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PLASTIC COMPOSITION

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Grace G. RyanNo Drawing. Application July 25, 1938,
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The present invention relates to a new composition of matter and more particularly to a plastic material peculiarly well adapted for use in numerous capacities in the dental art. This application is a continuation in part of my application Serial No. 163,256, filed September 10, 1937.

Practicing dentists of necessity employ numerous materials for the taking or making of impressions in the oral cavity and have at their disposal at the present time numerous products quite ill-fitted for the uses to which they are being put. For example, commonly used dental impression materials are calcined products such as plaster of Paris, Solvite, modeling compounds, waxes, and the more recent so-called hydro-colloids. The calcined materials and their modifications are in the first place disagreeable to use because they are uncomfortable to the patient and, further, because of the fact they tend to dehydrate the oral tissues, inaccurate impressions are often made. Aside from these objections, in many cases the impression must be fractured into several pieces to allow its removal from the patient's oral cavity, and after removal, when the parts are reassembled, great difficulty is encountered and not infrequently it is necessary to make the impression over.

The various modeling compounds available offer the disadvantage of not being sufficiently elastic to permit removal without distortion when the patient possesses a full or partial complement of teeth in the jaw, which leads to an inaccurate impression being made. Likewise, the waxes and other materials commonly used lead to inaccurate and otherwise imperfect impressions which prevent or at least make it extremely difficult for the dentist to construct the accurate dental appliances for the oral cavity he would like to make.

The hydro-colloid compositions of necessity are dispersed in large amounts of water, and experience has shown that while these materials give reasonably fair reproduction of the oral cavity, they are extremely difficult to use, are fragile, and must be handled with extreme care during removal from the patient's mouth. A further and major objection, however, results from the large water content, causing shrinkage or swelling, dependent upon the relative humidity of the air in which they are used. Not only does this render the impression inaccurate, but because of water loss voids are created, distortion takes place, and the practicing dentist is greatly inconvenienced or put at a disadvantage when he cannot pour his cast immediately or must of necessity ship the impression to a dental laboratory.

To state the matter simply, the art desires, and prior to the present invention has been without, an impression material which can be satisfactorily used without discomfort to the patient and without rendering too difficult the task of the dentist in taking the necessary impression or impressions with satisfactory accuracy. Obviously, if the dentist has at his disposal material which allows him to make accurate impressions, he will be able to furnish to his patient well fit dentures, making the burden much simpler and more pleasant for both the dentist and his patient.

An article showing the difficulties such as referred to appeared in the April 1938 issue of The Journal of the American Dental Association and the Dental Cosmos, pages 578-584.

An object of the present invention, therefore, is the provision of a plastic material overcoming the objections of previously used material and giving to the dental art for the first time a truly satisfactory impression compound.

I have found, after several years of experimentation, practical applications and tests involving the manufacture of hundreds of compositions, that a solid, high molecular weight fatty acid or wax, having added thereto a plastic material soluble therein, is a superior plastic for the dental art.

The solid, high molecular weight fatty acids such as stearic and palmitic, waxes, such as beeswax, Montan, carnauba, paraffin, etc., are by themselves absolutely worthless for even making approximate dental impressions. However, I have found that these materials will dissolve many of the artificial resins, and that when so used to dissolve these resins, the resulting compound, preferably with some plasticizer for the resin added, is an ideal composition of matter for use in the making of oral cavity impressions.

Originally I expected that some of the newer synthetic resins could be satisfactorily used as impression materials alone, but extended experiments with such resins proved otherwise. Some of the resins tried were the polyvinyl acetal resins, polyvinyl ester resins, polyacrylates, polymethacrylates, or copolymers of the same, polystyrene, copolymeric vinyl esters such as polyvinyl acetate chloride, to mention only a few, but all of these for one reason or another failed to meet the rigid requirements of an ideal dental impression material.

Broadly, my discovery resides in the fact that when synthetic resins are suitably dissolved by the solid, high molecular weight fatty acids or waxes, the resulting compound is unexpectedly

satisfactory as an impression material. In other words, standing alone, the solid, high molecular weight fatty acids, waxes, and the synthetic resins are not suitable, but when combined in accordance with my invention, the compound is unlike any of its constituents and serves remarkably well, as has been above stated.

Of the resinous materials employed by me, I prefer the polyvinyl acetal resins for compounding with the solid, high molecular weight fatty acids or waxes. These resins can be made by condensing either a wholly or a partially hydrolyzed polyvinyl ester with an aldehyde (formaldehyde, acetaldehyde, butyraldehyde, etc.). The present invention is in no way concerned with or limited to the particular method or ingredients employed in the production of the polyvinyl acetal resin, as the preparation of these is well understood in the plastic art. For sake of simplicity, the following examples will deal with the compounding of dental plastic from the polyvinyl acetal resins, solid, high molecular weight fatty acids, waxes, and plasticizers.

To produce my new compound, a solid high molecular weight fatty acid, for example stearic acid (or mixtures of said acids), may be introduced into a covered steam-jacketed kettle and melted, and the selected resin, preferably in a finely divided state, is added, the mixture being suitably agitated to bring about proper combination of the two. Almost simultaneously, plasticizer for the resin is included in the mixture, and heating and stirring is continued until a clear liquid is obtained. If an anodyne (pain reliever) or filler is to be included in the compound, it should be added at this time, and after formation of the clear liquid, it is preferably filtered to insure uniformity of product. The resultant mass is cooled as by pouring into water and kneaded or agitated to induce aeration thereof. Naturally, as the plastic is to be used in the oral cavity, reasonably pure ingredients should be used.

When using the polyvinyl acetal resin and stearic acid, a temperature range of approximately 100 to 150 degrees centigrade is sufficient to bring about proper working of the materials during mixing. When a suitable proportion of plasticizer for the particular resin is added, it will be found, when the new compound is cooled to room temperature, that it is exceedingly tough and elastic. The compound can be heated to a temperature of approximately 130 to 140 degrees Fahrenheit, placed in a dental tray, and inserted into the oral cavity for the making of exceedingly fine dental impressions. On cooling in the mouth to approximately body temperature, my improved compound sets to a tough but not too hard mass which can be readily removed from the mouth without destroying the desired accuracy of impression details. The materials so compounded are rubbery and elastic, which I consider an absolutely essential characteristic of an impression compound to permit the obtaining of accuracy especially where contour of teeth and severe undercuts are present in the mouth. Unlike the hydro-colloids and other prior art materials, my improved compound has good mechanical strength and does not tend to break and be permanently distorted during removal.

A further important property of the material resides in the fact that a dental impression can be made, taken from the mouth, and allowed to stand for an unlimited time without change in the impression made. This permits distant ship-

ment of the impression or other delay in making necessary castings, etc. Furthermore, the material has a long shelf life which is of importance to the dentist and distributor of dental supplies as it permits stocking of the compound without fear of deterioration. My tests have included exposure of samples of the compound to normal atmospheric conditions for well over a year without any apparent change in the characteristic of the materials having resulted from such exposure and lapse of time.

Numerous types of polyvinyl acetal resins can and have been produced, the particular type being dependent in the main upon whether polyvinyl alcohol or partially hydrolyzed polyvinyl acetate is used in the starting mixture and the particular aldehyde employed in the reaction. For example, the resin known in the trade as Formvar is made by condensing partially hydrolyzed polyvinyl esters with formaldehyde to the extent that at least 65% of the hydroxyl groups are reacted, and is an excellent resin for use in my compound. One preferred mixture is Formvar dissolved in stearic acid and plasticized with dimethyl phthalate. Likewise, the so-called Alvars, which are similar to Formvar except that acetaldehyde is employed, are also entirely satisfactory. Since the butyraldehyde type of polyvinyl acetal resin is compatible with a wider variety of plasticizers than the Formvar and Alvar types, there may be an advantage in using this type of resin. However, I wish to emphasize that all of these polyvinyl acetals, as well as the other resins mentioned above, are soluble to a greater or lesser extent in the solid, high molecular weight fatty acids and waxes, and of course plasticizers are known for each of said resins, so that all of said resins are contemplated for use in the carrying out of my invention.

To facilitate a clearer understanding of my compounds, a number of examples are given, and for sake of simplicity a butyraldehyde type of polyvinyl acetal resin is used in each. The analysis of the particular resin employed is as follows:

	Percent
Hydroxyl as polyvinyl alcohol.....	20.0
Ester groups as polyvinyl acetate.....	0.5
Butyralacetal as polyvinyl acetal.....	79.5

The polyvinyl alcohol used for making the resin was formed from polyvinyl acetate and is sold on the open market as Gelva 25.

As specific examples for formulas giving extremely excellent impression materials, I mention:

	Parts
(1) Stearic acid (triple pressed).....	100
Polyvinyl butyralacetal resin.....	40
Plasticizer (dibutyl phthalate).....	60
(2) Stearic acid (triple pressed).....	100
Polyvinyl butyralacetal resin.....	40
Oleic acid.....	30
Plasticizer (dibutyl phthalate).....	30
(3) Stearic acid (triple pressed).....	100
Resin.....	50
Plasticizer (oleic acid).....	100

The Formvar type of polyvinyl acetal resin can be plasticized with dimethyl and diethyl phthalates, triacetin (although only in limited amounts), benzyl benzoate, etc. As satisfactory plasticizers for the Alvar type of resins for this use may be mentioned the phthalate esters in general, triacetin, tripropionin, etc. The butyraldehyde type of polyvinyl acetal resin may be

properly plasticized for this purpose by the cited phthalate esters including the dibutyl and diamyl esters, glycerin esters, oleic and other high boiling liquid fatty acids, etc.

I have found that certain variations in the physical and chemical properties of the resin may occur when these materials are purchased in the open market, e. g., viscosity, molecular distribution, softening point, etc. and therefore the proportions outlined above should not be construed as indicative of specific limitations but rather by way of example, because variations in proportions of the materials may prove beneficial, depending upon the particular properties of materials purchased and used. Likewise, when another plasticizer is substituted, alterations in the proportions may be advisable to compensate for differences in plasticizing effect of the plasticizer on the resin.

My compound is not only well adapted for use as an impression material, but also as a duplicating material; that is, frequently the dentist is called upon to furnish a duplicate denture and he does this by making a master cast from the original impression of the oral cavity and then makes further working casts from the master cast which is called duplicating.

Also in certain dental procedures, it is often desired to obtain a registration commonly referred to as "the bite." To get the "bite," the dentist places a small amount of warmed impression material in the mouth of the patient who then closes his teeth to normal biting relation, thereby giving a registration of the teeth in this position. Unfortunately, the impression bite materials now available are unsatisfactory because the dentist always finds that on removal of the impression material from the patient's mouth, the septum between the biting surfaces is destroyed due to lack of toughness of the impression material. Further, most of the bite materials fail to give adequate accuracy and definition, due principally, I believe, to their lack of elasticity. I have found that my own improved compounds serve as excellent bite materials because, unlike waxes, they are tough and elastic. In view of the time element and the importance of having the bite material cool readily, I suggest modifying the composition from the impression material to give a bite material as follows:

	Parts
Stearic acid (triple pressed)	65
Polyvinyl butyracetal resin	15
Plasticizer (dibutyl phthalate)	20

or the following proportions will work equally as well.

	Parts
Stearic acid (triple pressed)	70
Polyvinyl butyracetal resin	15
Plasticizer (dibutyl phthalate)	15

or

	Parts
Stearic acid (triple pressed)	70
Polyvinyl butyracetal resin	15
Plasticizer (oleic acid)	20

These are examples of my compounds which, when used for "bite" study provide excellent definition, cool rapidly, and are sufficiently elastic to insure accuracy. Furthermore, these compositions provide a tough, accurate intermediate septum between the biting surfaces of the teeth, a property long sought for by the dentist and

not available to him prior to the discovery of the composition herein disclosed.

The compound also is desirable for use as a surgical pack. Oftentimes, after a tooth is extracted or other surgical work is done, proper blood clotting does not result, causing severe pain to the patient. To give relief in such cases, so-called packs are introduced into the surgical area, which may consist of gauze or cotton saturated with anodynes or lanolin gels containing anodynes. Naturally these remedies are of temporary nature because of their instability and/or wicking out or loss of anodyne, resulting in pain recurrence.

A serviceable and efficient surgical pack can be made by producing a compound from solid, high molecular weight fatty acids, polyvinyl acetal resin, and anodynes. One suitable example is:

	Parts
Stearic acid	20 to 60
Polyvinyl butyracetal	10
Anodyne (eugenol)	70 to 30

Although these proportions may be varied to give surgical packs of different hardness, it can be appreciated that because of the plastic nature and stability of the compound, these materials offer wide flexibility and can be easily introduced and removed from the surgical area. Many actual tests of these surgical packs have proved their consistent and prolonged efficacy.

In addition to the above dental uses, my improved compound, in a modified form, finds utility when serving in the capacity of a temporary stopping material. Oftentimes in the preparation of teeth for fillings and for bridge work, it becomes necessary for the dentist to temporarily fill the excavations pending completion and installation of the permanent filling or bridge work. Commercial temporary stoppings now available, such as gutta-percha metallic oxide mixtures, etc. possess poor adhesion to the walls of the excavation, allowing seepage which often results in soreness and pain, and further lack desired mechanical strength. Furthermore, these temporary stoppings do not ordinarily contain anodynes and in some instances the materials actually have an irritating or degenerative effect upon the nerve fibrilles of the walls of the excavation.

I have discovered that by adding fillers (inert toward the plastic), such as calcium sulphate (anhydrous or hydrated), barium sulphate, diatomaceous earth, and the like, to a mixture of solid, high molecular weight fatty acid or wax, polyvinyl acetal resin, plasticizer, and anodyne if desired, a very satisfactory efficient temporary stopping is obtained. Since the mixture is characterized by extraordinary adhesive qualities and plasticity, it is readily softened on the dental instrument by application of heat and can then be easily worked into the dental excavation. Removal of the temporary stopping offers no problem. Also, the ability to use anodynes such as eugenol or guaiacol, which also act like plasticizers, enables the dentist to insure his patient's comfort.

One suggested example of a temporary stopping is:

	Parts
Diatomaceous earth	30
Polyvinyl butyracetal resin	20
Plasticizer (dibutyl phthalate)	40
Stearic acid	8
Anodyne (eugenol)	2

By varying the proportions of these ingredients, temporary stoppings can be obtained with different physical properties such as hardness, softening point, etc.

It will be seen that in all of the examples given above, a solid, high molecular weight fatty acid or wax, a synthetic resin soluble therein, and a plasticizer therefor, constitutes an essential part of the composition. None of these ingredients can by itself serve as a useful material in the fields covered by the above disclosure. However, I have discovered that by dissolving the synthetic resin in a solid, high molecular weight fatty acid or an equivalent wax, and including some plasticizer for the resin, a new compound is obtained admirably well suited for use as an impression material having outstanding elastic, tough properties, permitting accurate, permanent impressions being made of the most difficult cases encountered in oral cavity work. Furthermore, the properties of the compound are such that a patient can be worked on without undue discomfort, and the dentist or other technician can perform his work without great difficulty and can be assured of accurate results.

In the preceding examples, I have included solid, high molecular weight fatty acids, but it will be understood that equivalent waxes can be substituted in whole or in part for such solid, high molecular weight fatty acids. Such waxes as carnauba, beeswax, Montan, Japan wax, and the like, are to be included. Further, although the solid, high molecular weight fatty acids are an essential ingredient, it will be noticed that some of the liquid, high molecular weight fatty acids can also be used more in the capacity as a plasticizer in some of the mixtures.

I wish to emphasize that I have discovered that what I term aeration of the plastic mass is vital to successful practice of my invention and discoveries. For example, I have made batches of the material identical in components and proportions in different ways and with different equipment with varying results, and invariably it has been my experience that when the plastic is not aerated, the results are not nearly as satisfactory as when aeration is included and in fact in most cases where the plastic was not aerated, it was entirely unsatisfactory. The word "aeration" is used herein and in the claims to signify broadly the incorporation of air or other gases in the product and this is preferably done in a way that bubbles or other evidence of entrapped air or gas is not apparent to the naked eye. I have definitely determined that this aeration results in a rather substantial reduction in the densities of the mixtures and compositions. To illustrate, a plastic mass was prepared in accordance with the invention hereinabove described using equipment and technique designed to avoid aeration; that is to say, the material was not stirred or beaten during mixing or compounding. The specific gravity of this particular mix referred to water at 25 degrees centigrade was found to be 0.9647. This material was unsatisfactory. Then a portion of the same batch of material was worked by agitation and kneading during cooling thereof and its specific gravity in the same terms was measured and found to be 0.8824. This represents approximately a decrease in density of 9% referred to the unworked material. This material was entirely satisfactory.

It will of course be understood that I do not intend to be limited to approximately a 9% den-

sity decrease, as obviously this will vary with the different formulas suggested in my application and also depends somewhat on presence of filler or the like if used as well as the nature of the constituents and amount of kneading or other treatment to which the materials are subjected. Likewise, it will be appreciated that the density of the materials themselves will vary so that it is emphasized that I consider I have made a basically new discovery in the matter of my aerated plastic masses.

Practically, aeration of the plastic is easy to accomplish as ordinary stirring and kneading equipment can be used to work the mass, or after heating of the solid, high molecular weight fatty acid or equivalent wax with the resin and other materials, it can be cooled by pouring into a moderate volume of water and vigorously stirred. Aeration of the plastic in a water medium is an extremely inexpensive and satisfactory way of accomplishing the desired results. It has been my experience, when aerating the plastic mass in a water body, that aeration takes place rapidly and only approximately 1% of water is taken up by the plastic, which amount of water can be easily tolerated in the plastic masses with which I have worked. Actually, it is quite customary, when using this material, for the dentist or other person to immerse the mass of prepared plastic in a body of hot water to bring it to the proper temperature and degree of softness.

I claim:

1. An elastic waxlike plastic composition comprising a waxy body selected from the group of high molecular weight fatty acids and waxes, solid synthetic resin soluble therein and plasticizer for said resin, the amount of waxy body being in excess of the amount of resin on a weight basis.

2. An elastic waxlike plastic composition, a plastic mass comprising solid fatty acid, solid synthetic resin soluble therein, and a plasticizer for said resin, the amount of solid fatty acid being in excess of the amount of resin on a weight basis.

3. An elastic waxlike plastic composition, a plastic mass comprising a waxy body selected from the group of high molecular weight fatty acids and waxes, solid synthetic resin soluble therein, plasticizer for said resin and an anodyne, the amount of waxy body being in excess of the amount of resin on a weight basis.

4. The process of producing an elastic waxlike plastic composition comprising the steps of dissolving solid synthetic resin in at least substantially an equal amount of a waxy body selected from the group of high molecular weight fatty acids and waxes on a weight basis, then adding plasticizer for said resin, and then aerating said plastic mass in the presence of water to reduce its density.

5. The process of producing an elastic waxlike plastic composition comprising the steps of heating a wax-soluble solid synthetic resin with substantially an equal amount of waxy body on a weight basis to produce a liquid, then adding plasticizer for said synthetic resin to the liquid, cooling the mixture, and working said mixture in the presence of water to permanently aerate the same.

6. The process of producing an elastic waxlike plastic composition comprising the steps of heating a waxy body selected from the group of high molecular weight fatty acids and waxes and a solid synthetic resin soluble therein to produce a liquid, then adding plasticizer for said solid synthetic resin to the liquid, cooling the mixture, and working said mixture in the presence of water to

permanently aerate same to reduce its density from the normal density of the material without aeration.

7. An elastic waxlike plastic composition comprising a plasticized polyvinyl acetal resin dissolved in a waxy body selected from the group of high molecular weight fatty acids and waxes, the amount of waxy body being in excess of the amount of resin.

8. An elastic waxlike plastic composition comprising solid fatty acid, polyvinyl acetal resin soluble therein, the amount of solid fatty acid being in excess of the amount of resin on a weight basis and plasticizer therefor.

9. As a new composition of matter, an aerated elastic waxlike plastic composition comprising a waxy body selected from the group of high molecular weight fatty acids and waxes, solid synthetic resin soluble therein, and plasticizer for said resin, the amount of waxy body being in excess of the amount of resin on a weight basis.

10. An elastic waxlike plastic composition comprising a plasticized polyvinyl butyr acetal resin dissolved in a waxy body selected from the group of high molecular weight fatty acids and waxes, the amount of waxy body being in excess of the amount of resin.

11. The process of producing an elastic waxlike plastic composition comprising the steps of heating a waxy body selected from the group of high molecular weight fatty acids and waxes and a polyvinyl acetal resin soluble therein to produce a liquid, the amount of waxy body being in excess of the amount of resin, then adding plasticizer for said solid synthetic resin to the liquid, cooling the mixture and working said mixture in the presence of water to permanently aerate the same to reduce its density from the normal density of the material without aeration.

12. The process of producing an elastic waxlike plastic composition comprising the steps of dissolving a plasticized polyvinyl acetal resin in a waxy body selected from the group of high molecular weight fatty acids and waxes, and then working said plastic mass in the presence of water.

13. The process of producing an elastic waxlike plastic composition comprising the steps of dissolving a plasticized polyvinyl acetal resin in a waxy body selected from the group of high molecular weight fatty acids and waxes, the amount of waxy body being in excess of the amount of resin and then cooling said plastic mass.

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