Title: COMPOSITIONS CONTAINING POLYVINYL PYRROLIDONE FOR TREATING DENTAL PULP AND FILLING ROOT CANALS

Abstract: Improved compositions for treating dental pulp and root canals comprising a mixture of particulate materials with water-based liquids containing polyvinyl pyrrolidone are provided. Homopolymers and copolymers of polyvinyl pyrrolidone can be used. Optionally, the composition may contain surfactants, humectants, stabilizers, and other additives. Examples of particulate powders include mixtures of calcium silicate, calcium aluminate, calcium sulfate, and hydroxyapatite. The compositions are particularly suitable for sealing and obturating dental root canals and root apices. The composition provides a stable barrier to bacterial and fluid leakage in the root canal system of a tooth.
COMPOSITIONS CONTAINING POLYVINYL PYRROLIDONE FOR TREATING DENTAL PULP AND FILLING ROOT CANALS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 60/900,475 having a filing date of February 9, 2007, the entire contents of which are hereby incorporated by reference.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] The present invention relates generally to improved dental compositions for treating the pulp and root canals in a tooth. The compositions contain a mixture of particulate materials such as calcium silicate, calcium aluminate, calcium hydroxide, and hydroxyapatite; and the water-soluble polymeric material, polyvinyl pyrrolidone.

Brief Description of the Related Art

[0003] The inner portion of a tooth includes a pulp cavity that contains soft living tissue or the “pulp” of the tooth. The pulp includes connective tissue, blood vessels, cells, and nerve endings. The pulp cavity comprises an upper pulp chamber and root canals that extend to the apex or apical section of the tooth deeper into the jaw. The outer (visible) portion of the tooth is referred to as the crown and has a covering of enamel. The hard enamel protects softer dentinal tissues in the upper portion of the tooth. The enamel
consists of a hard, calcium-based substance, hydroxyfluorapatite. The dentin tissue contains a matrix of minute hydroxyapatite tubules interspersed with collagen fibers that surround and protect the tooth pulp. The outer (non-visible) portion of the tooth root is covered with cementum, a thin hard tissue that joins the root to the surrounding bone through Sharpey’s fibers. Dental decay, or caries, is caused by bacteria accumulating on teeth and forming a biofilm (plaque). The biofilm produces acids that dissolve and weaken the hydroxyapatite of the tooth, thereby causing decay.

[0004] When dental caries are found in the enamel portion of a tooth, a dental professional will remove the caries to prevent further decay of the tooth. Then, the cavity is “filled” with a composite resinous material or amalgam filling. However, in some instances, the dental caries may be so deep that it penetrates to the dentin tissue. At this point, the bacteria and other microorganisms can migrate rapidly into the pulp tissue causing infection and inflammation. As a result, abscesses or inflammation may form in the pulp, and eventually in the periapical tissues surrounding the root apex. Provided that the dental disease is not too progressed, dental professionals will use root canal treatment procedures to remove the infected tissue from the tooth and replace it with an inert, biocompatible material. Otherwise, extraction of the tooth might be required.

[0005] The root canal system of a tooth is complex and many treatment methods can be used depending upon the condition of the patient and approach of the practitioner. In general, root canal treatment methods first involve drilling an opening in the crown of the tooth to provide access to the pulp cavity. Then, endodontic files are used to remove the pulp and clean and shape the root canals. The files are used with an irrigant. After using the files, an irrigant may be used to remove the smear layer created by the files. A sealer is coated on the wall of the root canals and then, the root canals are filled with a filling material. This sealing of the roots ideally prevents bacteria and other microorganisms from re-entering and causing infection of the living tissue surrounding the root tip. As a final step, the pulp chamber and opening in the crown of the tooth is sealed with a dental restoration such as a filling material. Preferably a permanent crown is placed over the opening in the tooth, such crowns being made of metal, porcelain-enamel metal, polymer-veneered metal, or ceramic. A post may be placed in the root for stability of the
crown, although this is usually done after the root canal procedure, and before the crown is made.

[0006] Some root canal treatment methods involve using portland cement to repair root defects such as iatrogenic perforations, or when apical surgery is performed to fill the root end. In general, portland cement contains a compound formed from calcia, silica, alumina, and iron oxide materials. Portland cement is commonly gray, but white versions, with lower iron content are known. The portland cement is combined with water to form a slurry-like composition that is introduced into the root canal defect. The composition solidifies to seal the canal. When portland cement materials are used to fill or seal the root canals, the cement particulates should have a small particle size. The fineness of a cement is represented by the surface area and one measurement thereof is the Blaine Number representing the ratio of the cement’s particle surface area to its weight (square centimeters of surface per gram).

[0007] Torabinejad et al., US Patents 5,769,738 and 5,415,547 describe using a portland cement composition having a Blaine number in the range of 4,000 to 5,500 cm$^2$/gram for various surgical and non-surgical root canal treatment procedures including sealing root canals, performing apicoectomies, and repairing root canal perforations. The '738 and '547 Patents disclose combining the portland cement with water to form a composition that is introduced into the root canal. There is no disclosure in the '738 and '547 Patents for making a composition containing water-soluble polymeric materials and portland cement.

[0008] In addition to portland cements, other biomedical cements have been developed for medical and dental applications. For example, Lu et al., US Patent Application Publication US 2007/0098811 discloses a biomedical cement containing at least one phosphate compound and at least one calcium silicate compound that does not contain any aluminum or magnesium compounds. Preferably, the cement contains 45 to 80 weight percent calcium oxide; 10 to 35 weight percent silica; and 1 to 30 weight percent phosphate. Hydroxyapatite can be added to form hydroxyapatite/calcium silicate hydrate
gel in situ at room temperature. Water-soluble polymeric materials are not added to the cement.

[0009] Kawahara et al., US Patent 4,647,600 discloses a dental cement that can be used for pulp-capping, base lining, root canal filling, and other applications. The composition is made of two parts. Part A comprises at least two powders - 100 parts by weight of a powder containing calcium oxide and alumina; and 2 to 70 parts by weight of calcium hydroxide powder. It is important that the powder particulates be surface-treated with organic and/or inorganic acids to increase the flowability of the particulate during mixing. Phosphoric acid, monobasic phosphates; pyrophosphoric acid, salicylic acid, various amino acids, myristic acid, and stearic acid can be mixed with the powder. Part B comprises an aqueous solution containing 0.01 to 70 wt.% of a water-soluble, high molecular weight substance that can be selected from many different polymeric materials including polyacrylic acid, sodium polyacrylate, polyvinyl alcohol, polyethylene glycol, polyethylene oxide, polyvinyl pyrrolidone, carboxymethyl cellulose, methyl cellulose, and hydroxyethyl cellulose.

[0010] Kawahara et al., US Patent 4,689,080 discloses a composition of alumina cement that can be used in dental pulp capping, root canal filling, sealing, alveolar bone reconstruction, and the like. According to the '080 Patent, the alumina cement is an industrial cement that can be mixed with other materials. The composition consists of: a) industrial calcium aluminate powder; b) calcium type powder hardening retarder such as calcium hydroxide, calcium chloride, or calcium oxide; and c) water-soluble polymer that can be selected from polyvinyl alcohol, polyvinyl pyrrolidone, gum arabic, acrylic acid, glycerine, sodium metasilicate, low-molecular fatty acid, and hydrophobic natural resin. A hardening retarder, preferably calcium hydroxide, must be added to the mixture. The calcium hardening retarder is added in a ratio of 1-20 parts by weight to 100 parts by weight of alumina cement powder.

[0011] Brothers et al., US Patent 5,454,867 discloses a dry, agglomerated cement material comprising portland cement particulate which is bonded together by a water-
soluble binder material. Examples of polymeric binder materials include: polyvinylpyrrolidone; polyvinylsulfonate; polyacrylic acid; polymethacrylic acid; poly 2-acrylamido-2-methylpropanesulfonic acid; polyacrylamide; polystyrenesulfonate; partially hydrolyzed polyvinylacetate; polyvinyl alcohol; copolymers thereof; and mixtures thereof. The cement material is made by fluidizing particles of the dry portland cement in a chamber by conducting gas through the chamber which causes the particles to separate and then introducing an aqueous solution (water/water-soluble binder) into the chamber. According to the '867 Patent, it is important that the agglomerated particulate has a surface area that does not exceed 0.300 m²/cc. The particles must be sufficiently agglomerated so that they can be used for industrial purposes.

[0012] Jefferies and Primus, PCT International Application Publication No. WO 2005/087178 discloses a polymer-infiltrated structure of calcium-based cement that can be potentially used as a pulp capping agent, root repair material, root canal sealer, and other clinical products. A self-etching/self-priming dental adhesive can be applied to the surface of an unset dental cement material to form a polymer-infiltrated structure. The surface infiltration permits stabilization of the cement before it fully sets. In another example, a portland cement material is described as being mixed with a solution of 2-10% polyvinyl pyrrolidone having a molecular weight between 40,000 and 1,300,000. There is no disclosure of the particle size or surface area of the cement particulate.

[0013] Another material that is used in surgical and non-surgical root canal procedures is ProRoot™ MTA root repair material available from Dentsply Tulsa Dental Specialties (Tulsa, OK). ProRoot MTA material has a composition similar to portland cement and does not contain any water-soluble polymeric materials. Particularly, the MTA material includes fine hydrophilic particles of dicalcium silicate, tricalcium silicate, tricalcium aluminate, tetracalcium aluminoferite, calcium sulfate dihydrate, and bismuth oxide that are combined with water to form a cement-like material. The MTA material is available in gray and white colored formulations. The oxides used in the MTA powder are of the highest purity to ensure that no heavy metals are included and used in the body. MTA root canal repair material is used in a wide variety of clinical applications. Particularly, the cement-like material has been used to repair root canal perforations during root canal
therapy; fill root ends; treat injured pulps in procedures known as pulp capping and pulpotomy, and repair root resorption.

[0014] Although MTA materials are generally effective in surgical and non-surgical root canal procedures, some dental literature has criticized these materials for having poor handling properties and a sand-like feel. There is a need for a composition having improved handling and placement properties. The material should promote the healing or repair of the pulp-tissue or the tissue surrounding root canal tips. The material should also provide a tight seal against the root canal dentin to prevent bacterial migration through the root canal. The present invention provides such improved materials.

**SUMMARY OF THE INVENTION**

[0015] The present invention provides improved compositions for treating the pulp and root canals in a tooth. The compositions can be used in various applications including the repair of root canal perforations, filling of root ends, treatment of injured pulps and repair of root resorption. In general, the compositions are made from a powdered particulate material and a liquid carrier comprising polyvinyl pyrrolidone and water. Copolymers of polyvinyl pyrrolidone, preferably a copolymer of polyvinyl pyrrolidone and polyvinyl acetate, also can be used. Optionally, surfactants can be added to the composition. The particulate material can be selected from the group consisting of calcium silicate, calcium aluminate, tetracalcium aluminoferrite, calcium phosphate, calcium sulfate, silica, alumina, calcium oxide, calcium hydroxide, and mixtures thereof. The powdered particulate is optionally blended with hydroxyapatite, a form of calcium phosphate, and other compounds such as radiopaque materials. Preferably, the particulate has a surface area of at least 0.5 m²/g and more preferably greater than 0.9 m²/g.

[0016] The compositions of this invention have many advantageous properties. The growth of new bone and tissue surrounding the root tip is enhanced in cases where an infection is present. In addition, the biocompatible compositions provide a stable barrier to bacterial and fluid leakage in the root canal system of a tooth.
BRIEF DESCRIPTION OF THE FIGURES

[0017] FIGURE 1 is a bar graph showing fluid microleakage data in root canal systems treated with a composition of this invention versus comparative, commercially-available root canal sealer materials.

[0018] FIGURE 2 is a bar graph showing adhesion strength in a root canal sealed with a composition of this invention versus comparative, commercially-available root canal sealer materials.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] The present invention provides new compositions suitable for use in healing diseased teeth. The compositions are particularly suitable for use in treating root canals. In addition, the compositions may be used for cavity lining or pulp-capping of carious teeth, treatment of traumatized teeth, or any procedure where bacterial leakage is to be minimized between the coronal and apical areas.

[0020] The composition of this invention is made from two parts. Part A of the product is particulate material selected from the group consisting of calcium silicate, calcium aluminate, tetracalcium aluminoferite, calcium phosphate, calcium sulfate, silica, alumina, calcium oxide, calcium hydroxide and mixtures thereof. Such particulate materials and mixtures thereof may be referred to herein as “dentalcrete” particulate. The dentalcrete particulate can be optionally blended with hydroxyapatite, a form of calcium phosphate, particulate. Compositions containing a combination of dentalcrete and hydroxyapatite particulate may be referred to herein as “phoscrete” particulate. Other compounds such as bismuth oxide, barium sulfate, tantalum oxide, cerium oxide, tin oxide, zirconium oxide, and radiopaque glasses that contain lanthanide or actinide compounds, tantalum, barium or strontium can be blended with the dentalcrete powdered particulate to make the material more opaque to x-rays as discussed further below.
[0021] The particulate material must contain particles of suitable size. To create a fine-powdered material, the particulate can be subjected to conventional air and solid media attrition techniques. This increases the surface area of the particles and reduces the particle size. The powdered particulate used in the composition of this invention preferably has a surface area of equal to or greater than 0.5 m²/g and more preferably greater than 0.9 m²/g. The particles generally have a surface area in the range of 0.5 to 3.0 m²/g and more preferably 0.9 to 3.0 m²/g. In one preferred embodiment, the particle size of the powder is reduced so that the maximum and average diameter sizes of the individual particles fall below 40 μm, more preferably below 15 μm, and most preferably below 10 μm. In some instances, the particles may be so fine that they have an average particle size of less than 1 μm. The average particle size of the particulate is preferably in the range of 10 times smaller than conventional portland cement particulate. Industrial and construction grade cement contain particles having an average particle size that is too large for the compositions of this invention. There also tends to be substantial agglomeration and aggregation of particles in such industrial cements. In contrast, the powdered particulate used in the present formulation comprises discrete and individual particles, which are not substantially agglomerated or aggregated. These particles are characterized by having small particle size and large surface area. The small, discrete individual particles in the composition provide several advantages over industrial cement particles.

[0022] For example, using such fine particles means that the hydraulic colloidal gel particles are more on a scale with dentinal tubules and lateral root canals in the tooth. The dentinal tubules in the root are microscopic, 1 to 3 μm in diameter, straight, and plentiful, with a density of 800 to 57,000 per square millimeter. Secondly, the fine particles can be blended easily and homogenously with the other ingredients of the composition. The small particles are mixed and distributed uniformly within the resin matrix. In contrast, the particles used in some traditional dental cements, for example, the cements described in the above-mentioned Kawahara et al., US Patent 4,647,600,
must first be surface-treated with inorganic or organic acids before they are mixed with other components.

[0023] Using a powder particulate having such a small particle size significantly improves the viscosity and handling properties of the ultimate composition as discussed further below. The preferred powder comprises particulate selected from dicalcium silicate, tricalcium silicate, tricalcium aluminate, tetracalcium aluminoferrite, calcium phosphate, calcium sulfate dihydrate, silica, alumina, calcium oxide, and calcium hydroxide, and combinations thereof. The powder may contain different amounts of the calcium phases such as the following compounds (listed from most to least amount of calcium phases): tricalcium aluminate, dicalcium silicate, tricalcium silicate, tetracalcium aluminoferrite, calcium hydroxide, and calcium sulfate dihydrate.

[0024] The above-described particulate (dentalcrete) can be mixed with other particulate powders in accordance with this invention. In such instances, the particle size of each of the powdered materials should be substantially equal. All of the particles dispersed in the resin matrix should have substantially the same fineness. For example, in one preferred version, the particulate is mixed with hydroxyapatite to form phoscrete as discussed further below. In another preferred embodiment, the particulate is mixed with a finely ground radiopaque material such as bismuth oxide, tin oxide, tantalum oxide, zirconium oxide, barium sulfate, barium or strontium-containing glasses, or other high atomic number, non-toxic, metal compounds including the lanthanides and actinides. Using such radiopaque materials, which absorb x-ray radiation, makes the composition visible in dental x-rays. The composition, which replaces the removed tooth structure, is made visible in the x-ray images. This helps the clinician confirm that the composition has been correctly placed in the teeth after the pulp-capping, pulpotomy, non-surgical, or surgical root procedure.

[0025] To form a phoscrete mixture, hydroxyapatite, a calcium phosphate compound, is added to the mixture of calcium compounds in the dentalcrete. In general, autogenous bone has two basic components, organic and inorganic. The inorganic component of
autogenous bone is primarily hydroxyapatite, and the organic component is primarily collagen. Hydroxyapatite powder is believed to help promote healing and repair of the bone and tissue surrounding the root tip, or in contact with dental pulpal tissue. Hydroxyapatite is compatible with the calcium compounds of dentalcrete and provides a stable, non-resorbable platform for bone and tissue repair. In the hydroxyapatite-containing dentalcrete composition of the present invention, the hydroxyapatite component has the same mineral composition as human bone, thereby providing a natural scaffold for bone and tissue regeneration. However, variations in the hydroxyapatite composition are equally suitable where the apatite is partially replaced by carbonate, or the hydroxyl is partially replaced by fluoride. Also, compositional variations with the calcium being partially replaced by strontium or barium are also in the spirit of the same invention. All of the compositions of this invention have good dimensional stability and will not cause expansion and stress on teeth, nor shrink to allow bacterial transit.

[0026] Part B of the product is a liquid carrier comprising polyvinyl pyrrolidone (PVP) and water. The compositions may comprise polyvinyl pyrrolidone homopolymer and/or polyvinyl pyrrolidone copolymer. For example, a copolymer of polyvinyl pyrrolidone and polyvinyl acetate can be used. The polyvinyl acetate units in the copolymer may be non-hydrolyzed. In one version, a copolymer of PVP and polyvinyl acetate (PVAc) (not hydrolyzed), wherein the ratio of PVP to PVAc is 60/40, is used in the composition. Of the many available water-soluble compounds that could be used to make the composition of this invention, it was found that polyvinyl pyrrolidone had the most desirable properties. The PVP homopolymers and copolymers thereof exhibit excellent adhesive properties, good film-forming characteristics, surface-active properties, and high solubility in water. Preferably, the molecular weight of the PVP material is in the range of 5,000 to 2,000,000. More preferably, the molecular weight of the PVP material is in the range of 8,000 to 1,500,000. For example, Plasdone® K-90 polyvinyl pyrrolidone homopolymer (available from ISP Chemicals, Inc.) can be used in the liquid carrier. The PVP material is preferably supplied in a powder form and has a glass transition temperature in the range of 100°C to 200°C. In another version, Plasdone® S 630 polyvinyl pyrrolidone copolymer (ISP Chemicals) is used. Preferably, the concentration
of PVP material is in the range of about 5% to about 40% by weight based on weight of the composition.

[0027] Optionally, surfactants can be added to the composition. Examples of suitable surfactants include, but are not limited to, alkyl sulfates (for example, sodium dodecyl sulfate (SDS)), fatty acid salts with C_{10} – C_{24} side chains, (for example, sodium stearate), alkyl ether sulfates, alkyl sarcosinates, alkyl betaines, and other anionic, cationic, and non-ionic surfactants having alkyl side chains suitable for human use. If surfactant is added, the concentration should be in the range of about 1 % to about 40% by weight based on weight of the composition. The ratio of surfactant to polymer should be no greater than 6 to 1.

[0028] Various additives such as, for example, plasticizers, softening agents, humectants, stabilizers, and anti-bacterial agents also can be added to the mixture. However, as opposed to some traditional cement materials, which require the addition of a calcium-type powder hardening agent such as calcium hydroxide, there is no need to add such hardeners to the composition of this invention. Calcium hydroxide particulate optionally can be added to the instant formulation, but it is not required. Rather, the formulation, by and in itself as described herein, has sufficient strength and other desirable properties. Of course, it should be understood that calcium hydroxide may form as a reaction product when the powdered particulate is mixed and reacted with the liquid carrier. For example, the powdered particulate may contain particles of tricalcium silicate, dicalcium silicate, and tricalcium aluminate hydrate. When these compounds react with water, they produce several reaction products including calcium hydroxide.

[0029] In practice, clinicians can dispense the powdered material (Part A) onto a pad; add the liquid carrier (Part B); and mix the components together using a spatula to form the composition of this invention. The concentration of powder particulate in the composition is generally in the range of about 1 to about 80 weight percent, and the concentration of liquid carrier is generally in the range of about 1 to about 50 weight percent. To prepare a surgical or repair composition the particulate powder is preferably mixed with the liquid carrier in a ratio of three (3) to one (1). That is, in one preferred
embodyment, the composition contains about 75 weight percent particulate and 25 weight percent liquid carrier. In other instances, the particulate powder can be mixed with the liquid carrier in different ratios such as, for example, four (4) to one (1) or five (5) to one (1). If the composition is intended to be used as a root canal sealer, the powder and liquid are preferably mixed in a ratio in the range of 1:1 to 2.5:1. In the final composition, the water content is generally in the range of about 1 to about 50 weight percent, preferably 15 to 30 and the water-soluble polyvinyl pyrrolidone homopolymer or copolymer is generally present in an amount of about 1 to about 50 weight percent, preferably 5 to 40 weight percent. If hydroxyapatite is present, it is preferably in a concentration of about 1 to about 30 weight percent. If a radiopaque component is present, it is preferably in a concentration of about 1 to about 60 weight percent.

[0030] Upon mixing the particulate powder with the liquid carrier, the particles, which are hydrophilic, react with the liquid to form hydrates. For example, the particulate powder preferably contains particles of tricalcium silicate, dicalcium silicate, and tricalcium aluminate. When these compounds react with water, they produce tricalcium silicate hydrate, dicalcium silicate hydrate, calcium hydroxide, and tricalcium aluminate hydrate. Each mineral compound reacts at a different rate. For example, the tricalcium silicate reacts relatively quickly, while dicalcium silicate hydrates more slowly. The material produced from the hydration reaction is a colloidal hydrate gel. Preferably, the particles dispersed in the gel have a very small particle size as discussed above. The product begins to harden and will eventually solidify to form a material having high compressive strength where the particles are mostly hydrated. Because the mixed material has good resistance to washout and displacement, the particulate material can react with the water and form a mass of relatively high compressive strength (>30 MPa) in situ. The material is able to resist washing out when the root canal system is rinsed with water or other fluid to complete a surgical procedure.

[0031] The composition of this invention has good handling and placement properties. The dental clinician can work with and handle the hydrated gel more efficiently before it
sets to form a rock-like substance in the root canal. Particularly, the composition has suitable rheological properties (for example, viscosity, setting time, elasticity, consistency, and the like) so it can be effectively used for treating vital and non-vital teeth. Good elasticity is very important for root canal sealers. The composition has good stability and holds the particulate in place, which is very important for surgical procedures. In general, the combinations of powder and liquid carrier compositions have either a putty-like or syrup-like consistency as discussed further below.

[0032] It should be understood that mixing the powdered material with a liquid carrier as described above is but only one possible method of preparing the composition of this invention. Other methods can be used. For example, the powdered particulate can be mixed with water (Part A) and then this mixture can be combined with the polyvinyl pyrrolidone (Part B).

[0033] In some root canal treatment cases, gutta-percha and root canal sealer materials can be extruded beyond the apex of a tooth. These materials can be irritants and cause residual discomfort until the body resorbs or encapsulates the material over a period of months or years. The compositions of this invention have good biocompatibility with the root canal system and promote normal healing of the bone and tissue surrounding the root tip, particularly if any of the material is extruded beyond the apex. The composition enhances the growth of new bone and tissue surrounding the root tip if an infection was present and is anti-microbial when it makes contact with bacteria. Adding the bioactive hydroxyapatite powder further enhances these phenomena to promote growth of cementum or reparative dentin, depending upon the application of the material.

[0034] The improved compositions of this invention can be either putty-like or syrupy in viscosity. When the composition is in the form of a putty-like material, it can be used in root canal indications such as apicoectomies, apexification, perforation repair, obturation, pulpotomies, or root-resorption repair. When the composition is in the form of an elastic material having a honey-like consistency, it can be used for root canal sealing or perhaps obturation. The rheological properties (viscosity, elasticity, and the like) of the powder-liquid combination are determined by the particle size distribution of
the powder, the composition of the liquid, and the powder to liquid ratio. Finer powders; more viscous liquids; more polymers; and a higher powder to liquid ratio all make a more putty-like material used for pulp-capping, cavity liner, root-end filling, obturation, pulpotomie, apexification, or treating perforations or root resorption. The composition of this invention is introduced into the tooth from the coronal or apical openings.

[0035] For example, the compositions can be used to seal at least a portion of the tooth; repair root perforations; repair root resorption; fill root ends; and cap at least a portion of the dental pulp that has been exposed. The composition also can be used to line a cavity preparation where pulp-exposure is possible. Moreover, complete obturation of root canals can be performed using the material of this invention. In addition, after a pulpotomy has been performed, the composition can be used to cover a root access opening in a root. In yet another example, the composition can be used to seal a root canal after gutta-percha has been introduced into the canal.

[0036] The invention is further illustrated by the compositions described in the following Examples, but these Examples should not be construed as limiting the scope of the invention.

**EXAMPLES**

**EXAMPLE A**

[0037] A root canal sealer was formulated with dentalcrete having 40 wt.% bismuth oxide and 60 wt. % of a mixture of calcium silicates, calcium aluminate, and calcium sulfate. (The approximate composition was 73 wt.% tricalcium silicate, 17 wt.% dicalcium silicate, 5 wt.% tricalcium aluminate, 1 wt.% tetracalcium ferrite, and 4 wt.% calcium sulfate.) The liquid carrier mixed with this powder contained 20 wt.% 2-pyrrolidone, 1-ethyl- homopolymer (polyvinyl pyrrolidone homopolymer - ISP Chemicals, Inc. Calvert City, KY) and 80 wt.% water. The powder was mixed with the liquid in a ratio of 2:1. The resulting root canal sealer formulation is identified as "Experimental Root Canal Sealer" (ES) in the In Vivo Study and Table 1 below.
IN VIVO STUDY

[0038] The endodontic biocompatibility of the experimental root canal sealer described in Example A was evaluated. Four dogs were the subjects of this protocol for root canal treatment. Non-surgical root canal procedures began with coronal access using a high speed round bur (#4 or 6) or fissure bur (#170). The root canals of the teeth were cleaned and shaped using a 1.3% sodium hypochlorite irrigating solution and Glide root canal lubricant, in conjunction with Gates-Glidden burs #1-4 and Profile .04 taper and .06 taper Nickel-Titanium instruments. Approximately half of the teeth had the working lengths established to the radiographic apex, using radiographs. The other teeth had the working length determination to where the delta formation commenced (1-2 mm away from the radiographic apex into the root).

[0039] After instrumentation, the root canals for the experimental materials were irrigated with BioPure MTAD root canal cleanser (Dentsply Tulsa Dental Specialties), as per the manufacturer’s instructions. In the control teeth, a 17% EDTA solution was used for irrigation and smear layer removal.

[0040] All canals were obturated with standard gutta-percha cones using a warm compaction technique to seal the apical portion, and a warm injectable technique to fill the coronal portion of the root canal. Canals were sealed and obturated with one of four material combinations:

a. gutta-percha (gp) with the control sealer (Pulp Canal Sealer; available from Kerr SybronEndo),

b. gutta percha (gp) with the experimental root canal sealer (ES), or

c. ES without gutta percha (gp).

[0041] Radiographs were made to confirm the adequacy of the intra-canal procedures and the apical position of the root canal filling materials. The subjects were sacrificed 65 to 70 days post-treatment. Healing was significant as seen by radiographic evidence of bone growth post-treatment. In the histology examination these characteristics were found for the experimental root canal sealer: low or no inflammation, periodontal
ligament regeneration, regeneration of new bone peripherally to the root apex, absence of bone or root resorption, formation of cementoid and cementum over the apical terminus of the canal and adjacent root structure, and insertion of Sharpey's fibers into the newly formed cementum. The grading of all the histological sections with the average scores for each procedure is shown in Table 1.

Table 1: Summary of Histological Results

<table>
<thead>
<tr>
<th>Tooth # or average</th>
<th>Periapical inflammation</th>
<th>Cementum</th>
<th>Bone quality</th>
<th>PDL</th>
<th>Material/treatment</th>
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</thead>
<tbody>
<tr>
<td>AVERAGE</td>
<td>0.4</td>
<td>0.3</td>
<td>0.9</td>
<td>0.7</td>
<td>ES/gp apex</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>ES obturation delta</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>0.1</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
<td>ES/gp delta</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>0.6</td>
<td>0.4</td>
<td>0.1</td>
<td>0.6</td>
<td>Kerr/gp apex</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.4</td>
<td>Kerr/gp delta</td>
</tr>
</tbody>
</table>

[0042] The average scores were very good for the experimental materials with all average scores less than 1 for any attribute. (A score of zero indicates normal healthy tissue that one would find with no treatment.) The only exception was one tooth that had been surgically treated immediately after the non-surgical treatment. The scores were numerically lower for the experimental sealer compared to the control sealer for the same procedure. Obturating to the delta with the experimental sealer without gutta percha gave the lowest score for teeth.

[0043] These general observations were made: 1) when any of the materials were kept within the root canal, the tissue had a normal appearance, no apical inflammation and no root resorption; and 2) the experimental materials did exhibit the formation of hard tissue within the extension of the pulp— that is, in the apical delta. In some specimens, significant hard tissue formed in the anatomical complexity, which indicates that root canal procedures of cleaning and shaping within the confines of the root fostered a positive healing and favorable tissue response apically.
MICROLEAKAGE STUDY

Preparation of Root Canals

[0044] The apical seal of single-rooted canals filled with the experimental root canal sealer of Example A and gutta-percha over two immersion periods in a phosphate-containing fluid (PCF) was investigated using a fluid leakage model and compared with two commercially available zinc oxide eugenol (ZOE)-based and epoxy resin-based sealers.

[0045] In this study, forty-six extracted human maxillary anterior teeth were stored in a solution of 0.9% NaCl and 0.02% NaN₃; the latter to prevent bacterial growth. The experimental design consisted of three experimental groups (n=10) for fluid leakage evaluation. Three teeth were used for each of the positive and negative control groups. Six additional teeth were employed for morphologic characterization.

[0046] Cleaning, shaping and filling were performed under an operating microscope (OPMI pico, Carl Zeiss Surgical, Inc., Thornwood, NY). Each experimental group contained 25% round canals and 75% oval-shaped canals, as determined by the use of buccolingual and mesiodistal radiographs. Canal patency was achieved with a size 15 Flex-o-file (Dentsply Maillefer, Ballaigues, Switzerland). Instrumentation was performed to 0.5 mm short of the radiographic apex with a crown-down technique using ProTaper nickel titanium rotary instruments (Dentsply Tulsa Dental Specialties) to size F4. The root canals were irrigated with 6.15% NaOCl between instrumentation, and with 5 mL of 17% EDTA under passive ultrasonic irrigation for 1 min to remove canal wall smear layers. Each debrided canal was dried with multiple paper points and trial-fitted with a F4 gutta-percha master cone with tug-back.

[0047] The three sealers evaluated for fluid leakage were Pulp Canal Sealer (PCS)
(SybronEndo, Orange, CA), AH Plus Sealer (Dentsply Caulk, Milford DE) and the experimental root canal sealer (Example A – referred to as Expt. Calcium Silicate Sealer in FIGURE 1.) The former two sealers were mixed according to the manufacturers' instructions. The experimental sealer was mixed with a liquid-to-powder ratio of 1:2 and covered with moist gauze to avoid evaporation of the water component. Each canal was filled with a warm vertical compaction technique using a System B heat source (SybronEndo), backfilled with gutta-percha using a Calamus unit (Dentsply Tulsa Dental Specialties) and restored with Cavit (3M ESPE, St. Paul, MN). The teeth were stored at 100% relative humidity for 6 days to allow complete setting of the sealers and then immersed in a PCF (0.17 g KH₂PO₄, 1.18 g Na₂HPO₄, 8.0 g NaCl, 0.2 g KCl in 1 L of deionized water containing 0.2 g of NaN₃ to prevent bacterial growth) for 24 hours prior to leakage evaluation.

[0048] For the positive control, each canal was cleaned and shaped in the manner previously described. A master cone was inserted to within 0.5 mm of the working length with tug-back without the use of a sealer. The gutta-percha was seared off from the canal orifice with the System B heat source. For the negative control, the canal was cleaned and shaped and filled with gutta-percha and AH Plus sealer. After filling, the entire root was dipped into molten sticky wax to seal the root surface and apex.

Leakage Evaluation

[0049] The filled teeth were decoronated using a slow-speed Isomet saw (Buehler Ltd., Lake Bluff, IL) under water-cooling to obtain 17 mm long root segments. Leakage was evaluated using a fluid filtration design upgraded with a Flodec measuring device (De Marco Engineering, Geneva, Switzerland) that permits digital data collection at 1.04 sec intervals. The Cavit was removed and the root segment was attached via its coronal orifice to an 18-gauge needle-perforated Plexiglas platform and sealed with cyanoacrylate glue. The external root surface was also covered with cyanoacrylate 2 mm coronal to the apical foramen. Nitrogen gas pressure was applied at 10 psi (69 kPa) via polyethylene tubing through the coronal end of the root segment. Fluid flow was recorded by monitoring the displacement of a water bubble inside the glass capillary tube of the
Fodeck device. Data was recorded as fluid flow over time and expressed as mean fluid flow (PL/min-l). After the initial fluid leakage evaluation, the root segment was carefully removed from the Plexiglas platform. The coronal orifice was restored with Cavit and the root segment was re-immersed in the PCF for an additional 28 days prior to the second period of fluid leakage evaluation at 35 days.

[0050] The fluid leakage results are shown in the bar graph of FIGURE 1. As shown in FIGURE 1, there are significant differences in fluid leakage among the experimental root canal sealer (designated as “Expt. Calcium silicate sealer”) and the two commercially available root canal sealers.

ADHESION TESTING

[0051] In this study, sixty recently extracted, intact, caries-free human canine teeth were cut into 1.1 mm thick longitudinal tooth slices. A 0.6 mm drill bit was used to prepare parallel holes in the radicular dentin along the coronal third, middle third and the apical third of the root, taking care that each hole was drilled in dentin and not in the pulp or cementum. Each parallel hole was enlarged sequentially with ProTaper S1, S2, F1, F2 and F3 nickel titanium instruments (Dentsply Tulsa Dental Specialties) under an operating microscope (OPMI pico, Carl Zeiss Surgical, Inc., Thornwood, NY) at 10X magnification until the D-16 diameter of a F3 instrument (1.0 mm) was achieved on the “coronal” aspect of the tooth slice.

[0052] Each tooth slice was immersed in 17% EDTA and ultrasonicated for 5 min to dissolve the smear layer created during the hole-shaping procedures. The slice was then immersed in 6.15% sodium hypochlorite and ultrasonicated for 5 min to remove organic debris and the demineralized collagen matrix created during EDTA irrigation.

[0053] All holes created in each tooth slice were completely filled with one particular type of root canal sealer to be investigated. Each tooth slice was placed over a Mylar strip. The corresponding endodontic sealer was mixed and placed inside a syringe attached to hub containing an 18-gauge needle. The sealer was injected into the holes so that each hole was filled with excess sealer. The surface of the tooth slice was covered
with another Mylar strip. The assembly was transferred to a humidor and weights were placed on top of the surface Mylar strip to enable the excess sealer to be expressed laterally from the surface and bottom Mylar strips. Tooth slices containing the sealer-filled holes were stored in 100% relative humidity for one week or until the sealer completely set.

[0054] Three sealers were investigated in this study: I) the experimental calcium silicate-based MTA root canal sealer of this invention; II) AH Plus “Jet” Root Canal Sealer (Dentsply Caulk, Milford, DE); and III) Pulp Canal Sealer (SybronEndo, Sybron Dental Specialties, Inc., Orange CA). Twenty tooth slices, each containing two holes in the coronal third, two holes in the middle third and two holes in the apical third of the root were prepared for each of the three groups to be examined.

[0055] After setting of the sealer, the Mylar strips were peeled off from each tooth slice to expose the set sealers. The twenty tooth slices from each group were randomly divided into two subgroups of ten slices each. One subgroup was tested immediately, while the other subgroup were immersed in a custom-prepared phosphate-buffered saline (0.17 g KH2PO4, 1.18 g Na2HPO4, 8.0 g NaCl, 0.2 g KCl in 1 L of deionized water) containing 0.02% sodium azide to prevent bacterial growth for three weeks. This solution is referred to as “SBF” in FIGURE 2.

[0056] Prior to push-out testing, the thickness of each tooth slice was measured. A carbon steel cylindrical push-out plunger with a diameter smaller than the wider “coronal” aspect of the truncated hole was selected for the push-out test. Each slice was secured with sticky wax in an “apical-coronal” direction to a metal support well along the top of a push-out testing device, so that the “apical”, smaller diameter side of the truncated hole was facing the plunger. The plunger and the hole to be tested were aligned by adjusting the X-Y stage beneath the well. As the plunger only contacted the set sealer on loading, shear stresses were introduced along the sealer-dentin interface, causing the set sealer to be dislocated from the root dentin wall. Each sealer-filled hole was subjected to compressive loading via a universal testing machine (Vitrodyne V1000 Universal Tester, Liveco Inc.,
Burlington, VT) at a crosshead speed of 10 μm/sec in order to displace the set sealer toward the "coronal" side of the hole. Failure was manifested by the extrusion of the intact cone of set sealer from the tooth slice. After performing push-out testing for the first hole, the tooth slice was carefully removed and re-secured with sticky wax for testing of a second hole. The procedure was repeated until the set sealers were dislodged from all the six holes within the tooth slice.

[0057] Referring to FIGURE 2, it can be seen that the experimental MTA sealer had significantly greater push-out strength, meaning better adhesion properties, than the comparative, commercially-available root canal sealers.

[0058] Workers skilled in the art will appreciate that various modifications can be made to the illustrated embodiments and description herein without departing from the spirit and scope of the present invention. It is intended that all such modifications within the spirit and scope of the present invention be covered by the appended claims.
CLAIMS

What is claimed is:

1. A composition for treating a root canal in a tooth, comprising:
   about 1 to about 80% by weight of particulate material selected from the group
   consisting of calcium silicate, calcium aluminate, tetracalcium aluminoferrite, calcium
   phosphate, calcium sulfate, silica, alumina, calcium oxide, calcium hydroxide, and
   mixtures thereof; and
   about 1 to about 50% by weight liquid carrier comprising polyvinyl pyrrolodine
   and water.

2. The composition of claim 1, further comprising about 1 to about 30% by weight of
   hydroxyapatite.

3. The composition of claim 1, further comprising about 1 to about 60% by weight of a
   radiopaque component.

4. The composition of claim 3, wherein the radiopaque component is selected from the
   group consisting of bismuth oxide, barium sulfate, tantalum oxide, cerium oxide, tin
   oxide, zirconium oxide compounds and radiopaque glasses containing tantalum, barium
   and strontium, and mixtures thereof.

5. The composition of claim 1, wherein the particulate material comprises a mixture of
   tricalcium silicate and dicalcium silicate particles.
6. The composition of claim 1, wherein the particulate material comprises about 20 to about 80 wt.% tricalcium silicate; about 20 to about 50 wt.% dicalcium silicate; about 1 to about 20 wt.% tricalcium aluminate, about 1 to about 8 wt.% tetracalcium aluminoferrite; about 1 to about 15 wt.% calcium sulfate dihydrate, and about 1 to about 50 wt.% radiopaque component.

7. A method of treating a root canal in a tooth, comprising the steps of:
   a) preparing the root canal in the tooth to be treated,
   b) providing a composition comprising a mixture of about 1% to about 80% by weight of particulate material selected from the group consisting of calcium silicate, calcium aluminate, tetracalcium aluminoferrite, calcium phosphate, calcium sulfate, silica, alumina, calcium oxide, calcium hydroxide and mixtures thereof and about 1% to about 80% by weight of a liquid carrier comprising polyvinyl pyrrolidone and water; and
   c) introducing the composition into the tooth from coronal or apical openings and allowing the composition to harden.

8. The method of claim 7, wherein the composition further comprises a humectant.

9. The method of claim 7, wherein the sealing composition further comprises about 1 to about 30% by weight of hydroxyapatite.
10. The method of claim 7, wherein the sealing composition further comprises about 1 to about 40% by weight of a radiopaque component.

11. The method of claim 10, wherein the radiopaque component is selected from the group consisting of bismuth oxide, barium sulfate, tantalum oxide, cerium oxide, tin oxide, zirconium oxide compounds and radiopaque glasses containing tantalum, barium and strontium, and mixtures thereof.

12. The method of claim 7, wherein the particulate material comprises a mixture of tricalcium silicate and dicalcium silicate particles.

13. The method of claim 7, wherein the particulate material comprises about 20 to about 80 wt.% tricalcium silicate; about 20 to about 50 wt.% dicalcium silicate; about 1 to about 20 wt.% tricalcium aluminate, about 1 to about 20 wt.% tetracalcium aluminoferrite; about 1 to about 15 wt.% calcium sulfate dihydrate, and about 1 to about 50 wt.% radiopaque component.

14. The method of claim 7, wherein the method comprises using the composition to seal at least a portion of the tooth.

15. The method of claim 7, wherein the method comprises using the composition to repair root perforations.
16. The method of claim 7, wherein the method comprises using the composition to repair root resorption.

17. The method of claim 7, wherein the method comprises using the composition to fill root ends.

18. The method of claim 7, wherein the method comprises using the composition to cap at least a portion of the pulp that has been exposed.

19. The method of claim 7, wherein the method comprises using the composition to line a cavity preparation where a pulp-exposure is possible.

20. The method of claim 7, wherein the method comprises using the composition to obturate root canals.

21. The method of claim 7, wherein the method comprises using the composition to cover a root access opening in a root after a pulpotomy has been performed.

22. The method of claim 7, wherein the method comprises using the composition to seal a root canal after gutta-percha has been introduced into the canal.
**FIG. 1**

- PCS sealer
- AH Plus sealer
- Expt. calcium silicate sealer

**Fluid leakage (µL/min)**

- 7 Days
- 35 Days
FIG. 2