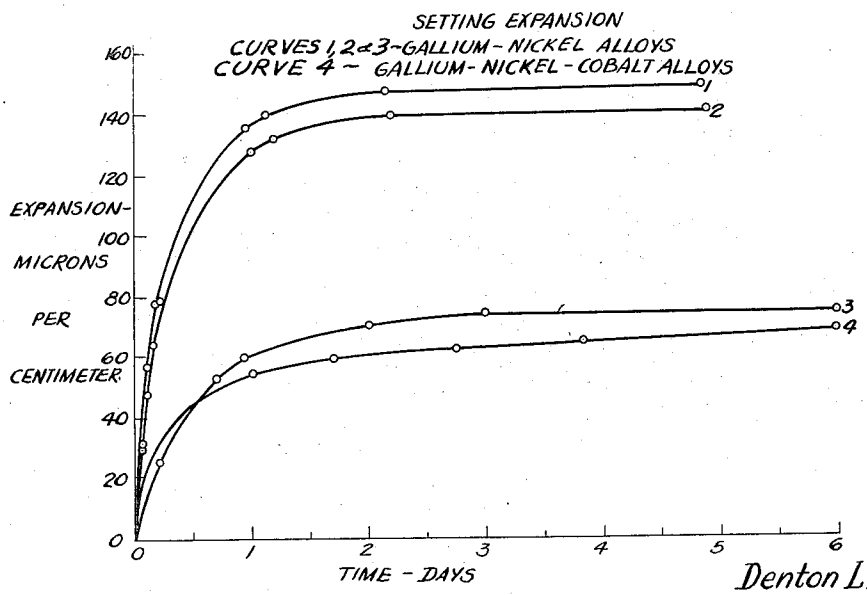
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COBALT-GALLIUM DENTAL ALLOYS

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COBALT-GALLIUM DENTAL ALLOYS

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This invention relates to alloys of gallium and particularly contemplates a novel composition in which liquid gallium or a liquid eutectic compound of gallium may be suitably alloyed with powdered metals and powdered-metal alloys to produce a pliable mastic alloy which can be shaped and which readily hardens at room or body temperature. The characteristics of such composition indicate its desirability for use in making impressions and in forming objects without requiring expensive machining or heat treating techniques. According to one embodiment of the invention, the resulting alloy possesses desirable characteristics of hardness, initial malleability and plasticity, nontoxicity, and low setting expansion as to suggest its use as a dental filling material in place of conventional dental amalgams.

It is accordingly an immediate object of this invention to provide a gallium alloy composition in which liquid gallium or a liquid eutectic compound of gallium is alloyed with powdered metals to form a readily pliable mastic which forms a hard alloy at room temperature.

It is a further object of this invention to provide an improved alloy of gallium which can be readily manipulated and deformed at room temperature and which subsequently sets at room or body temperature to form a hard alloy having a low setting expansion.

Another object of this invention is to provide a composition in which an eutectic compound of liquid gallium is combined with powdered metals at room temperatures to form a plastic mass which is readily adaptable as an impression material.

It is a still further object of the present invention to provide an improved alloy of gallium comprising a liquid component and powdered metal component which can readily be used and impressed in dental cavities to form a hard filling material having a low setting expansion.

Still another object of the present invention is to provide a filling material having a low setting expansion, low toxicity, and having a hardness at body temperatures suitable for dental use.

Other uses and advantages of the invention will become apparent upon reference to the specification and drawing which shows: a diagram of the expansion characteristics of certain gallium-nickel and gallium-nickel-cobalt alloys produced in accordance with the principles of this invention.

The physical characteristics of gallium indicate its desirability as an alloying element since its melting point is 29.78° C. (85.60° F.) while its boiling point is 1983° C. (3601° F.), thus giving it one of the longest liquid ranges of the metals. The metal has a low vapor pressure even at high temperatures, a pressure of 1 mm. of mercury being attained at 1315° C. (2399° F.). Gallium expands 3.4% in volume during solidification, the solid having a density of 5.90 g./cm.^{3}. Furthermore, it has the property of wetting many materials including tooth structure.

The true nature of the wetting property of gallium has not been determined but the wetting characteristic is generally attributed to a thin oxide film on the surface of the metal. It has also been determined that gallium is essentially nontoxic. See article by Meek, Harrold and McCord on "Toxicity of Gallium," Ind. Medicine, 12:7, January 1943.

Such exemplified characteristics and physical properties exhibited by gallium indicate its desirability as a component of a mastic material which can readily be molded or impressed and which subsequently sets at room or body temperatures into a hard mass. Materials of such characteristics which also possess low toxicity and low coefficient of thermal expansion is also suitable for use in dental restoration work. In the latter connection the composition should readily mix and condense, preferably using implements similar to those already familiar to the dentist. The gallium alloy should also harden at body temperatures within a reasonable length of time, and possess strength, dimensional stability and corrosion resistance equal to or greater than those of dental amalgams.

The allow compositions produced in accordance with the principles of the present invention were obtained by employing gallium metal of 99.9% purity. The constituents employed were obtained either from commercial sources or by alloying and comminuting in the Dental Research Section of the National Bureau of Standards. In addition, all metallic powders used in the composition passed a No. 325 sieve of the U. S. Standard Sieve Series. For laboratory control all mixing and condensing of specimens was performed at 37° C. (98.6° F.) or 21.1° C. (70° F.) which is above the melting point of gallium and the gallium-tin eutectic respectively. Mixing was accomplished either in a motar or by means of a mechanical amalgamator. All of the triturated mass was condensed. No liquid metal was expressed prior to or during condensation.

In accordance with the principles of the present invention, a liquid gallium or a liquid eutectic of gallium is combined with a powdered metal or metal alloy by trituration. The resulting plastically deformable mastic is suitably shaped or expressed and allowed to harden at room or body temperature to produce a hard solid mass in much the same manner as a conventional dental amalgam.

In the exemplified results to be detailed, determinations of the dimensional change were made at 37° C. (98.6° F.) using unrestricted specimens 10 mm. long and 5 mm. in diameter in a dental interferometer with a fiducial reading 15 minutes after mixing was started. The compressive strength was determined at 21.1° C. (70° F.) using cylinders 8 mm. long and 4 mm. in diameter. The strength of one series of gallium-nickel-silicon alloys was determined at 37° C. (98.6° F.) and at 50° C. (122° F.). The rate of loading of the compressive strength specimens was in all cases 80 lbs. (36.3 kg.) per minute.

The novel features of the present invention are described in further detail in the following illustrative examples.

Example 1: Gallium-cobalt alloy.—A mixture containing 40% liquid gallium was alloyed with 60% cobalt powder, formed and allowed to harden. The specimen contracted approximately 3 μ/cm. in 24 hours and was stable for four days thereafter. It should be observed that such specimen is the only gallium alloy of the various examples to be described that exhibited a negative setting expansion during hardening. The seven-day compressive strength of the gallium-cobalt alloy was 12,700 p. s. i. The negative setting expansion exhibited by the gallium-cobalt alloy while setting indicates its desirability for incorporation as a component of a dental filling material to control expansion.

Example 2: Gallium-nickel alloys.—Nickel powder that passed a U. S. Standard Sieve No. 325 was combined with liquid gallium in several proportions. A gallium content from 20 to 40% was found practicable. Less than 20% gallium resulted in a dry granular material that could not be readily packed and more than 40% gallium resulted in a sloppy alloy that was difficult to handle. The data on compressive strength and hardness of four gallium-nickel alloys are summarized in Table 1 below. When triturated 70 revolutions in 30 seconds, the 35% gallium alloy expanded from 128 to 136 μ/cm. from 2 to 5 days as illustrated by curves **1** and **2** in Fig. 1. Mixing this alloy in a mechanical amalgamator for 1 minute instead of a motor for 30 seconds results in a 24-hour expansion of about 60 μ/cm. as shown by curve **3** in the drawing. This increased to about 75 μ/cm. expansion after 3 days and remained constant for 14 days thereafter. Increasing the amount of work done on the mix appears to reduce the expansion and increase the compressive strength of the 35% gallium-nickel alloy.

The addition of either powdered cobalt or powdered silicon reduced the large setting expansion of gallium-nickel alloys. For example, an alloy of 35% gallium, 55% nickel, and 10% cobalt expanded about 55 μ/cm. at the end of 24 hours as shown by curve **4** of the drawing. It continued to expand for about 6 days until a total expansion of approximately 70 μ/cm. had occurred. No additional expansion had occurred at the end of 16 days. A specimen containing 36% gallium, 62% nickel and 2% silicon expanded 37 μ/cm. in 24 hours. However, this method of reducing the high expansion of the gallium-nickel alloys also reduced their strength. A comparison of the 24-hour compressive strengths is given in Table 2 below.

TABLE 1

Compressive strength and Brinell hardness of gallium-nickel alloys (Example 2)

Composition, Gallium-Nickel		Compressive Strength, p. s. i.	Baby Brinell hardness, 15 kg. load, 1/16" ball	Remarks
Wt. Percent	Wt. Percent			
23	77	14,000	48	Triturated 2 min. 3 lb. load on pestle specimen 3 days old.
33	67	32,000	90	Triturated 2 min. 3 lb. load on pestle specimen 1 day old.
35	65	49,000	90	Triturated 1½ min. 3 lb. load on pestle specimen 1 day old.
44	56	33,000	70	Triturated 2 min. 3 lb. load on specimen 1 day old.
------	------	62,000	100	As above except excess gallium was expressed during condensation.

Above values are individual or average of two determinations.

TABLE 2

Effects of addition of cobalt and silicon to the compressive strength of gallium-nickel alloys

Composition, wt. percent	Compressive Strength Average, p. s. i.
35 gallium 65 nickel	39,600
35 gallium 58½ nickel 6½ cobalt	31,100
38 gallium 60 nickel 2 silicon	25,500

All specimens made by trituration in a mortar, 70 revolutions in 30 seconds under a 3 lb. load.

It will be apparent that the embodiments shown are only exemplary and that various modifications can be made in construction and arrangement within the scope of invention as defined in the appended claims.

What is claimed is:

1. An alloy which is especially adapted to be plastically formed and subsequently hardened within a temperature range of 20 to 37° C. and which, after hardening is characterized by high compressive and tensile strength, high hardness and low setting expansion, said alloy consisting essentially of 20–40% of liquid gallium alloyed with 60–80% of powdered cobalt.

2. The invention of claim 1 in which said alloy contains about 40% gallium and about 60% cobalt.

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