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3,305,356

DENTAL AMALGAM

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7 Claims. (Cl. 75—134)

This invention relates to an improved dental amalgam and to a process for the preparation of such improved amalgam.

The conventional dental alloys are comprised basically of a silver-tin alloy compound (of about 75% by weight silver and about 25% by weight tin with some copper and zinc—up to 5% copper and 2% zinc by weight—replacing the silver-tin) amalgamated with mercury. However, this dental alloy, although satisfactory for many purposes, is not altogether suitable because of deficiencies in compressive strength, abrasion resistance and flow rate.

Features of the present invention, then include the provision of dental alloys having improved compressive strength and abrasion resistance and decreased flow rate, and to the process for preparing such alloys.

It has now been found that conventional dental alloys may be improved by mechanically dispersing a hard strong metal alloy throughout the conventional amalgam in the form of very fine particles. According to one aspect of the present invention there is now provided a dental amalgam having a compressive strength of about 60,000 to 65,000 p.s.i.g., a hardness of about 110 to 115 d.p.h., (preferably about 115 d.p.h.), and a flow of about 0.5 to 2% (preferably about 1%) in 21 hours, said amalgam comprising: about 30 to 45% (preferably 37.5 to 40.8%) of an alloy powder consisting of 75% by weight silver and 25% by weight tin having up to 7% of the silver-tin alloy replaced by up to 5% copper and up to 2% zinc; 5 to 25% (with a preferable range of 12.5 to 17.5%) of a dispersion phase silver base alloy containing at least 50% silver; and 40–60% (with a preferable range of 41.7 to 50% by weight) of mercury.

A dispersion phase alloy which may be used in this invention is any silver base alloy containing 50% by weight or more of silver. Examples include eutectic silver-copper alloy (72% by weight silver and 28% by weight copper) and an eutectic silver-copper-indium alloy (containing up to 30% by weight indium added to the eutectic silver-copper alloy). Other examples of suitable silver-base alloys include: silver-cadmium alloy having 5 to 50% by weight cadmium; silver-zinc alloy having from 5 to 50% by weight zinc; and silver-aluminum alloy having from 5 to 50% by weight of aluminum.

As used herein, the term "dispersion phase" refers to a metal alloy phase which is dispersed as particles throughout the matrix, and which remains largely intact in the set amalgam, forming a bond to the matrix by either diffusion and/or very slight amalgamation. It is distinguished from the silver-tin alloy phase which is mostly converted to new alloy phases by the action of the mercury during the trituration and setting of the amalgam. Only a very small fraction of the silver-tin compound may remain in the matrix in its original form, that is, in the form of a dispersed particle.

It has been found that the improvement achieved by the present invention is dependent upon, firstly, the size of the particles of the dispersion phase, secondly, the shape of such particles and thirdly, upon the amount of dispersion phase powder contained in the amalgam alloy base. Thus, it has been found that the compressive strength of the amalgam increases and flow decreases with decreasing particle size of the dispersion phase. The particle size of the dispersion powder should at least be passing

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400 mesh size (36 microns) or smaller. A coarser particle, although still improving the mechanical properties of the amalgam, introduces difficulties in the carving operation. The shape of the particle should preferably be spheroidal. The spheroidal shape is obtained by a metal atomizing technique which involves blasting liquid metal alloy drops as they enter a convergent gas stream emanating from several nozzles.

The gas atomization process can be described in general terms only since each alloy behaves differently in the atomization process, and the procedures giving optimum results must be determined by experimentation. In general, the greater the pressure of the atomizing gas (nitrogen which is the preferred gas used in this invention) the finer will be the average particle size of the alloy. The pressure determines the gas velocity emanating from the nozzles and the greater the velocity the more efficient the atomization. Hence it is the gas velocity that is the determining factor which, for a given number of nozzles of a given cross-section area, is determined by the inlet gas pressure. The maximum gas pressure should be used along with the greatest number of converging gas nozzles of smallest cross-section area possible. For the eutectic silver copper alloy the gas pressure used is 100 p.s.i.g., which is almost the maximum pressure that can be maintained in the present apparatus.

The temperature of the molten alloy is the next most critical factor in the atomization procedure. For eutectic alloys which have a constant freezing point, at least 100° C. superheat (degrees above the freezing point) is required. The eutectic silver-copper alloy is gas atomized from a temperature of approximately 900° C. For alloys which have a solidification range (all those mentioned except the pure silver-copper eutectic alloy) at least 150 to 200° C. superheat should be used. The extent of superheat is determined by the solidification range of the alloy. By solidification range is meant the temperature range beginning at the temperature at which the alloy first begins to solidify down to the eutectic or comparable temperature of the particular alloy. These ranges are obtained for binary alloys from the alloy constitutional diagrams given in the A.S.M. Metals Handbook, 1948 Edition. If the suggested superheat of 150 to 200° C. is not used for alloys having a solidification range spheroidization becomes very difficult. The eutectic silver copper alloy should be atomized from 1100° C. and the silver-copper-indium alloy from 800° C. The atomization procedure described above is about 20% efficient, that is 20% of the alloy powder will pass a 400 mesh screen. The remainder must be recycled.

In the preparation of the alloy particle in spheroidal form by the atomization process, it is preferred that the atomization process should be rapid. Exposure of the alloy to air at elevated temperatures for even short periods of time results in surface oxidation of the particles. The oxide film retards the surface diffusion process which increases unduly the setting time of the amalgam.

The atomizing process is better described in "Metal Progress" vol. 82, pages 107–110, 1962.

In addition, however, an irregular particle shape as obtained by either a filing or lathe turning technique can also be used with approximately the same beneficial effects. The silver-copper eutectic alloy containing 30 weight percent indium is sufficiently brittle that it is easily powdered by a filing or lathe turning technique. The lathe turning technique is most efficient. The alloy ingot should be turned at moderate to high speeds on a lathe and the tool cut should be as small as possible (one to several thousandths of an inch).

The eutectic silver-copper should be in the quench-cast condition, which will result if it is gas atomized. As used herein, the term "quench cast condition" is intended to

mean alloy solidified from the liquid state at a cooling rate exceeding normal cooling rates in still air, e.g. by water quenching or quenching in a rapid gas stream.

The quench cast microstructure of the silver-copper eutectic alloy is an extremely fine lamellar one. This condition imparts considerable strength to the alloy. An annealed or slowly cooled alloy coarsens the constituents of the alloy, and thereby decreases its hardness and strength. The dispersion phase alloy of sterling silver composition should be in its age hardened condition to obtain maximum strength for the amalgam. As used herein, the term "age hardened condition" is intended to mean a condition obtained by heat treatment which gives optimum hardness and strength levels to the alloy. This condition is obtained for the sterling silver alloy by gas atomizing the alloy, annealing the powder so obtained at 750° C. for 10 hours followed by water quenching (known as "solution heat treatment"), and then holding the solution heat treated alloy powder at 270° C. for 17 hours (aging). The heat treatment should be carried out in an inert atmosphere (nitrogen or argon) to prevent excessive oxidation of the alloy particles. It is also possible to obtain fairly high strength levels for the sterling silver alloy by the aging process described above, without the intermediate solution heat treatment.

There is an optimum amount of dispersion phase powder that can be added to the amalgam alloy base, below and over which the beneficial effects are diminished. The smaller the particle size the greater the amount of dispersion phase powder that may be added with improving results. For the silver-copper eutectic and the silver-copper eutectic alloy containing up to 30 weight percent indium, the optimum amount to be added to the amalgam alloy powder is approximately 30 weight percent for a particle size passing 400 mesh. More dispersion powder may be added if the particle size is substantially decreased; then, however, the present atomization process becomes economically prohibitive.

In the preparation of the improved alloy according to the present invention, the dispersion phase alloy is added to the conventional amalgam alloy powder as a mechanical mixture of powder of the two alloys. Mercury is added in the amount of 1:1 up to 1:14 mercury to total alloy powder ratio, and the mixture is triturated.

The trituration time is important for it determines the ultimate mechanical properties of the amalgam. For the silver-copper eutectic, sterling silver and the silver-copper indium alloys, trituration time should be at least 15 seconds but not exceed 30 seconds. The trituration method is further described in "The Science of Dental Materials" by E. W. Skinner and R. W. Phillips, W. B. Saunders Company, Philadelphia, Fifth Ed., Chapter 24, 1960, and as will be further described herein in the examples.

The following examples are given to illustrate the present invention:

EXAMPLE 1

A silver-copper eutectic alloy (72% by weight silver, 28% by weight copper) was atomized in a nitrogen atmosphere at 100 p.s.i.g. from a superheat temperature of 875° C. The resulting dispersion base alloy was analyzed for size. The results are given in Table I, as follows:

Table I.—Size analysis

	Percent
Retained on 150 mesh	41
Passing 150 mesh	59
Passing 200 mesh	43
Passing 250 mesh	34
Passing 325 mesh	23
Passing 400 mesh	17
Passing 500 mesh	8.5

EXAMPLE 2

This example is directed to determining the variation in compressive strength of the amalgam when the weight

ratio of silver-copper eutectic dispersion powder to standard alloy powder is varied. The silver-copper eutectic dispersion powder used was in the -400 to +500 mesh range. The mixture of dispersion phase alloy and of standard alloy are each in turn mixed with mercury in the weight ratio 5:7 and each is triturated for 30 seconds. The test specimens are condensed in a mold under 10,000 p.s.i.g. pressure and aged or allowed to set for seven (7) days before testing. The results of the tests under the above conditions are given in Table II.

Table II

Weight ratio dispersion to standard alloy powder:	Compressive strength, p.s.i.g.
0.0	48,500
0.2	57,000
0.32	59,500
0.40	62,000
0.50	64,200
0.60	63,200

This data shows the substantial increase in compressive strength possible through the use of the present invention.

EXAMPLE 3

An alloy mixture containing 0.3 weight ratio of dispersion powder to standard alloy powder was prepared. This alloy was in turn mixed with mercury in a weight ratio 5:7 and triturated for 30 seconds. The test specimens were condensed in a mold under 10,000 p.s.i.g. pressure and aged or allowed to set for seven days before testing. A series of tests was carried out under these conditions with the only variable being the mesh size of the dispersion phase particle mixed with the standard alloy. The variation in compressive strength of the amalgam with the differing mesh sizes of dispersion phase alloy is shown in Table III.

Table III

Dispersion Particle Size				Compressive Strength, p.s.i.g.
Mesh range		Micron range		
-150	+200	-103	+74	54,500
-325	+400	-44	+38	56,200
-400	+500	-38	+27	59,500
	-500	-27	+0	61,200

This data shows clearly the variation of compressive strength of the amalgam with size of dispersion particle, the greatest strength being evident when a particle of mesh size -500 is used.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A dental amalgam having a compressive strength of about 60,000 to 65,000 p.s.i.g., a hardness of about 110 to 115 d.p.h. and a flow of about 0.5 to 2% in 21 hours, said amalgam consisting essentially of:

- about 30 to 45% of an amalgamatable alloy consisting essentially of 75% by weight silver and 25% by weight of tin, said alloy having up to 7% by weight of the silver-tin alloy replaced by up to 5% by weight of copper and up to 2% by weight of zinc;
- about 5 to 25% by weight of discrete particles of a substantially non-amalgamatable alloy containing at least 50% by weight of silver, said alloy (b) being of substantially different chemical composition from said alloy (a), said alloy being present as a dispersion phase in the amalgam matrix and said alloy being in the form of discrete particles remaining essentially wholly intact in the set amalgam; and
- about 40% to 60% by weight of mercury.

2. The dental amalgam of claim 1 wherein said sub-

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stantially non-amalgamatable alloy consists essentially of a silver-copper alloy.

3. The dental amalgam of claim 1 wherein said substantially non-amalgamatable alloy consists essentially of a silver-copper eutectic alloy consisting essentially of 72% by weight silver and 28% by weight copper.

4. The dental amalgam of claim 1 wherein said substantially non-amalgamatable alloy consists essentially of a eutectic silver-copper-indium alloy containing up to 30% by weight indium added to the eutectic silver-copper alloy.

5. The dental amalgam of claim 1 wherein said substantially non-amalgamatable alloy consists essentially of a silver-cadmium alloy consisting essentially of 95-50% by weight silver and correspondingly 5-50% by weight of cadmium.

6. The dental amalgam of claim 1 wherein said substantially non-amalgamatable alloy consists essentially of a silver-zinc alloy consisting essentially of from 95-50% by weight of silver and correspondingly from 5-50% by weight of zinc.

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7. The dental amalgam of claim 1 wherein said substantially non-amalgamatable alloy consists essentially of a silver-aluminum alloy consisting essentially of from 95-50% by weight of silver and correspondingly from 5-50% by weight of aluminum.

References Cited by the Examiner

UNITED STATES PATENTS

2,271,264	1/1942	Kaufmann et al.	75—169
2,698,231	12/1954	Schulze et al.	75—173

OTHER REFERENCES

Smith: "The Chemistry and Metallurgy of Dental Materials," published by Blackwell Scientific Publications, Ltd., Oxford, England, pages 93-108, Dec. 29, 1947.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 33, after "45%" insert -- by weight --; same line 33, after "40.8%)" insert -- by weight --; line 35, after "7%" insert -- by weight --; line 36, after "5%" insert -- by weight --; same line 36, after "2%" insert -- by weight --; line 37, after "25%" insert -- by weight --; same line 37, after "17.5%)" insert -- by weight --; line 38, after "50%" insert -- by weight --; line 39, after "40-60%" insert -- by weight --; column 2, line 35, for "200° C. superheat should be used." read -- 200° C. Superheat above the first solidification temperature (liquidus line) should be used. --; line 46, for "1100° C." read -- 900° C. --; column 3, line 25, for "treatment." read -- treatment, for the latter is difficult due to a tendency for the powder to sinter at high solution heat treatment temperatures. --; line 43, for "1:14" read -- 1.4:1 --; line 44, after "powder" insert -- weight --; line 60, for "base" read -- phase --; column 4, lines 4 and 5, strike out "The mixture of dispersion phase alloy and of standard alloy are each in turned" and insert instead -- The mixtures of the dispersion phase alloy and of the standard alloy are each in turn --; line 61, after "45%" insert -- by weight --

Signed and sealed this 9th day of January 1968.

(SEAL)
Attest:

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