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PLASTIC HYDROCOLLOID COMPOSITION
AND METHOD OF MAKING

Johan Walter H. Stangenberg, Brevik, Sweden,
and Walter S. Crowell, Melrose Park, and
Charles Victor Gross, Penfield, Pa.; said Crow-
ell and said Gross assignors to The S. S.
White Dental Manufacturing Company, Phila-
delphia, Pa., a corporation of Pennsylvania

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Our invention relates to that class of composi-
tions that may be employed for taking impres-
sions and which are particularly applicable in
making replica casts of parts of the human body,
and is especially directed to the making of repro-
ductions of the form of the oral cavity.

For many years past it has been common prac-
tice in the taking of impressions of the oral cavity
to employ gypsum products, such, for instance,
as what is commonly known as "plaster of Paris".
Obviously, such material sets with unyielding
rigidity and therefore can only be withdrawn as a
unit where there are present no undercuts such
as any relatively inclined teeth would produce.
Consequently, an impression taken with such un-
yielding material must necessarily be cracked up
into pieces such as may be withdrawn, which
pieces must be subsequently placed together to
form the integral intaglio mold desired from
which the replica cast may be produced.

There are other disadvantages in the use of
gypsum products among them being the disagree-
able feeling experienced by the mud-like plaster
contacting with the tissues, that it requires
several minutes to set or solidify, and that the
breaking up of the cast is likely to injure the
permanent denture work that may be in the
mouth of the patient.

The principal objects of our invention are to
provide a cohesive impression taking and model
casting mold material that may be of such a
nature that it may readily conform to the most
minute furrows, ridges, indentations and crevices,
and that, in its solidified state, may be suffi-
ciently yielding in its nature to permit its with-
drawal as a unit and retain its intaglio form, in-
cluding all undercuts, with absolute precision.

Other objects of our invention are to produce
a plastic hydrocolloid mass so prepared and con-
stituted that it may be employed in the taking
of impressions of the mouth without the at-
tendant undesirable effect on the tissues and
denture work, and that in its solidified state
serves as an intaglio mold in which plaster casts
may be molded without interference with the
setting of the plaster and without tendency of
the plaster to adhere thereto. Or, to state it the
other way around, our hydrocolloid composition
when solidified is in adhesive toward plaster, so
that a mold formed of the composition does not
stick to a plaster cast molded therein.

Further objects of our invention are to pro-
vide a plastic hydrocolloid composition for form-
ing molds for plaster casts with an accelerating
agent tending to accelerate the setting of the

plaster molded therein and thereby counteracting
the normal retarding action of the mold form-
ing material upon the set of the plaster forming
the cast by its contact with the mold.

Our invention also comprehends a plastic
hydrocolloid composition for forming molds,
which has incorporated therein a precipitating
agent or fixing substance the excess of which is
susceptible of being removed by washing, and a
basic substance added to neutralize any traces
of said precipitating agent or fixing substance
which might remain after washing, and which
may progressively react with the other con-
stituents of the hydrocolloid, destroying their
jelly forming ability. This is more fully ex-
plained hereinafter.

As ordinarily prepared, compositions (other
than plaster of Paris, and the like), for use in
forming molds, such as those which yield for
making plaster casts, have a tendency to inter-
fere with the set of the cast forming material
such as plaster of Paris, alpha-gypsum, Keene's
cement, etc. When poured against the surfaces
of the mold for the purpose of making casts or
models, so that adhesion of the plaster or other
ingredients employed occurs with the result of
producing rough and inaccurate models or casts.
In some instances, particularly where a reversible
hydrocolloid material is employed, fixing agents,
such as alum and tannic acid, have been sug-
gested to prevent such adhesion.

We have found that the simple addition of fix-
ing substances either does not satisfactorily
remedy the difficulty, or deleteriously affects the
properties of the material to such an extent—
either when freshly made or shortly thereafter—
that it becomes unsuitable for the purpose in-
tended, or at least its efficiency is found to be
greatly impaired.

We have discovered after considerable research
and experimentation that the chief cause of the
adhesion of the plaster forming the cast is the
soluble organic substances present in the hydro-
colloid of which the plastic composition is largely
composed, which tend to retard the setting of the
plaster forming the cast.

Our plastic hydrocolloid impression composi-
tion may be produced from a reversible hydro-
colloid such as agar agar, water, glycerin or
sugars, fatty substances, waxes and the like, oils,
resins, vegetable fiber, mineral fillers, antiseptics,
flavoring agents and substances designed to ac-
celerate the set of plaster of Paris or other mate-
rial employed to form the cast, said plaster set
accelerating substances being employed to coun-

teract reaction of the retarding matter inherent in the agar agar type of hydrocolloid, which normally tends to retard the set of plaster of Paris, or other material, forming the cast.

- 5 A composition that has been found to be satisfactory may be compounded as follows:

Agar	10 parts (reversible hydrocolloid).
Paraffin wax	5 parts (wax).
Mineral oil	1 part (oil).
Common rosin	1/4 part (resin).
Cotton fiber	1/10 part (vegetable fiber).
Blanc fixé	10 parts (mineral filler).
Phenol or other antiseptic	1/100 part (antiseptic).
Flavoring oils	1/200 part (flavor).
Potassium sulfate	1 part (accelerator).
Water	q. s. to make 100 parts.

- 20 We have found that by washing the agar with cold water to remove the major portion of the organic substances that retard the setting of the plaster cast and by adding plaster setting accelerators to the mass to counteract or neutralize the effect of the remainder, satisfactory results may be obtained. Satisfactory results may also be obtained by adding chemical substances which react with and thus counteract the interfering organic substances, and preventing the action of these added substances on the other constituents of the agar by having present in the mixture, or subsequently adding thereto, a second protective agent or substance which arrests the deleterious action of the first on the other constituents of the agar but which does not arrest or reverse the action of the first on the interfering organic substances. In particular, the agar may be treated with a solution of a precipitating or fixing substance to fix or precipitate the interferent substances, subsequently washing the agar to remove excess and neutralizing any traces remaining, which might react on the jelly forming constituents of the agar to their detriment, by adding to the mixture a substance which arrests the deleterious action of the precipitatory or fixing substance on the other constituents of the agar but which does not arrest or reverse its action on the interfering organic substances. By either washing the agar agar hydrocolloid or treating it with a precipitating or fixing agent (as just described), the plaster-set-retardant matter which it includes is to all intents and purposes eliminated,—to a degree depending on the thoroughness of the washing, or on the sufficiency of the precipitant to counteract the retardant matter. In either case, therefore, the agar is pro tanto freed of the retardant matter as such.

- By "fixing or precipitating substance" is meant the provision of a substance capable of rendering the interferent substances innocuous either by combining therewith and providing a product which can be physically separated by precipitation or otherwise from the residue of the jelly, or by providing therewith a product which may remain in the jelly but does not have the capability of retarding the setting of plaster, or by producing a conjoint action with the retardant substances which compensates for this action.

- 70 In washing the agar agar, the agar agar is soaked in 160 parts of cold water until it softens and swells. The water is then drained off and replaced by fresh water. This operation may be repeated several times, or washing may be accomplished by passing a continuous current of

cold water through the agar for several hours. This removes about 20% by weight of the agar which includes most of the substances present which exert a retarding action on the setting of the cast of plaster or other materials employed. The prolonged treatment of the agar with water as described—whether by repeated soakings, or in a continuous current—removes the deleterious retardant matter by dialysis, rather than by washing in the ordinary sense: i. e., the water-soaked mass of agar behaves like a dialysing diaphragm or sack enclosing the impurities, which as they dissolve diffuse out through the wet agar into the surrounding water.

It is difficult to wash the agar free from all the offending substances without prolonged washing and excessive loss of material. Instead of doing so we may add to the compound which includes the washed agar a small quantity of a plaster set accelerator, such as potassium sulfate or other suitable substance. Obviously, other materials which are known to accelerate the set of plaster may also be used, for instance, magnesium sulfate, ferrous sulfate, various alums and other double salts, sodium chlorid, potassium chlorid, and a variety of other soluble sulfates and chlorids, with varying degrees of efficiency.

The washed agar is dissolved by boiling with 150 to 200 parts water. When solution is complete, it is boiled and stirred to get rid of excess water. When about 100–120 parts of water remain, the wax, resin and mineral filler hereinbefore referred to are added. The solution is violently agitated and the wax and resin added in the molten condition so that an emulsion is formed. The grain of the emulsion may be improved by passing it through a colloid mill.

Heating and stirring is continued while the cotton fiber is added and until all excess water is driven off. The plaster setting accelerator, such as potassium sulfate in solution in a small quantity of water, is then added. The mix is then cooled slightly and the flavoring material and the antiseptic added. After thorough mixing, the mass is allowed to cool and is then ready to package for sale. The accelerator is preferably added when the batch is nearly complete, so as to minimize any action it might have on the compound during the process of manufacture.

As already mentioned, the retarding action of the constituents of plastic hydrocolloid impression materials of the kind above described may be neutralized, by adding to them substances which react with the retarding constituents, precipitating or fixing them. The addition of such substances effectively prevents the undesirable action of the compound on the plaster cast, particularly if the added material is also an accelerator of the setting of the model material used. However, such substances, if present in sufficient quantity to accomplish the desired results, react with the jelly-forming constituents of the agar, commonly called pectin and gelose, and materially reduce or destroy the strength and elasticity of the jelly produced on cooling the mass. This action is progressive and is accelerated by increasing the temperature.

Thus, if the precipitating agent is added to the mass early in the process of manufacture and is present while the mass is being boiled to expel excess water, it will act on the agar to such an extent that the finished compound will not set to a jelly on cooling. If it is added near the end of the process, its action will be less and the

freshly made material will form a satisfactory jelly. On keeping at room temperature for some time and reheating for use, it will be found that the jelly strength is progressively reduced as the time of storage is increased.

We have found that the action of the precipitating and fixing agent on the pectin and gelose depends upon the acidity of the medium and that by adding to the mass the oxid, hydroxid or carbonate of a basic substance of such properties and in such quantities that the acidity is reduced during the process of manufacture to a value such that the pH determined by the usual methods is between 6 and 8, preferably between 6.5 and 7.5, the precipitating and fixing effect is accomplished and the deleterious action of the added substance upon the jelly-forming constituents of the agar is prevented.

We have found that the added basic substance acts most efficiently when added in the form of small particles, which particles are almost insoluble in water. Examples of sparingly soluble basic substances that may be added are carbonates of calcium, barium, strontium and magnesium, oxids or hydroxids of cobalt, nickel, zinc, cadmium, magnesium, beryllium and manganese. Such substances may be generally referred to as (basic) metal oxide agents, for reasons obvious to chemists.

Examples of precipitating and fixing agents are the sulfates (and double sulfates with the alkali metals) of iron, chromium, aluminium, zinc, nickel, cobalt, cadmium and manganese and the chlorids, nitrates and acetates of the same metals.

The basic substance may be added before the precipitating and fixing substance or afterwards, or at the same time, depending upon the amount of action of the precipitating substance on the gelose and pectin that is desired or permitted. It must be added in excess. The quantity of added substance that constitutes an excess depends upon the quantity of precipitating and fixing agent used and upon the acidity it produces in the mass. Thus, if 1% zinc sulfate is added to the compound as a precipitating agent, $\frac{1}{10}$ % zinc oxide is a sufficient excess, while if 1% potash alum is added, $\frac{1}{10}$ % calcium carbonate will be required.

The basic oxid may be added in great excess and may replace all or part of the mineral filler or pigment used.

The precipitating and fixing substance may be added at any time during the process of manufacture. The quantity of precipitating and fixing agent required depends upon the quantity of substances interfering with the set of plaster, etc., present in the agar. If this is reduced by washing, a correspondingly smaller quantity of precipitating and fixing substance is required than if unwashed agar is used. We have found that additions from a minimum of $\frac{1}{10}$ % to a maximum of 2% have been sufficient to produce the desired results. Exact proportions in a given case must be found by experiment.

For thus neutralizing the effect of substances contained in the agar on the set of plaster the agar may be treated in the cold with the precipitating and fixing substances,

In the following manner the agar is soaked for 12-24 hours in a solution of the precipitating and fixing substance at a temperature below 130° F. and then washed to remove the excess of precipitating and fixing substance which might have deleterious action on the jelly forming constitu-

ents of the agar. As a final step, a basic substance such as those described above is added to neutralize any traces which might remain after washing. The precipitating and fixing agents used are those described above and, in addition, tannic acid, tannin, and formaldehyde. The precipitating and fixing agent can be used as a solution varying in strength from a minimum of $\frac{1}{10}$ % to the maximum of a saturated aqueous solution of the agent used. The basic substance must be present in excess, as described above. We have found that $\frac{1}{10}$ % to 2% of the weight of the agar has been sufficient. A large excess can be used if it is desired to replace part or all of the pigment and filler with basic substance.

It may be here noted that the formula herein set forth is merely typical and that the specified number of parts therein set forth may be varied more or less and that other ingredients may be substituted for those specifically described.

Our invention is advantageous in that the process of taking impressions with the composition contemplated is much less irksome to both the patient and operator alike, as such composition greatly facilitates the operation and saves time, discomfort and expense, and produces more accurate results than by compositions heretofore known.

It is obvious that the invention is not limited to the specific material stated; but that it may be employed in many ways within the scope of the appended claims.

Having thus described our invention, we claim:

1. A method for preparing an improved plastic hydrocolloid composition, for taking impressions and forming molds for plaster casts, said composition comprising as its base a plastic agar-agar hydrocolloid including plaster-set-retardant organic matter; which method comprises washing the commercially pure hydrocolloid with cold water until substantially 20 percent of the substance thereof has been removed and therewith the major portion of such organic matter, and adding to the hydrocolloid an agent effective for neutralizing the retardant properties of any such organic matter remaining unremoved.

2. A method for preparing an improved plastic hydrocolloid composition, for taking impressions and forming molds for plaster casts, said composition comprising as its base a plastic agar-agar hydrocolloid including plaster-set-retardant organic matter; which method comprises washing the commercially pure hydrocolloid with cold water until substantially 20 percent of the substance thereof has been removed and therewith the major portion of such organic matter, and adding to the treated hydrocolloid an agent effective for neutralizing the retardant properties of any such organic matter remaining unremoved, said agent comprising a soluble sulphate or chloride.

3. A method for preparing an improved plastic hydrocolloid composition, for taking impressions and forming molds for plaster casts, said composition comprising as its base a plastic agar-agar hydrocolloid including plaster-set-retardant organic matter; which method comprises washing the commercially pure hydrocolloid to eliminate a portion of such retardant organic matter, and adding to the hydrocolloid a reagent effective for neutralizing the retardant properties of any such organic matter remaining unremoved, which reagent tends to act deleteriously on the jelly-forming constituents of the hy-

drocolloid, and adding a neutralizing agent for preventing deleterious action of such reagent on the hydrocolloid composition.

4. A method for preparing an improved plastic hydrocolloid composition, for taking impressions and forming molds for plaster casts, said composition comprising as its base a plastic agar-agar hydrocolloid including plaster-set-retardant organic matter; which method comprises
 - 10 washing the crude hydrocolloid to eliminate a portion of such retardant organic matter, and adding to the hydrocolloid a soluble metal salt effective for neutralizing the retardant properties of any such organic matter remaining un-
 - 15 removed; which salt tends to act deleteriously on the jelly-forming constituents of the hydrocolloid, and adding a basic metal oxide agent for preventing deleterious action of such salt on the hydrocolloid composition.
 - 20 5. A method of producing an improved, inadhesive plastic composition for taking impressions and forming molds for plaster casts, of the type characterized by a base of reversible hydrocolloid which includes plaster-set-retardant matter; which method comprises treating
 - 25 the hydrocolloid with a precipitating agent for its said plaster-set-retardant matter, which agent tends to act on its jelly-forming constituents; washing the treated hydrocolloid and thereby removing therefrom unreacted precipi-
 - 30 tating agent; and adding to the treated and washed hydrocolloid an agent tending to arrest the action of said precipitating agent on jelly-forming constituents of the hydrocolloid.
 - 35 6. A method for preparing an improved plastic hydrocolloid composition, for taking impressions and forming molds for plaster casts, said composition comprising as its base a plastic agar-
 - 40 agar hydrocolloid including plaster-set-retardant organic matter; which method comprises washing the agar-agar with cold water and adding thereto zinc sulphate and zinc oxide.
 7. An improved, inadhesive plastic composition for taking impressions and forming molds
 - 45 for plaster casts, comprising a base of reversible plastic agar-agar hydrocolloid which has been washed with cold water until substantially 20 percent of the jelly-forming constituents have been eliminated and therewith the major portion
 - 50 of plaster-set-retardant matter naturally present in the crude agar-agar, and also comprising one-tenth to 2 percent of an agent for counteracting the retarding effects of any unremoved remainder of such retardant matter.
 - 55 8. An improved, inadhesive plastic composition for taking impressions and forming molds for plaster casts, comprising a base of reversible plastic agar-agar hydrocolloid which has been freed of the major portion of plaster-set-retardant matter naturally present in the crude agar-
 - 60 agar, and also comprising a reagent for counteracting the retarding effects of any unremoved remainder of such retardant matter, said reagent tending to act deleteriously on the remaining
 - 65 jelly-forming constituents of the hydrocolloid, and a basic metal oxide agent for neutralizing the effect of said reagent upon the treated hydrocolloid.
 9. An improved, inadhesive plastic composition
 - 70 for taking impressions and forming molds for plaster casts, of the type characterized by a base of reversible plastic agar-agar hydrocolloid which naturally includes plaster-set-retardant matter; said composition comprising, besides the hydro-

colloid base, a soluble metal salt for counteracting such matter, which salt tends to act deleteriously on the jelly-forming constituents of the hydrocolloid base, and a proportion of basic neutralizing agent such that the pH of the composition lies between 6 and 8, said neutralizing agent being effective to arrest the action of said metal salt on the jelly-forming constituents of the hydrocolloid.

10. An improved, inadhesive plastic composition for taking impressions and forming molds for plaster casts, of the type characterized by a base of the reversible agar-agar colloid which naturally includes plaster-set-retardant matter; said composition comprising, besides the hydrocolloid base, one of the group of precipitating or fixing reagents consisting of the sulphates, chlorides, nitrates and acetates of iron, chromium, aluminum, zinc, nickel, cobalt, cadmium and manganese, and the double sulphates of said metals which include also an alkali metal base, said reagent tending to act deleteriously on the hydrocolloid base, and a basic metal oxide neutralizing agent for preventing deleterious action of said precipitating or fixing reagent upon the hydrocolloid base selected from the group consisting of the carbonates of alkaline earth metals and the oxides and hydroxides of cobalt, nickel, zinc, cadmium, magnesium, beryllium and manganese.

11. An improved inadhesive plastic composition for taking impressions and forming molds for plaster casts, of the type characterized by a base of agar-agar hydrocolloid which naturally includes plaster-set-retardant matter; said composition comprising, besides the hydrocolloid base, alum and zinc oxide.

12. An improved, inadhesive plastic composition for taking impressions and forming molds for plaster casts, of the type characterized by a base of agar-agar hydrocolloid which naturally includes plaster-set-retardant matter; said composition comprising, besides the hydrocolloid base, zinc sulphate and zinc oxide.

13. An improved, inadhesive plastic composition for taking impressions and forming molds for plaster casts, of the type characterized by a base of reversible plastic agar-agar hydrocolloid which naturally includes plaster-set-retardant matter; said composition comprising, besides the hydrocolloid base, a soluble metal salt for counteracting such matter, which salt tends to act deleteriously on the jelly-forming constituents of the hydrocolloid base, and a finely-divided sparingly-soluble basic neutralizing agent for preventing deleterious action of the metal salt on the hydrocolloid base.

14. An improved, inadhesive plastic composition for taking impressions and forming molds for plaster casts, of the type characterized by a base of reversible plastic agar-agar hydrocolloid which naturally includes plaster-set-retardant matter; said composition comprising, besides the hydrocolloid base, fatty substance, resin, anti-septic, flavor, vegetable fibre, and water, together with an agent for counteracting such retardant matter, said agent tending to act deleteriously on the hydrocolloid base, and a protective agent for preventing deleterious action of the first-mentioned agent of the hydrocolloid base.

J. WALTER H. STANGENBERG.
WALTER S. CROWELL.
C. VICTOR GROSS.

CERTIFICATE OF CORRECTION.

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JOHAN WALTER H. STANGENBERG, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 23, for "etc. When" read etc., when; page 3, first column, line 69, after "substances," insert the words and period in the following manner.; line 70, for "In the following manner the" read The; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 19th day of September, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.