Adhesive Bonding of Natural Stone

Section I: Basics of Stone Adhesion

Adhesive Theory

There are many theories concerning the forces that are at work in forming an adhesive bond between two (2) different substrates (in this case, natural stone and the adhesive). Most experts agree that the strength of an adhesive joint is determined by both a mechanical and chemical interaction between the adhesive and adherend.

A mechanical interaction appears to be a prime factor in bonding porous materials like limestone and most marbles. The surface of most materials is never truly smooth, but rather consists of a maze of microscopic peaks and valleys. If the adhesive is able to penetrate the open spaces of the substrate, known as wetting, and displace the air that is present, a mechanical bond is formed. The adhesive must fully wet the natural stone it is bonding in order to form a solid mechanical joint.

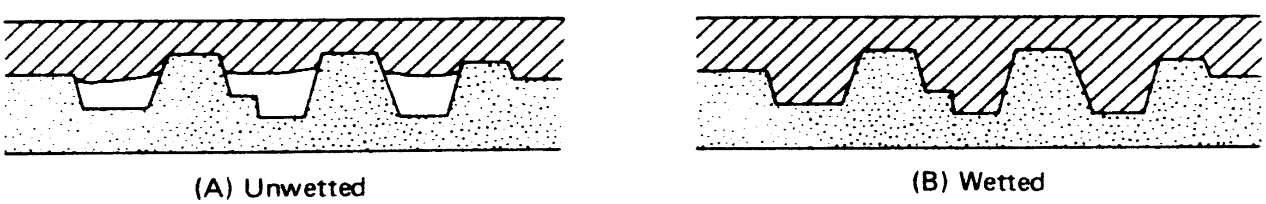

Figure 1: Visual schematic of adhesive wetting of substrates

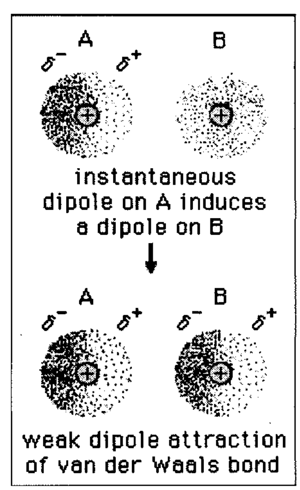

Figure 2: Van der Waals bonding

In joining extremely dense or non-porous materials like granite, the chemical interaction between the adhesive and the substrate becomes much more important than the mechanical interaction. The chemical interactions that dominate when bonding natural stone are based upon the adsorption theory and can be attributed to Van der Waals bonds. Similar to the phenomena of hydrogen bonding, Van der Waals bonds are secondary bonds (ionic, covalent, and metallic bond being considered primary bonds) that cause otherwise neutral molecules to be attracted to one another. As shown in Figure 3, some molecules exhibit stronger

Van der Waals bonding characteristics and adhesive formulations that contain a high concentration of these molecules tend to exhibit the strongest adhesive bonding strengths.

GROUP	STRUCTURE	VAN DER WAALS ATTRACTION
Organic acid	—C(=O)—OH	High
Nitrile	—C≡N	High
Amidc	—N(H)—C(=O)—	High
Hydroxyl	—OH	Medium
Ester	—O—C(=O)—	Medium
Acetate	—O—C(=O)—CH_3	Medium
Chloride	—C(Cl)(H)—	Medium
Ether	—C(H)(H)—O—	Low
Ethylene	—C(H)(H)—C(H)(H)—	Low

Figure 3: Van der Waals Bonding Attraction for Functional Groups

The chemical attraction created by Van der Waals bonding is dependent upon the adhesive and substrate being in close proximity to one another. Therefore, good wetting is essential for both the mechanical and chemical interactions to be effective.

Bonding Criteria for Natural Stone

The three (3) types of natural stone used in the majority of bonded stone applications are marble, limestone, and granite. Limestone and most marbles are considered porous materials and are generally easy to bond with many different types of adhesives. Granite and some marbles (especially green marbles) are much denser and considered to be non-porous materials. While a mechanical type of bond is normally sufficient for marble and limestone joints, granite and dense marbles require an adhesive capable of forming a strong chemical interaction in order to create an effective adhesive bond.

The success or failure of any stone lamination or repair is also dependent on the surface condition of the stone to be bonded. Water, oils, dust, and dirt can have a severe detrimental impact on the strength of both the mechanical and chemical interactions. These contaminants make wetting of the stone by the adhesive much more difficult and therefore greatly reduce the ability of the adhesive to mechanically bond to the stone. In addition, they interfere with the creation of Van der Waals bonds and thereby reduce the chemical interaction as well.

Abrading the stone prior to cleaning will significantly improve the strength of the bond by increasing surface area for mechanical interactions and by making the stone more receptive to chemical interactions. It should be noted, however, that this roughening of the stone surface should not be taken to an extreme. Uneven surfaces do not have the ability to form chemical interactions as effectively as even surfaces.

Section II: Adhesive Types

Three (3) types of adhesives are generally used for bonding natural stone. They are chemically classed as: 1) Polyesters, 2) Acrylics, and 3) Epoxies. Each has advantages and disadvantages for the stone worker.

Polyesters

A typical polyester system consists of polyester resin and styrene. When a benzoyl peroxide paste is added to this mixture, the polyester resin and styrene react to form a cured solid. They are fast reacting (generally curing in less than 30 minutes) and simple to use as the benzoyl peroxide paste can be added at a concentration of 2%-5% by weight without drastically altering the final properties of the bond. The cured product does contain some ester groups that provide the basis for a chemical interaction with the stone, but these groups are fairly shielded and in small concentrations. Therefore, polyesters will not normally exhibit strong chemical interactions and work mostly by establishing a mechanical bond. Since they are also subject to high shrinkage (roughly 1%-2%), stress is built up in the bond line during curing thus weakening the mechanical bond as well. In general,

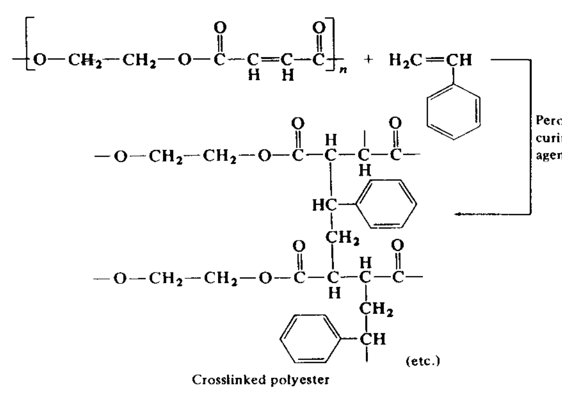

Figure 4: Polyester Reaction Scheme

polyesters should be restricted to use with porous materials like limestone and marble (some granites are also porous enough with proper surface preparation) where a fairly strong mechanical interaction can be developed between the adhesive and the stone. Price is the most common reason for polyester use as a typical polyester system costs roughly $10-$15 per quart depending on the curing properties. Unlike the other adhesive types, polyesters are subject to air interference during the cure and can exhibit a surface tack in some cases. This fact can pose problems during fabrication (grinding and polishing) of the stone after bonding if the polyester system has not been formulated to overcome the surface tack phenomena.

Acrylics

The acrylic type of adhesive, although similar to the polyesters in handling properties and cure speed, is based on a very different chemistry and therefore provides overall properties that are superior to polyesters. The acrylics also are cured using benzoyl peroxide (typically 1%-3%), but a polymerization reaction takes place rather than a cross-linking reaction. This results in each individual unit of the acrylic resin being bonded to the next in long chains. Since each acrylic unit contains an ester group, the acrylics are believed to show a much stronger chemical interaction with natural stone. Due to this fact, acrylics have shown the ability to bond even the densest granites with excellent success, even though they exhibit a fairly high shrinkage rate (also roughly 1%-2%). In addition, they have excellent weatherability, are UV stable, and are generally water clear in appearance. Since they can be formulated in a full range of viscosities (water thin to thick paste), they are excellent for nearly any application. Price is generally the limiting factor with acrylic use as a quart typically costs $25-$30.

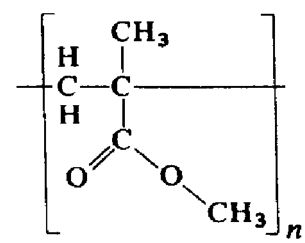

Figure 5: Typical Acrylic Resin Chain (Poly Methyl Methacrylate)

Epoxies

Completely different from either of the other two (2) adhesive types, epoxy systems have demonstrated the best overall bonding characteristics with natural stone. Most epoxy systems used with stone are based upon a reaction between an epoxy resin and a modified amine hardener. Unlike a polyester or acrylic, the reactive ingredients of an epoxy system are kept in separate containers until they are mixed for use. Although the ratios of resin to hardener (typically 2:1 or 1:1) can vary depending upon the product formulation, the mix ratio must be carefully followed to ensure a full cure and a good bond. If the ratio is off by more than 10%, a severe drop off in adhesive properties becomes evident. When used properly, epoxies provide the strongest bonds to natural stone due to very high concentrations of hydroxyl groups

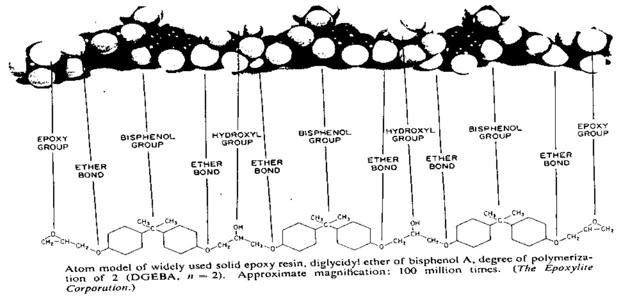

Figure 6: Standard Epoxy Resin

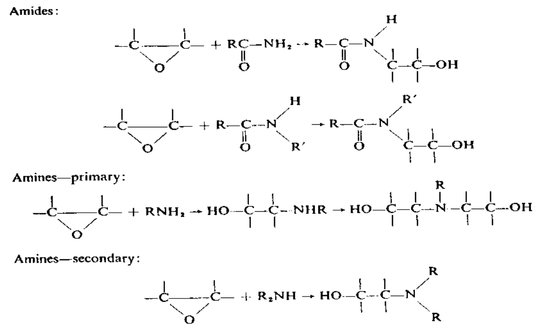

Figure 7: Typical Epoxy Reaction Schemes

available to establish a strong chemical interaction. In addition, they normally exhibit very little shrinkage during cure and therefore maintain a very good mechanical bond as well. Like the acrylics they provide good weatherability, although they are not truly UV stable and will normally chalk and discolor when exposed to sunlight. A relatively long curing time (3-8 hours) is the main disadvantage to using an epoxy system. Even the fastest setting systems do not approach the speed of either a polyester or acrylic. For this reason, epoxy usage is much less prevalent for fabrication applications. They provide the best overall properties, however, for structural applications outdoors. They range in cost from $15/quart to $25/quart, and are available in both flowing and paste consistencies.