(12) UK Patent Application (19) GB (11) 2 099 455 A

(21) Application No 8207282
(22) Date of filing 12 Mar 1982
(30) Priority data
(31) 56/039575
(32) 20 Mar 1981
(33) Japan (JP)
(43) Application published
8 Dec 1982
(51) INT CL[3]
C22C 5/06
(52) Domestic classification
C7A B230 B23X B23Y B279 B289 B309 B319 B320 B325 B327 B329 B32Y B331 B333 B335 B337 B339 B33X B349 B369 B389 B399 B419 B439 B440 B44Y B46Y B483 B485 B487 B489 B519 B539 B549 B559 B610 B611 B613 B616 B619 B621 B622 B624 B625 B627 B62X B630 B635 B63Y B661 B663 B665 B667 B669 B66X B670 B67Y
(56) Documents cited
None
(58) Field of search
C7A
(71) Applicants
Ishi Miura,
No. 21—6 3-chome,
Kamimeguro, Meguro-ku,
Tokyo, Japan,
G—C Shika Kogyo
Kabushiki Kaisha,
No. 76—1 Hasunuma-cho, Itabashi-ku, Tokyo,
Japan,
Atsushige Sato,
No. 24—3 4-chome,
Asagayakita, Suginami-ku, Tokyo, Japan
(72) Inventors
Ishi Miura,
Atsushige Sato,
Yasuhiro Kumei,
Osamu Okuno,
Bunsaku Yoshida
(74) Agents
Marks and Clerk,
57—60 Lincoln's Inn
Fields, London,
WC2A 3LS

(54) **Setting compositions for dental use**

(57) A setting composition for dental use comprises an alloy composed mainly of silver and tin, and including one or more of copper, zinc, indium, palladium and gold; mercury in an amount sufficient to amalgamate the alloy; and selenium. The selenium may be pre-coated with a metal showing an affinity for mercury, such as silver. The amount of selenium contained is preferably in a range of 0.005 to 5% by weight.

GB 2 099 455 A

FIG. 1

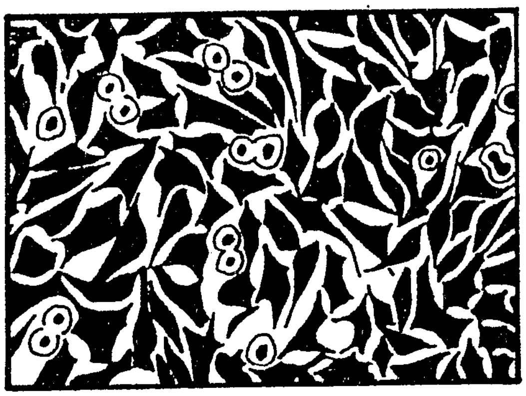


FIG. 2

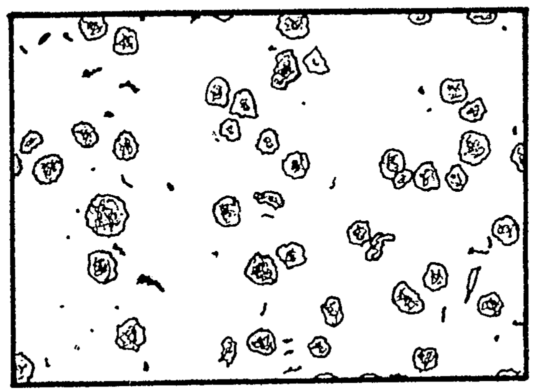
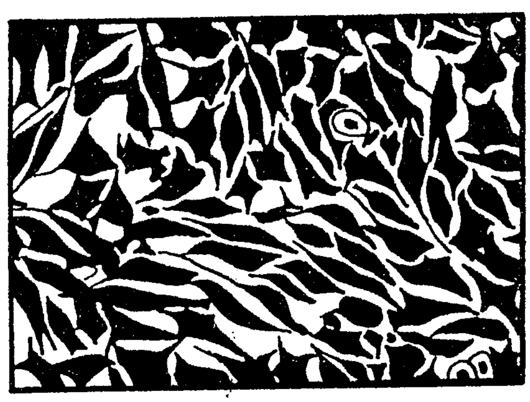


FIG. 3

FIG. 4



SPECIFICATION

Setting compositions for dental use

The present invention relates to setting compositions for dental use, that is to dental amalgam compositions.

Dental amalgams are prepared by triturating alloy powders composed mainly of silver and tin with mercury, and are condensed and set into the cavities of the teeth in the mouth.

In this specification, all percentages referred to are per cent by weight, unless otherwise noted.

Heretofore, alloys for dental amalgams have been composed mainly of not less than 65% silver, not more than 29% tin, not more than 3% mercury, and not more than 2% zinc, as specified by JIS T—6109. However, it has been found that such amalgam alloys have insufficient mechanical properties and corrosion resistance, since, once set, a phase of $Sn_{7-8}Hg(\gamma_2)$ is crystallized out, which is poor in strength and susceptible to corrosion.

Recently, it has been proposed to use high-copper or dispersion-strengthened type of amalgam alloys which cause no crystallization of such a phase. These alloys include copper in an amount exceeding the upper limit provided by the foregoing Japanese Industrial Standards (JIS), and have been developed to improve the mechanical properties by causing crystallization of Cu_3Sn (ε) or Cu_6Sn_5 (η) phase, while suppressing crystallization the $Sn_{7-8}Hg$ (γ_2) phase. However, these alloys do not take account of initial compressive strength after condensation and the toxicity of the leaching mercury. In other words, it takes several hours to make the condensed amalgam reach a strength sufficient to resist biting forces; in the meantime, there is a possibility that the condensed amalgam may break due to external forces, if applied. To add to this, the conventional amalgam has another disadvantage in that, during setting, it comes in contact with oral fluids, so that the harmful mercury leaches and accumulates in the body.

It has now been found that selenium is effective in increasing the initial compressive strength of a dental amalgam to prevent it from breaking due to biting forces and in suppressing the toxicity of the leaching mercury.

The present invention provides a setting composition for dental use, comprising a dental amalgam alloy composed mainly of silver and tin, and including one or more of copper, zinc, indium, palladium and gold; mercury in an amount sufficient to amalgamate the said alloy; and selenium.

Selenium is an element which is difficult to alloy with amalgamable elements, i.e. silver, tin, copper, mercury etc.; nevertheless, it reacts partly with mercury in an amalgam to provide a phase of SeHg. That reaction takes place only in the surface layer of the amalgam, however. This results in a lowering of the plasticity of the amalgam as the initial compressive strength thereof increases. This mechanism is comparable to that of concrete comprising pieces of stone, sand and cement, and provides an extremely firm structure. As a consequence, once set, the amalgam has improved mechanical properties such as compressive strength and flow. It is important that selenium is antagonistic to the toxicity of mercury leaching in oral fluids.

The amount of selenium contained in the amalgam composition according to the present invention is preferably in the range from 0.005 to 5% by weight relative to the total weight of the amalgam alloy and the mercury to amalgamate it. If the amount of selenium present is greater than 5%, the resulting composition may have inferior compressive strength to a selenium-free composition, whereas if the amount of selenium is less than 0.005% the selenium may have no substantial effect.

The amalgam alloy may contain selenium, or the amalgam alloy may be contained in advance with mercury in an amount of not more than 3% by weight, or selenium may be contained in the mercury to amalgamate the amalgam alloy, or selenium may be contained in advance in both the amalgam alloy and the mercury for amalgamation.

The amalgam compositions containing selenium are applicable with equal advantage not only to conventional alloys meeting the Japanese Industrial Standards but also to alloys of the dispersion-strengthened type or the high-copper type.

Selenium may be contained in an amalgam mixture in any suitable manner by, for example, (i) mixing selenium with powder of an amalgam alloy followed by triturating with mercury; (ii) pre-melting selenium in an amalgam alloy or mercury from one or both of which is obtained an amalgam; and (iii) mixing selenium-containing alloy powders of dispersion type and mercury. The selenium thus added has the effect of improving the initial compressive strength of the amalgam and reducing the toxicity of mercury.

In a particularly preferred method for the addition of selenium, selenium powder is pre-coated by vapour-deposition or plating with any one of silver, tin, copper, zinc, indium, palladium, gold and mercury or an alloy of one or more of these metals. This method makes amalgamation more uniform than do the above-mentioned three methods in which selenium is merely added.

The invention will be further described with reference to the following illustrative examples and comparative examples, in which samples are prepared as described and then subjected to testings. The test results are given also.

EXAMPLE 1

An amalgam alloy having a composition of silver 70%, tin 27% and copper 3% was melted and disintegrated by atomization in a nitrogen stream. The fine powder, which passed through a sieve of 270 mesh, was heat-treated, and then mixed uniformly with 0.2% by weight of selenium powder. The resulting mixture was added with mercury in a weight ratio of 1 to 0.75, and triturated mechanically by means of an amalgamator for ten seconds to prepare a Sample No. 1.

EXAMPLE 2

An amalgam alloy having a composition of silver 70%, tin 27% and copper 3% was melted and disintegrated by atomization in a nitrogen stream. The fine powder, which passed through a sieve of 270 mesh, was heat-treated, and then mixed uniformly with 0.2% by weight of selenium powder which had been pre-coated by vacuum-deposition with silver in a thin layer having a thickness of about five micrometers. The resulting mixture was added with mercury in a weight ratio of 1 to 0.75, and triturated mechanically by means of an amalgamator for ten seconds to prepare a Sample No. 2.

EXAMPLE 3

An amalgam alloy having a composition of silver 70%, tin 26%, copper 3%, zinc 0.5% and selenium 0.5% was melted, and poured into a mould to obtain an ingot which was in turn lathed. The fine powder, which passed through a sieve of 200 mesh, was heat-treated. The resulting mixture was added with mercury in a weight ratio of 1 to 1, and triturated mechanically by means of an amalgamator for ten seconds to prepare a Sample No. 3.

EXAMPLE 4

An amalgam alloy having a composition of silver 60%, tin 27% and copper 13% was melted and disintegrated by atomization in a nitrogen stream. The fine powder, which passed through a sieve of 270 mesh, was heat-treated, and added with 0.1% selenium-containing mercury in a weight ratio of 1 to 0.85. The resulting mixture was mechanically triturated by means of an amalgamator for ten seconds to prepare a Sample No. 4.

EXAMPLE 5

An amalgam alloy having a composition of silver 69.9%, tin 27%, copper 3% and selenium 0.1% was melted and disintegrated by atomization in a nitrogen stream. The fine powder, which passed through a sieve of 270 mesh, was heat-treated, and added with 0.1% selenium-containing mercury in a weight ratio of 1 to 0.75. The resulting mixture was mechanically triturated by means of an amalgamator for ten seconds to prepare a Sample No. 5.

EXAMPLE 6

An amalgam alloy having a composition of silver 70%, tin 27%, copper 2% and selenium 1% was melted and poured into a mould to prepare an ingot which was in turn lathed. The fine powder, which passed through a sieve of 200 mesh, was heat-treated. The powder was mixed mechanically with a second fine powder in a weight ratio of 6 to 4, the second fine powder being obtained by melting an amalgam alloy having a composition of silver 72%, copper 27% and indium 1% followed by atomization and sieving with a sieve of 270 mesh. The resulting powder was added with mercury in a weight ratio of 1 to 1.2, and triturated mechanically by means of an amalgamator for 15 seconds to prepare a Sample No. 6.

EXAMPLE 7

An amalgam alloy having a composition of silver 45%, tin 30% and copper 25% was melted and disintegrated by atomization in a nitrogen stream. The fine powder, which passed through a sieve of 270 mesh, was heat-treated and added with mercury in a weight ratio of 1 to 0.82. The resulting mixture was added with selenium powder in an amount of 2.0% relative to the total weight of the alloy powder and mercury, and triturated mechanically by means of an amalgamator for ten seconds to prepare a Sample No. 7.

Reference will now be made to Comparative Examples in which selenium is not contained, for the purpose of comparison.

COMPARATIVE EXAMPLE 1

An amalgam alloy having a composition of silver 70%, tin 27% and copper 3% was melted and disintegrated by atomization in a nitrogen stream. The fine powder, which passed through a sieve of 270 mesh, was heat-treated, and added with mercury in a weight ratio of 1 to 0.75. The resulting mixture was mechanically triturated by means of an amalgamator for ten seconds to prepare a Comparative Sample No. 1.

COMPARATIVE EXAMPLE 2

An amalgam alloy having a composition of silver 70%, tin 26%, copper 3% and zinc 1% was melted and poured into a mould to obtain an ingot which was then lathed. The fine powder, which passed through a sieve of 200 mesh, was heat-treated, and added with mercury in a weight ratio of 1 to 1. The resulting mixture was mechanically triturated by means of an amalgamator for ten seconds to prepare a Comparative Sample No. 2.

COMPARATIVE EXAMPLE 3

An amalgam alloy having a composition of silver 70%, tin 27% and copper 3% was melted and poured into a mould to obtain an ingot which was then lathed. The fine powder, which passed through a sieve of 200 mesh, was heat-treated. Apart from this, an amalgam alloy having a composition of silver 72%, copper 27% and indium 1% was melted and disintegrated by atomization in a nitrogen stream, followed by sieving with a sieve of 270 mesh. The first powder was mechanically mixed with the second powder in a weight ratio of 6 to 4 to form an alloy powder which was added with mercury in a weight ratio of 1 to 1.2. The resulting mixture was mechanically triturated by means of an amalgamator for 15 seconds to prepare a Comparative Sample No. 3.

Figures 1 to 4 of the accompanying drawings are phase contrast microphotographs of L cells, wherein figure 1 shows normal cultured L cells, figure 2 shows L cells applied with the amalgam of Comparative Sample No. 1, figure 3 shows L cells applied with the amalgam of Sample No. 3, and figure 4 shows L cells applied with the amalgam of Sample No. 1.

The samples obtained in the Examples as described above were tested as regards their manipulation time, compressive strength, flow, and cytotoxicity, and the results obtained are given in the Table below.

TABLE

Sample	Manipulation time (min.)	Compressive Strength (Kg/cm^2)		Flow (%)	Cytotoxicity *
		30 min.	24 hours		
1	8	637	4750	0.73	None
2	8	933	5070	0.70	None
3	6	710	4010	2.30	Slight
4	6	967	6160	0.31	None
5	8	625	4650	1.20	None
6	6	765	5530	1.05	None
7	8	772	5180	0.58	Slight
Comparative Sample					
1	8	403	4340	1.42	Marked
2	6	445	3770	2.80	"
3	6	534	5281	1.60	"

* See Figures 1 to 4

In the table, the manipulation time shall be taken as a period of time during which the samples are condensed and easily carved in a tooth model, and both the compressive strength and the flow were measured according to the American Dental Association Specification No. 1 (A.D.A.S. No. 1).

Testing of cytotoxicity was carried out on the basis of Spangberg's 51Cr release assay.

The test results indicate that Sample Nos. 1, 2, 5 and 7, although their manipulation time is identical with that of Comparative Sample No. 1, have a compressive strength after 30 min. about 1.5

to 2 times greater than that of Comparative Sample No. 1. This means that Sample Nos. 1, 2, 5 and 7 are advantageously prevented from breaking due to initial biting forces which may be applied after condensing. In addition, the compressive strength of the samples according to the invention continued to increase even after 24 hours, so that the flow was decreased. This means that the samples according to the invention provide condensed restorations which can resist biting forces over extended periods of time and, hence, are not broken. Similar results are obtained if Sample Nos. 3 and 6 are compared with Comparative Sample Nos. 2 and 3, respectively.

Example 2 shows the effect that is obtained by the selenium pre-coated with a metal showing an affinity for mercury. From a comparison between Sample No. 2 and Sample No. 1, it is found that the former has an initial compressive strength after 30 minutes about 1.5 times greater than that of the latter. Sample No. 2 increases its high final strength. Thus, the selenium coated in advance with a metal showing an affinity for mercury, such as silver, permits earlier uniform amalgamation with little danger of breaking of the condensed restoration at the initial biting.

The cytotoxicity tests reveal that Samples Nos. 1—2 and 4—6 show no toxicity at all, and Sample Nos. 3 and 7 show a slight degree of toxicity, whereas Comparative Sample Nos. 1—3 all show a considerable degree of toxicity.

Typical results of the toxicity tests are shown in Figures 1—4.

More specifically, figure 1 is a phase contrast microphotograph of normally cultured L cells, and figure 2 is a similar photograph of L cells to which Comparative Sample No. 1 was applied, showing that all the cells are exterminated. Figure 3 shows the cells to which Sample No. 3 was applied, showing that the cell density decreases slightly, yet the cell shape is similar to that of the normal cells, and hence the cytotoxicity is reduced. Figure 4 shows the cells to which Sample No. 1 was applied, showing that the cell density and shape are comparable to those of the normal cells and, hence, the cytotoxicity is completely eliminated.

It is thus found that selenium-containing dental amalgams show no or extremely little cytotoxicity as compared with the selenium-free amalgams, and provide condensed restorations well-suited to oral conditions.

As will be appreciated from the foregoing, the dental amalgams according to the present invention are superior to the prior art amalgams not only because the mechanical properties are improved but also because the cytotoxicity is reduced or eliminated, the compositions according to the invention having no or extremely little cytotoxicity.

CLAIMS

1. A setting composition for dental use, comprising a dental silver amalgam alloy composed mainly of silver and tin, and including one or more of copper, zinc, indium, palladium and gold; mercury in an amount sufficient to amalgamate the said alloy; and selenium.

2. A setting composition as claimed in Claim 1, in which the selenium is pre-coated with one or more of the said amalgam alloy ingredients.

3. A setting composition as claimed in Claim 1 or 2, in which the amount of selenium contained in the composition is in the range of from 0.005 to 5% by weight relative to the total weight of the amalgam alloy and the mercury to amalgamate it.

4. A setting composition as claimed in any of Claims 1 to 3, in which the said amalgam alloy contains selenium.

5. A setting composition as claimed in any of Claims 1 to 4, in which the said amalgam alloy contains mercury in an amount of not more than 3% by weight.

6. A setting composition as claimed in any of Claims 1 to 5, in which selenium is contained in the mercury to amalgamate the said amalgam alloy.

7. A setting composition as claimed in any of Claims 1 to 3, in which selenium is contained in both the said amalgam alloy and the said mercury for amalgamation.

8. A setting composition for dental use according to Claim 1, substantially as herein described with reference to any of the foregoing Examples Nos. 1 to 7.

New claims or amendments to claims filed on 20 May 1982.

New claim:

9. A setting composition for dental purposes comprising a dental silver amalgam alloy composed mainly of silver and tin, and including one or more of copper, zinc, indium, palladium and gold; and selenium, and said alloy is amalgamated when triturated with mercury.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1982. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained