EVOLUTION of DENTIN BONDING AGENTS

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Abstract:
This article describes the different types of bonding agents and its concepts of bonding to enamel, dentin, cementum. This also gives idea about different types of changes in chemical composition of bonding agents which varies between different generations. It also emphasizes about the importance of etchants and primers.

Keywords: Dentin bonding agents, Enamel Bonding, Cementum Bonding, generations of bonding agents, acid-etchant, primer.

INTRODUCTION
There are various materials available in dentistry like metallic or non metallic, aesthetic material or non aesthetic material,bonded or non bonded restorative material .

Esthetic dental appearance is one of the patients’ demands. This helped in the evolution of esthetic restorations, including the use of resin-based composite materials..Composite resin do not show an intimate microscopic contact with dentin when placed directly into the cavity. In order to overcome this, an intervening layer of fluid is used, which fills in the microscopic space, polymerizes and combines with the composite resin and components of dentin and thereby reducing microleakage.

The history of dental adhesives started as early as 1949, when Dr. Hagger, a Swiss chemist who patented a —Cavity Seall material (glycerolphosphoric acid dimethacrylate) used in combination with the chemically curing resin —Sevritonl, in 1951. Only dentin was initial substrate for bonding not the enamel. In 1952, it was postulated by Mclean and Kramer, that this material, —Sevriton Cavity Seall, chemically bonded to tooth structure. [1]

<table>
<thead>
<tr>
<th>Decade</th>
<th>Bonding agent introduced</th>
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<tbody>
<tr>
<td>1960s</td>
<td>First generation</td>
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<td>Sixth generation</td>
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<td>Early 2000s</td>
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<td>Eight generation</td>
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<td>2011</td>
<td>Universal bonding agent</td>
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**BONDING TO ENAMEL**

Enamel etching transforms the smooth enamel surface into an irregular surface with a high surface free energy (72 dynes/cm), more than twice that of unetched enamel. An unfilled or filled liquid acrylic (hydrophobic) resin with low viscosity wets the high energy surface and is drawn into the micro porosities by capillary attraction. After light curing, the bond between enamel and the restorative material is established by polymerization of monomers inside the microporosities and by copolymerization of remaining carbon – carbon double bonds with the matrix phase of the resin composite. Producing strong chemical bonds.

**BONDING TO CEMENTUM**

Very limited information exists on cementum-bonded restorations. [2] Treatment of intact and periodontitis-affected cementum with acidic (citric acid of pH:1, 37% phosphoric acid of pH:1) and neutral (24% EDTA pH:7) conditioners revealed a higher demineralization capacity of the EDTA solution on both substrates. Based on these findings, mechanical removal of the superficial layer of the exposed cementum prior to any periodontal regenerative treatment has been advised. This treatment mode may be applied to improve adhesive bonding as well. [Van Dijken et al]

X-ray photoelectron spectroscopy showed a strong reduction in the Ca/C ratio of intact cementum surfaces compared with smear-layer covered dentin surfaces (0.07 vs 0.43). These results imply that organic material predominates on the outmost cementum surface. Treatment of intact cementum surface with 17% EDTA (pH:7.4) further reduced the Ca/C (0.05) and the Ca/P (1.08) ratios due to demineralization. [3,4]

Also the arrangement of collagen fibers in cementum is much more irregular than dentin which restrict the proper infiltration of monomer into etched cementum, which compromises the bond strength. It seems that after demineralization the increased intrinsic fibril content of intact cementum surface creates an organic network that lacks the cohesive strength of demineralized dentin collagen, and although it is reinforced by resin infiltration. Bond strength to cementum is 0-35 Mpa. [5]

Traditional three-step multicomponent adhesives provided surface and interfacial characteristics of intact cementum more compatible with conventional dentin hybridization [6].

According to Okada H et al (2009) – the Micro shear bond strength to cementum are:

- 26.7 Mpa – Clearfil Tri S Bond
- 22.4 Mpa – G-Bond
- 35 Mpa – Clearfil AL
- 32.5 Mpa – Adper Single Bond

Bonding to dentin

*Definition of dentin bonding agents* -

Difunctional or multifunctional organic molecules that contain reactive group which interacts with dentin and the monomer of the restorative resin. [7,8]

*The Dentin bonding agents are classified as follows:*  
1. Based on generations  
2. Based on etching pattern  
3. Based on the treatment of smear layer
Classification-based on generation

Classification based on the treatment of smear layer
1. Smear layer modifying DBA, 2. Smear layer removing DBA, 3. Smear layer dissolving DBA

Classification based on etching pattern –
1. No etch adhesive
2. Total etch adhesive (etch & rinse adhesive)
3. Self etch adhesive,
   • 2 step self adhesives- e.g. Sixth generation DBA
   • 1 step self adhesives DBA e.g. Seventh generation DBA

Classification of adhesives based on type of solvent of primer or combined primer/adhesive resin:

<table>
<thead>
<tr>
<th>Solvent type</th>
<th>Example</th>
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<tbody>
<tr>
<td>Acetone</td>
<td>ABC Enhanced, EG Bond</td>
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<tr>
<td>Acetone and Water</td>
<td>AQ Bond</td>
</tr>
<tr>
<td>Water</td>
<td>ART Bond, Clearfil SE</td>
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<tr>
<td>Ethanol and water</td>
<td>Gluma</td>
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<tr>
<td>Ethanol</td>
<td>Excite, PQI</td>
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<td>Acetone and Ethanol</td>
<td>All-Bond 2</td>
</tr>
</tbody>
</table>

**COMPONENT OF BONDING SYSTEM OF COMPOSITE RESIN**
1. Etchants or conditioner
2. Primers
3. Adhesives
4. Initiators and accelerators
5. Fillers
6. Other ingredients

Etchants
Dr. Michael Buonocore (1955) made one of the important, advance in adhesive dentistry, by demonstrating that acid etching of enamel led to improve resin-enamel bond. He knew that concentrated (85 wt%) phosphoric acid was used in industry to pre-treat metal surfaces prior to painting or resin coating, thus, it was logical for him to use 85% phosphoric acid for 30 s to etch enamel followed by water rinsing. At that time, the presence of the smear layer was not known. However, Dr. Michael Buonocore (1955) knew that acid-etching removed something that interfered with good resin-enamel bonds.

Many researchers regarded Dr. Buonocore’s approach as unconventional at that time but over the next ten years, many investigators confirmed the utility of acid-etching enamel to increase resin-enamel bond strengths. The concentration of the phosphoric acid was subsequently reduced to 50% and then to 37%.
Etchant are chemicals used to etch enamel and dentin to make their surface more reactive. Enamel and Dentin both can be etched. Acid etching removes about 10 um of the enamel surface and creates a microporous layer from 5-50um deep.

**Enamel etching**
- Phosphoric acid is used in concentration of 37%.
- The etching time is 15 seconds.
- Placement done by a syringe or brush.
- Rinsing is done for 5-10 seconds with continuous water spray.
- On drying the enamel surface appears frosty and white.

ORGANIC (e.g Malie acid, Tartaric acid, Citric acid 10%, EDTA 0.1%, Acidic monomers)
- Polymeric (e.g. Polyacrylic acid 40%), Mineral acids (e.g. Phosphoric acid 37%, Hydrochloric acid, Nitric acid 10%, Hydrofluoric acid 10-16%)

Amongst the various agents that have been used as an etchant, phosphoric acid is the most commonly used acid at concentrations between 30 to 50 %, with 37 % concentration being the most accepted. At concentration > 50% formation of a layer of monocalcium phosphate monohydrate on etched surface which prevents any further dissolution.

Whereas <30% forms a precipitate of dicalcium phosphate dihydrate that can not be easily removed.

**Primers**
Primers are solutions containing hydrophilic monomer molecules dissolved in a solvent having surface tension less than the surface energy of the acid etched dentin. Monomers used are
1. HEMA (2-hydroxyethyl methacrylate)
2. NPG-GMA (N-phenyl-glycin-glycidyl methacrylate)
3. PMDM (pyromellitic dianhydride)
4. PENTA (Dipenta erythritol penta acrylate monophosphate)
5. 4-MET (4-methacryloyloxyethyl trimellitic acid)
6. 4-META (4-methacryloyloxyethyl trimellitic anhydride)
7. 4-AETA (4-acryloyloxyethyl trimellitic anhydride)
8. 10-MDP (10-methacryloxydecyl dihydrogen phosphate)
9. Phenyl-P etc.

Such monomers exhibit hydrophilic properties through phosphate, carboxylic acid, alcohol, or ester functional groups.

HEMA is a widely used primer monomer because of its high hydrophilicity and solvent like nature. It has 6.79 cps(Centiposes) viscosity at 20°C.

The rank of functional groups in their acidity is as follows:
- Sulphonic acid > phosphonic acid > phosphoric > carboxylic > alcohol
- Acidic primers containing carboxylic acid groups are used in self etching bonding agents
Solvents
Primers and/or adhesive resins tends to have a low viscosity, which is partly due to the dissolution of the monomers in a solvent which improves their diffusion ability in the micro-retentive tooth surface. Most commonly used solvents are:
1. Ethanol
2. Water
3. Acetone
4. ADHESIVES

Adhesives need to be hydrophobic so that fluid will not be allowed to permeate through the intermediate layer. At the same time adhesives require a certain hydrophilicity to defuse into the hydrophilic, primer –wetted dentin. Generally, adhesive resins are composed mainly of hydrophobic dimethacrylates e.g. Bis-GMA, TEGDMA, UDMA, and a small amount of a hydrophilic monomer such as HEMA.

Initiators
Polymerization can be initiated either through a photo initiator system consisting of a
1. Photosensitizer (e.g. camphoroquinone) in light cure system.
2. Chemical initiator (e.g. benzoyl peroxide, acetyl peroxide, lauroyl peroxide) in self cure system. Initiators may be about 1-2 wt% or less.

Fillers
The aim of filler addition to dentin adhesives are to -
1. Increase the mechanical properties and elastic modulus of adhesive.
2. Improve the distribution of the stresses induced by resin composite polymerization shrinkage and occlusal loading.
3. Incorporation of nanofiller particles to experimental adhesive system increased the micro tensile bond strength to dentin layer.

According to Kasraei et al. Incorporation of silica nanofiller increased bond strength to a certain degree. The optimum level of nanofillers to obtain maximum bond strength influenced by content, size, shape, and hydrophilicity of fillers. Kim et al showed that the maximum micro tensile bond strength is obtained at 1.0 weight percent fumed silica nanofiller with average particle size of 12 nm.[9]

Marketed nanofilled DBA’s. E.g.-
• Prime and bond NT (7nm fillers)
• Excite (12nm fillers)

Other ingredients
Sometimes additional ingredients are used with dentin bonding agents for a variety of purposes
• Glutaraldehyde –desensitizer
• 12-methacryloyloxydodecylpyridinium bromide (MDPB) and paraben—antimicrobials
• Fluorides—prevent secondary caries
• Benzalkonium chloride—prevent collagen degradation by prevent the action of matrix metalloproteinase enzymes which is responsible for denaturation of hybrid layer collagen.

DISCUSSION ABOUT THE BONDING AGENT BASED ON GENERATION
The concept of generation was used because of the complexity of bonding agents, the variety of classifications refers to when and in what order this type of adhesive was developed by the
dental industry. Each generation has attempted to reduce the number of bottles involved in the process, to minimize the number of procedural steps, to provide faster application techniques and to offer improved chemistry to facilitate stronger bonding.

First generation dentin bonding agents
The development of NPG-GMA (N-phenyl glycin-glycidyl methacrylate), a surface active co monomer was the basis of the first commercially available dentin bonding agent, Cervident(SS White). But the bond strengths produced by this agent were very low. Clinically, this agent did not successfully bond composite resins to dentin.

Theoretically, NPG-GMA was supposed to chelate with the calcium in dentin to form a water resistant chemical bond to dentin.

Second generation dentin bonding agents
Most of these agents were phenyl phosphorus, phosphorus, chlorophosphorus esters of unfilled resins such as BisGMA or HEMA.

The bonding mechanism involved improved wetting of surface and ionic interaction between the phosphate group and calcium of the tooth. Examples : Clearfil bond( solvent :ethyl alcohol solution),Scotchbond,Bondlite,Prisma Universal bond

Drawbacks in the first and second generation dba
1. Lack of adequate bond strength (only 2-3Mpa)that could overcome contraction stresses during polymerization.
2. Being hydrophobic in nature, close adaptation to the hydrophilic dentin could not be achieved.
3. Also lack of sufficient knowledge about the presence and nature of smear layer.

In 1975 McComb and Smith first described the smear layer using a scanning electron microscope. According to American Association of Endodontics (AAE): It is defined as a surface film of debris retained on dentin or other tooth surface like enamel, cementum after instrumentation with either rotary instruments or endodontic files. To obtain satisfactory bonding, the tooth surface should be treated to obtain a clean bonding substrate. Two strategies used to overcome low attachment strength of smear layer: 1. Removal of smear layer prior to bonding. 2. Use of bonding agents that can penetrate it and incorporate it into bonding layer. After removal of smear layer with an acid, dentinal permeability through the tubules increases more than 90%.

Third generation dentin bonding agents
These systems either modified or removed the smear layer to allow resin penetration into the underlying dentin.

• Etchants or conditioner
• Primers
• Adhesives

Definition of dentin conditioning: 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
• Modifications in organic matter.
• Decalcification of inorganic portion


The bond strength to dentin with these agents were usually higher (9-15MPa) and more durable thereby reducing microleakage. Examples:
• Scotchbond 2 (3M),
• Gluma (Heraeus Kulker Dental Products, South Bend, IN)
• Tenure (Den-Mat Corporation, Santa Maria, CA)
• Prisma Universal Bond 3 (Dentsply Caulk, Milford, DE)
• Syntac (Ivoclar Vivadent, Amherst, NY), and
• XR-Bond (Kerr)

Tenure was the first commercial oxalate bonding system, which utilized phosphoric acid in conjunction with aluminium oxalate and nitric acid as a dental conditioner. Mirage bond utilized conditioner of NPG (N-Phenyl glycine)+ 2.5% nitric acid followed by application of PMDM(Pyromellitic dianhydride). Dentin bond strength achieved was 10.9 Mpa.

Fourth generation dentin bonding agent
Fourth generation of dentin bonding systems appeared in the early 1990s and is still widely used. Most of these systems are based on the "total-etch" technique, or simultaneous etching of enamel and dentin, typically with phosphoric acid. Total etching and moist dentin bonding, concepts developed by Fusayama and Nakabayashi in Japan in the 1980s,and popularized by Kanca, are innovative hallmarks of the fourth generation adhesives.

When primer and bonding resins are applied to etched dentin, they penetrate the intertubular dentin, forming a resin-dentin interdiffusion zone, or —hybrid layer. This transforms the surface from a crystalline, acid sensitive, relatively hydrophilic structure, to an organic, acid-resistant, relatively hydrophobic layer. [Nakabayashi et al. 1982 ].The ultrastructure of dentin hybrid layers was first described by Van Meerbeek et al. and by Tay et al.

The bonding mechanism of the fourth-generation adhesive systems is a three-step process: (1) Etching, (2) prime, and (3) bond.

Examples include
1. All-Bond 2 (Bisco, Inc., Schaumburg, IL), Amalgambond (Parkell, Farmingdale, NY), Clearfil Liner Bond (Kuraray/J. Morita USA, Inc., Tustin, CA), EBS (ESPE America, Norristown, PA), OptiBond (Kerr), ProBond (Dentsply Caulk), Scotchbond Multi-Purpose Plus (3M).

Advantages of fourth generation dba
1. Many investigators have reported shear bond strengths for these materials that approach or exceed the typical enamel bond strength of 25 Mpa.
2. In addition, microleakage studies indicate that they provide a better marginal seal than earlier generations of adhesives.
**Drawbacks in the fourth generation dba**

1. Technique sensitive, requires post conditioning rinse, so risk of contamination.
2. Risk of over-wetting and over-drying.
3. Risk of over etching the dentin.
4. High degree of post operative sensitivity

Kanca discovered that if one left some residual water in acid-etched dentin, bond strengths could be doubled. Gwinnett revealed that wet bonding created thicker hybrid layers (i.e. more resin uptake into etched surfaces) than did dry bonding. Dry Bonding refers to the bonding in which the acid etched dentin is dry and uses the adhesive systems that provide water based primers.

- Too much water would rapidly re-expand the collagen network but would also dilute the monomer concentration.
- 35-50% HEMA in water provided the maximum bond strength.
- Water in these primers probably plasticized the stiffened, collapsed collagen network so that it reexpanded and increased its permeability to primer resins.

If the residual water in between collagen fibril is evaporated by air-drying, the collagen fibril network collapses into a relatively impermeable organic film that interferes with resin-infiltration.

Resin tags could still be formed, and gave some resin retention, but hybridization of the dentin between tubules (i.e. intertubular dentin) could not occur. Ineffective penetration due to collagen collapse has been observed ultra morphologically as a formation of a so called Hybridoid zone. The water often diffuses into the organic solvents so fast that the monomers can no longer remain dissolved in the solvents. They undergo phase changes that can lead to low bond strengths due to the formation of resin globules and poor resin tag formation, often permitting postoperative sensitivity. The number of mixing steps and the requirement for exact component measurements tend to confuse the process involved in Fourth Generation DBA. This led to the development and the great popularity of the fifth-generation dental adhesive.

**Fifth generation dentin bonding agents**

Uses two steps, i.e. Total etching + Application of primer and bonding agent. (Primer + Bonding agent are available in single bottle)

Examples are:
Prime & Bond, Opti Bond Solo, Single Bond

**Advantages**
1. Bond strength is sufficient (20 to 25 Mpa).
2. Simpler application procedure.
3. Post operative sensitivity is much less.
4. Some agents have incorporate fluoride.
5. Time saving and simple to use.

**Disadvantages**
1. Technique sensitive, requires post conditioning rinse.
2. Risk of over-wetting and over-drying.
Sixth generation dentin bonding agent
Researchers have thought to eliminate the etching step, or to include it chemically in one of the steps. The sixth-generation adhesives require no etching, at least at the dentinal surface.
Self-etching primer + adhesive:

Available in two bottles:
Primer and Adhesive

_Sixth generation dentin bonding agents are of two types_
Type 1
Type 2
Type 1–First liquid 1 (primer) applied to tooth surface followed by liquid2 (Adhesives).

Examples:
Clearfil SE Bond, AdheSE (Ivoclar Vivadent)
Type 2- Here both the liquid mixed first then that mixture will apply to the tooth surface.
Examples:
Xeno III, Prompt L PoP (3M), Brush and Bond F (Parkell)

_Advantages_
1. No need to acid etch with phosphoric acid.
2. No post conditioning rinsing required.
3. Reduced post-operative sensitivity
4. Less sensitive to degree of wetness and dryness.
5. Low technique sensitivity.

_Disadvantages_
1. Less effective bonding of enamel.
2. Initial bond might deteriorates with aging, which could lead to premature failure.

Seventh generation dentin bonding agent
All in one concept, i.e. components available as single component. Uses self etch primer. Same objective as the sixth generation systems except that they simplified the multiple sixth generation materials into a single component, single bottle one-step self-etch adhesive, thus avoiding any mistakes in mixing. Both the sixth and seventh generation adhesives are self etching, self priming adhesives which are minimum technique sensitive. The seventh generation DBAs have shown very little or no postoperative sensitivity. Examples are: I-Bond G-Bond Xeno IV etc.

_Advantages_
1. One-step procedure, no mixing or rinsing the tooth
2. Less postoperative sensitivity
3. Tolerant to moist or dry environments

_Disadvantages_
1. Some need refrigeration.
2. Decreased shelf life due to acidic formulation.
Eight generation dentin bonding agents
The number of parts in adhesive systems has been reduced over the years but performance has suffered as well. It was decided that a new system would be developed that had the best attributes of the fourth generation and the ease of the sixth-generation bonding systems, and that system is Eight Generation Dentin Bonding System. It is also Dual cure system. It consists of three bottles: an etchant/conditioner, a primer, and a separate hydrophobic bonding resin. In that regard, it resembles fourth-generation materials but the etchant/conditioner is not rinsed from the tooth. Thus, it also has characteristics of the sixth generation—the ease of a no-rinse system but the performance of a fourth-generation system Example : 1. Surpass 2. Futurabond DC Eight Generation Dentin Bonding system shows a dentin bond strength near about mid-50 MPa range according to University of North Carolina, Tufts University, and other testing institutions.

UNIVERSAL ADHESIVE
Universal adhesives introduced in 2011 have been described by some manufacturers as: ideally a single-bottle, no-mix, adhesive system that can be used in total-etch, self-etch, or selective-etch mode depending on the specific clinical situation and personal preferences of the operator. Also known as multi mode or multi purpose adhesive .It Contains the acidulated monomer MDP, which has proven to create excellent adhesion to enamel, greater product stability, and significant adhesion to metal and zirconium oxide.

Composition of universal adhesive
Matrix of universal is based on a combination of
1. Hydrophilic monomers (hydroxyethyl methacrylate /HEMA) hydrophobic (decandiol dimethacrylate /D3MA) and intermediate (bis-GMA) nature.
2. Methacryloyloxydecyl Dihydrogen phosphate (MDP) – is hydrophilic ,with mild etching property
3. Biphenyl dimethacrylate (BPDM),
4. Dipentaerythritol penta acrylate phosphoric acid ester (PENTA)
5. Polyalkenoic acid copolymer

Features of universal adhesive
1. The 10-MDP adhesive functional monomer have many positive attributes, including the potential to bond chemically to metals, zirconia, and to tooth tissues through the formation of non-soluble Ca++ salts.
2. Copolymerize with chemically compatible resin-based restoratives and cements
3.Its Hydrophilic characteristics properly —wet dentin, & at the same time be as hydrophobic to discourage hydrolysis and water sorption over time.
4. Film thickness of the polymerized adhesive is thin enough so not interfere with the seating of indirect restorations.
5. Acidic enough to be effective in a self-etching mode but not so acidic that they breakdown initiators needed for the polymerization of self- and dual-cure resin cements.
6. Contain water, as it is required for dissociation of the acidic functional monomers, inherent in all these systems, that makes self-etching possible.

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<tr>
<th>S.N</th>
<th>AUTHOR</th>
<th>INTERPRETATION</th>
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<tbody>
<tr>
<td>1</td>
<td>Loguerico et al(2015)</td>
<td>Concluded that selective enamel etching with phosphoric acid might not be crucial for universal bonding agent adhesion to enamel.</td>
</tr>
<tr>
<td>3</td>
<td>Takamizawa et al (2016)</td>
<td>Prime and Bond Elet(Dentsply: Milford DE, USA) performed better in total etch mode, whereas SBU (3M) and All-Bond Universal(Bisco Inc, Schaumburg, IL, USA) did not show a difference in performance in either</td>
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CONCLUSION
To satisfy the growing esthetic demands of today’s dental patients, improvements in materials and procedures have been made to make it possible to reproduce the natural appearance of natural teeth with direct and/or indirect esthetic restorations. Esthetic techniques involve a bonding step to ensure durability and reliability. Although important improvements in bonding have been made in the last 30 years, note that the requirements of an ideal bonding system are quite similar to those indicated by Buonocore. Apparently, the future has a sound background in the past.

REFERENCES
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