have complex compositions and application protocols which make dentin bonding an extremely technique-sensitive dental procedure.

SUMMARY OF THE INVENTION

An object of this invention is a more effective, simpler dentin bonding system based on the use of a special type of unsaturated amino acid. Another object of the present invention is providing a bonding system that includes a single composition dentin conditioner or etchant and a dentin primer. Yet another object of the present invention is the provision of a bonding system that includes both self-etching and radical-initiating properties in a single chemical agent.

The present invention is directed to a simple, effective method for bonding, preferably to mineralized dental tissue, such as enamel and dentin, which requires fewer steps, is less technique-sensitive than prior procedures, by virtue of less complex compositions and application protocols.

The present invention is directed to a composition suitable for preparing a substrate, such as skeletal tissue, particularly a tooth surface and most particularly, dentin, for subsequent adhesive bonding thereto. The compositions provide both a conditioning and priming function. In addition, these compositions provide self-etching and radical-initiating properties such that they eliminate the need for the use of a separate dentin conditioner and a primer and in many instances eliminate the need for a separate polymerization initiator and/or activator. Thus, the same composition may serve the dual functions of etchant and primer, and in many situations, may serve as a combined etchant, primer and initiator. The use of the methods according to the present invention reduces what is typically a 3 or 4 step procedure of preparing for and applying an adhesive used for preparing enamel and, particularly, dentin surfaces in current dental practice to a simple 1 or 2 step procedure.

The agent employed in the compositions of the present invention, a preferred type of amino acid, described below, has the ability in aqueous or water-containing solutions to both cleanse and activate a substrate surface, for example the surface of dentin, in a single step for subsequent bonding to resin-based materials. The agent employed in these compositions is a derivative of iminodiacetic acid and salts thereof. The "conditioning" and "priming" (or cleansing and activating) agent of the present invention has the general formula:

$$RN(CH_2YCO_2M)_2 \quad (I)$$

wherein $R=R^1$ or R^2;

R^1=an aromatic group;

R^2=a conjugated aliphatic group;

Y=a single bond, CH_2, $CHCH_3$ or $C{=}CH_2$; and

each M is independently H, an alkali metal, an alkaline earth metal, aluminum, a transition or redox metal or an alkyl group having 1 to 18 carbon atoms, with the proviso that when both M groups are alkyl groups, the compound corresponding to formula I be capable of being easily hydrolyzed or displaced with other reagents present in the etchant/primer composition.

These agents are dissolved in water or other polar solvents or mixed aqueous solvents, for example, low molecular weight ketones, such as acetone, or alcohols, such as ethanol and aqueous solutions thereof.

The present invention also includes two component kits including the aforementioned amino acid etchant and primer agent and an appropriate monomer system, each in an appropriate solvent.

It may be noted that the multi-step bonding protocols, typical of current commercial adhesive systems, generally tend to be a source of material waste and unreasonable technique sensitivity. The amino acid etchant/primer agents of the present invention not only reduce the number of steps normally involved in preparing a substrate surface and applying the adhesive monomer system thereto from 3 or 4 steps to 1 or 2 steps, but less waste and improved restorative or sealant results are obtained. Thus, although conventional aggressive etchants are effective in cleaning the surface of dentin for improved wetting by and diffusion of the components of the adhesive system, they can also weaken the underlying sound dentin by excessive demineralization and disruption of collagen fibrils. These types of etchants typically require an aqueous rinse step to remove residual acid and soluble by-products. Also, the depth of demineralized altered dentin resulting from the use of aggressive etchants may exceed the depth to which an adhesive resin can penetrate the dentin, resulting in a weakened, partially reinforced hybrid dentin zone, and thereby become vulnerable to failure. In contrast, the amino acid agents and solvent systems of the present invention are milder and may be used as single step etchant and primer compositions without subsequent rinsing since they are also effective in the presence of water and/or aqueous solvents. Furthermore, these amino acids demonstrate the ability to act as a free-radical initiator(s) for the types of adhesive monomer systems currently used as dental adhesives. Accordingly, while an aqueous rinse step, such as the type used with multi-step systems to remove residual acid and soluble by-products, may be used, it is unnecessary to employ such a rinse step. In addition, since the amino acid etchant/primer agents of the present invention are effective as free-radical initiators, they may, in fact, be combined with the adhesive monomer system immediately prior to application.

Several methods based on the properties of the etchant/primer compositions of the present invention provide for the preparation of a substrate surface, such as a dentin surface, for subsequent adhesion thereto, one of the methods including the formation of an adhesive bond thereto. Thus, one embodiment involves contacting the substrate surface with the etchant/primer composition of the present invention. Thereafter, either with or without a rinsing step with water, a conventional adhesive composition, typically including a free-radical initiator, may be applied thereto. After subsequent curing, a strong adhesive bond to the substrate is obtained. Such a method involves 2 basic steps, not including a rinsing step.

A strong adhesive bond to a substrate, such as dentin, may also be achieved according to another embodiment of the present invention in a single step. Thus, since the etchant/primer compositions of the present invention function not only to cleanse and condition the surface of a substrate, to a depth from about 1 to 5 microns, but also function as an initiator, for most adhesive monomers used to form an adhesive bond to a substrate surface, such as a dentin surface, it is unnecessary to include a separate initiator or accelerator. Accordingly, the etchant/primer composition of the present invention may be combined with an adhesive monomer system to form an etchant/primer/adhesive monomer system in a single composition. With this embodiment, rather than the 3 or 4 steps typically used to etch, prime and form an adhesive bond to a substrate surface, the etchant/primer/adhesive monomer system may be applied to the substrate by combining an etchant/primer composition