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PLASTIC ALLOY WHICH SETS AT ROOM TEMPERATURE

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This invention relates to an alloy composition which is plastic slightly above room temperature when first prepared but which hardens upon standing. These and other properties make the alloy suitable for forming molded products, especially compacted fillings used in tooth restorations.

Mercury-containing metallic compositions, known as amalgams, have been commonly employed heretofore where moldability at room temperature and subsequent hardening of the molded mass have been required. They have found special application in the filling of tooth cavities because of the hardness they attain and the tight fit which it is possible to achieve by packing the plastic body into a cavity and by the expansion which occurs during setting. However, the amalgams do not wet the tooth or form a bond therewith and consequently some separation may occur in time.

The amalgams are usually prepared by triturating together predetermined proportions of mercury and a solid metal or alloy in finely divided condition. Generally, more mercury is used than is required to form the final hardened body in order to insure a rapid and thorough mixing of the components and supply all the mercury that may be needed. Before the amalgam is molded or pressed into the desired shape, it is therefore necessary to squeeze out or express the excess mercury. The operation is time-consuming and wasteful.

Although dental amalgams have been extensively used, they are still open to the additional objections that mercury is toxic and amalgams do not harden with sufficient rapidity to permit polishing immediately after molding. In spite of these disadvantages, amalgams have been regarded as the only practical metallic materials for molding at room temperature. It is accordingly a principal object of this invention to overcome these disadvantages and to provide a new improved moldable mixture containing no mercury.

I have discovered that a superior hardened molded product can be made of an initially plastic composition consisting essentially of at least 49% by weight of silver, at least 18% tin, from 10 to 25% gallium, not over 6% nor less than 1% copper and not over 1.5% nor less than 0.05% zinc. Other elements may be present as impurities or intentional additions if they do not substantially alter the characteristics of the alloy. The alloy is non-toxic, hardens more rapidly within the range of room temperature to body temperature than conventional amalgams and

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forms a very tight bond with a tooth. Alloys within the foregoing range attain a Brinell hardness of 40 to 85 upon standing 48 hours after having been prepared and compacted. These hardness values refer to those obtained by use of a $\frac{1}{16}''$ diameter steel ball under a load of 12.61 kgs. applied for a period of 30 seconds. Furthermore, no excess gallium is required to prepare the composition. The alloy expands slightly during setting, within the limits specified for amalgams, which is of advantage in dental work.

In my preferred practices the alloy should consist of 49 to 65% silver, 18 to 25% tin, 10 to 25% gallium, 3 to 6% copper and 0.1 to 1.5% zinc.

The base alloy may be prepared by first melting together the silver, tin, copper and zinc components, preferably under non-oxidizing conditions. The proportions which have been found to give the best results are a minimum of 65% silver, a minimum of 25% tin, not over 8% copper and not over 2% zinc. Fusion together of these components in this manner is preferred rather than mixing the individual metals in powder form where the highest hardness is desired in the final product. The molten alloy is preferably cast in the form of a cylindrical body that can be subsequently machined to produce finely divided chips. It is often necessary or desirable to further comminute the chips by grinding or milling them under non-oxidizing conditions. Other methods of producing the comminuted alloy may be employed, of course, providing the proper particle size is obtained.

The finely divided particles of the alloy are then admixed with the required amount of gallium. Inasmuch as gallium melts at about 30° C. (87° F.), it is most convenient to warm it slightly to form a liquid and mix the liquid metal with the base alloy powder. However, solid gallium may be added to the alloy and the temperature of the mass raised to a point where the mass becomes plastic or the gallium melts. In any case, the gallium-containing alloy should be in a plastic condition when being mixed or triturated. Once the plastic alloy is prepared, there is generally no difficulty in maintaining the desired plastic condition long enough to permit molding or filling a cavity in a tooth.

The amount of gallium required to produce the desired plasticity and permit attainment of a minimum Brinell hardness of 40 in the hardened product lies within the range of 10 to 25% of the total weight of the alloy, and preferably the proportion should be 12 to 18%. Also, within these limits, all of the gallium is absorbed in forming the plastic mixture, consequently, there is no need for a preliminary squeezing or expression to remove excess gallium prior to molding or compacting the alloy.

The mixing or trituration of the gallium and silver alloy is preferably carried out in the conventional type of mortar and pestle apparatus employed in preparing amalgams. The period of mixing will vary, ordinarily, between ½ and 5 minutes, but should, in any event, be long enough to produce a uniform moldable mass.

The resulting alloy appears to be drier than the usual amalgam; however, it is still sufficiently plastic to be as readily formed or compacted as an amalgam. In spite of the apparent dryness of the alloy it has a greater wetting power than amalgams and tends to cling to a tooth, or other non-metallic material against which it is pressed. As a result, there is no zone of imperfect contact between the tooth or other wetted body and the gallium-containing filling and a firm lasting bond is thus assured.

Once the gallium-containing alloy is prepared it should be immediately molded or pressed into the desired shape. The compacting or condensing operation may be conducted in the same manner as that followed in handling the conventional dental amalgams. Generally, hardening progresses rapidly enough to permit polishing upon completion of the condensing operation, which is usually a matter of minutes. It has been observed that the gallium-containing alloy actually hardens more rapidly than an amalgam. If the alloy has been properly mixed and compacted, the final rigid product will meet the requirements of the Federal Specifications for dimensional change and flow of amalgams.

To obtain satisfactory properties in the final hardened product it has also been found to be necessary to employ a silver base alloy containing copper within the range mentioned hereinabove. Hardened alloys containing no copper, for example, those made from silver-tin alloys, do not possess the desired hardness and other properties essential to an acceptable dental alloy.

My invention may be illustrated by the following example wherein a silver base alloy in finely divided condition was used which consisted of 68.2% silver, 26.2% tin, 5.1% copper and 0.4% zinc. The alloy powder was triturated in conventional manner with 14% by weight of gallium at 35° C. for a period of 1 minute. The resultant alloy, which had a dry appearance, was packed in a mold with a tool and tested for dimensional change and flow according to Federal Specification U-A-451*a*. No excess gallium was expressed during the compacting operation. The dimensional change was found to be $+12.7\mu$/cm. and the flow percentage was 3.1, both values coming within the range set forth in the aforesaid Federal Specification. In addition it was found that the compacted product had a Brinell hardness of 48 after standing for 48 hours. It was also observed that the alloy could be polished within about 15 minutes after packing was started whereas this could not be done with a corresponding amalgam employing the same silver base alloy.

Having thus described my invention and one embodiment thereof, I claim:

1. A hardenable alloy composed essentially of not less than 49% silver, not less than 18% tin, 10 to 25% gallium, 1 to 6% copper and 0.05 to 1.5% zinc.

2. An alloy consisting of 18 to 25 per cent tin, 10 to 25 per cent gallium, 3 to 6 per cent copper, 0.1 to 1.5 per cent zinc and the balance silver in an amount of not less than 49 per cent.

3. An alloy consisting of 18 to 25 per cent tin, 12 to 18 per cent gallium, 3 to 6 per cent copper, 0.5 to 1.5 per cent zinc and the balance silver in an amount of not less than 49 per cent.

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