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Fluoride-releasing composite materials

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- (54) Title  
FLUORIDE-RELEASING COMPOSITE MATERIALS
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The invention relates to fluoride-releasing, polymerizable dental composite materials for permanent fillings having good mechanical stability, containing:

- (a) one or more ethylenically unsaturated polymerizable monomers based on di- or multi-functional (meth)acrylates;
- (b) initiators and optionally activators; and
- (c) usual fillers, and optionally pigments, thixotropic agents, plasticizers and other auxiliaries; and
- (d) one or more sufficiently water-soluble inorganic complex fluorides of general formula



where

A is a monovalent cation, M is a metal of the III-V main group or II-V sub-group, n is a whole number from 1 to 3 and m is a whole number from 3 to 6.

Abstract

The invention relates to fluoride-releasing, polymerizable dental composite materials for permanent fillings having good mechanical stability, containing:

- (a) one or more ethylenically unsaturated polymerizable monomers based on di- or multi-functional (meth)acrylates;
- (b) initiators and optionally activators; and
- (c) usual fillers, and optionally pigments, thixotropic agents, plasticizers and other auxiliaries; and
- (d) one or more sufficiently water-soluble inorganic complex fluorides of general formula



where

A is a monovalent cation, M is a metal of the III-V main group or II-V sub-group, n is a whole number from 1 to 3 and m is a whole number from 3 to 6.

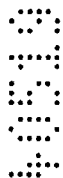


**AUSTRALIA**

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ORIGINAL  
COMPLETE SPECIFICATION  
STANDARD PATENT



Invention Title:



**"Fluoride-releasing composite materials"**



The following statement is a full description of this invention including the best method of performing it known to us:-

The formation of secondary caries on the edges of permanent dental fillings is a problem which has long been known in dental medicine. It has been shown that the tendency to form secondary caries in dental filling materials is reduced when they are able  
5 to release fluoride into the surrounding hard tooth substance. The reason for this is presumably the formation of caries-resistant fluorapatite by reaction of the hydroxylapatite in the tooth with released fluoride (R.S. Levine, The Action of Fluoride in Caries Prevention, British Dental Journal 140 (1976) 9-14).

10 There is no agreement in the literature as regards the question of what quantity of fluoride has to be released from a filling material in order that it has a reliable caries-inhibiting action (R.W. Phillips, Restorative Materials Containing Fluoride, Journal of American Dental Association 116 (1988) 762-763). In  
15 view of clinical findings with various fluoride-releasing filling materials it is however to be noted that the quantity of fluoride which is released by glass ionomer cements can reduce the formation of secondary caries to an extent which is clinically relevant (G. Wesenberg et al., J. Oral Rehabil. 7 (1980) 175-  
20 184). Also, it has been shown that in the case of so-called composite filling materials which display no or very little fluoride release, there is a particular susceptibility to attack from secondary caries (E.A.M. Kidd, Br. Dent. J. 144 (1978) 139-  
25 142). As a result of shrinkage of the resin during curing, an edge gap can form which favours the formation of caries.

There has thus been no lack of attempts to prepare composite filling materials which display a fluoride ion release which is comparable with glass ionomer cements.

High release rates of fluoride are relatively easy to achieve in  
30 glass ionomer cements. The material which cures out because of a reaction of fluoride-containing glass and an aqueous polycarboxylic acid solution forms a hydrated cement in the solid

state, which has ideal conditions for preparing and diffusing fluoride ions.

What is considerably more difficult to achieve is the release of fluoride from composite filling materials, which are also called  
5 resin fillings. In the cured form, composites essentially consist of a polymeric plastic matrix based on (meth)acrylate monomers and a high proportion of fillers. In order to protect the bond between plastic matrix and filler from the harmful effect of water (hydrolysis), composites are as a rule formulated  
10 to be non-polar and hydrophobic.

In contrast to the hydrous, hydrophilic matrix of glass ionomer cements, the hydrophobic matrix of composites prevents the release and diffusion of fluoride ions, however. Also, the introduction of fluoride-containing additives into composites is  
15 made difficult by the non-polarity and hydrophobic nature of these systems. This problem is described very vividly in B.F. Zimmermann et al., J. Dent. Res. 63 (1984) 689-692: "A major problem with incorporation of highly polar inorganic fluoride salts into low polarity polymer resins is phase separation and,  
20 consequently, loss of mechanical integrity...".

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polymerizable dental materials, containing yttrium fluoride and/or sparingly water soluble complex heavy metal fluorides, such as e.g. barium hexafluorozirconate. These compounds serve exclusively to increase the X-ray opacity of the dental materials.

K. Aleksieva et al. (CA 103(6): 42608e) describe prosthesis plastics based on polymethyl methacrylate which contain sodium fluoride or potassium hexafluorotitanate. They found that, in contrast to sodium fluoride, potassium hexafluorotitanate weakens the tensile strength of the polymer. They come to the conclusion that the potassium hexafluorotitanate-containing material is less well suited for producing dental prostheses than the sodium fluoride-containing material. In addition, sodium fluoride is known to be toxic.

DISCLOSURE OF THE INVENTION:

In one aspect, the present invention is directed to polymerizable dental materials, containing:

- (a) one or more ethylenically unsaturated polymerizable monomers based on di- or multi-functional (meth)acrylates;
- (b) initiators and optionally activators;
- (c) usual fillers, and optionally pigments, thixotropic auxiliaries, plasticizers and other auxiliaries;
- (d) one or more sufficiently water-soluble inorganic complex fluorides of general formula



where

A is a monovalent cation, M is a metal of the III-V main group or II-V sub-group, n is a whole number from 1 to 3 and m is a whole number from 3 to 6.



A is preferably an alkali metal ion or  $\text{NR}_4^+$  with R =  $\text{C}_1\text{-C}_{18}$  alkyl, phenyl or substituted phenyl.

The substituents for phenyl are preferably selected from the group consisting of  $\text{C}_1\text{-C}_6$  alkyl groups,  $\text{C}_1\text{-C}_6$  alkyl groups which  
5 are substituted by halides or nitrogen- or oxygen-containing groups, halides,  $\text{C}_1\text{-C}_6$  oxyalkyl groups and  $\text{C}_1\text{-C}_6$  azaalkyl groups.

A is particularly preferably a sodium or potassium ion and R is particularly preferably  $\text{C}_1\text{-C}_6$  alkyl.

$\text{MF}_m$  is preferably selected from the group  $\text{SiF}_6^{2-}$ ,  $\text{TiF}_6^{2-}$ ,  $\text{ZrF}_6^{2-}$ ,  
10  $\text{AlF}_6^{3-}$ ,  $\text{ZnF}_3^-$ ,  $\text{PF}_6^-$  or  $\text{BF}_4^-$ .  $\text{ZnF}_3^-$  is particularly preferred.

••••• The complex fluoride is contained in the materials preferably up  
••••• to 2 to 25 % by wt., more preferably 5 to 15 % by wt. and  
••••• especially 5 to 10 % by wt., relative to the total weight of the  
••••• material (components (a) to (d)).  
•••••

15 ••••• The initiators and optionally activators according to component  
••••• (b) constitute 0.01 to 10 % by wt., in particular 0.1 to 5 % by  
••••• wt. of the total weight (components (a) to (d)), and the fillers  
••••• are contained in the materials according to the invention in an  
••••• amount of preferably 40 to 85 % by wt. and in particular 50 to  
20 ••••• 80 % by wt., relative to the total weight (components (a) to  
••••• (d)).  
•••••

••••• The at least bifunctional acrylic acid and/or methacrylic acid  
esters to be used as constituent (a) according to the invention  
can contain monomeric and polymeric acrylates and methacrylates.

25 ••••• The long-chained monomers of US-A-3 066 112 based on bisphenol-A  
and glycidyl methacrylate or their derivatives resulting from  
addition of isocyanates can for example be advantageously used.  
Also suitable are compounds of the bisphenol-A-  
diethoxy(meth)acrylate and bisphenol-A-dipropoxy(meth)-  
30 ••••• acrylate type. The oligo-ethoxylated and oligo-propoxylated  
bisphenol-A-diacrylic and dimethacrylic acid esters can also be

used.

Also well suited are the acrylic acid and methacrylic acid esters of at least bifunctional aliphatic alcohols, for example triethylene glycol-di(meth)acrylate, ethylene glycol-di(meth)-  
5 acrylate, hexanediol-di(meth)acrylate and trimethylol propane-tri(meth)acrylate.

Particularly suitable are also the diacrylic and dimethacrylic acid esters of bis(hydroxymethyl)-tricyclo[5.2.1.0<sup>2,6</sup>] decane and the diacrylic and dimethacrylic acid esters of the compounds of  
10 bis(hydroxymethyl)tricyclo[5.2.1.0<sup>2,6</sup>] decane extended with 1 to 3 ethylene oxide and/or propylene oxide units, as cited in DE-C-2 816 823.

Well suited monomers are also the methacrylic acid esters described in EP-A-0 235 826, e.g. triglycolic acid bis[3(4)-  
15 methacryloyloxymethyl-8(9)-tricyclo[5.2.1.0<sup>2,6</sup>]-decylmethyl esters].

Naturally, mixtures of monomers and/or of unsaturated polymers produced therefrom can also be used.

Suitable as constituent (b) are initiator systems which effect the radical polymerization of the at least bifunctional monomers, e.g. photoinitiators or so-called redox initiator systems.  
20

Suitable as photoinitiators are for example  $\alpha$ -diketones, such as camphor quinone, in conjunction with secondary and tertiary amines, or mono- and bisacyl phosphine oxides, such as 2,4,6-  
25 trimethyl benzoyl diphenyl phosphine oxide and bis(2,6-dichlorobenzoyl)-4-n-propylphenyl phosphine oxide. However, other compounds of this type are also suitable, as are described in European patent publication specifications EP-A-0 073 413, EP-A-0 007 508, EP-A-0 047 902, EP-A-0 057 474 and EP-A-0 184 095.

30 The concentration of the photoinitiators is in particularly

preferred manner 0.1 to 3 % by wt. and particularly 0.1 to 2 % by wt., relative to the total weight of (a) + (b) + (c) + (d).

Suitable as redox initiator systems are organic peroxide compounds together with so-called activators. Coming into  
5 consideration as organic peroxide compounds are in particular compounds such as lauroyl peroxide, benzoyl peroxide and p-chlorobenzoyl peroxide and p-methyl benzoyl peroxide.

Suitable as activators are for example tertiary aromatic amines such as the N,N-bis-(hydroxyalkyl)-3,5-xylidines known from US-A-  
10 3 541 068 and the N,N-bis-(hydroxyalkyl)-3,5-di-t-butyl-anilines known from DE-A-2 658 530, particularly N,N-bis-( $\beta$ -oxybutyl)-3,5-di-t-butyl-aniline and N,N-bis-(hydroxyalkyl)-3,4,5-trimethyl aniline.

Well suited activators are also the barbituric acids and  
15 barbituric acid derivatives described in DE-B-1 495 520 and the malonyl sulphamides described in EP-A-0 059 451. Preferred malonyl sulphamides are 2,6-dimethyl-4-isobutyl malonyl sulphamide, 2,6-diisobutyl-4-propyl malonyl sulphamide, 2,6-dibutyl-4-propyl malonyl sulphamide, 2,6-dimethyl-4-ethyl malonyl  
20 sulphamide and 2,6-dioctyl-4-isobutyl malonyl sulphamide.

For further acceleration, polymerization is preferably carried  
out in this case in the presence of heavy metal compounds and ionogenic halogen or pseudo-halogen. Copper is particularly  
suitable as heavy metal, the chloride ion as halide. The heavy  
25 metal is suitably used in the form of soluble organic compounds. Likewise, the halide and pseudo-halide ions are suitably used in the form of soluble salts, for example the soluble amine hydrochlorides and quaternary ammonium chloride compounds may be cited.

30 If the polymerizable dental materials according to the invention contain as (b) a redox initiator system of organic peroxide and activator, peroxide and activator are preferably present in parts

of the dental material according to the invention which are spatially separated from each other and homogeneously mixed together only directly prior to using the dental material according to the invention. If the dental material according to 5 the invention contains organic peroxide, copper compound, halide and malonyl sulphamide alongside one another as (b), it is especially useful that organic peroxide, malonyl sulphamide and the combination of copper compound/halide are present in three constituents spatially separated from one another. For example, 10 organic peroxide, polymerizable monomers and fillers can be kneaded to give a paste and the other components can be kneaded in the manner described above in each case with a small quantity of fillers or in particular thixotropic auxiliaries, such as silanized silica, and a plasticizer, for example phthalate, to 15 give two separate pastes. On the other hand, the polymerizable monomers can also be present together with copper compound/halide and fillers. Constituent (d) can, if the dental material according to the invention is present in constituents spatially separated from one another, be present in each of these 20 constituents.

25 Apart from the at least bifunctional acrylic acid and methacrylic acid esters (a) and the initiator system (b), up to 85 % by wt., relative to the total weight of (a) + (b) + (c) + (d), of organic and/or inorganic fillers, pigments, dyes, thixotropic auxiliaries, plasticizers and other auxiliaries are contained.

30 Inorganic fillers can for example be quartz, ground glasses, non-water-soluble fluorides, such as  $\text{CaF}_2$  or  $\text{SrF}_2$ , silica gels and silica, in particular pyrogenic silica or its granules. They are preferably contained in the dental materials in a concentration of 40 to 85 % by wt., quite particularly preferably 50 to 80 % 35 by wt., relative to the total weight of (a) + (b) + (c) + (d). For better incorporation into the polymer matrix it can be advantageous to make the fillers and optionally X-ray opaque additives hydrophobic. In a preferred embodiment, all the inorganic fillers used are silanized, preferably with

trimethoxymethacryloxypropyl silane. The quantity of silane used is usually 0.5 to 10 % by wt., relative to inorganic fillers, preferably 1 to 6 %, quite particularly preferably 2 to 5 % by wt., relative to inorganic fillers. Usual hydrophobing agents are  
5 silanes, for example trimethoxymethacryloxypropyl silane. The maximum average grain size of the inorganic fillers is preferably 15  $\mu\text{m}$ , in particular 8  $\mu\text{m}$ . Quite especially preferably used are fillers with an average grain size of  $< 3 \mu\text{m}$ .

Suitable as fillers are also ready-pigmented polymethyl  
10 methacrylate beads or other pulverized organic polymers. To increase the flexibility of the materials it can also be advantageous to use soluble organic polymers. Suitable are e.g. polyvinyl acetate and the copolymers based on vinyl chloride/vinyl acetate, vinyl chloride/vinyl isobutyl ether and  
15 vinyl acetate/maleic acid dibutyl ether. Well suited as additional plasticizers are for example dibutyl, dioctyl and dinonylphthalates.

20 The materials according to the invention can be used inter alia as permanent filling materials, sealing materials, cements or as materials for temporary fillings or crowns and bridges.

25 The polymerizable fluoride-releasing dental materials according to the invention have good mechanical values (compressive and bending strengths), good long-term stability of the cured material and excellent aesthetics. Their fluoride ion release is comparable with that of a standard commercial glass ionomer cement.

Examples

Series 1: Preparation and testing of conventional and fluoride-releasing composite tooth-filling materials with tooth-like coloration.

Preparation of a pre-mix

5 A pre-mix is kneaded from 70 parts by weight bis-acryloxymethyltricyclo(2.5.1.0<sup>2,6</sup>)-decane and 30 parts by weight 2,2-bis-4-(3-methacryloxypropoxy)-phenyl propane (modified bis-GMA), 24 parts by weight silanized pyrogenic silica, 0.3 parts by weight camphor quinone, 3 parts by weight N-dimethyl  
10 aminoethyl methacrylate and 110 parts by weight YF<sub>3</sub>.

••••• Control example

••••• 3.9 g of the pre-mix and 6.1 g silanized tooth-like pigmented  
••••• quartz (grain upper limit approx. 3 μm, average grain size  
••••• approx. 1.5 μm) are kneaded to give a conventional tooth-filling  
15 material with a uniformly pasty consistency.

••••• Example and comparative example 1

••••• 3.9 g of the pre-mix are treated, for the paste according to the  
••••• invention, with 1.6 g pulverized potassium hexafluorotitanate  
and, for the comparative paste, with 1.6 g pulverized sodium  
20 fluoride and in each case 4.5 g silanized, tooth-like pigmented  
quartz (average grain size 1.5 μm) to give a tooth-filling  
material with a uniformly pasty consistency.

Comparative example 2

25 3.9 g of the pre-mix are treated with 0.4 g pulverized sodium  
fluoride and 5.7 g silanized tooth-like pigmented quartz (average  
grain size 1.5 μm) to give a tooth-filling composition with a  
uniformly pasty consistency.

The tooth-colored pastes of the control example, of the example according to the invention and of comparative examples 1 to 2 were moulded to give testpieces according to the instructions given below the following Table 1, and cured. The compressive strength, the bending strength and the opacity of the testpieces were then determined. The results of the investigations are summarized in Table 1 below.

TABLE 1

Mechanical properties of the cured tooth-colored composites (Series 1: Control example, example and comparative examples 1 and 2)

	Control example	Example	Comparative example 1	Comparative example 2
Compressive strength <sup>1)</sup> [MPa]	420	410	340	360
Bending strength <sup>2)</sup> [MPa]	110	102	87	90
Opacity <sup>3)</sup> [%]	92.0	93.3	99.8	98.0

- 1) Compressive strength measured according to ISO 9917
- 2) Bending strength measured according to ISO 4049
- 3) Opacity measured with a Cielab colorimeter (Testpiece disks diameter 2 cm, height 3.5 mm)

In further investigations the fluoride ion release of the cured tooth-colored composites of the control example, of the example according to the invention and of comparative examples 1 and 2 and of a standard commercial glass ionomer cement was determined.

The results are summarized in Table 2 below and represented graphically in Figure 1. The fluoride ion release is surprisingly high and comparable with that of the standard commercial glass ionomer cement.

TABLE 2

5 Fluoride release<sup>1)</sup> of the composites of series 1 (ppm F/d)

	1 day	7 days	14 days
GIZ Ketac-Fil	3.60	1.00	0.62
Control example	0.05	0.01	0.01
Example	5.16	0.82	0.19
Comparative example 1	15.90	6.00	4.10
Comparative example 2	4.00	1.50	1.00

1) two testpieces (Ø 15 mm, h 1.5 mm) are stored freely suspended in 50 ml distilled water at 36° and, after the appropriate period, the fluoride concentration is measured using ion-sensitive electrodes. After each measurement the water is changed. The data refer to the daily release.

Series 2: Preparation and testing of conventional and fluoride-releasing composite tooth-filling materials without coloration

Preparation of a pre-mix

15 A pre-mix is kneaded from 70 parts by weight bis-acryloxymethyltricyclo(2.5.1.0<sup>2,6</sup>)-decane and 30 parts by weight 2,2-bis-4-(3-methacryloxypropoxy)-phenyl propane, 24 parts by weight silanized pyrogenic silica, 0.3 parts by weight camphor quinone, 3 parts by weight N-dimethylaminoethyl methacrylate and  
20 110 parts by weight YF<sub>3</sub>.

Preparation of the composite pastes

The quantity of pre-mix given in Table 3 is treated in each case with the given quantities of fluoride-releasing filler and non-pigmented quartz to give tooth-filling materials of comparable pasty consistency. The consistency is controlled with reference to the viscosity.

Properties of the composites

Table 3 shows the compositions of Examples 1 and 2 and of the control example and of comparative examples 1 to 4 of series 2. At a comparable content of fluoride-releasing filler and comparable viscosity (processing properties), the composites according to the invention have an increased total filler content. As a result, the polymerization shrinkage attributable to the plastic matrix is reduced compared with less filled systems (cf. Table 4). This can counteract the tendency towards edge gaps formation.

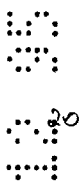
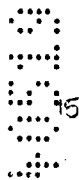


Table 4 shows that the composites according to the invention also have good aesthetics (= low opacity) in addition to excellent mechanical values in the non-colored state. Compared with the materials with sodium fluoride (comparative examples 2 and 3), which appear dull and lifeless, the materials according to the invention have partly tooth-like transparency and aesthetics.



In particular, the comparison of the  $K_2TiF_6$  with the NaF-containing materials is surprising. K. Aleksieva et al. report that NaF as fluoride-releasing constituent weakens the mechanical values of PMMA prosthesis plastics significantly less than  $K_2TiF_6$ . Unexpectedly, the opposite is found for the composite materials based on difunctional (meth)acrylates.

Table 5 shows that in a hydrolysis stability test (10 h storage in water at 100°C) the surface hardness of the materials according to the invention increases in a clearly more marked

manner (so-called secondary curing effect) than in the case of the comparative examples.

Table 6 gives an overview of the fluoride release from the composites. Figure 2 shows this graphically. With the composites according to the invention, release rates are achieved which are comparable with commercially obtainable glass ionomer cements (e.g. Ketac Fil, ESPE, Seefeld). With NaF as fluoride-releasing filler (see comparative example 2) yet higher release rates are of course possible in principle but, because of the poor mechanical values and the deficient aesthetics (cf. Tables 3 and 4), NaF-containing materials are clearly inferior to the composites according to the invention.

The preparations according to the invention thus permit the formulation of composites as dental materials which well satisfy the following requirements:

- Fluoride release comparable to glass ionomer cements
- good mechanical values
- excellent aesthetics
- high stability in an aqueous medium

and which thus represent a significant improvement compared with the state of the art.



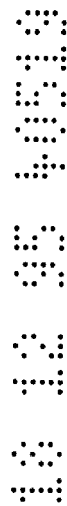


TABLE 3 Composition of the composites from Series 2

	Fluoride-releasing filler	Fluoride-releasing filler [g]	Pre-mix [g]	Non-Pigmented quartz [g]	Total filler content [%]	Viscosity <sup>3)</sup> [mm]
Control example	-	0	42.9	57.1	81.0	0.65
Example 1	K <sub>2</sub> TiF <sub>6</sub>	15.0	36.5	48.5	83.8	0.65
2	KZnF <sub>3</sub>	15.3	37.1	47.6	83.6	0.82
Comparative example 1	BaZrF <sub>6</sub>	15.9	38.5	45.6	83.0	0.98
2	NaF	15.0	47.5	37.5	78.9	1.12
3	NaF	4.0	47.2	48.8	79.1	0.62
4	MEM HF	3.6	36.7	59.7	80.1 <sup>2)</sup>	0.68

1) Total filler content =  $\Sigma$  (amount of filler in the pre-mix + quartz + fluoride-releasing filler)

2) MEM HF is a liquid, its amount is not included in the fillers

3) Measurement of the viscosity by "extrusion compression": 0.6 g of the paste in the form of an extrudate of 4 mm diameter are loaded with 200 g between two plates for 60 s. After 60 s the distance between the two plates is measured.



TABLE 4 Mechanical values of the composite from series 2

	Fluoride-releasing filler	Content [%]	Compressive strength [MPa]	Bending strength [MPa]	Volume shrinkage [%]	Opacity [%]
Control example	-	0	474	146	2.53	76.4
Example 1	$K_2TiF_6$	15.0	438	127	2.12	81.1
2	$KZnF_3$	15.3	464	121	1.81	89.0
Comparative example 1	$BaZrF_6$	15.9	441	127	1.92	81.2
2	NaF	15.0	348	93	1.31	98.5
3	NaF	4.0	422	106	2.24	90.3
4	MEM HF	3.6	416	112	2.39	78.4

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TABLE 5 Surface hardness of the composites from series 2 before and after storage in water for 10 h at 100°C

	Surface hardness [MPa]		
	Before	After	Change
Control example	383	547	+ 43 %
Example 1	478	765	+ 60 %
2	479	638	+ 33 %
Comparative example 1	479	638	+ 33 %
2	166	174	+ 5 %
3	383	383	± 0 %
4	383	383	± 0 %

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TABLE 6 Fluoride release<sup>1)</sup> of the composites from series 2 [ppm F/d]

	Fluoride release [ppm/d]				
	1d	1 week	2 weeks	3 weeks	4 weeks
Comparative example	< 0.1	< 0.01	< 0.01	< 0.01	< 0.01
Example 1	5.1	0.59	0.89	0.51	0.59
2	2.5	0.42	0.57	0.44	0.46
Comparative example 1	0.3	0.04	0.03	0.01	0.02
2	20.5	2.64	1.71	1.14	0.92
3	3.3	0.17	0.16	0.13	0.13
4	0.4	0.11	0.07	0.06	0.05
Commercial glass ionomer cement "Ketac Fil" (ESPE, Seefeld)	3.6	0.87	0.63	0.3	0.27

1) Two testpieces (Ø 15 mm, h 1.5 mm) are stored freely suspended in 50 ml dist. water at 36°C and, after the appropriate period, the fluoride concentration in the water is measured using ion-sensitive electrodes and converted to the quantity released daily. After each measurement, the water is changed.

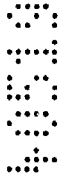
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. Polymerizable dental material containing:
- a) one or more ethylenically unsaturated polymerizable monomers based on di- or multi-functional (meth)acrylates;
  - 5 (b) initiators and optionally activators;
  - (c) usual fillers, and optionally pigments, thixotropic auxiliaries, plasticizers and other auxiliaries; characterized in that it additionally contains
  - 10 (d) one or more sufficiently water-soluble inorganic complex fluorides of general formula



where

A is a monovalent cation, M is a metal of the III-V main group or II-V sub-group, n is a whole number from 1 to 3 and m is a whole number from 3 to 6.



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2. Dental material according to claim 1, characterized in that A is an alkali metal ion, preferably a sodium or a potassium ion, or  $NR_4^+$  with R =  $C_1-C_{18}$  alkyl, phenyl or substituted phenyl.



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3. Dental material according to Claim 2, characterized in that R is substituted phenyl and the substituents for phenyl are selected from the group consisting of  $C_1-C_6$  alkyl groups,  $C_1-C_6$  alkyl groups which are substituted by halides or nitrogen or oxygen-containing groups, halides,  $C_1-C_6$  oxyalkyl groups and  $C_1-C_6$  azaalkyl groups.

4. Dental material according to Claim 2, characterized in that R is a  $C_1-C_6$  alkyl group.

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5. Dental material according to Claims 1 to 4, characterized in that the group  $MF_m$  is selected from  $SiF_6^{2-}$ ,  $TiF_6^{2-}$ ,  $ZrF_6^{2-}$ ,  $AlF_6^{3-}$ ,  $ZnF_3^-$ ,  $PF_6^-$  and  $BF_4^-$ .

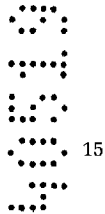
6. Dental material according to Claims 1 to 5, characterized in that it contains

- 5 10 to 55% by wt. component (a),  
0.01 to 10% by wt. component (b),  
40 to 85% by wt. component (c) and  
2 to 25% by wt. component (d).

7. Dental material according to Claims 1 to 6, characterized in that it contains

- 10 14 to 44% by wt. component (a),  
0.1 to 5% by wt. component (b),  
50 to 80% by wt. component (c) and  
5 to 15% by wt., component (d).

8. Dental material according to claim 7 wherein component (d) is in an amount of 5 to 10% by wt.



- 15 9. Use of one or more sufficiently water-soluble inorganic complex fluorides of general formula



where A is a monovalent cation, M is a metal of the III-V main group or II-V sub-group, n is a whole number from 1 to 3 and m is a whole number from 3 to 6, for producing polymerizable, fluoride-releasing dental materials, which, in addition to the inorganic complex fluoride, contain:



- 20 (a) one or more ethylenically unsaturated polymerizable monomers based on di- or multi-functional (meth) acrylates;  
25 (b) initiators and optionally activators; and  
(c) usual fillers, and optionally pigments, thixotropic auxiliaries, plasticizers and other auxiliaries.

Dated this 23rd day of February 1999

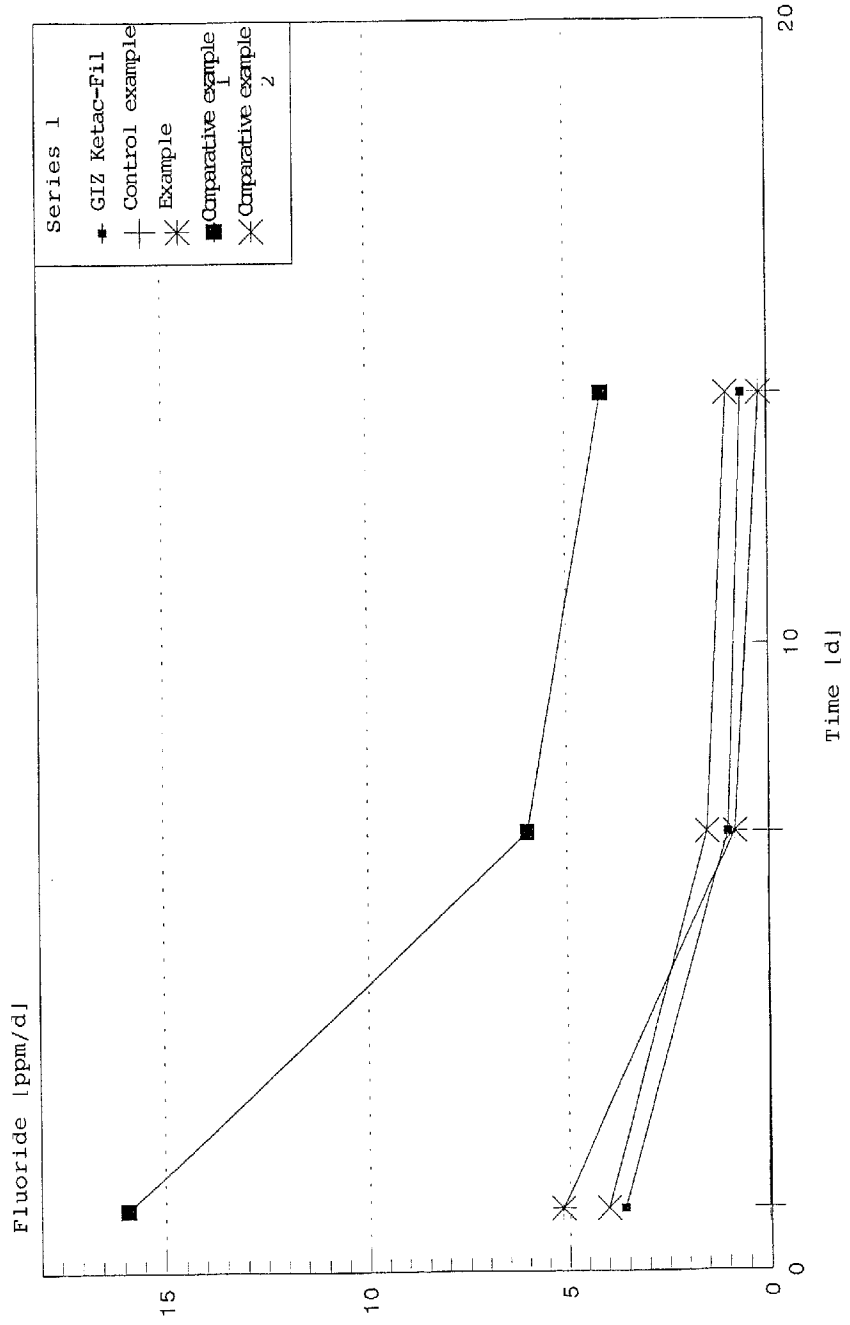
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Figure 1



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Figure 2

