

## BIOCOMPATIBLE CEMENTITIOUS DENTAL COMPOSITIONS

### FIELD OF INVENTION

The present invention relates to improvements in dental compositions, and, more particularly, to high strength cementitious materials suitable for use as luting agents, sedative and insulating bases, temporary and long term restoratives, endodontic sealants, pulp capping materials, soft tissue packs, impression pastes and adhesives for dental composites and hard tissues. Specifically, the present invention relates to highly biocompatible, high strength, low solubility, insulating bases and restoratives containing syringic acid esters dissolved in chelating agents and metal oxides that adhere to metals and resins.

The invention also relates to silanized glass-filled cementitious materials suitable as intermediate, semi-permanent restorative materials and as a restorative in the repair of fractured porcelain or porcelain to metal crowns and bridges.

### BACKGROUND OF THE INVENTION

Oil of cloves has been used in the treatment of dental caries since the XVI century and its inclusion in combination with zinc oxide in dental cements, commonly referred to as luting agents, was reported over 100 years ago. Analysis revealed that oil of cloves contains approximately 85% by weight of eugenol. It is this latter compound which is used in zinc oxide-eugenol (hereinafter referred to as ZOE) dental cements. ZOE compositions have found wide application in dentistry including temporary restoratives, sedative bases, cementing media for crown and bridge work, in pulp capping, soft tissue packs in oral surgery and periodontics, root canal sealants in endodontics and with modifying agents as impression pastes.

ZOE cements possess much better biocompatibility than most other dental materials. They have excellent sealing characteristics and their bacteriocidal effectiveness has been well demonstrated. The cement acts as a palliative or anodyne and as a mild non-irritant antiseptic. Unfortunately, these materials have low strength, which are often insufficient to resist forces of mastication. Their lack of resistance to wear and disintegration, partially because of their high relative solubility in oral fluids of the mouth, further deters their more extensive use as temporary restorations or fillings. These materials also inhibit free radical polymerization because of the presence of an electron-rich phenolic hydroxyl group in the eugenol molecule. Thus, acrylic resins, and to a lesser extent composites, in contact with a ZOE cement do not polymerize completely. This incomplete cure results in polymer surface regions having poor physical properties such as low surface hardness. ZOE cements adhere only weakly to acrylic restorations, bone or dental tissues. Moreover, eugenol has shown no evidence of inhibiting caries formation.

Although the eugenol ingredient is relatively non-toxic (LD<sub>50</sub> of 0.5 g/kg for white mice), free eugenol has some inflammatory characteristics. Thus, when injected into the abdominal integument and eyes of rabbits, eugenol produces severe inflammation. It produces leucocytic infiltration and polymorphonuclear responses, and in direct contact with the pulp or periodontal tissue eugenol can act as a coagulant. In vitro

tests it shows a hemolyzing, protein precipitating action.

A further disadvantage is that eugenol has a penetrating long-lasting odor and lingering taste which is unpleasant to many patients. In addition, incompletely hardened cements containing much residual eugenol can produce irritation and toxic cell reactions.

To overcome some of these deficiencies, especially to improve the mechanical strength of the ZOE cement, research has been directed to either replacing eugenol altogether with a more suitable substitute or towards including additives in the ZOE compositions which alleviate some of the problems. However, the use of eugenol substitutes has often resulted in cements possessing poor physical properties.

Zinc oxide will react with many chelate forming compounds, especially those containing o-methoxyphenol (guaiacol) groups to yield cementitious products. Cements obtained from o-ethoxybenzoic acid (referred to hereinafter as EBA) and zinc oxide have found a considerable number of applications in dentistry because of their strength and excellent biocompatibility, especially as luting agents and as bases. However, under clinical conditions the materials still disintegrate too rapidly to be employed for more permanent conditions.

Recently, Brauer, Argentar and Stansbury (U.S. Pat. No. 4,362,510; also see Brauer, G. M.; and Stansbury, J. W.; and Argentar, H.: Development of High-Strength, Acrylic Resin-compatible Adhesive Cements, *J Dent Res* 62, 366 (1983).) have developed cements comprising a liquid made up of vanillic ester such as n-hexyl vanillate, a chelating agent and a zinc oxide-aluminum oxide and hydrogenated rosin powder. Vanillate esters such as n-hexyl vanillate (HV) dissolved in o-ethoxybenzoic acid react with zinc oxide powders to yield high-strength, adhesive cements, which are much less soluble than ZOE cements, do not inhibit polymerization of acrylic monomers and can be formulated with them. Such cements, with or without the resin or polymer, have excellent strength and adhere well to non-precious metal, resins and porcelain. However, n-hexyl vanillate has shown no evidence of inhibiting caries formation.

Syringic acid (3,5-dimethoxy-4-hydroxybenzoic acid) has a molecular structure somewhat similar to vanillic acid with an additional methoxy group in the "5" position of the aromatic ring. The acid, when used as a feed additive for rats, has shown a larger reduction in caries of the rats than any other phenolic compounds and amino acids studied (Thompson, Vogel and Phillips, *J. Dent Res* 44:596-599, 1965). Other phenolic compounds such as eugenol as well as amino acids did not inhibit caries formation at the level tested.

Various phenols including vanillin and syringic acid have been tested for their inhibitory effects on the polymerization of methyl methacrylate (Chem. Abstracts 83: 179694t, 1975), the tested phenols having activities lying between the extremes produced by hydroquinone and vanillin.

Intermediate restorations are commonly used in dentistry, especially in pedodontics. Often for patients with rampant caries, gross cavities should be repaired expeditiously to alter the oral flora and arrest the caries process. When this has been accomplished permanent restorations can be placed. Removal of the caries until completion of the restorative work may take several months or longer. An intermediate restorative is used during this time to protect the teeth and should have a