United States Patent Office 3,141,761 Patented July 21, 1964

3,141,761

PULVERIZED SILVER ALLOYS FOR USE IN PRODUCING DENTAL AMALGAMS

Fritz Röhm, Stuttgart-Kaltental, Germany, assignor to Firma Dr. Walter u. Schmitt G.m.b.H., Schwabisch Gmund, Germany

No Drawing. Filed Feb. 20, 1963, Ser. No. 260,065
Claims priority, application Germany Feb. 23, 1962
5 Claims. (Cl. 75—.5)

The present invention relates to improved pulverized silver alloys and more particularly to such alloys which are suited for the production of dental amalgams.

For many years dental amalgams (mercury-silver-tin alloys) of varying compositions have been used for restoring lost tooth structure. Such amalgams usually are prepared by mixing a pulverized silver-tin alloy with mercury shortly prior to their use. Such dental amalgams have in general proved quite satisfactory because of their hardness, edge strength and good margin sealing properties. However, it was found that the known dental amalgams in which the silver content of the pulverized silver alloy usually was between 50 and 70%, often in the course of time become discolored or show evidence of corrosion. Also in some instances such amalgams give rise to discolorations in high carat gold alloy crowns and bridges because of electrolytic action in view of the differences in potential between the amalgam and the gold alloys.

In measurements in the mouth, differences in potential between various amalgam fillings and other metal dental work, such as crowns and bridges of high carat gold alloys, as high as 100 millivolts and more have been found in extreme cases. In these cells the saliva forms the electrolyte. Similarly, often cells occur in the amalgam fillings themselves as the hardened silver amalgams of the usual composition consist of a number of phases, some of which are not noble. In connection with such corrosion the almost silver free tin rich γ_2 phase of the binary mercury alloys is the most unfavorable component.

Often it has been reported that pulverized silver alloys with a higher silver content than 70% hardly can be processed to an amalgam usable by a dentist and that such alloys with a silver content higher than 75% cannot at all be used for such purposes. The reasons given for this are that the alloying with the mercury only proceeds with great difficulty and that upon amalgam formation immediate hardening takes place.

According to the invention it was found unexpectedly that a silver alloy powder containing 80 to 99.5% of silver and the remainder 0.01% to 6% of copper, zinc, cadmium, indium, mercury and tin, either singly or combined, and 0.001% to 19% of gold, palladium and platinum, either singly or in combination, upon trituration with mercury, will provide plastic tooth filling masses usable by dentists.

Especially, such alloys which contain silver contents of 95% and over are also advantageous. Such alloys, for instance, can be of the following composition: 95–99% Ag, 0.1–0.5% Pt and/or Au, 0–0.5% Cu and 1–4.8% Sn; or 97–99.5% Ag, 0.01–0.1% Cu, Cd, Zn and/or Sn and 0.5–3% Au, Pd and/or Pt. However, alloys having a silver content at the lower end of the range according to the invention are admirably suited, such as, for example, alloys of the following illustrative composition: 94–80.2% Ag, 3–17% Pd, 3–17% Au, 0–1% Pt, 0.01–3% Cu, Cd, Zn and/or Sn and 0.5 to 2% Hg.

A portion, up to 1%, of the noble metals gold, palladium and platinum in the alloys according to the invention can, if desired, be replaced by rhodium, iridium, ruthenium or osmium and a portion, up to 0.5%, of the base metals can be replaced by nickel, cobalt, chromium or silicon. The diameter of the individual particles of the

powdered silver alloy according to the invention is below 0.2 mm.

The following procedures can, for example, be employed in the preparation of the silver alloy powders:

(1) After smelting the alloys are cast to bars and then comminuted mechanically, for example, by filing or milling. In such filing or milling operation the bars are converted to filings or cuttings whose individual sizes should be as close as possible as that of the desired grain size of the final powders. In order to obtain a powder having a grain size of under 0.2 mm. in diameter from such filings or cuttings as is desired, they are passed through appropriate sieves.

(2) Such silver alloy powders can also be produced chemically from corresponding solutions, for example, by reduction. Under appropriate conditions the screening of the powders produced may be omitted as the grain sizes obtainable are within the desired range.

(3) The silver alloy powders according to the invention can also be obtained by plasma spraying which is similar to the metal spraying techniques known in the art. The metal is sprayed with a special metal spraying pistol having an appropriate nozzle into a liquid, such as, water and depending upon the temperature, nozzle size, spraying pressure and discharge velocity, a metal powder of appropriate grain size is obtained.

(4) The silver alloy powders according to the invention can also be prepared by electrochemical processes, such as, for example, by cathodic deposition. The process is similar to the known metal electrolyses for the production of pure metals. It is possible to obtain alloy powders the grain size of which are very uniform and within the desired range by appropriate control of the current density and the concentration of the solution electrolyzed.

It was also found that it often is advantageous to subject the silver alloy powders obtained by the different processes to an aftertreatment. It is possible in this way to increase the hardening time, that is, the time required for hardening after the silver alloy powder has been mixed with the mercury, to the desires of the individual dentist. Such aftertreatment consists in a heat treatment, known per se, the temperature of which and duration depends upon the composition of the powder concerned and its method of preparation. The aftertreatment of a silver alloy powder according to the invention can, for instance, be carried out at 130 to 360° C. over a period of 1 to 5 or more hours, depending upon its method of production, grain size and desired properties. For instance a silver alloy powder according to the invention produced by milling having an average grain size of 80μ, after heating for 4 hours at 320° C., was suitable for the preparation of a dental amalgam by trituration with mercury in a proportion of 5 parts powder to 8 parts mercury. The resulting plastic mass was workable for 16 minutes and after packing into a cavity hardened to a filling of a hardness of $H_{B2.5}$ 80–90 kg./mm.^{2} and of an expansion below +15 to +20μ/cm. Under load it exhibited a flow of 1.2%. The potential of such amalgam against a hydrogen electrode is +0.7 to +0.8 volt.

With some silver alloy powder compositions and methods of preparation the heat treatment can be carried out at higher temperatures up to just below the melting point thereof.

In electrolytic silver alloy powders according to the invention containing 99.5% silver, it was found advantageous to employ a heat treatment at 800–950° C. for 30 minutes to 2 hours, expediently under an inert gas, such as pure argon, or under high vacuum to prevent surface oxidation. The powder thus obtained with a grain size of 120μ when triturated with mercury in a proportion of 5 parts powder to 7 parts mercury gave an amal-

gam composition which was workable for 12 minutes and which after hardening had a hardness of $H_{B2.5}$ of 90–100 kg./mm.^{2}, an expansion of +20 to +30μ/cm. and a flow of 0.8%.

Also, it can be of advantage to subject the cast alloy bars to a homogenization before the powders are produced therefrom. The temperature and duration of such homogenization treatments can vary greatly within wide limits depending upon the alloy composition concerned.

Illustrative silver alloys for the silver alloy powders according to the invention are:

(1) 99.5% Ag, 0.1% Pt, 0.4% Sn
(2) 98.0% Ag, 0.25% Pt, 0.25% Cu, 1.5% Sn
(3) 95.0% Ag, 0.25% Au, 4.75 Sn
(4) 95.0% Ag, 0.25% Pt, 0.25% Au, 0.5% Cu, 4.0 Sn
(5) 95.0% Ag, 0.5% Pd, 3.5% Sn
(6) 85% Ag, 9.5% Pd, 1.0% Au, 1.5% Pt, 1.5% Cu, 1.2% Sn, 0.3% Zn
(7) 95% Ag, 4.9% Sn, 0.1% Au
(8) 95% Ag, 4.9% Pd, 0.1% Cu
(9) 95% Ag, 0.5% Pt, 1.0% Cu, 3.5% Sn
(10) 90% Ag, 9.8% Pd, 0.2% Cu

When 5 parts of alloy 6 were triturated with 6 parts of mercury an amalgam was obtained which after hardening exhibited a hardness of $H_{B2.5}$ of 92 kg./mm.^{2}, an expansion of +15 to +25μ/cm. and a flow of 0.9%. The powder was one obtained by mechanical comminution and an after heat treatment for 4 hours at 210° C. under vacuum.

The alloys given in the specific examples as well as many others within the purview of the invention after amalgamation with mercury have such a favorable potential against a hydrogen electrode that no corrosion occurs.

I claim:

1. A method of producing a dental amalgam which comprises triturating a silver alloy powder in which the diameter of the individual alloy particles is less than 0.2 mm. consisting essentially of an alloy of 80–99.5% silver and the remainder 0.01–6% of at least one metal selected from the group consisting of copper, zinc, cadmium, indium, mercury and tin and 0.001 to 19.9% of at least one noble metal selected from the group consisting of gold, palladium and platinum, with mercury in a proportion of about 5 parts by weight of the silver alloy powder to 6–8 parts by weight of mercury.

2. The method of claim 1 in which said silver alloy powder essentially consists of an alloy of 95–99% of silver, 0.1 to 0.5% of gold, 0.1–0.5% of copper and 1–4.8% of tin.

3. The method of claim 1 in which said silver alloy powder essentially consists of an alloy of 95–99% of silver, 0.1 to 0.5% of platinum, 0.1–0.5% of copper and 1–4.8% of tin.

4. The method of claim 1 in which said silver alloy powder essentially consists of an alloy of 95–99% of silver, 0.1 to 0.5% of gold and platinum, 0.1–0.5% of copper and 1–4.8% of tin.

5. The method of claim 1 in which said silver alloy powder has been subjected to a heat treatment effective to increase the hardening time of the amalgam produced therefrom.

References Cited in the file of this patent

UNITED STATES PATENTS

1,574,714	Vogt	Feb. 23, 1926
1,719,365	Gray et al.	July 2, 1929
1,720,216	Gray et al.	July 9, 1929
1,847,941	Gray et al.	Mar. 1, 1932
1,965,012	Taylor	July 3, 1934
2,058,857	Emmert	Oct. 27, 1936
2,151,905	Emmert	Mar. 28, 1939
2,353,254	McCandless	July 11, 1944
2,698,231	Schulze et al.	Dec. 28 ,1954
2,734,823	Sheff	Feb. 14, 1956
2,791,498	Brundin et al.	May 7, 1957
2,805,155	Gelb et al.	Sept. 3, 1957
2,935,401	Anderson et al.	May 3, 1960