## United States Patent [19]

## Wolf

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## [56] References Cited UNITED STATES PATENTS

#### 3,532,521 10/1970 Bakan et al. ..... 75/169

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#### [57] ABSTRACT

A novel dental restorative is described which achieves improved physical properties by employing a combination of amalgamatable silver-copper-tin dental alloys in the trituration with a minimum of mercury where one of the silver-containing alloys contains between 15 percent and 30 percent copper by weight of the single alloy component.

#### 1 Claim, No Drawings

### 1 **DENTAL ALLOY**

#### BACKGROUND OF THE INVENTION

The mainstay restorative material used in the midst 5 of rapidly advancing technology in the health care fields is still dental amalgam made by triturating a silver, tin alloy with mercury to form a coherent settable mass. This use of this material remains the standard technique used by the dental profession in repairing 10 carious tooth structure. The oral environment has proven to be hostile and difficult for the newer materials designed to replace the amalgam restoration.

Likewise, newer amalgamatable dental alloys have been developed which improve on the classical advan-15 tages of this type of restoration. Improvements in compressive strengths, reduction in static flow or creep of the set amalgam, corrosion resistance and controlled expansion in a professionally acceptable material for dental restoration techniques are all sought in any new 20 materials.

The novel restorative product of the present invention achieves improved properties in the foregoing areas by employing an alloy composition made up of a mixture of at least two silver, copper and tin-containing 25 dental alloys where the copper content of one of the alloys is at least 15 percent by weight of that alloy and that alloy comprises at least 50 percent by weight of the total of all the amalgamatable silver-containing alloys 30 used.

The following examples demonstrate the preferred alloy compositions which can be used to make the dental restorative material of the present invention.

#### **EXAMPLE 1**

A dental restoration according to the present invention was prepared by triturating 45 percent by weight of mercury with 55 percent by weight of a specially prepared dental alloy in a capsule on a mechanical mixer which is operated for approximately 10 seconds. The  $^{40}$ resulting coherent mass of unset triturated amalgam is then placed in a standard mold cavity and condensed by applying a dead load of 2,030 psi for 90 seconds. The load is then removed and the amalgam permitted to set upon standing for at least 15 minutes. The exact 45 procedural details of testing can be determined with reference to 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 50 publication, 211 East Chicago Avenue, Chicago, Illinois, 60611, pp 168-171).

Tensile strength measurements are taken at 15 minutes, flow at 3 to 24 hours, and dimensional change is 55 measured at 5 minutes to 24 hours, according to the ADA Specification hereinbefore identified.

The specially prepared alloy of this example was prepared by spraying two different molten alloy compositions at approximately 2,000°F, sizing according to a 60 preselected particle size distribution, annealing the resulting alloy when desired and then blending the separate alloys in a predetermined proportion. The first alloy component was prepared by spraying molten alloy having the composition by weight, 70 percent sil-65 ver, 22 percent copper and 8 percent tin in a conventional manner, i.e., such as described in U.S. Pat. No. 3,305,356, issued Feb. 21, 1967 at Column 2, lines 9

et seq through Column 3, line 25. The alloy is then collected and sized by Vortec brand air classification equipment which separates the alloy into two fractions approximately 20 microns and larger and the second 20 microns and smaller.

Typically, the 20 micron and larger fraction is then sieved in a 325 mesh sieve and the fraction containing particles over 20 microns in size and under 44 microns in size are all retained and blended with the fraction containing particles of 20 microns and under in predetermined proportions which help to establish set time in the final alloy.

Typically, a three to five minute work time before set with approximately 40 to 50 percent by weight of mercury is desired and can be accomplished by using an alloy comprising 80 percent by weight of the larger particle size fraction and 20 percent by weight of the smaller particle size fraction.

The second alloy component used is similar to conventional dental alloy used today, i.e., L. D. Caulk Spherical Alloy, which conforms to the ADA standard for such alloys and comprises approximately 65 percent silver minimum and a maximum of 29 percent tin, a maximum of 6 percent copper and a maximum of 2 percent zinc. The alloy is classified as the first component by preparing two fractions with a Vortec brand air classifier, one having particle sizes 15 microns and larger, and one having particle sizes 15 microns and smaller. Again, the larger particle size fraction is sieved with a 325 mesh sieve resulting in a fraction having particle sizes from 15 microns to 44 microns in size. To control work time in the final alloy mixture, the 15 micron to 44 micron fraction is annealled by heating at 320°F for between 1 and 6 hours. The smaller particle size fraction is annealed to a dead soft condition by heating at 680°F for 24 hours. The two particle size fractions are thus blended to a composition typically containing 50 percent by weight of each fraction with variations being possible depending on the length of annealling of each fraction, as well as the relative particle size distribution in the fractions.

The first and second alloy components are then blended to a composition comprising 60 percent by weight of the first alloy component and 40 percent by weight of the second alloy component.

The foregoing composition, when evaluated according to the ADA Specification and other tests, shows superior properties as shown in the data in Table I and compared to the standard for dental amalgams.

#### **EXAMPLE 2**

An amalgam was prepared as in Example 1, using a first alloy component of 70 percent silver, 25 percent copper and 5 percent tin with the results shown in Table 1.

#### EXAMPLE 3

An amalgam was prepared as in Example 1, using 85 percent of a first alloy component comprising 70 percent silver, 25 percent copper and 5 percent tin with the results shown in Table 1.

#### EXAMPLE 4

An amalgam was prepared as in Example 1, using 60 percent of a first alloy component comprising 70 percent silver, 20 percent copper and 10 percent tin with properties similar to those shown in Table 1.

#### EXAMPLE 5

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A satisfactory amalgam restoration is prepared as in Example 1, using 60 percent of a first alloy component comprising 70 percent silver, 15 percent copper and 15 percent tin.

#### EXAMPLE 6

A satisfactory amalgam restoration is prepared as in Example 1, using 50 percent of a first alloy component 10 comprising 60 percent silver, 30 percent copper and 10 percent tin.

#### **EXAMPLE 7**

A satisfactory amalgam restoration is prepared as in 15 Example 1, using 60 percent of a first alloy component comprising 80 percent silver, 15 percent copper and 5 percent tin.

#### **EXAMPLE 8**

A satisfactory amalgam restoration is prepared as in Example 1, using 60 percent of a first alloy component comprising 75 percent silver, 23 percent copper and 2 percent tin.

#### EXAMPLE 9

A satisfactory amalgam restoration is prepared as in Example 1, using 90 percent by weight of a first alloy component comprising 70 percent silver, 15 percent copper and 15 percent tin. Alternatively the presence of tin provides the setting mechanism by the reaction of  $Ag_3Sn$  with mercury to give the most desired noble properties in the finished restoration.

<sup>1</sup>C. E. Guthrow, L. B. Johnson and K. R. Lawless, J. Dental Research 46:1372-1381, 1967; and G. E. Stoner, K. R. Lawless and F. Wawner, J. Dental Research 50:519

Accordingly, it is important that sufficient tin is present in the dental alloy to produce Ag<sub>3</sub>Sn, while it is undesirable for any substantial amount of tin to be present in a form which is available for the formation of the Gamma 2 phase product of tin and mercury.

While it is not certain at the present time what the exact mechanism may be, it is postulated that the addition of copper in the manner described herein has a twofold beneficial effect on amalgamatable silver-tincontaining dental alloys.

First, the copper is in a form in the first alloy component which permits it to preferentially react with the tin 20 of the second component before any substantial amount of Gamma 2 has been formed. Secondly, it appears that besides scavengering tin, the copper tends to harden the resultant amalgam, thus reducing dynamic creep or flow, and reducing the phenomenon of "ditch-25 ing" in the placed dental restoration. This occurs when the forces of mastication or chewing work the more flowable restorations over the edge of a restorative cavity with subsequent fracturing of the extruded material and exposure of the margin of the restoration to carious 30 attack. The reduction in dynamic creep, which the

	ADA STD.	Example 1	Example 2	Example 3
Tensile — psi:			-	
15 minutes	290 psi	1232 psi	639 psi	372 psi
1 hour 24 hours	minimum	3246 psi 7324 psi		1. J. C.
Compressive Strength – 0.02 in/min. Crosshead Speed				
1 hour 24 hours		30,582 59,105	22,471 64,846	23,710 57,596
Compressive Strength – .002 in/min.				
24 hours	<del></del> 11 total (	47,041	49,874	48,761
Dead Load Flow Between 3 and 24 hours	- 3%	0.3%	0.35%	0.5%
Expansion	maximum			
Microns/cm	±20	0.94	+8.3	-0.8

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#### TABLE 1

The amalgam prepared according to the present invention possesses many superior features over present commercially available dental alloy amalgam preparations. For example, it is now considered important to avoid amalgam preparations which permit significant amounts of tin in the dental alloy to react with mercury because of tin's propensity to form a phase of a specific mercury-tin compound  $(Sn_7Hg_8)$ , known as Gamma 2 phase. This Gamma 2 phase is the situs for the corrosion which contributes to the failure of present dental amalgams in service.<sup>1</sup> It has been recognized that a reduction in the amount of this phase present enhances the corrosion resistance of the amalgam restoration.

hardening effect of copper has in these systems, thereby provides an unexpected benefit in the reduction of carious attack on margins.

Further, the surface of the resultant amalgam restoration is relatively corrosion-free and capable of being burnished. However, the margins of the amalgam restoration seem, for some reason, to provide for an environment which is conducive to the ionization of the metals present at the surface. This ionization permits compound formation at the surface of the restoration which is contiguous to the tooth cavity, enhancing the mechanical fit of the restoration and tending to reduce margin seepage.

Likewise, the ionization seems to provide a bactericidal environment at the margin which discourages further carious attack at the margin of the tooth cavity next to the restoration.

The present invention has been described in terms of 5 the presently known preferred embodiments, and it is intended that compositions which may depart from those presently preferred which demonstrate the equivalent novel advantages in use, are to be included within the scope of the appended claims. 10

I claim:

1. A dental composition amalgamatable by tritura-

tion with mercury comprising a mixture of amalgamatable silver-containing alloys wherein one of said alloys contains between about 60 and 80 percent by weight of the alloy weight of silver, between about 15 and 30 percent by weight copper and between about 2 and 15 percent by weight tin and a second alloy comprises between 68 and 72 percent by weight of the alloy of silver, between about 22 and 28 percent by weight of tin and between about 1 and 8 percent by weight of copper.

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