INTRODUCTION

DENTINE BONDING AGENTS Introduction: It has rightly been said, that the only thing that remains constant in this world is change. Since the advent of time, and particularly since the dawn of the 20th century, man has been faced with the opportunity to change and improve upon pre-existing ideas and inventions in order to progress and evolve. The field of Dental Materials has not been exempt from this challenge, and this is best reflected by the evolution seen in Dentine Bonding Agents. However, change for its own sake is unwise and unnecessary. Is it prudent to tamper with a current system if it functions adequately? In order to answer this question, we must first have a sound understanding of where we stand in the field of Dentine Bonding Agents today. How we determine improvement depends on our perception of it. In today’s times, the objectives of restorative dentistry are vastly different from those of yesteryear and we are called to challenge the pre-existing paradigm and make way for a new one. Earlier performance standards were based on the concept of longevity: the longer the restoration lasts, the fewer the number of times the tooth will require a change of restoration. Therefore, pursuing a material whose chief function is to effectively withstand the rigors of the oral environment has long held our attention. The materials commonly used for restorative purpose in order to achieve this end were amalgam, gold foil and cast restorations. However, changing times have also meant a change in objective: Increasing public awareness of tooth-colored restorations has led to a rising demand for more esthetic, biocompatible materials such as composites, glass ionomer cements and porcelain. Of all the innovative materials available today, the direct placement of resin composites has assumed its place as the current technique of choice in restorative dentistry. One of its principal advantages is its bondability to enamel and dentin, which has been made possible by the use of Dentine Bonding Agents. The advent of Dentine Bonding Agents, with its property of adherence to the tooth structure by both micro-mechanical and chemical means, has heralded a new era in the field of dentistry owing to. The formulation of this path-breaking material has been attributed to momentous contributions by great scientists like MICHAEL BUONOCORE, RAFEL BOWEN, NUBO NAKABAYASHI and FUSYAMA. Recent improvements in adhesive systems have generated a revolution in dentistry, placing adhesive restorations on the front stage. Clinicians have had to rise to the challenge of confronting this continuous and rapid change. There has also been a surge in the development of more refined and diverse restorative materials. These materials along with the new, improved bonding agents have left the clinician spoilt for choice and he is faced with the daunting aspect of determining which offers the most advantages. This Library dissertation discusses Dentin Bonding Agents, with a complete coverage of bonding systems with the hope that it will contribute to a better understanding of these systems and thus empower dental professionals with the ability to make more effective treatment and material choices. Acknowledgement: Several people have contributed towards the inception, compilation and final completion of this library dissertation and I would like to take this opportunity to gratefully acknowledge them all. Firstly, I extend heartfelt thanks to Dr. Baskar Rao, Principal of S.D.M. College of Dental Sciences and Hospital, for providing us not only with excellent facilities but also with his help at all times. I am extremely grateful to Dr. Nageshwar Rao, Head of Department of Conservative Dentistry, S.D.M. College of Dental Sciences and Hospital and my mentor for his unwavering support, guidance and invaluable suggestions which have been instrumental in the successful completion of this dissertation. I would also like to sincerely thank all the other members of the staff of the Department of Conservative Dentistry for their timely help and advice. I am grateful to Mr. Javale, (Neha, put his college designation here.. statistician, I think) for helping me with the monumental task of typing this manuscript. My sincere thanks to my parents and my sister, for being a constant source of love and encouragement without which I would not be where I am today.
Lastly, but definitely not the least, I am grateful to my friends (Neha, their names come here) for their help, support and inspiration.
As we more through time, we are continuously faced with the opportunity to change this is true for our restorative materials, as it is for anything else. In order to know whether or not we should change, we must have an understanding of where we are currently. If the change mill not precede improvement is it mice to presence.

How we determine improvement depends on our paradigm, our new of the objectives of restorative dentistry traditionally, dentists have as much as possible is the ideal permit we have in the time that challenges that paradigm.

The earlier performance standard is rendered on the concept of longevity. The longer the restoration lasts, the fever the number of times a tooth mill require restoration in a lifetime. Therefore, pursuing a material that will withstand the rigors of oral environment has long held our attention.

The materials commonly used for restorative purpose are amalgam, gold foil and cast restorations in ‘colour’. Increasing environmental consumes and public awareness for tooth colored materials have heralded patients to demand more esthetic, biocompatible materials such as rempastes glass inomer cements and porcelain.

Of all the innovative esthetic materials available today, the direct placement of rein composite has assumed the cement thrust in restorative dentistry one of the principle advantages in the use of these resin composites is the hondalility to the enamel and dentin; which has been possible due to mostly improved bonding systems.

Dentin bonding agents have created a new in the field of dentistry, owing to its property of adherence to the tooth structure by both micromechanical and chemical means. This momentous change like Michal Buroocore, Rafel Bomen, Nubo Nakahayashi, Fusyama.

Recent improvement in adhesive systems have generated a revolution in dentistry, placing adhesive restorations on the front stage clinicians have been confront4d with this continuous and rapid turnover is adhesive materials. These has been an angering process in developing more refined and diversfied restorative materials along with the production of steadily improving bonding agents creating confusion as to which and is letter.

This library dissertation discusses dentin bonding agents, with complete coverage of the bonding systems, hoping that this would help dental professionals better in understanding bonding systems.

HISTORY

Dentin Bonding Agents have developed over several decades. The various historical events, with took place have led to our present day DBA.
1938  -Development of epoxy molecule by Castan
1951  -Development of glycerophosphoric acid dimethacrylate molecule by Dr.Oscar Hagger. This molecule permitted resin adhesion to dentin.
1952  -Usage of glycerophosphoric acid dimethacrylate by Kramer and Mclean (earliest description of hybrid layer)
1955  -Buonocore introduces etching of teeth any phosphoric acid; he found that an acrylic resin; bonds well with etched enamel.
1956  -Buonocore pioneers the work on adhesion to dentin. Initial dentin bonding agent’s developed were lased on the glycerophosphoric acid dimethacrylate molecule and bonds to hydrochloric acid etched dentinal surfaces, but bond strength diminishes greatly on immersion in mater.
1957  -Bowen starts work on bio-phenol glycidyl methacrylate (BIS-GMA) resin systems.
1962  -Bowen conducts first workshop dental materials.
1965  -Causton describes how primers work.
1982  -Bowen, Cobb, Rapson develops the multilayer adhesive system.
1982  -Nakabayashi reports the presence of hybrid layer.
1987  -Fusayama described the concept of total etching and boning.
1997  -Ferrari et al established the bonding mechanism of one bottle adhesive system to conditioned dentin.
2000  -Evaluation of bonding ability of the sixth generation bonding systems done by Ferrari et al.
2003  -Seventh generation by Ferrari et al.
ENAMEL

Enamel is the hardest of the mineralized tissues of the body. It covers the anatomical crown of the tooth. This tissue is very brittle in nature but protects the underlying structure, i.e. dentin and pulp.

The inorganic component of enamel is principally appetite it its, hydroxy, fluoro carbonate forms. Calcium and phosphate are the two major inorganic elements (Brudevold, Steadman and Smith 1960). Minor variations occurs is composition in which aluminum, barium, magnesium, strontium, radium and vanadium among others can be found in the lattice.

Crystallites are embedded is an organic matrix with comprises less than 1% of the volume of mature enamel (Estoe, 1963). Less than one half of the organic component contains protein; high glutamic acid with significant amount of proliferation and glucose (Deutch&Pe’er,1982). During mineralization of the crown, a significant shift occurs in the value of organic material. The ameloblasts produce large amounts of organic matrix among early phases of enamel development, then as crown saturation proceeds, the volume of organic matrix decreases while the volume of inorganic material increases. A mineralization gradient (Crabb and Darling 1960) exists in mature enamel, thus the outer portion of enamel is relatively more mineralized than the inner portions.

Water exists in enamel in a significantly larger amount (up to 4% by value). About 25% of water is loosely bound to the crystallites.

A dynamic gradient involving fluid exists between the pulp and oral environment (Bergman 1963) in which enamel participates through its porous permeable structures,but enamel is selectively permeable (Darling and Others, 1961) allowing the passage of water and ions but excluding large molecules (Poole, Tachy and Berry, 1963).

Histochemical studies have shown the complex nature of the surface integument. This fully reacted low energy surface confers significance in the bonding equations, as does the traumatically or operatively imposed tissue. An understanding of the micro-morphological properties have been significant is remaining interactions between enamel and bonding agents.

DENTIN

Dentin forms the largest portion of the tooth structure. It is covered by the enamel and cementum on the outer surface and internally it forms the walls of the pulp cavity.

The dentin comprises of dentinal tubule that are small canals that extend across the entire width of dentin, from dentinoenamel junction(DEJ) or dentinoecemental junction(DCJ) to the pulp. Each tubule contains cytoplasmic cell
process (Tomes Fiber) of an odontoblast. Each dentinal tubule is lined with a layer of peri tubular dentin that is much more mineralized than the surrounding intertubular dentin. The number of tubules increases from DEJ (15000-20000/mm2) to the pulp (45000-65000/mm2). The dentinal tubules are filled with dentinal fluid which makes it difficult to bond.

The chemical composition of dentin comprises of 75% inorganic, 20%, 5% H2O and other minerals. It is less mineralized than enamel but more mineralized than cementum or bone. As age advances there is a structural change in dentin. The mineral content of dentin increases with age. This mineral phase is composed primarily of hydroxyapatite crystallites. The organic phase is primarily collagen (Type I with traces of type IV collagen). They consist of carboxy, amino, hydroxyl surface groups. The other non-collagenous constituents that can be found are dentin phospho-protein, sialoproteins and osteocalcins.

Dentin permeability is highly variable. Variation in permeability may arise from tubular irregularities associated with mineral deposits, organic components of the odontoblastic processes. An outward flow of dentinal fluid occurs because of a small but positive pulpal pressure (10-15 mm Hg). The permeability characteristics of dentin are of crucial importance in dentin bonding because most of the current bonding systems rely on resin penetration or infiltration into dentin (Transdentinal Permeation). Resin penetrates into tubules to form tags that can contribute to resin adhesion. More important factor is permeation of resin into intertubular dentin (Intradentinal permeation).

Dentinal permeability is reduced with age and also in caries affected dentin as the lumina becomes narrow/may get obliterated by deposition of intratubular crystals and apposition of irregular sclerotic or reparative dentin.

Adhesion
Adhesion is defined by the “American society for testing and materials as “A substrate capable of holding material together”. The word adhesion is derived from the Latin word adherer, which means ad-to and hearer- to stick. Adhesion refers to the attraction between the atoms and molecules at the contacting surface of different materials (De Brayer et al 1951, Wake 1982).

In adhesive terminology adhesion or bonding is the attachment of one substrate to another. The surface of the substrate that is adhered to is termed as adherent. The adhesive or bonding agent may be defined as the material that when applied to the surface of the substrate can join them together, resist separation and transmit loads across the bond.

An important requirement for any of these interphase phenomenons to take place is that two materials being joined must be sufficiently in close and intimate contact and besides this sufficient wetting only occurs if its surface energy of adhesive is less than the surface energy of the adherent. If the adhesive had a high surface tension, then it would roll up into a droplet and which will prevent adhesion.

Based on this theory of wetting and surface free energies, adhesion to enamel is much easier to achieve than adhesion to dentin. This is because enamel is primarily made up of hydroxyapatite which has a high surface free energy whereas dentin has a low surface free energy because it is compared of two distinct material hydroxyapatite and collagen. Hence, wetting is easy for enamel than for dentin.

In the oral cavity, the tooth surface is normally covered by a pellicle. This salivary pellicle is organic in nature and has a low critical surface tension that impairs adequate adhesion. Moreover, instrumentation of the tooth substrate during tooth preparation produces a smear layer which has a low surface free energy. Hence, the natural tooth surface should be thoroughly cleaned and penetrated prior to bonding procedures to increase the surface free energy.

Types of Adhesion
Van Noort in 1994 suggested that one or more of the following of mechanism can create an adhesive bond:
1. Mechanical Adhesion
Here, retention is by the interlocking of one phase into surface of another. This type of adhesion can be due to
a. Geometrical effects
These are caused by microscopic porosity or roughness of the surface, i.e. mechanical locking provided by undercuts, grooves etc.
b. Rheological effects
   This is caused by flow of materials in both liquid and semisolid phases. Mechanical adhesion also referred to as micro-mechanical adhesion results from the presence of surface irregularities that give rise to microscopic undercuts. The liquid adhesive can penetrate these undercuts and once set is locked in them. A prerequisite for this form of adhesion is that the adhesive can readily adapt to the surface of the substrate. The adaptation is determined by the wettability of the adhesive on the substrate, the ideal situation being that of perfect wetting when the adhesive spreads spontaneously over the surface. The degree of penetration of the adhesive may also depend on the pressure used during application of the adhesive that helps to force the adhesive into surface irregularities.

II. Physical Adhesion
When the two surfaces come in close proximity to one another, secondary forces of attraction can be generated through dipole-dipole interactions. The polar reaction occurs as a result of attractive forces between the positive and negative charges on the molecules. The magnitude of the interaction energy is dependent on the mutual alignment of the dipoles. This type of bonding is a rapid and reversible process because the molecules remain chemically intact on the surface. Therefore, this weak physical adsorption is also easily overcome by thermal energy and is not suitable if a permanent bond is desired. It follows that non-polar liquids will not readily bond to polar solids and vice-versa, because there is no interaction between the two substances at the molecular level even if there is good adaptation. A familiar example of this problem is the inability of hydrophobic silicone rubber impression materials to adapt to the hydrophilic moist surfaces of the soft tissue (This problem is overcome by the use of surfactant).

III. Chemical Adhesion
If an absorbed molecule dissociates on contact with a surface and constituents alone rearranges themselves in such a way that as for covalent, a strong adhesive bond can result. This form of adhesion is called as chemisorption. The feature that distinguishes the chemical bond from the physical type of interaction described previously is that a chemical reaction takes place between the molecules and the surface molecules of the substrate. Adhesives must be strongly attracted chemically to the surface of application to form strong bond and require identical reactive groups on both surface.

IV. Adhesion through molecular entanglement
So far it has been assumed that there is a distant surface between the adhesive and the substrate. In effect, the adhesive as adsorbed on the surface and can be considered surface active. If the substrate is permissive the adhesive is able to penetrate through the surface of the substrate and absorb into rather than adsorb onto the substrate. If the absorbing molecule is a long chain molecule or better still forms polymers in the pretreated layer, the resultant enlargement between the adhesive and the substrate is capable of producing very high bond strength. This approach is being adopted for resin bonding systems.

CHEMISTRY OF ADHESIVE SYSTEMS
Dentin bonding systems contain monomers that have hydrophilic and hydrophobic groups these provide a stable link with the dentin and the restoration. The chemistry of adhesive agents can be explained as.
Adhesion based on ionic polymers
Adhesion by coupling agents
Adhesion by grafting reaction
TYPES OF Chemical adhesion
There are two types of chemical adhesion
Primary Valence Forces
Covalent Bonds
Co-ordinative Bonds
Ionic Bonds
Secondary Valence Forces
Intermolecular adhesion (Vander Waal’s Forces)
Hydrogen Bonds.

Adhesion by coupling agents
Coupling agents utilizing the concept of hydrophobic and hydrophilic groups are the monomers based on phosphate or phosphonate.
The hydrophilic PO4 group interacts with Ca+ ions in dentin. This type of adhesion is seen to occur with the non-electrolyte adhesion. Bonding can be accomplished with the inorganic part of the dentin, hydroxyapatite, or to the organic part. Use of coupling agents for bonding leads to only minor improvement in the bond strength. One coupling agent; 3-methacryloyloxy propyl trimethoxysilane. Another coupling agent; butylacrylate acrylic acid copolymer with free carboxylic acid groups. NPG-GMA is another coupling agent used.

The coupling agent utilizes the concept of hydrophilic and hydrophobic groups i.e. it consists of a bi-functional molecule, where the outer part into a chemically unites with the tooth surface whilst the other attaches to resin. The coupling agents have basically the formula.

M-R-X

M- Methacrylate group, which eventually becomes bound to the resin by copolymers.
R- is the clearing and spacing group spacing group must be able to provide the necessary flexibility to the coupling agent to enhance the potential for bonding of the reactive group. If the molecule is excessively rigid, the ability of the reactive group to find a satisfactory conformational arrangement is jeopardized, such as hydrocarbon chains.
X- represents a reactive or functional group with interacts with the tooth surface. The reactive groups are end groups.

CLINICAL FACTORS AFFECTING ADHESION

Salivary or blood contamination

Although dentin is a wet substance, the constituents of saliva and blood create an environment that can destroy dentin bonding. These contaminants act in a negative manner for adhesion.
- Rubber dam and other dry field aids should be used to prevent contamination.

Moisture and Oil contamination from Handpiece

During cavity preparation, there may be water or oil contamination. This should be prevented by using a three way syringe and maintaining the air compressors well.

Surface Roughness of tooth structure

Increased surface area created by surface roughness results in better bonds with dentin. Mechanical retention may be increased by the microscopic roughness produced on dentin or enamel by rotary cutting instrument.

Mechanical undercuts in tooth preparation

The mechanical undercuts placed in the tooth structure hold the restorative material from bodily displacement from the preparation and by microscopic movement caused by thermal or polymerization influences. This type of retention is further augmented with the current generation dentin bonding agents.

Flouride content of teeth

Increased flouride content in enamel is considered to be resistant to acid etching but it was found that if the etching time was made double, the same effect would be produced.

Dentinal canal characteristics

Dentinal canals at the external surface of tooth roots or near the dentinoenamel junction have small diameters. As dentinal canals are observed closer to the dentinal pulp, they become larger. Older dentin has small dentinal canals, while younger dentin has larger dentinal canals. Superficial abraded dentin may have occluded canals. If the canals are small, attachment is less and vice versa. Bonding agents use mechanical attachment into dentinal canals as well as chemical bond. If canals are small, attachment would be less whereas if canals are large, attachment is enhanced.

Presence of plaque, calculus, extrinsic stains or debris

Any enamel or dentin surface that requires bonding must be scrupulously cleaned before the bonding procedure begins. Plaque present on the tooth surface prevents etching. Penetration of plaque by the acids used in DBA’s is not possible and will result in a clinical adhesive failure. Tooth surface stains and dental calculus if not removed will not permit bonding.

Presence of bases or liners

The presence of varnish eliminates the potential to bond restorative material to the tooth surface. Liners may result in creating moderate bonds with dentin but the bond strength is significantly lower than that created by placing resin on acid etched enamel surfaces.

Tooth dehydration
Overdrying the tooth preparation before placing bonding agents should be considered to be a negative factor. Drying only till the obvious shine of moisture remains is a good clinical guide.

Constituents of temporary cements
If a temporary cement is present since a long time in the tooth, the liquid portion of the cement is rendered inert. Etching is done above the cement, which results in better adhesion.

DENTIN BONDING AGENTS
The dentin bonding agents are di or multifunctional organic molecules that contain reactive group, which interacts with dentin and the monomer of the restorative resin.

Components of DBA
- Conditioner
- Primer
- Adhesive

Requirements of DBA
Ideally, dentin-bonding system should have:
- Sufficient bond strength, optimum 17-20 Mpa
- Be compatible with dental tissues
- Provide an immediate permanent high strength bond to dentin
- Minimize microleakage at the margins of the restoration
- Prevent recurrent caries and marginal staining
- Easy to use and less technique sensitive
- Reasonable shelf life
- Compatible with all resins
- No reduction in bond strength when applied to moist surface
- No potential for sensitization of patient on operator

Problems in Bonding to dentin
The developments of adhesives that adhere to dentin have still been and still remain a challenge to researchers. Dentin consists of 50% inorganic hydroxyapatite, 30% organic material and 20% of fluid. Dentinal hydroxyapatite is randomly arranged in an organic matrix. The high fluid content of dentin places certain requirements on restorative dental material (resin are hydrophobic).

The tubular nature of dentin provides a variable area through which the dentinal fluid might flow to surface and adversely affect adhesion.
Sclerosed dentin if present is difficult to penetrate (results from aging or mild irritation and causes a change in the structure of primary dentin, i.e. the peritubular dentin becomes wider, gradually filling the tubular with calcified material. The areas are harder, denser, less sensitive).
Presence of intertubular and peritubular dentin, (each tubule is surrounded by a collar of hyper-mineralized dentin called peritubular dentin. The less mineralized dentin between the tubules is called intertubular dentin). The presence of smear layer complicates dentin bonding. The smear layer is present on cut dentin surface and is of limited strength so it must be either removed or penetrated by the resin.
Permeability of dentin differs at different sites. Variation in permeability may arise due to tubular irregularities associated with mineral deposits. It also increases near the pulp and pulp horns than the adjacent areas.

CLASSIFICATION OF DBA
1. According to generation
2. According to their adhesion strategy towards enamel, dentin or on the basis of number of clinical application
3. Depending on chemical composition
4. According to treatment of smear layer
5. According to chronology, chemistry and shear bond strength
6. According to mode of curing
7. According to type of solvent
1. On the basis of Generations:
   1. First Generation Dentin Bonding Agents
   Developed by Bowen - 1965.
   Agents used in this generation are:
   a. Glycerophosphoric acid dimethacrylate,
   b. Cyanoacrylates
   c. NPG - GMA
d. Polyurethanes

Buonocore four decades ago found that a resin containing GPA-DMA could bond to HCl etched dentin surfaces. However, the bond strength was by water. To overcome this problem Bowen synthesized NPG-GMA a surface-active comonomer that theoretically produced water resistant bonds. NPG-GMA acted as an adhesion promoter between the tooth structure and resin material by chelating with surface calcium.

Disadvantages:
- Poor clinical results
- Hydrolysis of GPA-DMA in oral environment
- Difficulty in bulk polymerization of cyanoacrylates
- Instability of NPG-GMA in solution
- Hydrophobic resin
- Low bond strength (2.1 - 2.8 Mpa)
- Ex: Cervident (S.S.White Co.)

First commercially available dentin bonding agent.
Cosmic bond (Amalgamated Dental)
Palakav (Kulzer, USA)

2. II Generation Dentin Bonding Agents:

In general, the second-generation dentin bonding agent was much improved compared with the first generation. These were developed during the early 1980's.
Most of the agents were primarily - (polymerizable phosphates in BIS-GMA) resin
1. Halophosphorous esters of BIS-GMA. Hence they were called as phosphate-bonding systems.
2. Polyurethane based compounds were also used.
The bonding mechanism involves a surface wetting
Phenomenon as well as ionic interaction b/n phosphate groups and dentinal calcium.
The II-generation systems had the smear layer intact. This was to create a Ca+ rich layer where the phosphate can combine with Ca+.

Disadvantages:
1. Low bond strength (1-3 Mpa) (studies by Relief and others 1986 and Solomon & Beech)

A major reason for the poor performance of these bonding agents is the fact that these bond to the smear layer rather than to the dentin itself.
Ex: Scotch bond dual cure ('OM Dental)
Bond Lite, (Kerr)

Dentin Bonding Agent (Johnson &. Johnson) Prima Universal
Creation Dentin Bonding Agent
Clearfil (Kuraray)

3. III generation Dentin Bonding Agents

Developed in mid 1980's.
The third generation dentin adhesives showed increased bond strength and improved clinical performance.
These systems resulted either total or partial removal of the dentinal smear layer.
In addition they required a surface-conditioning step. They used a solution or a series of solutions to increase the wettability of dentin (i.e. priming solution).
Their mechanism of bonding to dentin was by penetration of smear layer i.e. they used micro mechanical means of adhesion rather than the unreliable chemical bonding of previous material.

Disadvantages:
- Time consuming (More of number of steps)
- Technique sensitive

Ex:
Gluma (Bayer Dental)
Conditioner: EDTA 17%
Primer: 35% 1-iEMA (Adhesion Promoter)
5% Glutaraldehdye
Adhesive: 55% BISGMA 45% TEGDMA
Bonding was achieved by Glutaraldehyde bonds to amino groups in collagen
Charge compounds Reacts with OH group of HEMA

And causes mechanical interlocking in the opened ends of dentinal tubules

2. Tenure:
Oxalate was the first available dentin-bonding agent developed by Bowen.
Conditioner: 2.5% nitric acid + ferric oxalate (stains the teeth).

SYSTEM CONDITIONER ADHESION PROMOTER
1 Gluma  17% ED'FA  35% HEMA  5% GA  55% BISGMA TEGDMA
2 Scotchbond  55% HEMA  2.5% Maleic acid  BIS-GMA HEMA
3 TENURE  (10.2-18.2 Mpa)  1% Nitric acid  2% Phos. Acid  2.5% Aloxalate  5% NTG-GMA PMDM
BIS-GMA TEG- DMA
4 4. Prisma Univ. Bond 2  30% HEMA  6% PENTA  50% UDMA  25%TEG- DMA  4.5% PENTA  0.5% GA

4. Fourth Generation Dentin Bonding agent:

In these systems there was complete removal of smear layer.
These bonding systems involved the "Total etch" technique that is simultaneous etching of enamel and dentin with phosphoric acid or other acids. An improvement in dentinal bond strength by etching was first demonstrated by Fusayama in 1979 and became common in Japan. This gained acceptance in US much later. This is because etching of dentin has been traditionally discouraged because of pulpal inflammation but it is found that very little acid actually penetrates dentin.
These systems were also known as Universal bonding systems as these bonds to dentin, enamel, amalgam, porcelain and composite.
Mechanism of bonding
1. Acid Etching
   - Removes the smear layer
   - Opens the dentinal tubules
   - Increases dentinal permeability
   - Decalcifies intertubular and peritubular dentin

Depth of decalcification is affected by
- PH of the acid
- Concentration
- Viscocity
- Application of time of etchant

Removal of hydroxyapatite crystals leave a collagen meshwork that can collapse. After the conditioner is rinsed off, primer (containing hydrophilic resins) is applied.
   - The primer wets and penetrates the collagen meshwork raising it to almost its original level. The primer also increases the surface energy and hence the wettability of the dentinal surfaces. Then the unfilled resin is applied and penetrates the primed dentin co-polymerizing with the primer to form a intermingled layer of collagen and resin termed as hybrid layer or resin reinforced zone or resin infiltrated layer.
This is thought to be the primary bonding mechanism of current adhesive systems.
Ex:
   - All Bond (BISCO)
   - Amalgam Bond Plus
   - Scotchbond Multipurpose
   - ProBond
   - Liner Bond 2

ALL BOND 2
   - All Bond 2 is a unique development in the field of adhesive. It is a universal bonding system that will bond composite to all dental related surfaces.

i.e.
   - Dentin
   - Enamel
   - Metal Alloy
   - Amalgam
   - Porcelain
   - Composite

ALL BOND 2 (BISCO)

Conditioner: SA+HEMA(4.4)
Primer: 2% NTG-GMA
16%BPDM
Adhesive: BIS-GMA, UDMA, HEMA

SCOTCHBOND MULTIPURPOSE
Conditioner: 10% Maleic acid
Primer: HEMA + Polyalkenoic acid
Adhesive: Hydrophobic BIS-GMA
Hydrophilic HEMA
Photoinitiators

AMALGAM BOND
Conditioner: 10% Citric acid
19% Ferric Chloride
Primer: HEMA with water
Adhesive: 4-META
MMA-TBB

Advantages:
- Bond strength - 18 Mpa
- Wets better
- Bonds to wet surface

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

In the case of 4th generation bonding systems, the clinician had the option of converting the dentin bonding agents from a light curing to a dual curing one. This was carried out by incorporation of a self-activating agent (sulfinic acid derivative) to the bonding agent (1:1 ratio).

Fifth Generation Dentin Bonding Agents

To simplify the clinical procedure by reducing the bonding steps and thus the working time, a better system was needed. Also, clinicians needed a better way to prevent collagen collapse of demineralized dentin. So, the 5th generation bonding systems were made.

Here, the primer and adhesive are combined in one step. These were marketed as one bottle bonding systems. However, etching was required so these are not treated as one bottle system.

The etching is carried out for 15-20 secs. This system creates a mechanical interlocking with etched dentin by means of resin tags, hybrid layer formation.

Ex: Primer & Bond NT (Dentsply)
- Opti Bond Solo Plus (Kerr)
- One Step (Ivoclar)
- Single Bond (3M)
- Scotchbond MP Plus (3M)

1. PRIME & BOND NT
Conditioner: 35% Phosphoric acid
Adhesive: PENTA, UDMA, Resin
R5-62-1, T&D Resin
Nanofiller, Cetylamine
FL & Acetone

Sixth Generation Dentin Bonding Agents

The sixth generation dentin bonding agents were introduced in the late 1990’s (1999). Here, the primer and etchants are combined in one step (self etch primers - SEP’S)

The sixth generation bonding systems are characterized by the possibility to achieve a good bond to enamel and dentin using only one solution. The first evaluation of these systems showed sufficient bond to conditioned dentin while bond to enamel was less effective. This may be due to the fact that the sixth generation systems are composed of an acidic solution that cannot be kept in place, must be refreshed continuously and have a pH that is not enough to properly etch enamel.

Recently, a H2O based bonding has been introduced which combines with the functions of a conditioner, the primer and the adhesive in a so called self-conditioning primer adhesive. The active solution is mixed from two components resulting in the formation of an acidic (self-conditioning) monomer which superficially etches dentin and enamel. The dentin bond mediated by this bonding agent seems to be adequate. However, the etching pattern of enamel appears to be less retentive than that produced by phosphoric acid etching.

Ex:
Prompt -L-Pop
It has 3 compartments
- Compartment 1: Containing methacrylated phosphoric acid, esters, photo initiators, stabilizers
- Compartment 2: Contains water, complex fluoride and stabilizers
- Compartment 3: Has a micro brush

The blister is activated by squeezing compartment 1, thereby releasing its content into compartment 2. The mixing ratio is 4:1 and the freshly mixed solution is released on the micro brush into compartment 3.

On applying this to dentin, the smear layer will be dissolved. Then the demineralized dentin is loaded with prompt-l-pop monomers leading to the formation of a hybrid layer.

Seventh generation Bonding Agents
- This is the latest addition in the series of bonding systems.
- According to manufactures, it a fluoride releasing, self-etching type of bonding agent. It also has a colour changing capacity.
- The etching, priming and bonding is a simple application with no rinsing or drying. It is available in two bottles, which have to be mixed and filled in the cavity.
- It is being manufactured by a company called J Monta (USA) and the product is ONE UP BOND F.
- This is the only bonding system, which provides visual confirmation of complete polymerization by color charge.

Yellow  Pink  White
(Liquid A and B)  (Liquid A & B mixed)  (Completely cured)

Manufactures are claiming that this bonding system also blocks postoperative sensitivity.

Another manufacturing company H KULZAR have brought a product “BOND” in the market. This Is a single bottle system having self etch priming and bonding along with desensitizing capacity.
- It has the advantage of single bottle system and no need of mixing of any liquids.

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

This new classification based on adhesion strategies has been given by Van Meerbeek&Others, 1998, 2000

1. Total etch adhesives
   - 3 step
   - 2 step

2. Self etch adhesives
   - 2 step
   - 1 step

3. Resin modified glass ionomer adhesives

TOTAL ETCH ADHESIVES

These adhesives involve a separate etch & rinse phase. The conditioning step is followed by a priming step and application of adhesive resin. This results in a 3 step total etch adhesive (4th generation)

In the 2 step total etch adhesive, primer & adhesive are combined in one application, i.e.
- Conditioning (I Step)
  - primer + adhesive (II Step)

This correlates with the 5th generation of adhesives

Mechanism of adhesion

Bonding to acid-etched enamel enamel requires an air-dried surface to allow the photo-polymerization hydrophobic bonding agent to be drawn by capillary attraction into the pits created by acid-etching. As a result, two kinds of tag-like resin extensions are formed (Permans & Others, 1999; Van Meerbeek & Others, 2000b)

   Macrotags are circularly formed between enamel prisms and peripheries. Microtags are formed at the cores of enamel prisms where the resin cures into a multitude of distinct crypts of dissolved hydroxyapatite crystals.

The underlying mechanism for the 3-step &2-step total etch adhesive is alike. The dentin smear layer produced during cavity preparation is removed by etch & rinse phase, which results in 3-5m deep demineralization of the dentin surface. Coolagen fibrils are completely removed from hydroxyapatite and form a microretentive
network for micromechanical interlocking of monomers (Hybrid Layer).

Advantages and Disadvantages of 3-step total etch adhesive

Three Step Total Etch Dentin Bonding Agents

Ex

? All Bond 2 (Parkell)
? Clearfil Liner Bond (Kurry)
? Gluma BS (Bayer)
? Scotch BondMP Plus (3M)

Advantages

Separate application of conditioner, primer & adhesive
Low technique sensitivity
Bonding to enamel is good
There is a possibility of particle filled adhesive
Most efficient & consistent results

Disadvantages

Risk of overstretching of collagen fibres
Time consuming procedure
Post conditioning, rinse is required
Sensitive to over-dry*over-wet conditions
Weak monomer-collagen interaction

Two Step Total Etch Dentin Bonding Agents

Ex

Gluma Comfort Bond (Kulzer)
Prime&Bond NT
Prime&Bond 2.1

Advantages

Simpler application
Possibility for particle filling
Possibility for single dose packaging

After priming, the surface should appear glossy without any dry spot. This is a clinical indication that resin is adequately and sufficiently applied.

Monomers are sufficiently applied not only to saturate the exposed collagen network but also to establish a thick resin layer on top of the hybrid layer. This layer may act as a flexible intermediate shock absorber. This shock absorber may also help to protect the adhesive joint against early failure.

Prime&Bond NT

This is a successor of prime*bond 2.1. It contains nanofillers which have a diameter of about 7m. These nanofillers help to
form a uniform resin film that stabilizes the hybrid layer.

They also serve as an additional cross-linker, i.e. the average dentinal tubule is about 8m in diameter and the channels between the collagen fibrils is about 20nm wide with a diameter of 5-10nm. The nanofiller is able to penetrate these channels to provide nanoretention. This is a fluoride releasing mechanism.

SELF ETCH ADHESIVES

This adhesive system is based on the use of non-rinse acidic monomers that simultaneously condition & prime dentin and enamel. The concept of self-etch primers was first introduced by Scotchbond 2 (3M), in the early 90’s. However, this system was advocated to be applied on dentin alone, and therefore required clinically selective enamel etching in a separate step.

More recently one step SEP’s or all in one adhesives are available that combine the conditioning, priming and application of adhesive resin into a single application.

Two step SEP
Ex: Clearfil Liner Bond 2V (Kuray)  
Prime&Bond NT+NRC  
Scotchbond (3M)  
Optibond (Kerr)

One step SEP
Ex:  
Prompt-L-Pop (ESPE)  
Syntac  
Etch&Prime 3.0 (Degussa)

Single component DBA

Advantages
- No acid etching required
- No light curing of DBA
- Well defined hybrid zone
- High bond strength
- Depth of demineralization corresponds to depth of penetration

Disadvantages
- High cost
- Used only with direct resin restoration

Depending on pH and etching potential SEA are classified into

Mild SEA (pH 2.0) and Strong SEA (pH 1.0)

Mechanism of bonding

The mechanism of bonding differs for mild and strong self etch adhesives

Mild SEA

Here, two types of bonding are seen, hybridization + intermolecular bonding
The hybrid layer is of sub-micron size and resin-tag formation is less pronounced. In the hybrid layer, hydroxyapatite is not removed completely because of the weak acid. So, a second type of bonding occurs, i.e. hydroxyapatite acts as a receptor for additional molecular interaction with specific carboxyl or phosphate groups.

Ex, the primary ionic bonding of Unifil Bond GC; 2 carboxyl groups of 4-META with hydroxyapatite were confirmed in XPS and TEM.
This two-fold mechanism may be advantageous in terms of restorative longevity.
Strong SEA

This is similar to the total etch bonding system. Mechanism of bonding is by hybrid layer formation, i.e. nearly all hydroxyapatite is removed from the collagen and thus any chemical reaction between hydroxyapatite and functional monomer is excluded.

GLASS IONOMER ADHESIVES

A third adhesion strategy that differs from the former approaches (persued by resin-based systems), as it involves glass-ionomer based interaction with the tooth substrate, with the development of resin modified glass ionomer adhesives that can bond resin to the tooth structure.

A two-fold mechanism is predicted with this system with a short polyalkenoic acid pretreatment which cleans the tooth surface, exposes surface collagen to a depth of 0.5-1.0m. Here, a micromechanical bond; due to resin interdiffusion and a chemical bond; due to ionic interaction of the carboxyl groups of polyalkenoic acid with calcium of hydroxyapatite that remained attached to collagen fibrils, takes place. The underlying mechanism of glass ionomer adhesives is similar to that of mild etch adhesives.

A network of “hydroxyapatite-coated” collagen fibrils interspread by pores is typically exposed to a depth no deeper than 1m. Upto 0.5m thick layer, often referred to as gel-phase remains attached to the tooth surface despite the conditioner being rinsed off.

3. According to their chemical composition (Craig)
   - Polymethanes
   - Polyacrylic acids
   - Organic phosphonates
   - Mellitic anhydride and methylmethacrylate (4-META)
   - Hydroxyethyl methacrylate + Gluteraldehyde (HEMA+GA)
   - Ferric oxalate + NPG-GMA (N-phenyl glycine and glycidyl methacrylate)+PMDM pyromellitic dianhydride and 2HEMA)

4. On the basis of treatment of smear layer
   The smear layer of limited strength, so it must be either removed or modified before application of bonding agent
   a. Removed
      Example: -
      Tenure (nitric acid)
      Mirage bond
      Clearfil liner bond systems
   b. Modified
      Example: -
      All bond
      Scotch bond 2
      XR bond
   c. Preserved
      Example: -
      Scotch bond dualcure
      Prisma universal bond

5. On the basis of shear bond strength (Eick et al.)
   Included dentinal adhesives without produce shear bond strength of 5-7Mpa
   Example: -
   Dentin adhesit
   Scotch bond dual cure
   Gluma

Category 2
   Included the experimental and commercial products derived from Bowers work with ferric and aluminium onalalates and have produced shear bond strength between 8-14 Mpa
Example: -
  Tenure
  Mirage bond

Category 3
Included dentinal adhesives, without produced shear bond strength values of about 17-20Mpa
Example: -
  Super bond
  Scotch bond 2
  Scotch bond multipurpose
  All bond
(Decreased failure was cohesive in nature)

6. According to their mode of curing
Chemical cure
Example: -
  Amalgabond plus
Light cure
Example: -
  One bond
  Gluma comfort bond
Dual cure
Example: -
  Clearfil linear bond 2V
  Prime and bond NT dual cure

SMEAR LAYER

Introduction
Knowledge of the nature, structure and composition of the prepared surfaces of the teeth is the key to the
formulation and understanding of adhesive restorative systems.
Smear layer was first suggested by Skinner (1961). It was first described in detail and termed as “smear layer” by
Boyde et al (1963)
The smear layer encompasses of any debris remaining on enamel, dentin after conventional methods of cavity
preparation.

The smear layer can be discussed under the following:

? Composition
? Formation
? Size
? Attachment to dentin
? Potential advantages/disadvantages

Composition
Smear layer is composed of debris generated during cavity preparation. Sculein lists the following as its components.
  Inorganic tooth particles
  Bacteria and tissues
Saliva
Blood

Smear layer is rich in nitrogen, sulphur, carbon. The organic component consists of coagulated proteins denatured by frictional heat during cavity preparation. The presence of hydroxyapatite crystals in smear layer is because of its breaking away from the organic matrix and then resetting in the smeared matrix.

Formation

Smearing occurs when hydroxyapatite within (the tissue) is either plucked out or broken or swept along the resets in the smeared out matrix.

Studies have shown that temperature will rise up to 6000°C in dentin when it is cut without a coolant. This value is significantly lower than the melting point of appetite (15000°C - 18000°C) and has led to conclude that smear layer formation is a physiochemical phenomenon rather than a thermal transformation of appetite involving mechanical shearing and thermal dehydration of the protein. Plastic flow of hydroxyapatite is believed to occur at low temperatures than its melting point.

Size

The smear layer thickness is about 5-10 microns but according to some studies it may range from 1-5. The size of the smear layer is influenced by the type of bur used, it speed of rotation and presence or absence of coolants. The steel and tungsten carbide bur produce an undulating pattern. There is a rapid deterioration of the cutting edges. The cutting efficiency of these burs increase the frictional heat resulting in the smear layer formation.

This smear layer formed is irregular in shape and non-uniform in size and distribution, and remains on the prepared surface even after thorough leavage with water.

The diamond burs produce relatively deep and uniform groves. Significant difference exists between diamond burs used with and without a coolant (water spray). The smeared debris does not form a continuous layer but exists as localized islands with discontinuities exposing the underlying dentin. The water spray does not prevent smearing but significantly reduces its amount and distribution.

The smear layer consists of two separate layers
Superficial layer (outer) loose debris
Layer loosely attached to underlying dentin (Inner) plug formation

Attachment to the underlying tissue

The smear layer is not always firmly attached to or continuous over the substrate. It may lift free in come cases.

Potential Advantages & Disadvantages of the smear layer

The main advantages of the presence of smear layer on dentin.
Reduction of dentin permeability to toxins and oral fluids.
Reduction of diffusion (usually inwards) & convection (outwards by hydrostatic pressure or inwards eg. by cementing restorations) of fluids, prevents wetness of cut dentin surfaces.
Bacterial penetration of dentinal tubules is prevented.

The main disadvantages are:
It may harbour bacteria, either from the original carious lesions or saliva which may multiply taking nourishment from the smear layer or dentinal fluid.
The smear layer is permeable to bacterial toxins.
The smear layer may prevent the adhesion of composite resin systems, bonding agents, glass ionomer and polycarboxylate cements.

Hybrid layer

Bonding to acid etched tooth surface requires an air-dried surface to allow the photo-polymerizable hydrophobic bonding agent to be drawn by capillary attraction into the pits created by acid etching. As a result, two kinds of tag-like resin extensions are formed.
Macro-tags are circularly formed between enamel prisms and peripheries.
Micro-tags are formed at the cores of enamel prisms where the resin cures into a multitude of distinct crypts of dissolved hydroxyapatite crystals. The underlying mechanism of dentin is alike for three or two step total etch adhesives. The dentin smear layer produced during cavity preparation removed by the etch and rinse phase which results in a 3-5m deep demineralization of the dentin surface. Collagen fibrils are nearly completely uncovered from hydroxyapatite and form a macro-retentive network for micromechanical interlocking of monomers. This interlock was first discussed by Nakabayashi, Kojima & Masuhma in 1982 and is commonly referred to as HYBRID LAYER.

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

Three specific ultra morphologic features have been described as resulting from this hybridization process.

Shag carpet appearance stands for the loose organization of collagen fibrils that are directed towards the adhesive resin and often unraveled into their micro-fibrils. This feature typically appears when the dentin surface, after being acid-etched, has been actively scrubbed with an acidic primer solution. The physical rubbing action combined with chemical action of the citric acid was found to enhance the removal of acidically dissolved inorganic dentin material and surface debris. This resulted in a deeply tufted collagen fibril surface whose topography is similar to appearance of a shag carpet. The combined mechanical or chemical action of rubbing the acid etched dentin with an acidic primer dissolves additional mineral while fluffing and separating the entangled collagen at the surface. This active rubbing application is thought to promote infiltration of monomers into the loosened collagen scaffold by a kind of “massaging effect”.

A second typical hybridization characteristic has been termed as tubule-wall hybridization and represents the extension of the hybrid layer into the tubule wall area. Resin tag formation in the opened tubules is circularly surrounded by a hybridized tubule orifice wall that is thought to be favourable in hermetically sealing the pulpo-dentinal complex against microleakage and the potential subsequent ingress of microorganisms. This effect may be especially protective when the bond fails either at the bottom or top of the hybrid layer, which are considered the two weak links in the micromechanical attachment. Then, the resin tags usually break off at the hybrid layer, surface keeping the dentin tubules and thus the direct connection to the pulp sealed.

Thirdly, lateral tubule hybridization has been described as the formation of tiny hybrid layer into the walls of lateral tubule branches. This micro-version of a hybrid layer typically surrounds a central core of resin, called a microresin tag.

Reverse Hybrid layer

The acid etched surface of dentin is further subjected to treatment with sodium hypochlorite. This results in dissolution of the collagen fibrils that are exposed. 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 unlike the normal hybrid layer where the collagen fibers are encapsulated by resin, and so this layer thus formed is termed as reverse hybrid layer.

Inter-tubular Bonding

The hybrid layer has been considered to provide micromechanical bonding to dentin but resin tag formation may also contribute to the bond strength. Penetration of the bonding agent into the tubules may provide increased retention, as there will be no path of withdrawal until same tags fracture. So, dentin near the pulp has more retention due to increase number of tubules.

The action of these mechanisms is by:

? The resin tags, which significantly increase the bonding width.
? Hybrid layer, which creates an elastic layer between the restoration and dentinal tissue (elastic bonding).

Conditioning of dentin

Conditioning of dentin can be defined as only alteration done after the creation of dentin cutting debris, termed the smear layer. The objective of this is to create a surface capable of micromechanical and possible chemical bonding to a dentin bonding agent.

The principal effects of conditioning of dentin may be classified as

a) Physical changes.
b) Chemical changes.

Physical changes are principally
Removal or modification of smear layer.
Opening of dentinal tubule orifices.

Chemical changes are principally
Modifications of the fraction of organic matter.
Decalcification of the inorganic portion.

Removal of smear layer generally results in increased permeability of the dentin (Pashley, Michelich, Kehl 1981). The small particles comprising of smear layer have a large surface to volume ratio. The particles dissolve more easily then the intact dentin. If the smear layer and smear plugs within the tubules are lost, the exposed dentin becomes more permeable and sensitive. For clinical success the conditioned dentin must be sealed to prevent sensitivity and pathology (Brannstrom 1981).

Conditioning of dentin same be done by
1) Chemicals
   a) Acids
   b) calcium chelators
2) Thermal
   Lasers.
3) Mechanical
   Abrasion.

Acid conditioners
  Manufacturers generally use the terms conditioners or etchant to describe agents that are rinsed off the dentin.

Mode of action of chemical conditioners
  It has been suggested that mineralized collagen matrices have appetite crystallites arranged not only around collagen fibrils but also within them. The depth of demineralization depends on the type of dentin present. In sclerotic dentin because of either hypermineralization or formation of more acid resistant forms of calcium phosphate (Pashley 1992), more time and stronger acid is required for etching.

Effect of chemical conditioners
  Chemical conditioners remove the smear layer and expose a microsporous scaffold of collagen fibrils thus increasing the microporosity of intertubular dentin. Because this collagen matrix is normally supported by the inorganic dentinal fraction, demineralization causes it to collapse. In intertubular dentin the exposed collagen fibrils are randomly oriented and are often covered by an amorphous phase with relatively few microporosities and variable thickness. Sometimes fibrous structures probably remanants of odontoblastic processes are pulled out of the tubules and smeared over the surface. With aggressive acid etchants, the acids may tend to pull the collagen fibers away from the intact dentin or unaffected dentin leaving a submission space termed as hiatus. With increasing aggressiveness of the conditioning agent, a circumferential groove may be formed at the tubule orifice separating a cuff of mineralized peritubular dentin from the surrounding intertubular dentin. Alternatively, the mineralized peritubular dentin may be completely dissolved to form a funnel shape structure.

  Historically, several acids have been used as dentin conditioners. These include hydrochloric acid, pyruvic acid, phosphoric, citric and nitric, acids.

Phosphoric acid
  It was the first dentin conditioner that was successfully used to remove the smear layer, etch the dentin and restore with adhesive composite resin by Fuzayama and Others (1979). This helps in removing the surface dentin, leaving a clean, well-defined etching pattern where the tubules are enlarged into a funnel shape. Phosphoric acid is the acid of choice recently for the etching purpose. However, the controversy remains about the optimal concentration of this acid. The most widely used concentration in clinical practice is 37% of H₃PO₄. Chow and Brown (1973) demonstrated that the application of phosphoric acid solutions greater than 50% resulted in the formation of monocalcium phosphate monohydrate that is not readily soluble and would not be completely washed away in the clinical situation.

  If H₃PO₄ is applied on dentin when 50 of dentin was remaining it resulted in pulpal damage as the acid liberated gas that passed through the pulp producing thrombus and haemorrhage (Kozam and Burnett).

NITRIC ACID
It is stronger than phosphorus acid. Easily removes the smear layer. Concentration of 2.5% causes funneling of the orifice of dentin to a depth of 5m in 40 seconds.

**CITRIC ACID**
10% citric acid is used for the purpose of removing the smear layer. It has been reported by Nakabayashi (1989) that such treatment tends to lower the porosity or permeability of the demineralized surface, possibly by denaturing the collagen.

Nakabayashi developed 10% citric acid plus 3% ferric chloride combination. The divalent cation seems to stabilize the dentin matrix during its demineralization by citric acid. This combination was found to be particularly effective for methacrylate based adhesives containing 4-META. Ferric appears to be necessary since the citric acid alone yield poor results with this system. The higher bond strengths of 4-META/MMA-TBB products conditioned by 10% citric acid and 3% ferric chloride solution can also be achieved by substituting cupric chloride for the ferric ions, example Super Bond C and B metabond and amalgam bond.

Kuraray Introduced 10% citric acid and 20% calcium chloride in the latest generation of clearfil linear bond system. This high concentration of calcium may stabilize collagen during surface etching. It also decreases the extent of the demineralization of hydroxyapatite by a common ion effect. Here, the depth of decalcification is about 8-microns compared to the phosphoric acid etching which results in 16-micron depth of decalcification (Inokshi and others 1989).

**PYRUVIC ACID**
Pyruvic acid and pyruvic acid buffered with glycine have been reported to satisfactory acid etch both enamel and dentin (Asamussen and Munksgaard, 1988) when using the Gluma Bonding system. Glycine was used to adjust the pH and perhaps to facilitate polymerization reactions.

**MALEIC ACID**
It removes the smear layer but not the smear plugs. It is used in scotch bond 2 and Dexthesive as a conditioner. Although it is grate acidic, it does not appear to decalcify deeply. The hybrid layer formed in this is comparatively thin. (10% maleic acid is used).

**POLYACRYLIC ACID**
These acids are being used more recently. A 10 second application of Durelon liquid (40% polyacrylic acid) results in opening of dentinal tubules. There is no chance of potential harm to the dental pulp here, due to the large molecular size which prevents the acid to more through the dentinal tubules.

**HYDROCHLORIC ACID**
The hydrogen ions from these acids diffuse into the dentin while etching. The surface reactions are violent as carbonate is converted to carbon dioxide and as calcium and phosphate are liberated. These products may be liberated faster than they can diffuse from the site leading to formation of reaction products that may limit further penetration of protons. Further, the hypertonic solutions when osmotically draw the fluid from the dentin towards the surface could restrict the inward proton diffusion.

**CALCIUM CHELATOR**
Chelators are used to remove the smear layer without decalcification or significant physical changes to the underlying substrate as apposed to the strong acid etchants.

**EDTA(ETHYLENE TRIAMINE TETRAACETIC ACID)**
Brannstrom’s concern that bacteria might be incorporated into smear layer and infect the dentin surfaces of cavities led him to develop a dentin conditioner containing 0.1% ethylene diaminetetraacetic acid and 0.15% Benzalkonium chloride as a surface active disinfectant (1980). This agent was marked under the name “Tubulicid”. It is scrubbed on the surface of the smear layer for a few seconds, then left passively for another 60 seconds followed by additional scrubbing. Such treatment removes the smear layer and generally leaves the smear plug intact. The dilute solution of EDTA removes some calcium that is thought to be important in the mechanism of bonding. This was probably responsible for the fall in bond strength. EDTA was developed for its use in the Gluma system by Munksgaard and Asmussen in 1984. It removes the smear layer but does not form significant surface concavity nor is the funnel shape change associated with phosphoric acid evident. The smear plugs in the dentinal tubules are not for removed completely by 30 secs of application of the conditioner.
Thermal Modifications

Lasers

Hard tissue lasers in dentistry are an emerging technology. A pulsed Nd:YAG laser will not disturb the pulp, even if the approach is as close as 1m. Heat is dissipated between the 10 to 30 secs pulses per second. Most of the research has been conducted on dry dentin, but the laser operates on dentin immersed in saliva or H2O. The mechanism of dentin removal is through microscopic explosions caused by the thermal transients. The carbonized, black soot that results is easily washed off with water. Lased surface results in desensitized dentin, presumably by occlusion of the open and permeable dentinal tubules. Microorganisms and organic debris are eliminated from the lased surfaces. The laser decreases the organic fraction of the dentin surface.

The bond strength is increased by about 60% when this was done presumably by increasing the bondable inorganic fraction of the dentin surface. The laser may create micro-mechanical retention.

Mechanical Modifications

It is a mechanical mean of modification of dentin aluminum oxide is used for the purpose of micro-abrasion. It removes healthy as well as diseased dentin and results in a smear layer. Its abrasion action depends on the particle size as well as the velocity. The 0.5-micron or larger particles create a smear on the dentin and increase the surface area (Blacke, 1991). The smear layer formed might be used to eliminate the bond strengths of smear layer mediated dentin bonding agents.

Primers

Major advances have been achieved by the introduction of primers that promote wetting of the dentin with the bonding agent, and penetration of the bonding agent into the dentin.

Primer monomers are bifunctional molecules i.e they contain
1. hydrophilic groups (eg- OH-2-COOH) for better compatibility of the resin monomers with the moist dentin,
2. hydrophobic methacrylate groups for the co-polymerization with the bonding resin Primers are monomer dissolved in solvents such as acetone, alcohol and water and are capable applied to the etched or conditioned dentin substrate last are not rinsed off. Organic solvents aid in displacing water, expanding or re-expanding the collagen network and thus promoting the infiltration of the monomer into the submicron or nanometer sized spaces with in the collagen fiber network. The first dentin bonding mechanism that gave reliable, high bond strengths reported by Nakabayashi et al (1982) was based on the use of 4- META/ methyl methacrylate tri-n butyl borane (MMM- TBB) and 3% ferric chloride in 10% citric acid as a conditioner.

Effective primers contain monomers with hydrophilic properties that have an affinity for the exposed collagen fibril and hydrophilic properties for co-polymerization with adhesive resins. The objective of this step is to transform the hydrophilic dentin surface into a hydrophilic state. Besides HEMA primers contain other monomers, such as NTG-GMA, PMDM, BPDM an PENTA. Present day primers also include a chemical or photo polymerization initiator so that these monomers can be polymerized in situ.

Solvents used in adhesives

ACETONE
- Highly volatile
- Excellent water chaser
- Strong drying agents (risk of over-drying dentin)
- Storage and dispense problems
Ex- One Step (Bisco)
Prime and Bond NT (Dentsply)

Gluma One Bond

ETHANOL
- Excellent penetration capacity
- Good compromise in respect of evaporation
- Good surface energy
Ex- Excite(Vivadent)
Optibond Solo Plus(Kerr)

WATER
- Good penetration capacity
- Enables self-etching of acid monomers
- Slow evaporation difficult to remove
- Remaining H2O may hamper the resin penetratum air polymerization
Ex- Amalgam bond plus (Parkell)
Prompt-L-Pop
Etch bond multipurpose
Solvents may also be used in combination i.e.

- Acetone -H2O
  - Ex- tenure-quick
- Acetone-Ethanol
  - Ex-All Bond 2(BISCO)
- Ethanol-water
  - Ex-Gluma comfort bond
  - Scotchbond

**DRY BONDING**
This refers to the bonding in which the acid etched dentin is dry and uses adhesive systems that provide water based primers. These rehydrate and re-expand the collagen fibres, allowing the resin to infiltrate.

**WET BONDING**
This refers to the bonding in which the acid etched dentin surface is moist. This uses acetone based primers which have water chasing capacity. This technique was introduced by Kanca(1992) and Gwinnet(1992).

There are 2 types of bonding systems
**Water Based Primers**
The first approach to create a hybrid layer in wet dentin is the use of water-soluble primers containing HEMA.
Examples of this type of monomer are Scotch bond 2, Scotch Bond Multipurpose. After application of the water-HEMA mixture, the surface is air-dried to evaporate the H2O. As the H-2O concentration falls, the HEMA concentration rises, until theoretically there should be no H-2O and 100% HEMA on the surface. Water has a much higher vapour pressure than does HEMA. In fact, at atmospheric pressure, HEMA can be regarded as almost volatile. This permits its retention as a solvent; water is evaporated during air-drying.

**Use of water Miscible primer solvents**
The second method of creating hybrid layers in this category of bonding is to sequentially acid etch, rinse, leave moist on dry prime and then bond then HEMA will be in 2 types
1) 35% HEMA in water
2) 13% polyalkenoic acid copolymer in 50% HEMA.

The intrinsic wetness of dentin varies from about 1% in superficial to about 22% in deep dentin. Tay et al using all Bond 2, Bisco, have described the consequences of applying acetone based primers to overwet dentin; the authors found that small globules were formed within dentinal tubules. These were formed when the first one or two layers of primer were applied, i.e. in the tubules filled with dentinal fluid there was too much water available to dilute the acetone with result that the monomer came out of the solution. As more globules formed, they accumulated on the walls of the tubule, reducing the permeability of the tubules, permitting successive primer applications to dehydrate the tubules enough to form normal resin tags.

If successive extrinsic water is left on to surface prior to the application of primer (All Bond 2), which tends to bridge the excess water droplets to four a tiny blister. This prevents resin tag formation in those tubules beneath the water droplet, clinically if the clinician sees a rough texture on the primed surface that might be caused by this phenomenon, these droplets can be destroyed with the tip of brush, which can be used to add more primer.

**Steps for effective priming**
- Microscope examination of attachments produced by primer has shown deficiencies like
  - Incomplete surface coverage
  - Incomplete interfibrillar saturation within the hybrid zone
  - Incomplete penetration to a full depth of demineralized dentin

Steps
A - One method of improving surface coverage and diffusion of the primer is by the application of multiple coats. A second coat of primer is shown to increase the shear bond strength significantly.
B - The surface of dentin should not be over dried or over wet.
C - The etching time should not exceed the time recommended by the manufacturers.
The primer reacts with the side chain grouping of the amino acids in the collagen structures especially -NH2, -OH2 and COOH. Masuhara and coworkers developed analysis bonding agents containing the polymerization initiator tributyl boron,
which is said to induce grafting of the monomers and polymers on to the collagen structure.

WET BONDING

Earlier, placement of restoration on wet surface may have caused confliction between the dentist and his training. However, the picture has changed now.

When the etched dentin is air dried the collagen network will collapse & the micro-channels opened by the removal of the appetite systems will be closed from a compact coagulate that is impenetrable to resin.

Resulting in a layer of imperfect bonding termed as “Hybridoid region” (Tay, Guinett, 1995). This results in microleakage at nanometer level (1/1000 th of a micron called “Nanoleakage”)

This type of bonding results with the bonding systems containing hydrophilic resin such as HEMA, which tolerate moisture.

This clinical technique commonly referred to as wet bonding has been introduced by Kanca and Gwinett, 1992.

In acetone containing primers, when the acetone comes in contact with water; the bonding point of acetone is raised and boiling point of water is lowered (AZEOTROPISM), which causes evaporation of both the acetone and water and resin is left behind.

Alternatively conditioned dentin may be air dried and remoistened with water or an antibacterial collection such as chlorhexiden.e Also an aqueous solution of HEMA (35%) (Aquaprep BISCO) are affective for compensating the dryness induced on dentin surface by air drying.

Over wetting phenomenon

When amount of water is present on dentine surface, this may interfere with the bonding because when primer is applied the solvent evaporates leaving the resin, if water is not completely replaced by primer, polymerization is affected.

In such conditions excessive water causes phase separations of hydrophobic and hydrophilic components resulting in blister and globule formation at the resin dentin surface.

Advantages of wet bond

It is a technique sensitive procedure. Firstly, acetone quickly evaporates from the primer bottle, so that bottle should be immediately closed and the dispersed solution is should be applied immediately on the etched surface.

The evaporation of solvent will increase the ratio of monomers to the acetone solvent that will have an effect on the eventual permeability of monomers in the exposed collagen network.

To prevent this, primers are be available in pre-dosed single patient use capsules Ex Primer and Bond NT Quix (Dentsply).

In contrast to adhesive systems that provide acetone based primers and show a restricted “window of opportunity” as far as precise amount of water that should remain post-conditionally on the dentin surface for efficient bonding to be achieved, adhesive systems that provide H2O-based primers appear less technique sensitive and bond equally well to varying degree of surface dry and wetness. Bonding to dry dentin has the advantage of being the clinically accepted and utilized standard used by most clinicians.

ADHESIVES

The resin component of a bonding system consists of a combination of resins such as BIS-GMA or otherdimethacrylate resins. These penetrate the primed dentin and co-opolymerize with the primer to form a hybrid layer. Some of these systems may contain fillers, which may be silica or glass, or fillers of nano size.

This is the final step of bonding process; application of adhesive layer. Spreading of the adhesive resin over the surface to which it is bonded should be done preferably with a brush rather than air spray. The adhesive is copiously placed and evenly spread with a brush tip that can be separately squeezed out between a paper tissue. The optimal thickness of adhesive is about 100μm when placed in a sufficiently thick layer, the adhesive resin may, due to its relatively high elasticity, acts as a stress relaxation buffer. This will absorb by elastic elongation, in part, the tensile stresses imposed by polymerization contraction of the resin composite subsequently placed over the adhesive resin.

The polymerization contraction stress generated during the placement of composite restoration was found to be absorbed and relieved by the application of an increasing thickness of low-stiffness adhesive. Blowing the adhesive resin layer may reduce its thickness too much, decreasing its elastic buffer potential to relieve polymerization contraction stress. A filled adhesive has

Greater film thickness
Greater ability to flex
Helps dissipate stress of polymerization
AMALGAM BONDING

Although retention and resistance forms were the hallmark of traditional amalgam preparations, modern conservative philosophy and the desire to extend the use of amalgam to more extensive restorations have stimulated a search for improved methods for retaining amalgam restorations. Mechanical adjuncts, including threaded pins or retentive grooves placed in dentin have served well for years towards these ends. More recently, bonding agents employing M-R-X type coupling agent have achieved some clinical success where,

M = a methacrylate molecule which bonds to the composite resin
R = a linking molecule
X = a molecule which interacts with the dentine surface or smear layer

One system uses 4-methacryloxyethyl trimellitate anhydride (4-META). However, the mechanism for responsible for the bonding amalgam to resin is predominantly mechanical in nature. It is produced by condensing the plastic amalgam mass into an inset adhesive resin layer, thus producing an intimate mechanical interlocking as macroretentive areas are produced within the resin after the resin has polymerized.

The results of controlled clinical trials have been mixed, but surely amalgam-bonding agents have placed an adjunct to conventional retentive areas if properly employed.

BIOCOMPATIBILITY OF DENTIN BONDING AGENTS

Bonding of restorative materials to tooth structure, either directly or through an intermediate has been a prime concern of dental researchers and scientists for a long time. A material with good bonding capabilities will minimize gap formation and microleakage between the tooth and the restoration and thereby reduce the risk of recurrent caries and pulp injury.

A good understanding of the biological aspects of DBA is important for their proper use in dental practice. Many dentin bonding agents require total or partial removal of the dentinal smear layer, resulting in opening of the dentinal tubules, which may increase the dentinal permeability of the dentin extensively. An increased dentin permeability enhances the possibility of pulp insult, either by bacterial products diffusing into the pulp, or by cytotoxic leachables from the restorative material, since we know that some components of these adhesive systems are capable of penetrating dentinal tubules up to 200-300µm in pulpal direction.

Biological testing of DBA is a delicate and complex process. Unlike most dental materials dentin bonding systems are made up of more than one material. Usage testing of DBA is further complicated by the fact that physical properties of the test material may influence the results. Poor bonding leading to gap formation, thus allowing bacterial ingrowth, may lead to an adverse pulp response which could be a result of an effect of the test material, of the bacteria, or of a combination of both. All this may complicate the interpretation of results.

SUMMARY and CONCLUSION

Quoting from the Broadway musical “South Pacific”, “If you don't have a dream, how are you going to have that dream come true?” Although reality almost always seems to fall short of conceptualization, a variety of dental researchers have, in their separate ways, brought a long-standing dream to fruition -- that of providing the profession with adhesives that can effectively bond dental composites to dentin and enamel simultaneously. Perfection has not been achieved by any of them and much hard work remains as they seek to improve their various systems. But, given the high tensile strength of dentin (Bowen & Rodriguez, 1962), the progress made in the last decade, and the currently recognized need for dentin as well as enamel bonding, it is reasonable to expect that before the end of this decade the intensive and extensive research efforts will succeed in providing clinicians with completely satisfactory materials and methods for preventive and restorative dentistry by way of adhesive bonding to both dentin and enamel. This dissertation comprehensively describes a number of dentin bonding systems already available to practitioners that are beneficial for increased versatility toward improving the performance of restorative materials. The question of which current dentin bonding system has the best evidence supporting it remains unresolved; the clinician is called upon to put each system on trial before deciding which one is most suitable.

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