

# DENTAL CAVITY FILLING COMPOSITE MATERIAL

## FIELD OF THE INVENTION

This invention relates to a filling composite material having highly improved mechanical properties, and being very low in polymerization shrinkage, thermal expansion coefficient and water absorption. More particularly, it relates to a dental filling composite material which is easy to be filled into loss cavities of front teeth and molars, quick to be polymerized, low in polymerization shrinkage, thermal expansion coefficient and water absorption and may be readily polymerized and cured to form a polymer of high compressive strength, flexural strength and hardness.

## BACKGROUND OF THE INVENTION

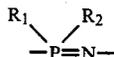
Materials such as amalgam and silicate cement have hitherto been used as dental filling materials. These materials, however, have no adhesiveness to tooth substance but have liability to cause secondary caries. Further, some uncertainty with regard to durability and fear of injuriousness to the pulp or soft tissues have compelled these materials to be replaced by resin type filling materials. In other words, a monomer to be used as the dental filling material is a mixture of polymethyl methacrylate and methyl methacrylate, of bisphenol-A glycidyl dimethacrylate and ethyleneglycol dimethacrylate, or of urethane dimethacrylate, 2,2-di-(4-methacryloxy ethoxy phenol)propane and triethylene glycol dimethacrylate. Such mixture is incorporated with fillers such as silica powder and amines such as dimethyl-p-toluidine and p-tolyldiethanolamine, as well as peroxides such benzoyl peroxide. Then, the resulting mixture is polymerized by amine-peroxide system to form the filling materials.

As well-known in the art, however, such monomer has a C—C homo bond in its chain and skeleton and therefore produces a polymer of high flexibility and bending, but has disadvantages of high thermal expansion coefficient and low heat-resistance. In other words, the resulting polymer is low in strength and hardness, large in polymerization shrinkage and low in softening point. Consequently, if the above-mentioned mixture of monomers is filled into dental cavities, gaps may be produced between cavities and polymers due to polymerization shrinkage and temperature change upon eating and drinking, thereby to cause secondary caries. In addition, the polymer has poor hardness and strength, resulting in ready wearability and poor durability.

## SUMMARY OF THE INVENTION

A general object of the invention is to completely solve the problems as described hereinabove and to provide an improved dental filling composite material which is not injurious to the pulp and the soft tissues and forms an eternal prosthesis.

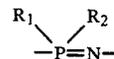
A principal object of the invention is to provide a filling composite material containing 10 to 99% by weight of phosphazene of the formula:



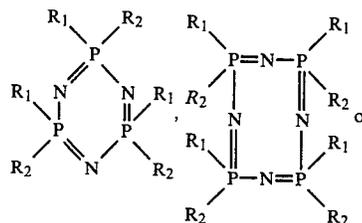
in which at least one of  $R_1$  and  $R_2$  represents radicals having not less than 3 carbon atoms and being polymerizable.

## PREFERRED EMBODIMENT OF THE INVENTION

In accordance with the invention any phosphazene of the formula:

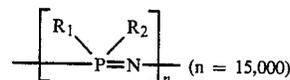


in which  $R_1$  and  $R_2$  are defined hereinabove, may be used but it is preferred to select the following phosphazene:



(I)

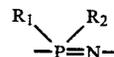
(II)



(III)

In the above formulae, at least one of the radicals  $R_1$  and  $R_2$  has not less than 3 carbon atoms and polymerizable groups. As the polymerizable groups, there may be mentioned those compounds that can be polymerized by polycondensation, addition polymerization and by ring-opening polymerization, especially those compounds having vinyl groups that can be polymerized by radical polymerization. Further, it has been found that those compound whose  $R_1$  or  $R_2$  has 1-3—NH<sub>2</sub> groups show adhesiveness, while those having 1-3 phenol groups show highly improved heat-resistance.

Compounds having



bonds are, as is generally known, of hetero bond which has a higher bonding energy than that of homo bond, and inhibits molecular rotation. Thus, the compounds show inorganic properties, such as low flexural strength, high hardness, poor flexibility and high decomposition point and hence are called inorganic oligomers or inorganic high polymers.

It will be apparent from the foregoing that polymers of the compounds according to the present invention have highly improved mechanical properties, and other preferable properties such as polymerization shrinkage and thermal expansion coefficient, as well as excellent durability and practical usefulness and thus show excellent properties as dental filling composite materials.

The invention may be embodied by reaction of organic compounds having vinyl groups with phosphazene as described hereinabove, or by polymerization of