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3,268,348

## DENTAL IMPRESSION MATERIALS

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23 Claims. (Cl. 106—38.5)

This invention relates to dental impression compositions particularly of the alginate type and is a continuation-in-part of my applications, Serial No. 158,943, filed December 8, 1961; now abandoned; and more particularly Serial No. 375,957, filed June 17, 1964, which is a continuation-in-part of the former, now U.S. Patent No. 3,234,033.

A primary objective is to produce compositions which provide dental impressions possessing the qualities of elasticity and resilience as well as rigidity and toughness or strength so balanced that precision dental impressions may be made and removed from undercuts without rupture or permanent deformation. A specific requirement in dentistry is making dentures, both full and partial, as well as bridges, in accurate dental reproduction with maximum comfort to the patient, and this is also a general objective of my invention.

It is among the further objectives of this invention to produce models or casts from such impressions that possess hard smooth surfaces free from chalkiness and dusting in handling during use of the same or in storage.

Another important objective of my invention is the production of a dental impression composition which is readily wetted and mixed with water to a smooth consistency with controlled setting time.

A further objective of the invention is to produce dental impression compositions which have long storage and shelf life, that is they show minimum or no deterioration with age during use and normal exposure to atmospheric conditions including warm and humid conditions.

Moreover the impressions made from my compositions require no fixing or after treatment in special solutions or baths which involve additional time and material and increased cost generally. The fixing operation refers to treatment of the impression after it has been made. In the earlier developments and until comparatively recently, this operation was necessary before pouring or applying the dental "stone" (generally a composition containing some form of plaster of Paris) to the impression to make a satisfactory model or cast. The fixing baths consisted of aqueous solutions of various inorganic salts and these materials, as well as the time and cost, are eliminated by the use of my composition.

Among the essential ingredients or components of my invention in its major or primary aspect are (a) the alginates especially the water soluble types such as the alkali metal alginate, e.g., sodium or potassium or ammonium alginates, (b) calcium sulphate preferably in the dihydrate form, although the anhydrous and hemi-hydrate types also give good results; and (c) I also as a principle feature of my invention make use of certain selected fluorides specifically barium fluoride, which I believe I am the first to use in dental impression mixtures of the type noted above. I also make use of the oxides of magnesium and aluminum in the mixture particularly the former. These oxides generally have the property of neutralizing acids. These and other novel combinations hereinafter referred to are employed by me. The amounts of barium fluoride used in my impression mixture may vary from about 1% to about 10% by weight, and preferably from about 1% to about 5%.

The calcium sulphate in the mixture reacts with the water soluble alginates to form an elastic and resilient impression base on the one hand, and it also reacts with the fluorides to form the insoluble calcium fluoride. The specific reactions and interreactions of these essential ma-

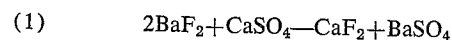
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terials and those disclosed herein generally appear to be a prime requirement to produce the superior results I obtain, and to meet the foregoing objectives. In addition to these essential ingredients, I also make use of retarders, generally salts of an alkaline character such as tetrasodium pyrophosphate to control the rate of the reactions and to prevent premature setting; and I also make use of fillers such as diatomaceous earth (and other generally inert and water insoluble materials), for bulk and as a diluent of the more active ingredients. All of the materials are thoroughly mixed and in a finely divided state of subdivision, and when it is desired to use the resulting composition, it is admixed with water in proper proportions to form the impression, the details of which are fully described hereinafter. These and other aspects of my invention will be discussed and set forth more fully below.

The soluble salts of alginic acid (which is the essential gel forming material in various marine algae or plants), especially the potassium, sodium and ammonium alginates or mixtures of the same are suitable for my invention. The commercial product known as "Improved Kelmar" has been found very satisfactory. Calcium sulphate in the form of the anhydrous salt ( $\text{CaSO}_4$ ), or the hemihydrate ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) and preferably the dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) may be employed. The soft soluble alginate is converted into the resilient and elastic insoluble type in an aqueous medium by interaction with calcium sulphate. The retarder which controls the rate of setting of the impression mixture may comprise a salt having an alkaline reaction generally such as sodium carbonate or trisodium orthophosphate or meta phosphate but I prefer the tetrasodium pyrophosphate for this purpose. With regard to the fillers, I prefer diatomaceous earth (e.g., the commercial product referred to as Hyflo-Super-Cal). However, (although less desirable) other substantially inert and water insoluble materials such as calcium fluoride, carbonate or triphosphate, as well as various finely divided earths or clays and minerals, e.g., bentonite, talc, kaolin, etc., and various silicates such as those of the alkaline earth metals and those of aluminum and the heavier metals, e.g., lead silicate, and as stated previously water insoluble oxides such as, for example, aluminum oxide or magnesium oxide alone or in admixture with the diatomaceous earth, or with each other, could be employed with varying results, especially in addition to diatomaceous earth.

In its principal aspects and as a major feature of my novel impression mixtures, I make use of barium fluoride in combination with the use of the aforementioned alginates and with calcium sulphate as essential ingredients of my composition. The principal reaction of calcium sulphate with the soluble alginate has already been referred to. The reactions which may occur between the calcium sulphate and barium fluoride may be explained as follows:

Calcium sulphate is soluble in water to the extent of 0.2%, and the fluoride of barium for example, is dissolved to the extent of 0.16%. However calcium fluoride is soluble in water only to the extent of 0.002%, and the free calcium and fluoride ions furnished by the calcium sulphate and barium fluoride respectively are considerably in excess of the concentration required to precipitate them as calcium fluoride. The reaction thus goes forward until one of the other of the reactants is exhausted. It is thus noted that even with such a small concentration of fluoride ions as those furnished by the relatively insoluble barium fluoride will cause precipitation of the even less soluble calcium fluoride.



Whatever may be the explanation of the reaction in an aqueous medium or sequence of reactions in the mixture

in relation to the physical properties of the impression and the "stone" model or cast made from the same, the result is an impression which is smooth and accurately defined and may be readily removed without breakage or distortion. Moreover, the model or cast made from these impressions are of a high degree of precision and part cleanly from the latter without adhesion and have glossy, flintlike non-dusting and non-chalking surfaces surfaces of a highly superior type.

I believe in this connection that I am the first to use barium fluoride and the combinations mentioned herein, in impression mixtures containing them and in addition containing the other essential ingredients namely the soluble alginates and calcium sulphate.

The amounts of barium fluoride which I may incorporate in my impression mixtures may vary from about 1% to about 10% by weight with a preferred range of from about 2% to about 5% more or less.

It may be noted particularly that the results observed with my new dental compositions employing barium fluoride and various combinations of the same are greatly superior to the use of mixtures containing the fluorides of the prior art namely those of sodium and potassium or zinc when used singly.

I am aware that potassium and sodium fluorides have been disclosed in the prior art and despite the fact that they are both alkali fluorides the former is soluble in water to the extent of 92.5% while sodium fluoride dissolves much less to the extent of 4.5%. Potassium fluoride is very difficult to handle because it is highly deliquescent, and moreover the results of making impression mixtures and impressions are somewhat unreliable because of unpredictable working ranges in time of mixing, effect of temperatures, setting times and other control difficulties. Mixtures employing sodium fluoride alone are somewhat better in these respects than potassium but the results with regard to impressions and casts in both cases leave much to be desired; and in fact when used alone, i.e., as the sole fluoride additive both potassium and sodium fluoride dental impression compositions have been found to be impractical in actual commercial use. Moreover I have found that the addition of barium fluoride to dental impression mixtures containing either of these two fluorides improves the overall results obtained with them. The latter feature comprises another aspect of my invention namely adding barium fluoride to dental impression mixtures containing sodium or potassium fluorides.

It is noted also in connection with the prior art that dental impression compositions containing zinc fluoride as the sole fluoride give much better results than either potassium or sodium fluoride compositions so far as control and quality of impression and the cast are concerned but such compositions have been found to be notoriously unstable or have a short shelf life especially in warm and humid environments rendering the product useless. In general basic oxides of low water solubility are used.

In still another aspect of my invention I may add basic metal oxides to the mixture containing barium fluoride or other basic oxides such as those of magnesium and aluminum which function as neutralizing agents.

The selected neutralizing agent (which functions under adverse conditions to stabilize the mixture) may be a metal oxide, or hydrated oxide, or carbonate, e.g., of oxides of magnesium, aluminum and the like. These neutralizing agents are insoluble in water or only slightly soluble and neutralize acids. Some further examples of these are calcium oxide or carbonate in small amounts and the hydroxides of magnesium or aluminum.

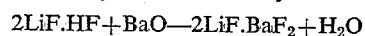
The amounts of these substances used for illustration may be from about 1% to about 10% by weight or preferably about 1% to about 5%. It is to be noted in the above connection and in general with this aspect of my invention that I refer to these oxides as metal oxide neutralizers because in general they (as well as

the other compounds referred to below) show an alkaline reaction in neutralizing acids, e.g., HF.

Of all of these the oxides are preferred, especially magnesium oxide. Also in those cases where the addition of an oxide or similar acid neutralizing agent is indicated the fluorides corresponding to the oxide added are very sparingly soluble in water. Moreover in general I may add metal oxides, or the other types of compounds mentioned on a selective basis with regard to the type and various proportions of the components of the mixtures employed by me.

Various combinations may be made, as another feature of my invention with barium acid fluoride and the oxides of lithium, magnesium, aluminum, zinc and others, or by other suitable methods to produce the corresponding double fluorides and/or intimate mixtures of the same. Examples of these are  $\text{BaF}_2 \cdot \text{MgF}_2$ ;  $\text{BaF}_2 \cdot \text{AlF}_3$ ;  $\text{BaF}_2 \cdot 2\text{LiF}$ ; and  $\text{BaF}_2 \cdot \text{ZnF}_2$ , etc.

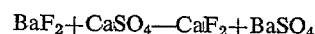
The reactions may be illustrated by the following:



The results obtained are satisfactory in either case whether the fluorides combine as a loose chemical combination or are used in intimate admixture with each other.

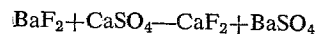
The amounts of each of the combinations shown above used in the impression mixture referred to above may vary from about 1% to 10% with the preferred range of 2% to 5%.

The fluoride of barium as pointed out is very much less soluble in water than that of potassium (92.5%) and comparatively is much less soluble than sodium fluoride being respectively 4.44% for the latter and 0.16% for barium fluoride. The differences in chemical and physical properties no doubt account for its superiority in the present connection. The reactions with the mixtures containing alginates and calcium sulphate with particular reference to the latter are as follows:



The amount of barium fluoride in the type of impression mixtures used herein are in proportions of from about 1% to about 10% (with 2% to 5% preferred). I may also use the complex addition compounds or mixtures of the type previously referred to in the same range.

It is especially to be employed as stated above in connection with my present invention that I may employ barium fluoride (solubility in water 0.16%) as the fluoride component of my dental impression mixture, containing the other components as outlined above in the mixture; and moreover it is inherent in this aspect of my invention that barium fluoride and calcium sulphate must both be specifically present in the mixture to obtain the desired results. The reaction with calcium sulphate (hydrated) is shown below:



It is noted particularly in this reaction that the novel feature is presented of the formation of two practically insoluble substances namely calcium fluoride already referred to, and barium sulphate which has the extremely low solubility in water of 0.00035%.

Strontium fluoride (solubility in water 0.12%) reacts similarly to barium fluoride (although the latter is definitely preferred) to form strontium sulphate on reaction with calcium sulphate, the solubility of strontium sulphate being about the same order as strontium fluoride; and I may if desired use the latter in the dental impression mixture shown. However it is noted that for several reasons I prefer the use of barium fluoride as an additive. Complex fluorides may also be formed with acid fluorides and oxides in these cases. In all cases it is desirable to use neutralizing agent of the types described above including basic metal oxides, hydroxides and the like preferably magnesium oxide.

It is also emphasized that none of the fluorides mentioned herein are in any sense equivalents.

Having described the various materials which may be employed in connection with my invention, and pointed out certain variations in the practice, I shall proceed to show more particularly the steps of the process of its applications together with the preferred materials and their preparation to obtain best results.

Reverting to the manner in which my impression mix-

Specific examples

The table shows a number of specific examples in connection with various compositions and ingredients each in general being to some degree dependent on the specific type of fluoride employed, although they need not necessarily be widely different for best results and, on the other hand, may vary considerably, in accordance with desired results.

| Ingredients, Percent by Weight          | BaF <sub>2</sub><br>Barium<br>Fluoride | BaF <sub>2</sub><br>Barium<br>Fluoride | BaF <sub>2</sub> ZnF <sub>2</sub><br>Barium<br>Zinc<br>Fluoride | BaF <sub>2</sub> .2LiF<br>Barium<br>Lithium<br>Fluoride | BaF <sub>2</sub> .MgF <sub>2</sub><br>Barium<br>Magnesium<br>Fluoride | 2KF.BaF <sub>2</sub><br>Potassium<br>Barium<br>Fluoride |
|-----------------------------------------|----------------------------------------|----------------------------------------|-----------------------------------------------------------------|---------------------------------------------------------|-----------------------------------------------------------------------|---------------------------------------------------------|
| Potassium Alginate.....                 | 13.5                                   | 13.7                                   | 13.8                                                            | 13.5                                                    | 13.5                                                                  | 13.5                                                    |
| Calcium Sulphate Dihydrate.....         | 12.8                                   | 12.6                                   | 13.5                                                            | 12.7                                                    | 12.3                                                                  | 12.5                                                    |
| Retarder Tetrasodium Pyrophosphate..... | 2.0                                    | 2.0                                    | 2.3                                                             | 2.3                                                     | 1.5                                                                   | 2.2                                                     |
| Fluoride, etc. (see above).....         | 4.2                                    | 4.2                                    | 4.2                                                             | 4.5                                                     | 4.0                                                                   | 4.3                                                     |
| Magnesium Oxide.....                    | 0.0                                    | 3.5                                    | 4.5                                                             | 5.5                                                     | 0.0                                                                   | 4.5                                                     |
| Filler Diatomaceous Earth.....          | 67.5                                   | 64.0                                   | 61.7                                                            | 62.0                                                    | 68.8                                                                  | 63.0                                                    |
| Example #.....                          | (1)                                    | (2)                                    | (3)                                                             | (4)                                                     | (5)                                                                   | (6)                                                     |

Remarks: Good but non-equivalent results may be obtained also with—(a) Compositions like Example 6 in which 2NaF.BaF<sub>2</sub> is the fluoride used; (b) Compositions like Example 5 in which BaF<sub>2</sub>.AlF<sub>3</sub> is the fluoride used; (c) Substitutions of filler and type of calcium sulphate may be made with some adjustment of other materials; (d) Variations in the amount of MgO used.

tures may be used and to the most suitable proportions for their use: The ingredients or components of the compositions of my impression mixtures which I have referred to above as preferred materials, i.e., the soluble alginate, e.g., potassium alginate (a suitable form is Improved Kelmarmar), calcium sulphate dihydrate; the retarder, tetrasodium pyrophosphate; and barium fluoride.

All of the materials should be in finely divided form, and thoroughly mixed. On a generalized basis, the proportions of materials may vary considerably. Satisfactory results may be obtained within the following illustration of range and intermediate compositions shown for convenience in parts per one hundred parts by weight or percent; although I am not limited thereto.

| Material                                 | Parts by Weight or percent |                           |      |
|------------------------------------------|----------------------------|---------------------------|------|
|                                          | Range                      | Intermediate Compositions |      |
|                                          |                            | (1)                       | (2)  |
| Potassium Alginate.....                  | 12-15                      | 13.5                      | 13.0 |
| Calcium sulphate dihydrate.....          | 12-16                      | 12.5                      | 15.0 |
| Retarder (Sodium Pyrophosphate).....     | 1-5                        | 2.0                       | 3.5  |
| Barium Fluoride.....                     | 2-5                        | 4.2                       | 2.9  |
| MgO Oxide (Metal Oxide Neutralizer)..... | 0-6                        | 1.5                       | 5.0  |
| Filler—Diatomaceous Earth.....           | 73-53                      | 66.3                      | 60.6 |

Variations in the proportions of ingredients may be on an even wider basis than shown in the above illustration for example as already pointed out, barium may vary from about 1% to 10% and the calcium sulphate, dependent on the type and the extent of hydration and other ingredients from about 10% to about 20%. The filler will vary in amount with the variation in the other ingredients; and where the diatomaceous earth is supplemented by some other filler, e.g., bentonite, kaolin, calcium or magnesium carbonate, etc., the proportions used of the former are less. All of these data are by way of examples and are not to be construed as limiting.

In the production of the dental impression material all components or ingredients are reduced to finely divided or powdered form and sieved to about 80 mesh in size, or finer. After mixing in a suitable type of mechanical mixer (such as a rotary helicoid ribbon type or double cone or other efficient tumbling type) the lumps may be broken down by passing through a coarse mechanical sieve. At this state, the material is ready for packaging and distribution for use. Flavoring or coloring materials may be introduced after mixing with a small amount of diatomaceous earth, calcium or magnesium carbonate or magnesium oxide.

When used by the dentist, the impression material prepared as described is mixed with water generally at room temperature to the consistency of a somewhat heavy, smooth, creamy paste-like material. Spatulation of the wet mixture may take place in about one half to one minute, and it is then transferred to the tray to be applied to the mouth. Generally, the latter operation takes place in about a minute or a minute and a half, and the material is allowed to set for about three and one-half to four minutes in the mouth; the whole operation consuming about six minutes. The proportion of water used is about 10 to 10.5 gms. of the powdered impression mixture to about 25 cc. of water, or generally a ration of about 2.5 parts of water to 1 part of the material. All of these data are illustrations only.

All of the above data on use may vary somewhat, those shown being illustrative of satisfactory conditions for good results.

The temperature of the water, as well as the room temperature, though not critical, have very appreciable effect in the setting time, decreasing with increase in temperature and vice versa. This is in accord with effect of temperature generally on reaction rates. Generally room temperatures, depending on individual taste, varies between about 68° F. and 74° F. and this is satisfactory working range, although good results may be obtained in a somewhat wider range with minor adjustments.

Any suitable dental "stone" (generally a plaster of Paris composition) of which there are a number available, made up to proper consistency with water, may be employed in making the "stone" cast or model. Moreover, as previously stated, fixing is eliminated, that is the impressions made with my compositions do not have to be treated in a fixing bath or solution prior to making the cast or model, and the latter, with the use of my invention, are hard, smooth and durable.

There may be many modifications of my invention without departing from the spirit and scope thereof, and any limitations to be imposed should be only those in accordance with the appended claims.

I claim:

1. A dental impression composition consisting essentially of a mixture of an alkali metal alginate, calcium sulphate, a metal fluoride and an inert filler, the said fluoride consisting of barium fluoride, and being present in an amount of from about 1% to about 10%, said fluoride being adapted to eliminate fixing of said composition while maintaining controlled setting time and minimizing deterioration with age, and to provide smooth and accurate impressions and casts.

2. A dental impression composition consisting essentially of a mixture of an alkali metal alginate, hydrated

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amount of from about 1% to about 10% said fluoride being adapted to eliminating fixing of said composition while maintaining controlled setting time and minimizing deterioration with age, and to provide smooth and accurate impressions and casts.

17. A dental impression composition consisting essentially of a mixture of an alkali metal alginate, hydrated calcium sulphate, a metal fluoride and an inert filler and a metal oxide neutralizer, the said fluoride consisting of barium fluoride combined with another fluoride selected from the group consisting of potassium fluoride, sodium fluoride, lithium fluoride, magnesium fluoride, aluminum fluoride and zinc fluoride and being present in a total amount of from about 1% to about 10% said fluoride being adapted to eliminating fixing of said composition while maintaining controlled setting time and minimizing deterioration with age, and to provide smooth and accurate impressions and casts.

18. A dental impression composition consisting essentially of a mixture of an alkali metal alginate, hydrated calcium sulphate, a metal fluoride, a neutralizer consisting of magnesium oxide, an inert filler consisting of diatomaceous earth, and a retarder consisting of sodium pyrophosphate, the said fluoride consisting of barium fluoride combined with another fluoride consisting of zinc fluoride and being present in a total amount of from about 1% to about 10% said fluoride being adapted to eliminating fixing of said composition while maintaining controlled setting time and minimizing deterioration with age, and to provide smooth and accurate impressions and casts.

19. A dental impression composition consisting essentially of a mixture of an alkali metal alginate, hydrated calcium sulphate, a metal fluoride and an inert filler, a retarder and a metal oxide neutralizer consisting of magnesium oxide, the said fluoride consisting of barium combined with another fluoride consisting of zinc fluoride and being present in a total amount of from about 1% to about 10% said fluoride being adapted to eliminating fixing of said composition while maintaining controlled setting time and minimizing deterioration with age and to provide smooth and accurate impressions and casts.

20. A dental impression composition consisting essentially of a mixture of an alkali metal alginate, hydrated calcium sulphate, a metal fluoride, a metal oxide neutralizer consisting of magnesium oxide, an inert filler and a retarder, the said fluoride consisting of barium fluoride and being present in an amount of from about 1% to about 10%, said fluoride being adapted to eliminate fixing of said composition while maintaining controlled setting time and minimizing deterioration with age, and to provide smooth and accurate impressions and casts.

21. A dental impression composition consisting essentially of a mixture of an alkali metal alginate, calcium sulphate dihydrate, a metal fluoride, a metal oxide neutralizer consisting of magnesium oxide, an inert filler, consisting of diatomaceous earth, and a retarder in the said fluoride consisting of barium fluoride and being present in an amount of from about 1% to about 10%, said fluoride being adapted to eliminate fixing of said composition while maintaining controlled setting time and minimizing deterioration with age, and to provide smooth and accurate impressions and casts.

22. A dental impression composition consisting essentially of an alkali metal alginate, calcium sulphate, a metal fluoride and an inert filler, the said fluoride being selected from the group consisting of barium and strontium fluorides and being present in an amount of from about 1% to about 10%, said fluoride being adapted to eliminate fixing of said composition while maintaining controlled setting time and minimizing deterioration with age, and to provide smooth and accurate impressions and casts.

23. A composition for taking dental impressions of the type described in claim 1 wherein the said composition is dispersed in an aqueous medium.

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