuraray)

Mixing ratio is 4:1

Demineralized dentin is then loaded with prompt L pop monomers which will form hybrid layers.

Prompt L pop:

It has 3 compartments

- Compartment 1: Containing methacrylated phosphoric acid, esters photoinitiators, stabilizers.
- Compartment 2: Contains water, complex fluoride and stabilizers.
- Compartment 3: Has a microbrush.

Brush and Bond

•Chemically impregnated bristles which when come in contact with the liquid triggers a co catalytic action and improves subsequent cure.

•Stops sensitivity.

Features:

- Single step application
- Visual confirmation of polymerization.
- Low film thickness- 10 Microns
- Stable adhesion in moist or dry conditions.
- Fluoride releasing

A

A and B Mixed

Polymerization completed

Liquid A:
2-hydroxyethyl methacrylate (HEMA), Purified Water, EthanolUrethane dimethacrylate resin, Butylated hydroxy toluene (BHT), Highly dispersed silicon Dioxide

Liquid B:
Phosphoric acid modified polymethacrylate resin, Mono fluoro phosphazene
modified methacrylate resin, Urethane dimethacrylate resin, Butylated hydroxy toluene (BHT), Camphorquinone, Ethyl-4-dimethylaminobenzoate

INDICATIONS
Single step self-etching adhesive for direct, light-cured

CONTRAINDICATIONS
1.History of severe allergic reactions to methacrylate resins..
2. for direct or indirect pulp capping.
3. for use with self-cure or with dual cure composites

Advantages of Sixth Generation Bonding agent:

- No need to acid etch with phosphoric acid.
- No post conditioning rinsing required.
- Reduced post operative sensitivity
- Simultaneous demineralization and resin infiltration.
- Less sensitive to degree of wetness and dryness.
- Single dose packaging possible. So less chance of cross infection.
- Possibility for particle filled adhesive.
- Low technique sensitivity

Disadvantages of sixth Generation Bonding Agents:

- Less effective bonding of enamel:
- Instrument enamel in some way.
- Initial bond might deteriorate with aging, which could lead to premature failures.
- Bonding to Sclerotic and caries affected dentin might be problematic
- May inhibit set of self cure or dual cure resin materials.
- Insufficient long term research.

Time Saving?

Several applications may be suggested by the manufacturer.

Beware!

Self etch adhesives may inhibit the set of chemically cured or Dual cured composites

Seventh Generation Bonding systems:

They are truly all in one self etch adhesives that require no mixing.

Eg:

I bond(Heraeus Kulzer).

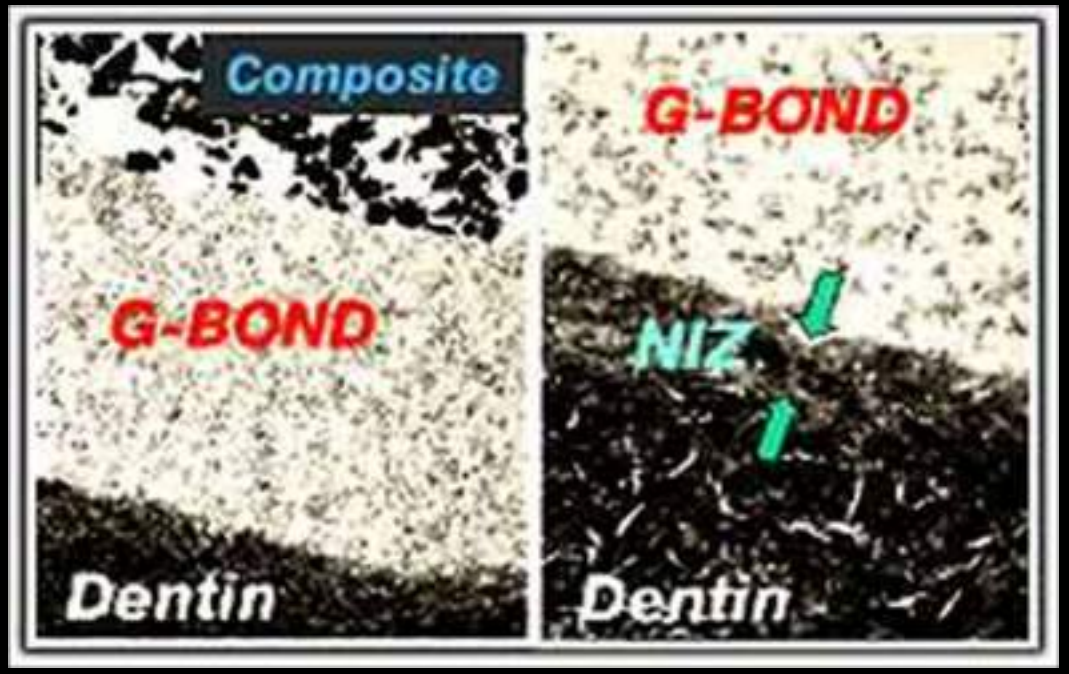
G Bond(GC America).

iBond(Heraeus Kulzer):

Single step no mix bonding system

Five in one solution:

- Etch
- Disinfect
- Desensitize
- Prime and
- Bond



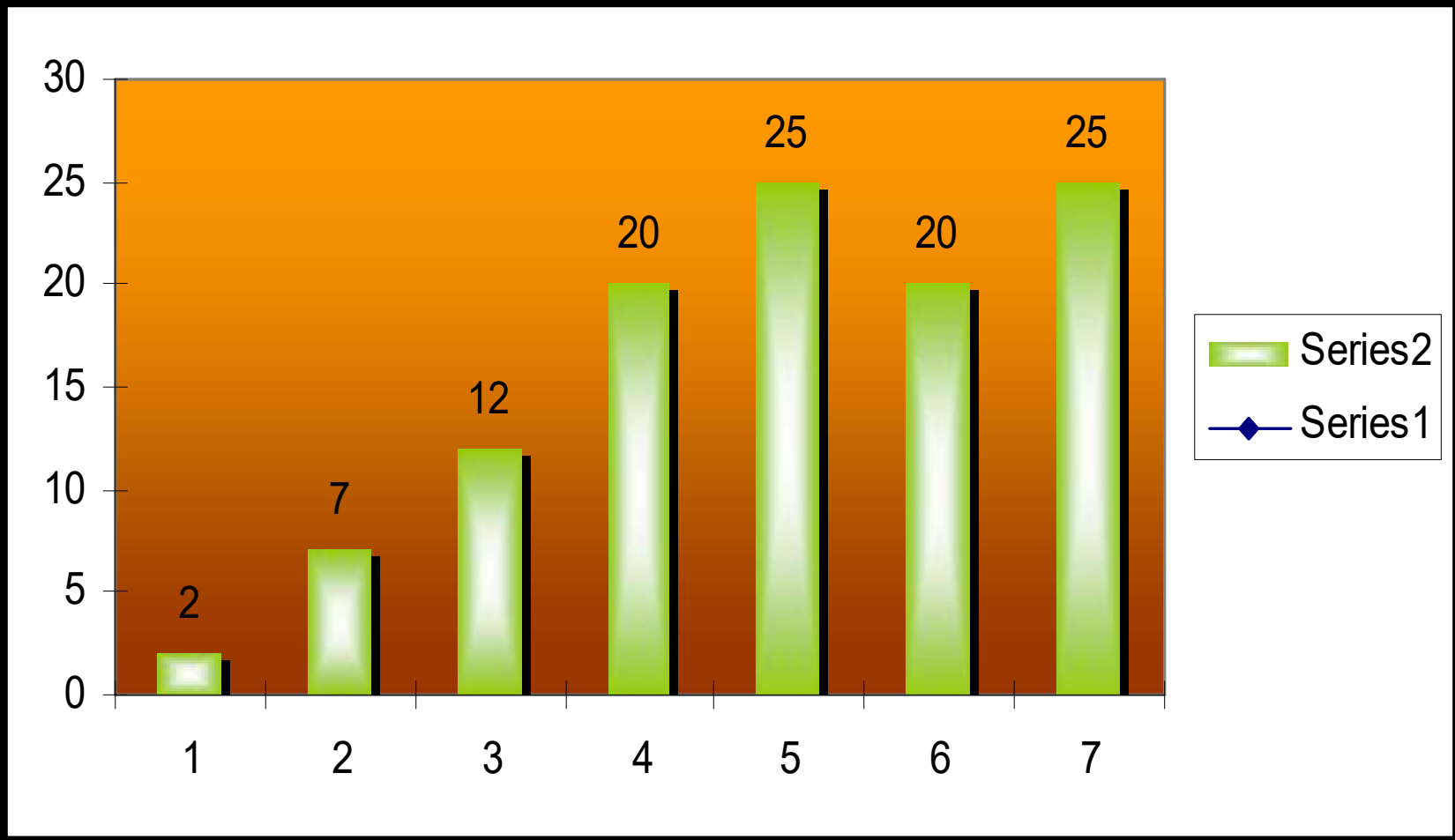
GC s G bond:

4 MET monomer :strong consistent bond to dentin

Phosphoric acid ester monomer : Consistent bond to enamel.

Nanointeraction 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,


30
25
20
15
10
5
0
2
7
12
20
25
20
25
1
2
3
4
5
6
7
Series2
Series1

Classification based on the number of clinical application steps and how they interact with tooth structure

Van Meerbeek and others 1998, 2000.

Classification based on adhesion strategies

- **Total etch adhesives:**
- 3 step
- 2 step
- **Self etch adhesives:**
- 2 step
- 1 step.
- **Resin modified glass ionomer adhesives**

Total etch concept.

Total etching is the simultaneous etching of enamel and dentin.

Advocated by Fusayama in Japan.

3 step Total etch:

- Conditioning
  - Priming
  - Application of adhesive resin

  Fourth generation of dentin bonding agent

- All bond 2(Bisco Dental)
- Amalgam- bond(Parkell)
- Clearfil Liner Bond(Kuraray)
- Imperva Bond(Shofu Dental)
- Optibond(Kerr)
- Scotch bond multipurpose(3M Dental)

2 Step total etch

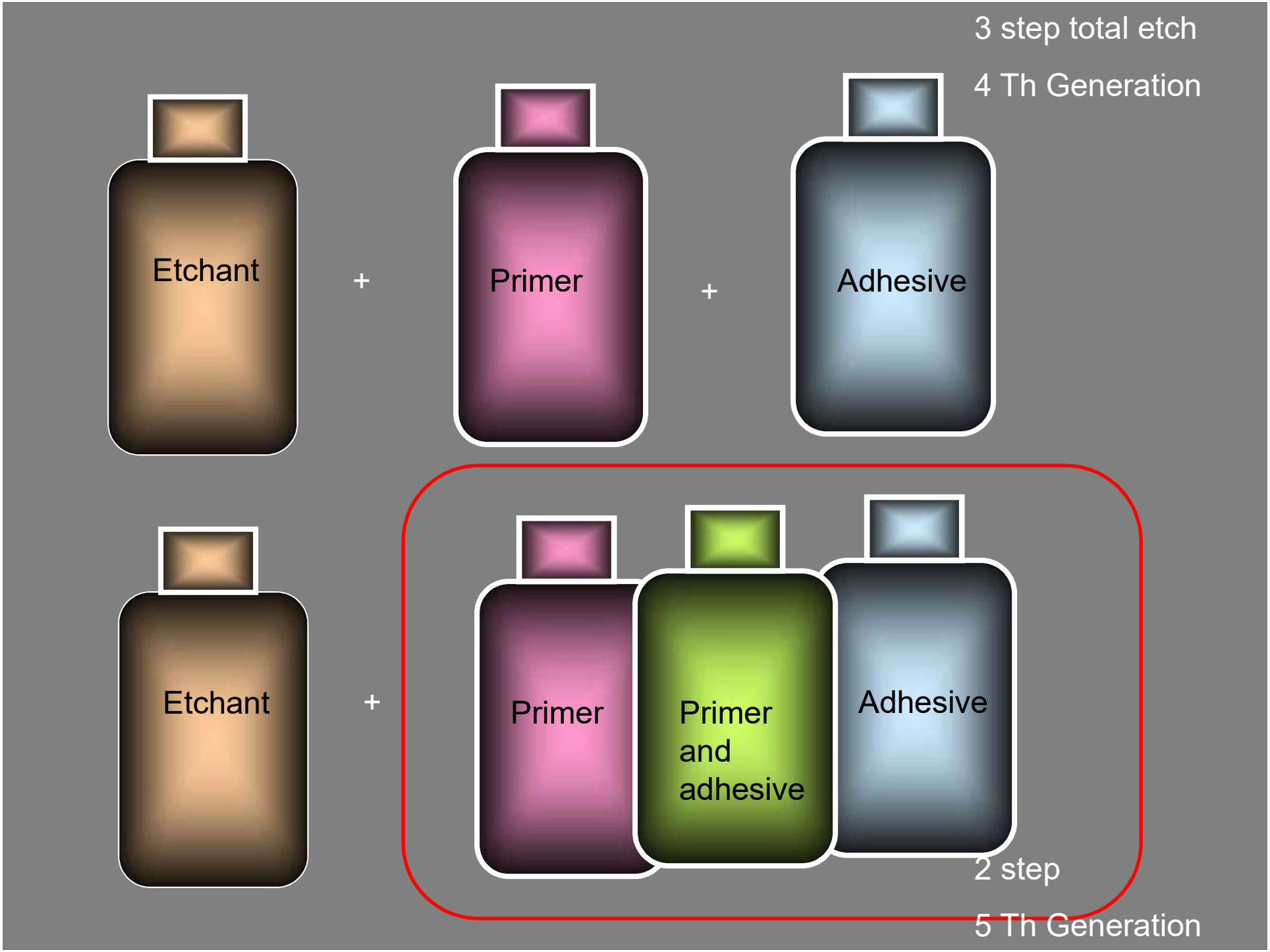
- Conditioning
- Primer and adhesive

Fifth generation of dentin bonding agent.
Eg:

- Gluma comfort bond(Kulzer)
- Prime and bond NT
- Prime and bond 2.1

Ph of the adhesive formulations:2.5-4.5

Separate acid etching step


3 step total etch
4 Th Generation
Etchant
+
Primer
+
Adhesive
Etchant
+
Primer
Primer and adhesive
Adhesive
2 step
5 Th Generation

Wet bonding/ Moist bonding:

- Dr. John Kanca and Gwinnet in 1992.

The reason for collapse of collagen network:

- Acid etched dentin shrinks 65% vol.
- Stiffness of mineralized dentin is about 19,000MPa
- Stiffness of acid etched dentin matrix is about 1Mpa.
- The resulting layer of imperfect bonding is known as **Hybridoid region.**

- Residual water is left in the acid etched dentin, then bond strength could be doubled. **Kanca**

- The primer solvent should be water or water miscible.
- The primer monomer should be amphiphilic or hydrophilic because they must compete with water and , in fact , diffuse through water in the depths of demineralized zone.

Azeotrophism:

- In acetone containg primers
- the boiling point of acetone is raised
- the boiling point of water is lowered(**azeotrophism),**
- evaporation of both water and acetone and the resin is left behind.

Dry Bonding:

refers to the bonding in which the acid etched dentin is dry and uses the adhesive systems that provide water based primers. These rehydrate and reexpand the collagen fibers , allowing the resin to infiltrate.

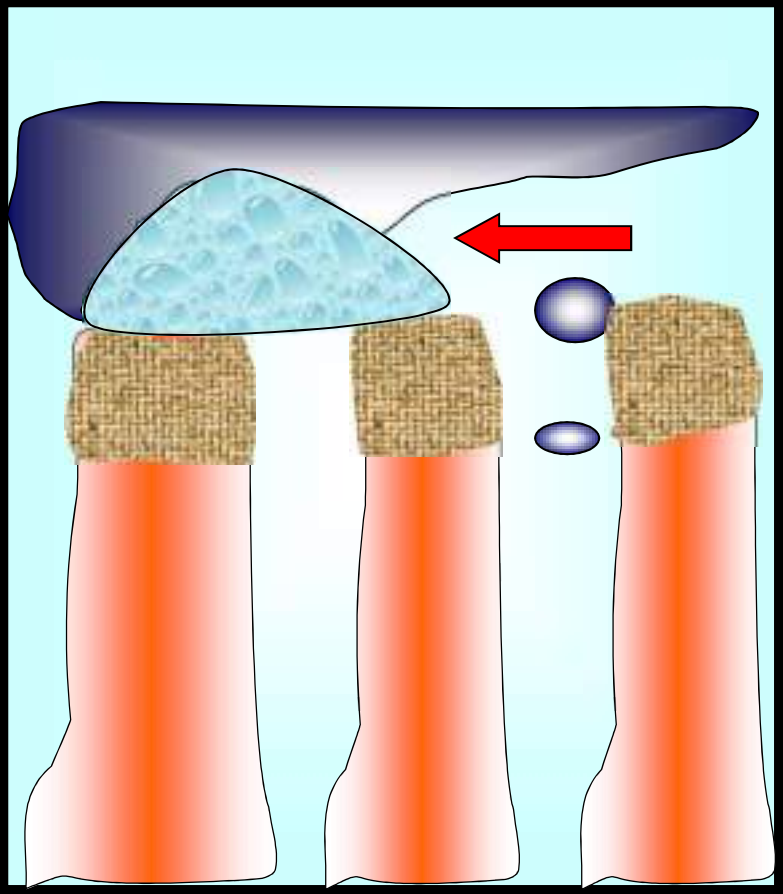
Advantages of total etch system:

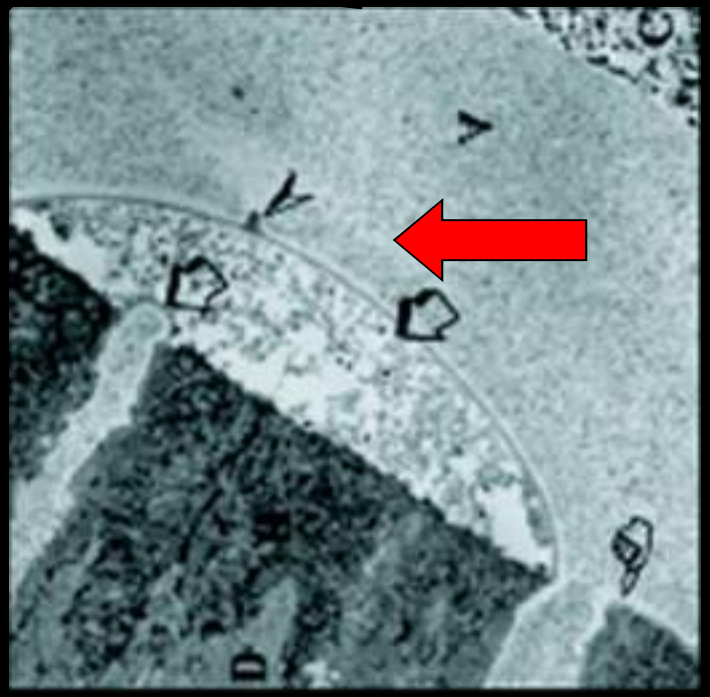
- Bonding to enamel is good.
- There is possibility of particle filled adhesives.
- Most efficient and consistent results.

Disadvantages:

- Risk of overwetting and over drying
- Overetching phenomenon leading to nanoleakage.
- Weak monomer collagen interaction.
- High degree of post operative sensitivity
- Technique sensitivity, Requires post conditioning rinse.

Over wetting phenomenon





Post operative sensitivity because of lack of resin tag formation.

- Acetone based products show a restricted **window of opportunity** as compared to water based primers.

- The biggest advantage of next two systems is that their efficacy does not depend on the hydration of dentin.

- **How wet or how dry?**

Hence total etch products were known to be **technique sensitive.**

Overetching phenomenon: A condition where in demineralization is too deep for monomers to penetrate.

Nanoleakage:
Incomplete primer penetration into the zone of demineralization is the significant cause of nanoleakage which could ultimately lead to failure of the adhesive interface

Self etch adhesives:

Based on the use of non rinse acidic monomers that simultaneously condition and prime dentin and enamel.

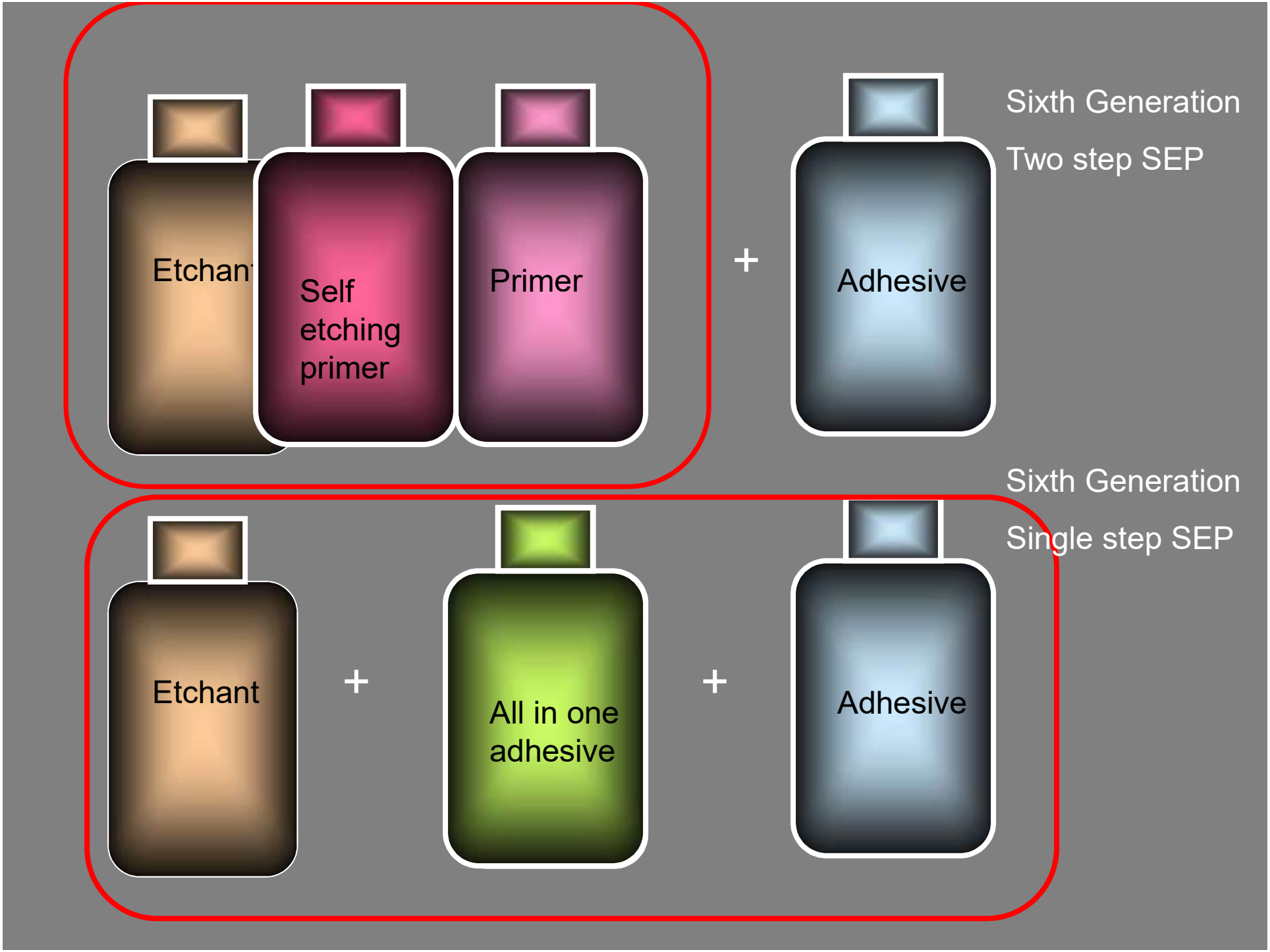
- Concentration of acidic monomers from 5-10% wt to 30-40% wt
- Acidic monomers were dissolved in 30-40% HEMA,
- Formulation that was both self etching and self priming
- pH low enough to etch through the smear layers to underlying dentin.

- If the solution not well agitated: Smear layer incorporated into the hybrid layer.
- If the solution is scrubbed onto the surface, the smear layer is removed.
- Most importantly self etched and self primed surface is not rinsed water

Technique:

- The surface is scrubbed for 20 sec and then gently air dried .
- The dried surface is then covered with a relatively hydrophobic adhesive layer and then light cured.

- Self etching primers can be used in deep cavities as liners and bases when an intermediary resin composite such as Clearfil Protect liner F is used.


Etchant
Self etching primer
Primer
+
Adhesive
Sixth Generation
Two step SEP
Etchant
+
All in one adhesive
+
Adhesive
Sixth Generation
Single step SEP

Two step SEPs:

The first marketed modern self etching primer was Scotch prep(**Scotch bond 2)**

Primer:2.5% maliec acid and 55% HEMA in water.

relatively short shelf life and the acidity of maliec acid accelerated the breakdown of HEMA.

- **Clearfil liner bond 2:**

The first contemporary self etching light cured product(1992)

Its acidic monomer copolymerized with other methacrylate comonomers.

- **Clearfil liner bond 2V:** Dual curing self etching primer.
- **Clearfil SE bond.(** Kuraray)
- **AdheSE(**Ivoclar Vivadent)
- **FL bond(Shofu)**
- **Optibond solo plus self etch adhesive system(Kerr)**
- **Nanobond(** Pentron technologies
- **GC unifil bond(GC** America).

One step SEPs:

One step SEPs are " All in one systems" which attempt to incorporate all the primary components of adhesive system into a single container

.

Eg:

- Prompt L pop(3M ESPE)
- Touch and bond(Parkell)
- Brush and Bond(Parkell)
- One up Bond F(J Moritas)
- Xeno iii(Dentsply , Caulk

Advantages of single step SEPs

Fast and easy to use.

Disadvantages:

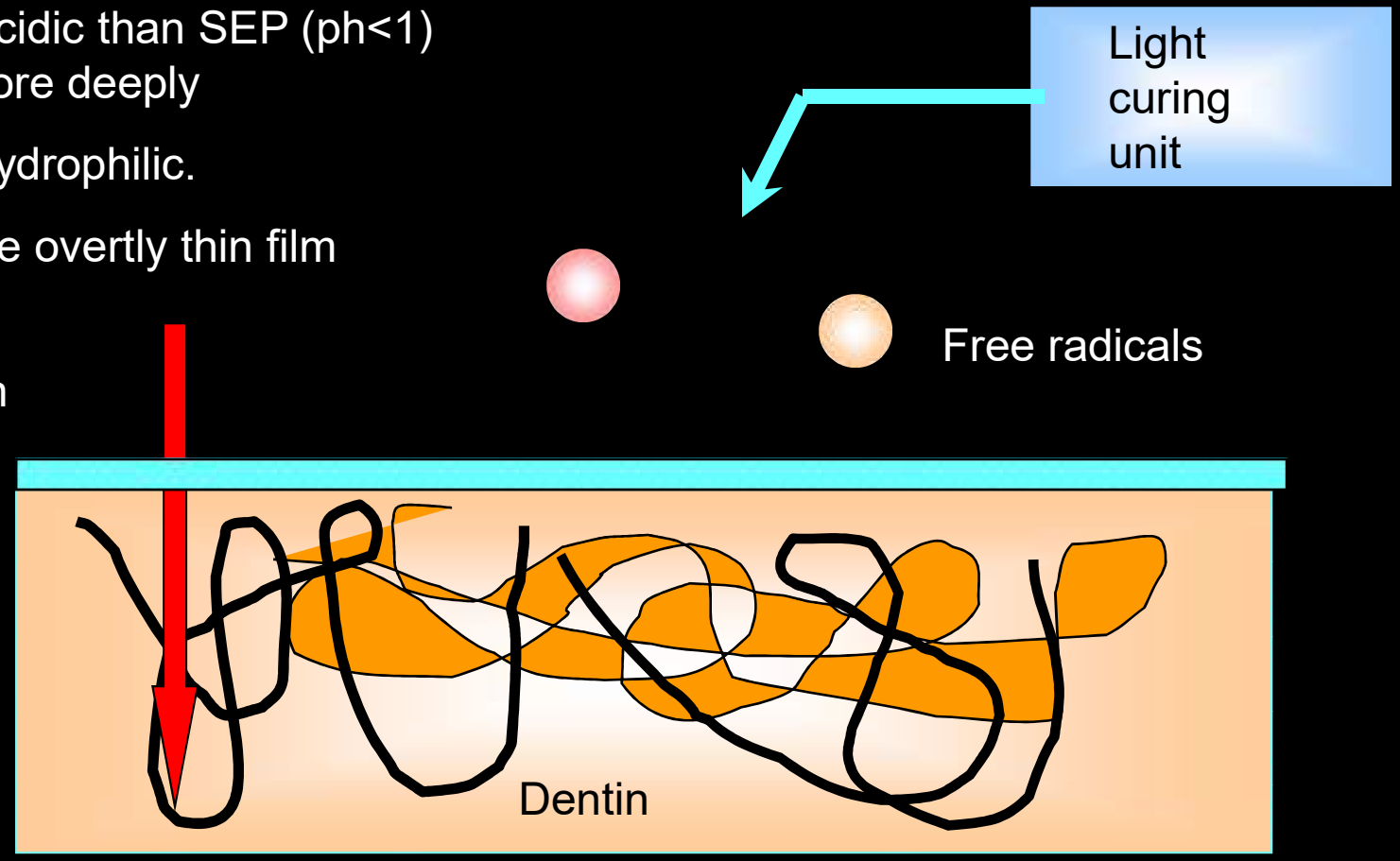
- Marginal staining and debonding may occur in some of the systems.May not bond durably to enamel.
- May not be compatible with self cure and dual cure composites.
- Lack of polymerization.
- Water trees phenomenon.

Lack of polymerization

More acidic than SEP (ph<1)
etch more deeply

More hydrophilic.

Produce overtly thin film



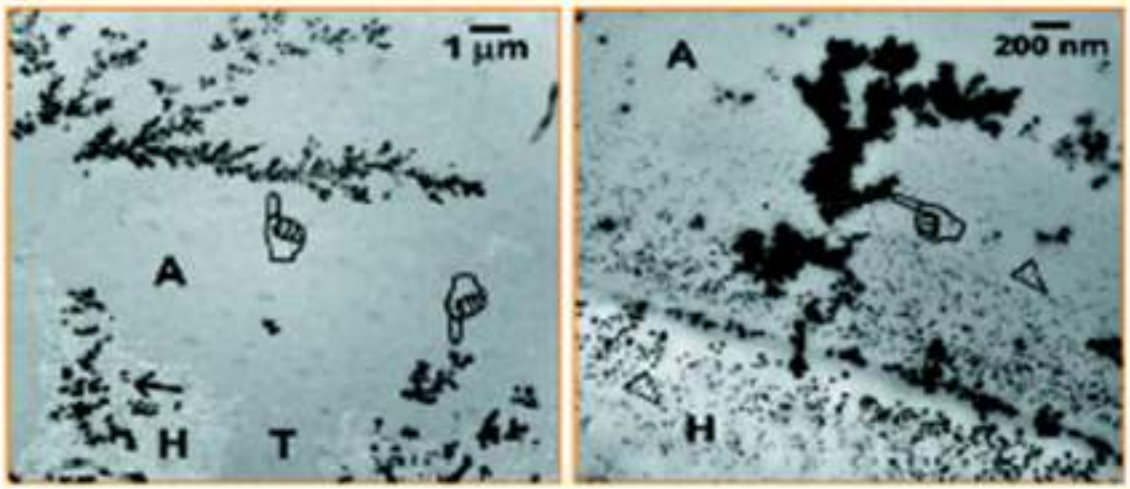


Figure 8 Transmission electron micrographs of dentin bonded with an all-in-one adhesive, then placed in 37°C water for 24 hrs prior to soaking in silver nitrate to demonstrate the presence of water-filled (now silver-filled) channels called "water trees" (finger-pointers) extending from the hybrid layer (H) and passing through the cured adhesive layer. The black silver deposits indicate where there were water-filled channels. Such water trees do not form in self-etching primer adhesives23. Courtesy of Dr. Franklin Tay, University of Hong Kong, with permission.

Water trees phenomenon

- Acidic
- Hydrophilic
- Leaching of unpolymerized monomers

This phenomenon does not occur in self etching primers because the etched and primed dentin is covered by a comparatively thick hydrophobic resin layer

In such a case a resin modified glass ionomer is used before placing composite restorations.

Rating Self-etching Bonding Agents

Product	Company	Type of Cure	Unit Dose	Filler, Wt. %	Fluoride Release	Refrigeration Required or Recommended	Number of Steps	Total time, seconds	Bond Strength, Enamel, MPa†	Bond Strength, Dentin, MPa†	Cost, $/ml*	Rating
6th-generation - Type I *(Self-etching Primer and Adhesive)*												
ADHESE	IVOCLAR VIVADENT	LC	No	2	No	No	6	61	16	21	21.00	94%
CLEARFIL LINER BOND 2V	KURARAY AMERICA	DC	No	10	No	Yes	6	66	26	35	32.00	87%
CLEARFIL SE BOND	KURARAY AMERICA	LC	No	10	No	Yes	5	46	29	28	21.80	96%
CONTAX	ZENITH/DMG	DC, LC	No	0	Yes	No	3	60	20	20	33.30	ce
FL-BOND	SHOFU	LC	No	17	Yes	No	5	33	21	27	30.00	91%
GC UNIFIL BOND	GC AMERICA	LC	No	0	Yes	Yes	4	38	20	30	19.83	88%
NANO-BOND	PENTRON CLINICAL TECHNOLOGIES	DC, LC	No	—	No	Yes	5	63	14	20	14.99	84%
ONE-STEP PLUS WITH TYRIAN SPE	BISCO	LC	No	8.5	No	No	6	50	na	na	15.83	na
OPTIBOND SOLO PLUS SELF-ETCH ADHESIVE SYSTEM	SDS/KERR	DC, LC	Yes	16	Yes	No	7	76	28	25	41.60	ce
6th-generation - Type II *(Self-etching Adhesive)*												
3M ESPE ADPER PROMPT L-POP SELF-ETCH ADHESIVE	3M ESPE	LC	Yes	0	No	No	4	38	22#	12#	15.99	89%
BRUSH&BOND	PARKELL	LC	No	0	No	No	3	33	10	15	33.00	89%
ONE-UP BOND F	TOKUYAMA DENTAL CORP./J. MORITA USA	LC	No	10	Yes	Yes	3	35	22	21	10.90	91%
TENURE UNI-BOND WITH GLOSS-N-SEAL	DEN-MAT	LC	No	0	No	No	5	38	na	na	13.25	ce
TOUCH&BOND	PARKELL	LC	No	0	No	Yes	4	38	12	2	18.00	na
XENO III	DENTSPLY/CAULK	LC	No	4.8	Yes	No	4	38	31	29	20.00	96%
7th-generation *(No Mix Self-etching Adhesive)*												
iBOND	HERAEUS KULZER	LC	Yes	0	No	Yes	3	60	19	12	25.00	90%

na=not available, ce=currently being evaluated

*Costs are listed for comparison only and are not used to calculate the ratings. All costs are listed in U.S. dollars.

†24-hour tensile bond strengths

#Bond strengths are based on a 1-coat technique; instructions for use now indicate a 2-coat technique.

THE DENTAL ADVISOR Recommends:

6th-generation, Type I – ***Clearfil SE Bond, AdheSE, FL-BOND***

6th-generation, Type II – ***Xeno III, One-Up Bond F***

7th-generation – ***iBOND***

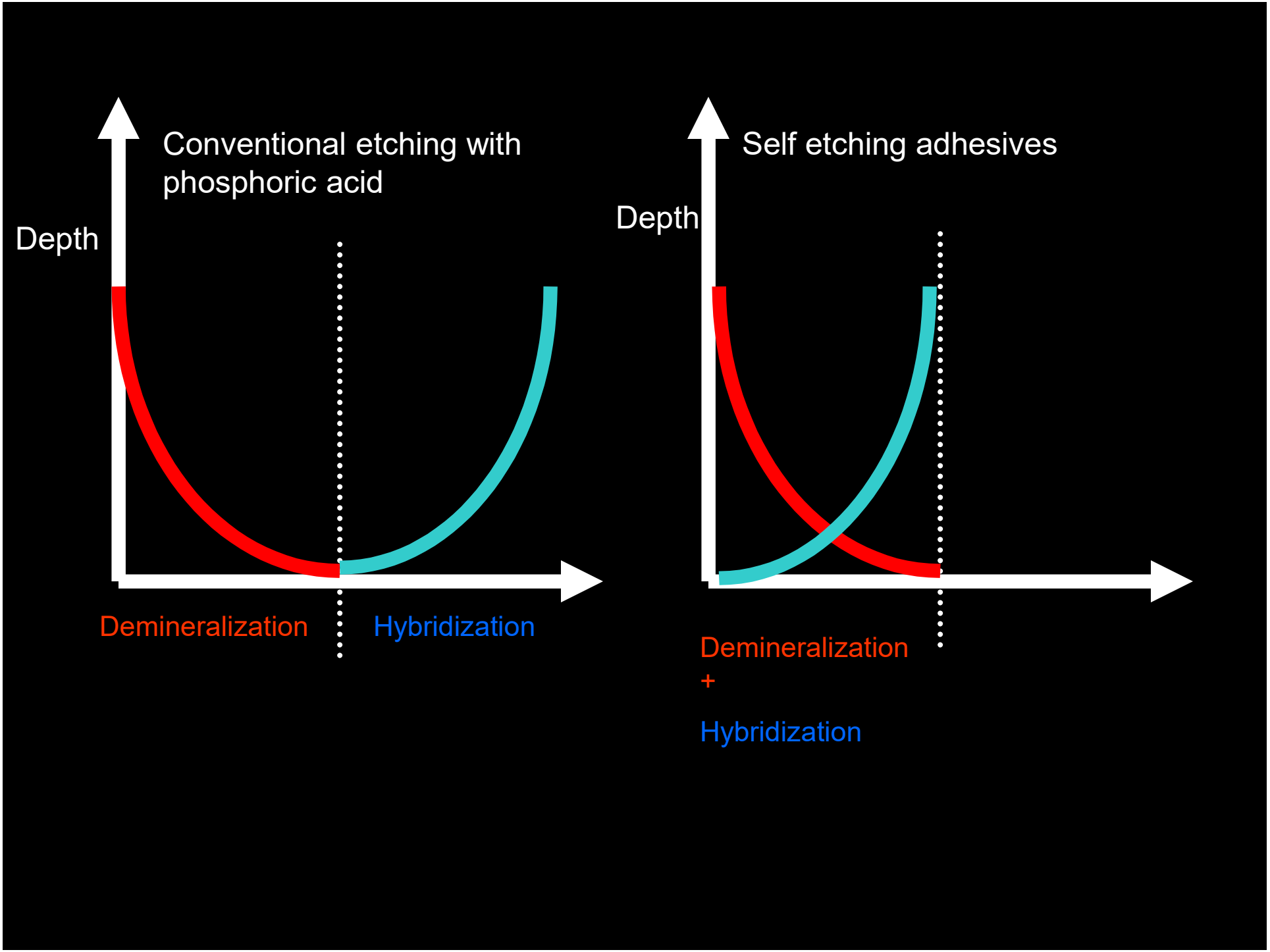
Advantages of self etching:

- Their efficacy does not depend on the hydration of dentin. The self etching primers are designed to be used on dry dentin.

- They do not etch very far into the dentin beneath the smear layers. This avoids the removal of smear plugs in the dentinal tubules and
seems to be responsible for lack of post operative sensitivity

- The shallow etch ensures good resin infilteration.

- Even though the hybrid layer is thin, the dentin bond strengths is comparatively high.


Conventional etching with phosphoric acid
Depth
Demineralization
Hybridization
Self etching adhesives
Depth
Demineralization
+
Hybridization

Disadvantages of Self etch adhesives:

- Less effective bonding of enamel:
- Instrument enamel in some way.
- Initial bond might deteriorate with aging, which could lead to premature failures.
- Bonding to Sclerotic and caries affected dentin might be problematic
- May inhibit set of self cure or dual cure resin materials.
- Insufficient long term research.

Depending on the ph (after Van Meerbeck et al 2003)

- **Mild SEA(Ph2)**
- **Intermediary strong(Ph of 1.5)**
- **Strong SEA(Ph1)**

pH appears to affect properties and behaviour of the material.

Mild SEAs:
Hybridization and intermolecular bonding.

Hybridisation: Hybrid layer is of submicron size and resin tag formation is less

Intermolecular bonding: Hydroxyapatite acts as a receptor for additional molecular interactions with specific carboxyl or phosphate groups of monomers like 4 META and 10 MDP

Intermediary adhesives(1.5)

Are more acidic than " mild" adhesives, so achieve greater micromechanical interlocking at the enamel surface, although the hybrid layer produced at the dentin surface is thin, at around 1 micron.

Strong SEA(1 or less):

The mechanism of bonding is similar to total etch, with the formation of hybrid layer and no chemical reaction may take place, since the hydroxyapatite is entirely removed.

Adhesives	pH
Strong (1 or less) NRC(Dentsply) Adperprompt	1 0.4
Intermediary(1.5) Xeno III(Dentsply) AdheSE primer(Vivadent) Optibond Solo Plus SE primer(Kerr) I Bond	1.4 1.4 1.5 1.6
Mild(around 2) Clearfil SE Panavia ED primer mixed(Kuraray)	1.9 2.6

According to chemical composition(Craig)

- Polyurethanes(1-6 Mpa)
- Polyacrylic acids(2-4 Mpa)
- Organic phosphonates
- 4 META (3-7 Mpa)
- HEMA+GA(11-17 MPa)
- Ferric oxalate+ NPG GM(4-12.5 Mpa)

PMDM+2HEMA..

On the basis of treatment of smear layer:

Smear layer	Eg
Smear layer removed	Tenure Mirage Bond Clearfil liner bond
Smear layer modified	Scotch bond 2 All bond
Smear layer preserved	Scotch bond dual cure Prisma universal bond

On the basis of shear bond strength(Eick et al)

- **5-7 Mpa:**

Scotch bond dual cure
Gluma

- **8-14 Mpa**

Tenure
Mirage bond

- **17-20 Mpa**

Scotch bond 2
Scotch bond multipurpose
All bond

Dentin Bonding Systems

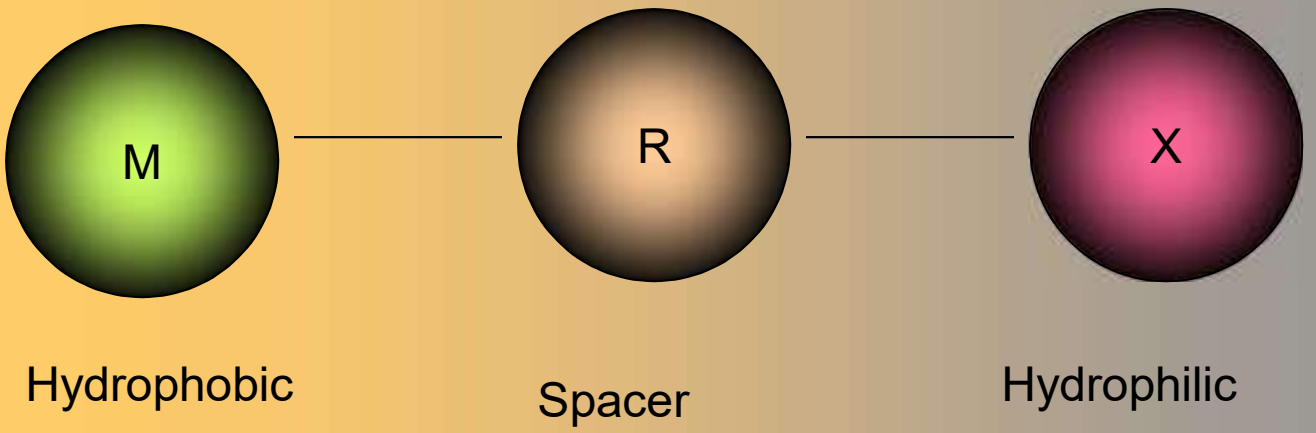
According to their mode of curing:

- **Chemical cure:**
Amalgabond plus

- **Light cure:**
One bond
Gluma comfort bond

- **Dual cure:**
Clearfil liner bond 2V
Prime and Bond NT dual cure.

Mechanism of dentin bonding:



- Dentin smear layer produced removed by etch and rinse phase.
- 3-5 micrometer deep demineralization of dentin.
- Collagen mesh work uncovered from hydroxyapatite to form a microretentive network for monomers.

Nakabayashi, Kojima and Manihara 1982

Hybrid layer, Resin reinforced zone, or resin infiltrated layer

Hybrid layer is **the hydrophilic resin infiltrated surface layer of collagen fibers in demineralized dentin.**

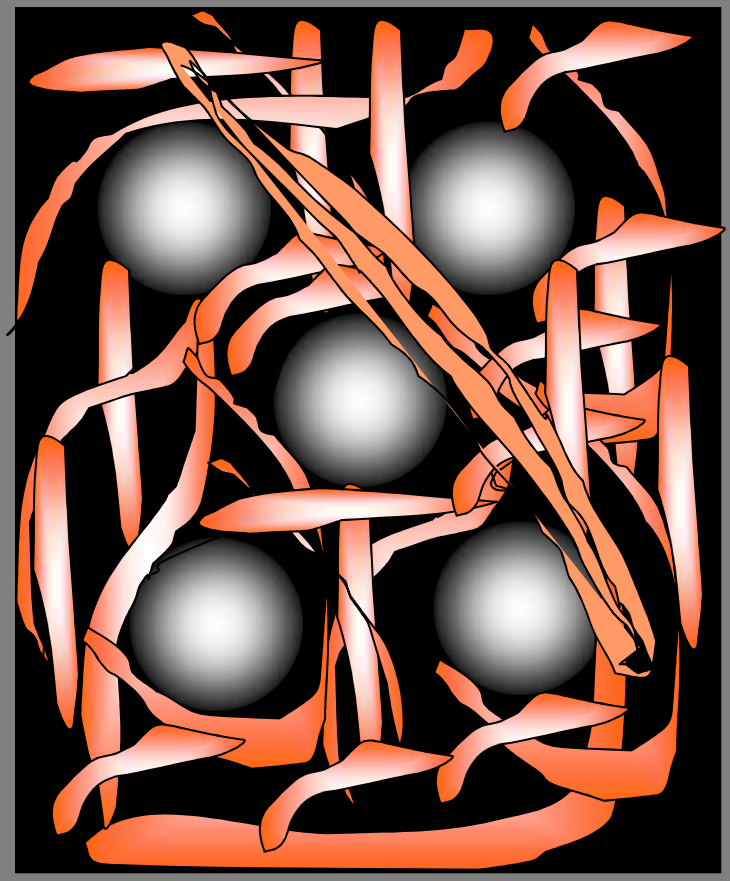
Concurrent with hybridization, the resin tags seal the unplugged dentinal tubules and offer additional retention through hybridization of tubule orifices.

Shag carpet appearance

Appears when dentin surface after being acid etched is actively scrubbed with an acidic primer solution.

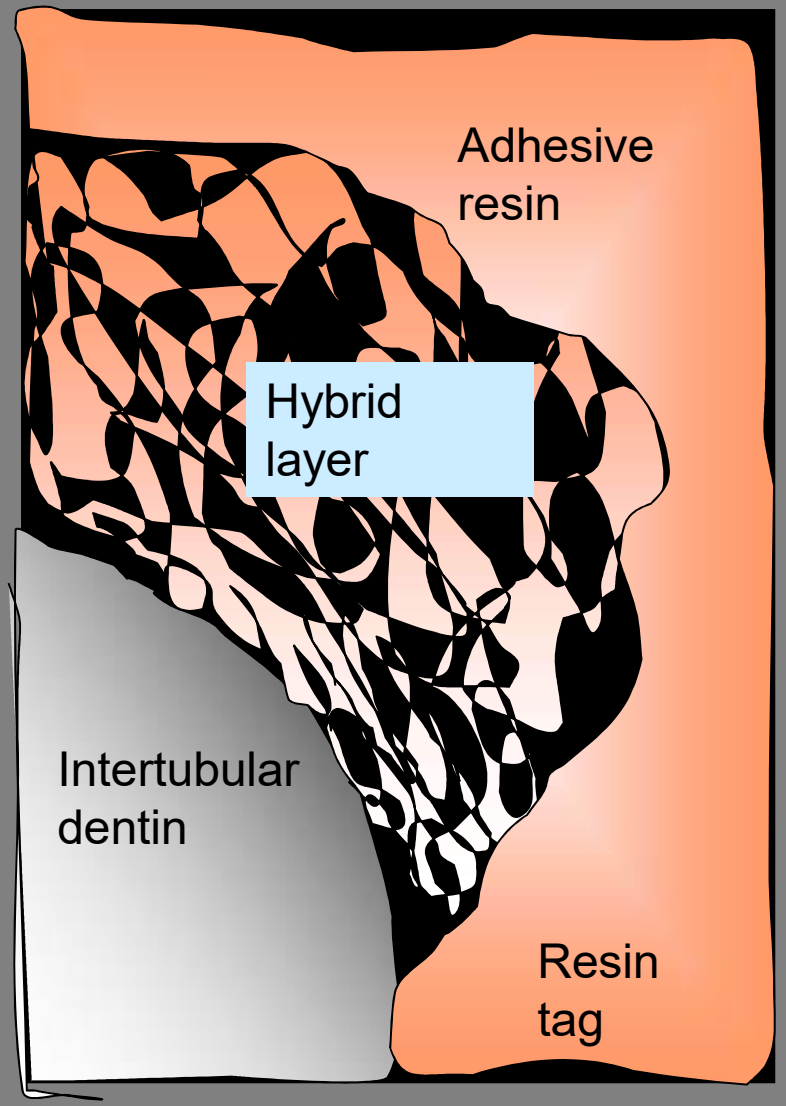
Mechanism of action:

The combined mechanical and chemical action of rubbing the acid etched dentin with an acidic primer dissolves additional mineral salts while fluffing and separating the entangled collagen at the surface.



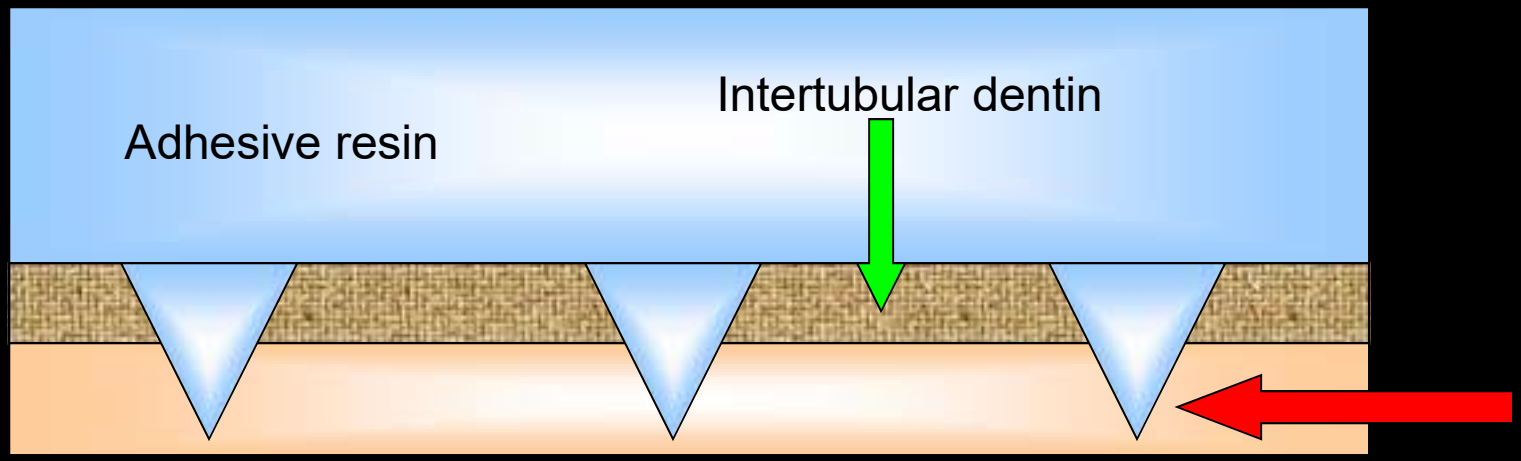
Tubule wall hybridization:

- Extension of the hybrid layer into tubule wall area.
- Hermetically sealing the pulpodentinal complex against microleakage
- Especially protective when bond fails at top or bottom of the hybrid layer
- The resin tags keep tubules sealed as they break off at the level of hybrid layer. This is attributed to tubule wall hybridization which ensures a leakage free seal of tubules.

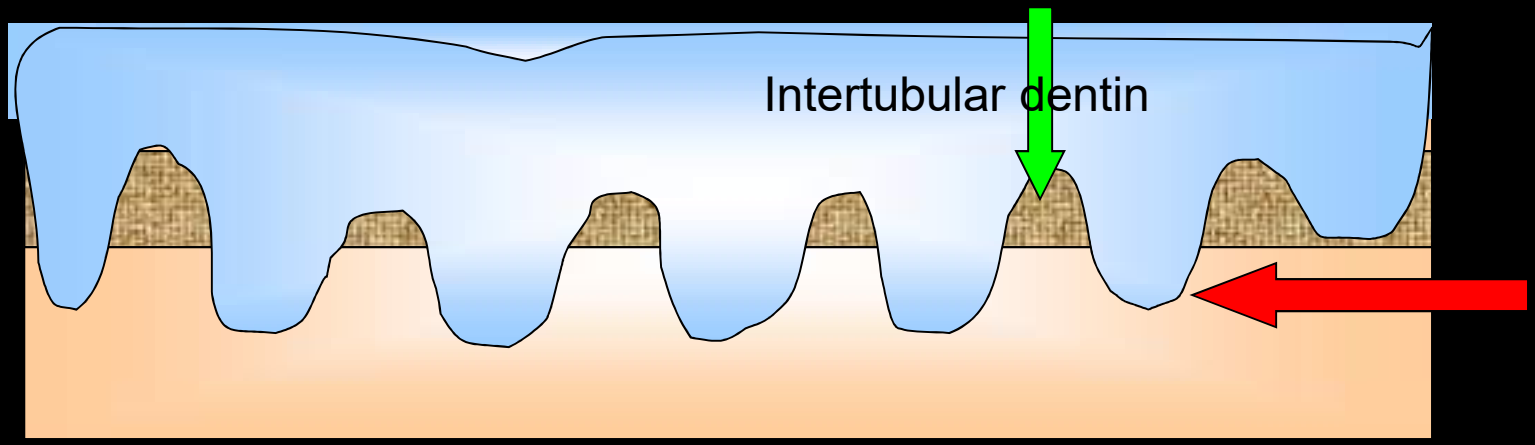


Lateral tubule hybridization :

- Formation of tiny hybrid layer into the walls of lateral tubule branches.
- This microversion of hybrid layer typically surrounds a central core of resin called microresin tag.



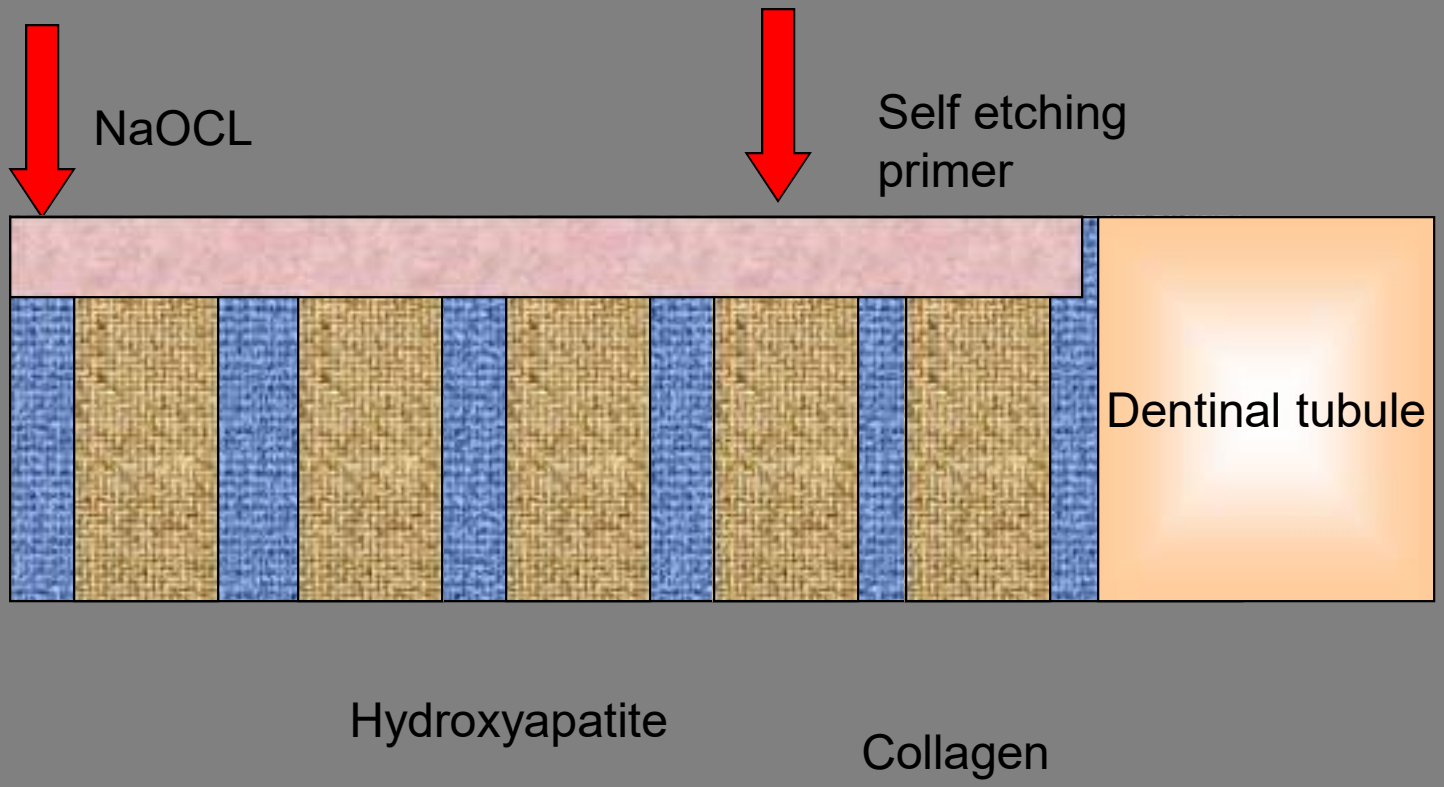
Superficial dentin hybrid layer



Deep dentin hybrid layer

Ghost hybrid layer:
Formed due to incorporation of air bubbles at the substrate adhesive interface.

Reverse Hybrid layer: Hybrid layer is surrounded by more inorganic material.



Elastic Bonding concept:

- The resin layer on the top of the hybrid layer when it reaches an optimal thickness due to high elasticity may act as a stress relaxation buffer.

- Absorbs by elastic elongation the stresses caused by polymerization contraction of the resin.

Composition of dentin bonding agents

- Etchants
- Primers
- Adhesives
- Initiators and accelerators
- Fillers
- Other ingredients.

Etchant or a conditioner:

Definition:
Alteration of dentin surface including smear layer with the objective of producing a substrate capable of micromechanical and possibly chemical bonding to dental adhesives

Physical changes after conditioning:
Removal or modification of smear layer.
Opening of dentinal tubule orifices

Chemical changes after conditioning:
Modifications in organic matter
Decalcification of inorganic portion

Conditioning of the dentin

- **Chemicals**

Acids
Calcium chelators

- **Thermal:**

Lasers

- **Mechanical:**

Abrasion

The various acid etchants used are:

Organic
- Maliec acid
- Tartaric acid
- Citric acid
- EDTA
- Acidic monomers

Polymeric
Polyacrylic acid

Mineral acids
- Hydrochloric acid
- Nitric acid
- Hydrofluoric acid

Conditioners

Free flowing/ gel etchants

Calcium chelators:

- Remove smear layer without decalcification or significant physical changes in the underlying dentin substrate.
- No funnel shaped changes are seen.

EDTA

pH of 7.4

Tublicid

0.1% EDTA

0.15% Benzalkonium chloride

- Scrubbed on the surface for a few seconds,
- then left passively for another 60 seconds followed by additional scrubbing.
- Smear layer removal, smear plug intact

Lasers:

Nd: YAG lasers used at 10-30 pulses per second. The lased surface is desensitized by occlusion of open and permeable dentinal tubules.

Air abrasion:

Aluminium oxide particles are used for air abrasion of a particle size of 0.5 Microns.

Primers
Surface tension less than the surface free energy of the acid etched dentin.

Amphiphilic bifunctional molecules.

Monomers used are
- HEMA
- NPG-GMA
- PMDM
- BPDM
- PENTA

Acidic primers containing carboxylic acid groups are used in self etching bonding agents.

The solvents used in primers

- Acetone
- Ethanol/ water
- Primarily water.

In some primers solvent levels can be as high as 90%.
A few fourth and fifth generation bonding agents are solvent free.

- **Acetone – H2O**
- Eg: Tenure- quick
- **Acetone- ethanol**
- Eg: All bond 2 (Bisco)
- **Ethanol- water**
- Eg: Gluma comfort bond
- Scotchbond

Dentin Bonding Systems

Solvent	Advantage	Disadvantages	Eg
Acetone	Excellent water chaser, Dries quickly	Evaporates quickly after being dispensed. Can evaporate from the container. Sensitive to wetness of dentin(risk of over drying. Multiple coats may be required. Offensive odour. Volatile, bond strength may be significantly reduced.	One step(Bisco) Prime and Bond NT(Dentsply) Gluma one bond.

Dentin Bonding Systems

Ethanol/ water	Evaporates less quickly, less sensitive to wetness of dentin. Good surface energy and good penetration.	Extra drying time.	Excite(Vivadent) Optibond solo plus(Kerr)
Water	Slow evaporation, not sensitive to wetness of dentin. Have capacity to raise collapsed fibers.(9%-50%)	Long drying time. Water can interfere with adhesive if not removed	Amalgabon d plus(Parkell) Prompt l pop Scotch bond multipurpo se
Solvent free	No drying, single coat	Higher film thickness	

Adhesives

- Hydrophobic, dimethacrylate oligomers
- Diluted with lower molecular weight monomers.

Commonly used are:

Bis GMA, UDMA, TEGDMA, Methacrylated phosphates, PENTA.

- Minimal thickness of 100 Micrometers
- Applied using brush.
- Act as a stress relaxation buffer to relieve polymerization contraction stresses.
- May contain fillers.(Optibond solo, Prime and bond NT)

Initiators and Accelerators:

- Light cured: camphoroquinone and an organic amine.
- Dual cured bonding agents :catalyst to promote self curing.

Fillers:

- Most unfilled
- inorganic fillers 0. 5% to 40% by wt.
- microfillers, or nanofillers, and submicron glass.

Do not scatter light. Provide radioopacity

- The filled bonding agents tend to produce higher in vitro bond strength.

Functions of nanofillers:

1. Prevents nanoleakage.
2. Causes uniform thickness of adhesive layer
3. Better flexibility to adhesives
4. Better dissipation of forces
5. Scatter of light is prevented.

Other ingredients:

- Flourides
- Antimicrobial ingredients
- Glutaraldehyde as a desensitizer.

Bond strength:15-35 Mpa

Problem	Solution
Dentin surface too dry	Use moist cotton pellet to rehydrate surface
Dentin surface too wet	Gently air dry to achieve glistening surface
Contamination with saliva and blood	Rinse, re etch if contamination is moderate or greater
Contamination with caries detector, handpiece lubricant or hemostatic agent	Rinse and reetch
Contamination by eugenol	Avoid eugenol containing provisional materials and temporary cements.
Remaining caries affected dentin	Remove caries

Surface does not glisten after application of primer	Apply additional coats of primer
Self cured composite debonds from adhesive	Use dual cure bonding agent with self cured composite or resin cement
Bonding agent under cured	Cure recommended time with properly maintained light curing unit, be sure the bonding agent is compabtible with light curing unit.
Recent bleaching procedure	Wait one week after bleaching.
Flourosed teeth	Double the etching time
Smooth single surface lesions lack of bonding	Create surface roughness and mechanical undercuts

Clinical properties

The success of a bonding agent is evaluated indirectly, for

- Post operative sensitivity
- Interfacial staining
- Secondary caries
- Retention or fracture from insertion to 18 months.

These clinical trials test short term retention and initial seating.

.

Biological properties

Typically skin irritants.

HEMA is not considered biocompatible as a monomer.

local and systemic reactions.

- Wearing gloves
- Immediately replacing contaminated gloves
- Using high volume evacuation
- Keeping all bottles tightly closed.
- Disposing of materials in such a way that the monomers cannot evaporate into office air.

Even with double gloves, contact with these aggressive solvents and monomers will produce actual skin contact in a few minutes.

Follow all reasonable precautions, and if unwanted contact occurs, immediately flush the affected areas with copious amounts of water and soap. Once the material is polymerized, there is very little risk of side effects.

Bonding to dentin and enamel

Where does it stand in 2005?

Gordon J Christensen JADA, vol 136, Sep 2005.

"Have our concentration on "bond" and " microleakage" and the endless publications on these subjects gone too far? How much bonding is enough bonding, and when is bonding not important at all? Is microleakage reduction effected by bonding agents really so vital clinically?"

Dentin Bonding Systems

Bond with the Best

Dr. Rafael Bowen with a volunteer participant in a clinical trial of an adhesive material to bond composite restorations to dentin and enamel.