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Wolf

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[54] **METHOD OF PREPARING DENTAL RESTORATIVE MATERIAL**

[75] Inventor: **Donald Timothy Wolf,** Milford, Del.

[73] Assignee: **Dentsply Research & Development Corporation,** Milford, Del.

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[58] **Field of Search** ..... 29/192 CP, 199, 192 R; 117/100 M; 106/35; 75/169, 173

[56] **References Cited**

UNITED STATES PATENTS

157,140	5/1874	Southworth	75/169 X
249,880	11/1881	Bonwill	75/169 X
485,280	11/1892	Juterbock	29/199 X
1,164,997	12/1915	Davis	29/199 X
1,963,085	6/1934	Gray	75/169 X
2,991,176	7/1961	Clancy	117/100 M X
3,154,413	10/1964	Dow	117/100 M UX
3,305,356	2/1967	Youdelis	75/169 X

Primary Examiner—L. Dewayne Rutledge
Assistant Examiner—O. F. Crutchfield

[57] **ABSTRACT**

Dental amalgam material and method of making the same in which a silver alloy particle is formed and coated with gold. Upon the addition of mercury, the gold coating retards the formation of the silver alloy-mercury amalgam, thus extending working time.

10 Claims, No Drawings

METHOD OF PREPARING DENTAL RESTORATIVE MATERIAL

BACKGROUND OF THE INVENTION

This invention relates to dental amalgams and methods for the production thereof.

The prior art is replete with various suggestions for providing dental amalgams, and includes various possibilities as to compositions and modes of manufacture.

In searching for improved combinations, a number of formulations have been proposed. As noted in U.S. Pat. No. 1,574,714, the so-called "amalgam" or "silver" dental fillings are usually made of an alloy of silver and tin often containing small percentages of copper and zinc which is mixed with mercury to form the amalgam. That patent, for example, discloses an alloy formula comprising 67 parts silver, 27 parts tin, 5 parts copper and 1 part zinc, and suggests the addition of elements from the fifth, sixth or seventh group of the periodic system, such as chromium, vanadium, manganese, tungsten, molybdenum and tantalum, to increase hardness.

Other prior art patents suggest alternative amalgam combinations comprising, in addition to silver and tin, elements such as gold, nickel and palladium. See, e.g., U.S. Pat. Nos. 2,460,595; 249,880, 109,173; 1,215,678; 1,022,596 and 485,280. Many of these patents discuss the use of gold, which is also discussed in "Research and Development" magazine, August, 1971 (P.6) and "Dental Industry News," November, 1971.

It has also been suggested that the mechanical properties of conventional alloy materials can be materially affected by processing techniques. For example, see U.S. Pat. No. 3,305,356, which discusses the preparation of spheroidal alloy particles through an atomizing process and the use of various cooling methods.

Notwithstanding all of the various formulations and processes discussed in the prior art, including the literature mentioned above, the dental amalgams presently in use are subject to certain drawbacks in that none ideally meets all of the characteristics desirable for such materials. This, however, is not particularly surprising since the ideal material must possess a wide range of attributes, such as excellent corrosion resistance, durability and hardness, high tensile strength, shear resistance and compressive strength, proper working time, flow rate and expansivity for dental purposes, resistance to crushing and the like.

BRIEF SUMMARY OF THE INVENTION

The broad object of the present invention is the production of a dental amalgam material possessing the foregoing desired attributes to a degree which surpasses that of prior art formulations:

Essentially, it has been discovered that an improved dental amalgam can be formed by initially making spherical silver alloy particles of more or less conventional composition by any of the known particle-forming techniques. Then, in a sharp departure from the prior art, the particles are plated or coated with gold. Subsequently, when the coated particles are mixed with mercury, the gold layer controls the rate of penetration of the mercury into the silver-tin core, providing for longer work time, punctuated by a quick-setting mechanism as the mercury-gold layer provides a vehicle for rapid diffusion of mercury into the core accelerating the amalgamation of the silver-tin alloy.

The mechanism obtained, using the alloy of this invention, permits the use of alloy materials in the core capable of developing higher strength in the set amalgam. For example, unannealed alloys impart better properties to the set amalgam restorations than annealed alloys but are generally not professionally acceptable because the work time of the amalgam is too short for proper placement of the restoration. Therefore, the amalgams prepared with unannealed gold-plated alloy possess significantly greater strength, corrosion resistance and hardness (among other desirable qualities) in comparison with prior art materials.

Thus, it is the object and purpose of this invention to provide an improved dental amalgam and method for making the same. This object and purpose, and others attendant thereto, will be more fully understood by reference to the following detailed specification and claims,

DETAILED DESCRIPTION

Following prior art procedures and formulations, there are almost inevitably formed several phases of the mercury-silver alloy amalgam upon trituration. These appear to be a first phase of silver-mercury composition, e.g., Ag_2Hg_3, and a second phase of tin-mercury, e.g., Sn_7Hg_8. The second phase is highly undesirable because, among other reasons, it corrodes easily and is weak.

While it is thus necessary to reduce or eliminate the second (tin-mercury) phase, this cannot be accomplished by removal of the tin, since this element prevents undue size change as the amalgam sets.

It has been discovered that the troublesome mercury-tin phase can be virtually eliminated without the necessity of disposing with the use of tin. Broadly, this is accomplished through the preparation of a silver alloy, comprising at least about 65% silver, and not more than about 29% tin, with minor proportions of copper (e.g., 6%) and zinc (e.g., 2%), and forming the same into particles by one of several known methods, such as by lathe cutting to produce irregular shapes, or by spraying, to produce spheres and coating the alloy with a thin layer of gold, i.e., no more than 3% by weight of the alloy.

Initially, the uncoated alloy particles are separated into fractions according to size. For example, three fractions may be selected: fines (below 10–15 microns), medium (about 10–15 microns to about 30–44 microns) and coarse (about 30 microns to about 50–60 microns). Good results have been achieved by annealing the fine fraction at high temperatures (e.g., 250°C to 400°C) for more than one hour until the alloy is lightly annealed.

It should be noted that the amount of annealing which may be used with the present invention is substantially less than that employed in conventional technology relating to the preparation of silver alloys. In the conventional process, the substantial annealing is required to slow down the amalgamation of the mercury and silver, but results in a weakening of the amalgam. In particular, the annealing conventionally used reduces compression strength, thereby making the filling susceptible to cracking.

Thus, the present invention provides a means for extending working time, i.e., the period from mixing the mercury with the silver particles until setting of the resulting amalgam, without loss of strength. Moreover,

for the first time, the setting time is selectively controlled by the gold coating on particles of the present invention in which the thickness of the coating varies, thereby affecting the time required for the mercury to "penetrate" the enteric gold coat to join with the silver alloy.

Indeed, with the novel gold coated particles of the present invention, one can select the desired working time, at the end of which there occurs a so-called "snap set." When the working time is expressed graphically, it appears as a virtually horizontal line on the hardness/time coordinates, followed by a sharply rising curve, representing the snap setting. Such graphic depiction makes it even clearer that the setting is a function of how long it takes the mercury to penetrate through the gold coating to the silver alloy particle. This selective setting and extensive working time is something never before achieved in the art and of great value, since conventional compositions afford very little latitude in terms of time.

In more detail, the conventional alloy develops viscosity slowly and, at some point between one and one-half to three minutes, the material becomes unpackable. At some point between 4 to 8 minutes, conventional alloys become carvable.

By contrast, the gold-plated alloy of the present invention has a working time of (preferably) 2 to 3 minutes after which it snap sets and can be carved almost immediately. The material is susceptible to carving for about 3 minutes, according to the preferred formulations, after which it becomes very hard. Such initial high hardness is continued through the life of the material.

As indicated, with the present invention, it may be desirable to use different thicknesses of gold coating. More particularly, it has been found advantageous to use a gold coat of from about 0.5 to about 3% gold (expressing the weight of the gold as a percentage of the total weight of the particle). The gold-plating or coating can be applied by a number of known methods.

The gold plated alloy can also be treated, if desired, with from 0.05 to 3% mercury by plating or by vapor deposition. This mercury coating improves the solution characteristics of the gold-plated alloy and gives better mixes and lower mercury ratios.

Additionally, the judicious selection of particle sizes will also improve the mechanical properties of the amalgam of the present invention. Good results have been achieved with the following mixtures of particles according to the following sizes:

Coarse	0–30%
Medium	40–70%
Fine	30–60%

After the particles are formed and gold-plated as hereinbefore generally described, they are blended. Thereupon, the blend is ready to form an amalgam. Thus, when the dentist has prepared the tooth cavity, he mixes the gold-plated particles with mercury and the amalgamation process begins at the rates heretofore described. He may select working time by adjusting the particle blend, i.e., by using heavier or lighter gold coatings, the working time can be controlled, or by varying the time of trituration which directly modifies working time.

It is novel and of substantial commercial importance that a superior amalgam can be formed using between 35 to 50% mercury. Indeed, excellent results are obtained by using from about 38 to 44% mercury, and no known alloy will form a suitable amalgam with so little mercury as that set forth in said range. This low mercury ratio is significant advantage per se.

The invention can be further understood by reference to the following examples which illustrate, but do not limit, the concept.

EXAMPLE I

A dental alloy prepared according to the American Dental Association Specification No. 1 for alloy for dental amalgam with June 1970 revision (see Guide to Dental Materials and Devices — 6th edition, American Dental Association publication, 211 East Chicago Avenue, Chicago, Ill. 60611, pp 168–171), comprising a minimum of 65% by weight silver, a maximum of 29% tin, a maximum of 6% copper, and a maximum of 2% by weight zinc, was obtained in spherical form by spraying as described in U.S. Pat. No. 3,305,356. The resultant alloy was sized by air classification in a Vortec brand air classification apparatus to obtain two fractions, one having particle sizes 15 microns and larger, and one having particle sizes 15 microns and smaller. Typically, the larger particle size fraction is sieved with a 325 mesh sieve to produce a fraction having particle sizes from 15 microns to 44 microns. This fraction and the smaller particle size fraction are blended into a bimodel distribution in the ratio of up to about 60% by weight of the larger particles and up to about 40% by weight of the smaller particles.

The resulting alloy was plated with between 0.5% by weight gold and 3% by Weight to form a product having the ability to be amalgamated with as little as 38 to 44% by weight of mercury and was able to be carved for about 3 minutes after a 3-minute work time with nearly full strength being developed within approximately 30 minutes. Likewise, the set amalgam exhibits superior corrosion resistance due principally to the reduction in the amount of Gamma 2 formed during the setting reaction.

Other proportions of alloy are, of course, possible to make for optimum properties in a given application, while still employing the novel teaching herein. Likewise, it is possible to coat various alloys with other amalgamatable materials to achieve the advantages of the present invention in the same or different applications, using, for example, copper, palladium, platinum, indium, nichel, cadmium and silver.

I claim:

1. A method of making a dental amalgam comprising the steps of:

a. providing a plurality of silver-tin alloy spheres;

b. coating the individual silver-tin alloy spheres completely with gold; and

c. triturating the gold coated silver-tin alloy spheres with mercury to form an amalgam.

2. The invention of claim **1** wherein the particles comprise up to 30% by weight of particles between about 30 microns to about 60 microns; between 40 to 70% by weight of particles between about 10 microns to about 44 microns; and between 30 to 60% by weight of particles of less than about 10–15 microns.

3. The invention of claim 1 wherein the silver-tin alloy spheres also contain a small amount of one or more of the following: copper, zinc, mercury.

4. The invention of claim 1 wherein mercury is added to comprise about 30 to about 50% of the amalgam.

5. The invention of claim 1 wherein mercury is added to comprise about 38 to about 44% of the amalgam.

6. The invention of claim 1 wherein the silver-tin alloy spheres are coated with from about 0.05 to about 3% gold.

7. The invention of claim 1 wherein the spherical cores are under approximately 60 microns in size.

8. A method for preparing dental restorative material having a controlled working time prior to set comprising the steps of:

a. forming a test group of alloy spheres;

b. sub-dividing the test group;

c. coating each sub-divided test group with a different thickness of gold;

d. applying an amalgamating substance to the spheres of each test group;

e. measuring the working time elapsed from the application of the amalgamating material to the penetration thereof through the gold coatings of the spheres and until the alloys of the spheres set in each test group;

f. forming a working group of alloy spheres;

g. applying to said working group of spheres a gold coating having a thickness corresponding to the aforesaid test group most approximating the desired working time, prior to final setting of the coated spheres by application of an amalgamating material thereto.

9. The invention of claim 8 wherein the amalgamating material is mercury.

10. A method for making dental restorations comprising the steps of:

a. manufacturing spherical particles having spherical inner alloy cores individually covered with substantially uniform gold coatings, said particles having a capacity to snap set after a period of working time upon trituration with mercury, said working time being variable in accordance with the length of trituration;

b. determining the working time required to complete the restoration; and

c. triturating mercury and the coated particles for a preselected length of time to produce the required working time.

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