

silicon dioxides, for example of the "Aerosil" type, the various boron and barium silicate glasses, aluminium silicate and glass ceramic fillers etc., such as disclosed, for example, in U.S. Pat. Nos. 3,801,344, 3,808,370 and 3,975,203 and in DE-A 2,347,591.

A suitable precipitated or pyrogenic silicon dioxide, a so-called microfiller, is disclosed, for example, in DE-A 2,403,211 and EP-A 60,911.

The dental filling materials according to the invention are particularly suitable for use as light-curing products, i.e. products which are present in a single phase and polymerize under the influence of light.

Such compositions contain one or more photopolymerization initiators. Suitable compositions are particularly carbonyl compounds such as benzoin and its derivatives, particularly benzoin methyl ether, benzil and benzil derivatives, for example 4,4-oxydibenzil and other dicarbonyl compounds, for example diacetyl, 2,3-pentanedione or metal carbonyls, quinones, particularly camphorquinone, or their derivatives. The proportion of the photopolymerization initiator is about 0.01 to about 5% by weight based on the total composition.

These light-curable, i.e. photopolymerizable preparations preferably also contain so-called polymerization accelerators. These are substances which speed up the polymerization reaction in the presence of polymerization initiators. Examples of known accelerators are amines such as p-toluidine, N,N-dimethyl-p-toluidine, N,N-di(hydroxyethyl)-p-toluidine, trialkylamines such as trihexylamine, polyamines such as N,N,N',N'-tetraalkylalkylenediamines, barbituric acid and dialkylbarbituric acids and sulphimides, preferably in an amount of about 0.01 up to about 5% by weight based on the total composition.

Suitable accelerators are described, for example, by G. M. Brauer et al., *Journal of Dental Research*, Vol. 58, No. 10 (1979), pp. 1994-2000.

It is of course also possible to use the dental filling materials according to the invention in the form of a two-phase preparation, one phase containing a polymerization catalyst, for example a peroxide, and the other phase containing an accelerator for this peroxide, for example an organic amine, in which case the two phases are mixed immediately prior to the tooth being filled and the polymerization occurs in the drilled cavity to be filled, which is preferably provided with a lining or bonding material.

Suitable peroxides which decompose at the start of the polymerization forming radicals, are, for example, aryl peroxides such as benzoyl peroxide, cumene hydroperoxide, urea peroxide, tert-butyl hydroperoxide or tert-butyl perbenzoate and silyl peroxides, preferably in amounts from about 0.01 to about 5, particularly about 0.5 to 2.5% by weight based on the total composition.

If one phase of the two-phase agent contains a polymerization initiator, then an accelerator of the type described above, preferably an amine, or barbituric acid or its derivatives, for example a dialkylbarbituric acid, is expediently added to the other phase.

Basically any suitable compounds suggested for this purpose may be used as a polymerizable monomer in the dental filling materials according to the invention. Such compounds are particularly the known products obtained by reacting bisphenols, particularly bisphenol A, with glycidyl methacrylate, known under its abbreviation of bis-GMA, the various alkanediol dimethacrylates such as 1,6-hexanediol methacrylate, 1,4-butanediol dimethacrylate, triethylene or tetraethylene

glycol dimethacrylate, bis(2-methacryloxypropyl) phthalate, isophthalate or terephthalate, trimethylolpropane dimethacrylate and trimethacrylate, as well as particularly the reaction products obtained by diisocyanates and hydroxyalkyl methacrylates, such as are described, for example, in DE-A 2,312,559, adducts from (di)isocyanates and 2,2-propane-bis[3-(4-phenoxy)-1,2-hydroxypropane] 1-methacrylate according to US-A 3,629,187 and the adducts of isocyanates and methacroyl alkyl ethers, methacroyl alkoxy benzenes and methacroyl alkoxy cycloalkanes, such as described in EP-A 44,352.

It is of course also possible to use mixtures of suitable monomers.

It is also expedient to use at the same time, as a component of the mixture of monomers, small amounts of brominated methacrylic acid esters, such as those described in EP-A 143,362, in order to improve the opacity to X-rays of the filling.

It is finally expedient to add UV stabilizers to the dental filling materials based on synthetic resins in order to prevent darkening during the ageing of the fillings. A particularly suitable UV stabilizer is 2-hydroxy-4-methoxybenzophenone. Another preferred material is 2-(2'-hydroxy-5'-methylphenyl)benzotriazole; but basically any physiologically inert UV absorbent is suitable for this purpose. Suitable examples are, inter alia, hydroquinone, p-benzoquinone and p-butylhydroxytoluene. The last-mentioned compound may also act in the filling as, for example, an antioxidant.

A survey of the substances conventionally used in dental filling materials can be found in the paper by R. L. Bowen in *Journal of Dental Research*, Vol. 58/5 (May 1979), pp. 1493-1503, and in the immediately following supplementary paper by J. F. Lann, pp. 1504-1506.

To obtain an appearance as natural as possible of the filled areas of the teeth, the composite materials necessarily also contain a small amount of dyes or pigments.

The examples below serve to elucidate further the invention.

PREPARATION OF THE FILLERS

EXAMPLE A

An ethanolic solution of 1000 g (4.8 mol) of $\text{Si}(\text{OC}_2\text{H}_5)_4$ and 24.8 g (0.1 mol) of methacryloxypropyltrimethoxysilane is stirred under reflux. 500 ml of strength NH_3 solution are added dropwise to the boiling solution. After stirring for 30 minutes the precipitate is treated with water and stirring is continued for a further 4 hours. The cooled precipitate is filtered off, again treated with 500 ml of NH_3 solution and introduced into a glandless reaction vessel to undergo a post-reaction. The washed precipitate is dried in a rotary drier in an atmosphere of argon and is then ground.

EXAMPLE B

An ethanolic solution of 1000 g (4.8 mol) of $\text{Si}(\text{OC}_2\text{H}_5)_4$ and 29.8 g (0.2 mol) of $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ is stirred under reflux. 500 ml of a 5% strength NH_3 solution are added at boiling temperature. After stirring for 30 minutes the forming precipitate is treated with water and stirring is continued for a further 4 hours. The cooled precipitate is filtered off, again treated with 500 ml of NH_3 solution and introduced into a glandless reaction vessel for post-condensation. The washed pre-