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CARBOXY ALKYL CELLULOSE IMPRESSION MATERIALS AND IMPRESSIONS MADE THEREFROM

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This invention relates to impression materials, and more particularly to dental impression materials, to substances and compositions in producing such impressions, to impressions made with these substances and compositions, and to methods of making such substances, compositions and articles, and methods of utilizing the substances and compositions.

Various substances and compositions have been suggested in the prior art for the production of impression compositions and materials. The more exacting the art is in which such impression material is employed, the fewer are the satisfactory materials that have been employed for such purposes. For example, considering the exacting requirements of the dental impression art, there are few compositions which have proved satisfactory in practice and for the most part they have been based on alginate containing compositions although pectates have also been proposed. The compositions have not always been satisfactory, many of them exhibit limited shelf-life, and are subject to other deficiencies.

Considering the requirements for impression material in such exacting arts as the dental impression art where it is necessary to make exact replicas, a number of requirements exist that must be considered. The impression material should be easily brought into condition for use; it should not require heat for such purpose at least most desirably should not do so; it should be of such physical character that it can be inserted into cavities and fissures and readily removed therefrom without mutilation or destruction when set; it should set in a suitable time, not too short to prevent proper manipulation in application, nor so long as to cause discomfort to a dental patient; it should form a sharp accurate impression of the structure to which it is applied; it should set to a tough rubbery or flexible state so that it may be stripped from the structure to which it has been applied even when undercuts are present; and the dry powder composition should be stable over a substantial period of time before mixture with water for use.

Few compositions have been found to be usable in the art. In some of them compressional strength is obtained at a sacrifice of flexibility. In some, the gel structure obtained is not satisfactory because it is rather loose and open in character. In some cases ions formed act as retarders for plaster which comes in contact with the impression. Because of these and other considerations, prediction is of little value and actual test is required to determine the actual value of any composition for the exacting requirements in this field. Whether or not the set obtained is weak or strong, and other factors mentioned above, must be investigated.

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Among the objects of the present invention is the production of impression materials from substances giving satisfactory gel structures enabling impression materials to be produced without the defects exhibited by prior art materials.

Other objects include the production of impression materials which possess high compressional strength and extreme flexibility when set.

Still further objects include molded impressions from such impression materials.

Many other objects and advantages in the invention will appear from the more detailed description set forth below, it being understood that such more detailed description is given by way of illustration and explanation only, and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

In accordance with the present invention, impression materials are produced particularly suitable for dental impression use, from carboxy alkyl cellulose employed in a composition containing a salt of a metal forming a gel with the carboxy alkyl cellulose, the combination yielding a satisfactory gel structure when set from a paste with water. The carboxy alkyl celluloses differ radically from alginates and related materials heretofore used in the art in that the alkaline earth metal salts of the carboxy alkyl celluloses, namely, the calcium, strontium and barium salts are soluble in water as well as the alkali salts thereof, thus distinguishing the carboxy alkyl celluloses from alginic acid and similar materials heretofore used in the art in requiring their utilization under essentially distinct conditions.

The carboxy alkyl celluloses include carboxy methyl cellulose, carboxy ethyl cellulose, and other carboxy alkyl celluloses but for present purposes it is preferred to use a carboxy alkyl cellulose in which the alkyl group does not contain more than 4 carbon atoms, that is, not above the carboxy butyl cellulose and more desirably the carboxy methyl cellulose is employed although the carboxy ethyl cellulose may also be satisfactorily utilized. For illustrating the invention, since it is particularly eminently suitable for use in this direction, the invention will be illustrated by the use of the carboxy methyl cellulose.

The carboxy alkyl celluloses individually or in mixture most desirably are used for present purposes in the form of a water-soluble salt. Any soluble salt may be employed including the salts of the alkali metals, ammonium, the salts of the alkaline earth metals, and salts of amines or alkanol amines. The choice of salt is dependent in part on the particular field in which the impression material is to be employed. For dental

impression work, long chain amine salts would not normally be employed because they give a soapy product in water. Consequently for dental impression work, the salts of sodium, potassium, ammonium, short chain amine and alkylol amines such as ethanolamine salts are desirably employed.

The strength of the impression which is obtained by the use of the carboxy alkyl celluloses, is dependent at least in part on the viscosity of the soluble carboxy alkyl cellulose which is employed. Here too the carboxy methyl celluose may be used as exemplary. Carboxy methyl cellulose is available with a viscosity as high as 2000 C. P. S. at 1% and carboxy methyl cellulose of that viscosity gives the strongest impressions. It is most desirably employed although lower viscosity carboxy alkyl celluloses may be employed, as for example, that having a viscosity at 1000 but below 1000 the strength drops off rapidly and at least for dental impression work a lower limit of from 500 to 700 C. P. S. may be mentioned although the highest viscosity materials as set forth above give the most desirable impressions from the strength standpoint.

With the carboxy alkyl cellulose, a setting agent is employed. Since the alkaline earth salts of the carboxy alkyl celluloses are soluble in water, they are not avaiable as setting agents. The setting agents employed should be a salt or mixtures of salts of a metal or metals forming a gel with the carboxy alkyl cellulose when set from a paste with water. The metals, salts of which can be used for forming strong gels are more particularly those in classes I*b*, III*a*, IV*b*, VI*a*, and group VIII of the periodic system as exemplified for example, by copper, lead, aluminum, iron and chromium, which are capable of forming strong gels with the cellulose solution. The salts employed of such metals for setting purposes include for example, the halides, sulfates, silicates, acetates, etc. Thus chromic sulfate, lead halides, lead mono-silicates and other slightly soluble lead salts, aluminum salts such as its salts with organic acids particularly the acetates and more specifically the basic aluminum acetates, etc., may be used. Salts which give the production of gels of satisfactory strength and compositions which are light or white in color are preferred since they may be pigmented readily to any color to meet commercial acceptance.

Aluminum acetate may be employed to give excellent compositions for these purposes with for example, carboxy methyl cellulose. In some instances the aluminum triacetate by itself may be too rapid in setting and may be retarded by basic retarding agents such as the alkali metal carbonates and phosphates, as for example, sodium carbonate or sodium phosphate. The best results, however, have been obtained by the use of basic aluminum acetates.

The speed of setting of the composition depends mainly on the degree of basicity of the aluminum acetate. This varies considerably in commercially available basic aluminum acetates. The acetic acid content of the basic aluminum acetate, therefore, affects the speed of setting of the ultimate composition produced. If the basic aluminum acetate employed is relatively slow in its action, more of it may be employed with for example, sodium carboxy methyl cellulose in order to increase the setting time of the composition. For example, considering proportions of basic aluminum acetate to sodium carboxy methyl cellulose where a 1:1 ratio gives too slow a setting time, the amount of basic aluminum acetate may be increased for example, to a ratio of 5:1 or acidic accelerators such as the alkali metal bisulfates for example, potassium bisulfate may be incorporated in order to speed up the setting time. Where the basic aluminum acetate is too rapid in its action, retarders may be incorporated, namely, basic retarding agents such as the alkali metal carbonates and phosphates for example, sodium carbonate or sodium phosphate. Basic aluminum acetates produced in the laboratory may be controlled from the standpoint of their basicity to give the desired set. Commercially available basic aluminum acetates may be heat treated to reduce their acetic acid content where the commercially available material is too rapid in its action, reduction in the acetic acid content materially affecting the rapidity of action. For example, in one commercial basic acetate which had an aluminum oxide content of 33.4% and which was somewhat too fast in setting time without the use of a retarder, such basic aluminum acetate heated for 42 hours at 140° C. lost an appreciable amount of acetic acid and gave excellent results when used even in equal parts by weight with the sodium carboxy methyl cellulose for example.

To exemplify the basicity of basic aluminum acetate, reference may be made to the commercial material which usually shows an analysis that corresponds roughly to the formula

$$Al(OH)(C_2H_3O_2)_2$$

combined with 1.5 to 2 moles of water. Stabilizers, such as boric acid, may be added to the aluminum acetate and for that purpose small amounts only are necessary. If desired, substances such as soluble sulphates, particularly potassium sulphate, which accelerate the setting of plaster, may be included in the impression composition, in small amounts as for example, from 0.5 to 5% by weight.

Thus it is possible to adjust the setting time of these compositions, as for example, by the character of the basic aluminum acetate or other setting agent which is employed or by the presence of accelerators or retarders, etc. The illustrative setting times referred to herein are particularly stated from the standpoint of the utilization of these compositions for the production of dental impressions where it is desirable that the composition should show characteristics which enable them to be used so that there is available one minute for mixing and a setting time of about 3 minutes.

As exemplifying other setting agents that may be employed the following is given. Chromic sulphate may be used as the setting agent. It exists in a variety of forms which are not all equally effective for these purposes. Of these varieties, the most important for use in compositions made under this invention particularly for dental impression materials, may be characterized as the green chromic sulphates which are hydrated salts. In their most desirable form, they contain at least one sulphate which does not precipitate with barium chloride, and there may be 1, 2 or 3 such unreactive sulphate groups present. Those having from 5 to 8 mols of water of hydration are particularly valuable and a specific salt of that character is the chromic sulphate having an SO_4/Cr_2O_3 ratio of about 2.9/1 and having 7.4 mols of water of hydration. In general any deliquescent chromic sulphate is not desirable but the non-deliquescent salts are used. Any of the

hydrated chromic sulphates may be used, including the violet colored salt with 18 mols of water of hydration, if first heat treated, as for example, at temperatures of from 90 to 150° C., or preferably from 90 to 110° C. convert them into lower hydrates particularly of green color. The rose colored anhydrous salt is desirably converted into a hydrated material for use in the present invention.

While the chromic sulphate employed may be produced in any desired way, as for example, heat treatment of higher hydrates within temperature ranges as indicated above for periods of say about 5 hours, or by direct preparation in appropriate ways, the following example illustrates one manner of preparation of a satisfactory material for use herein without any intention of limitation to that example.

Sulphur dioxide gas is passed into an aqueous solution of CrO_3 until substantially no further reaction occurs. The resulting solution is slowly evaporated and the crystals obtained dried at about 180° F. for about 24 hours, while mixing every hour to expose the material evenly to the heat. Or vacuum drying may be employed. A chromic sulphate particularly effective for use in the present invention is that illustrated by the following analysis:

	Per cent
Cr_2O_3	26.17
Basicity	21.77
Acidity (as H_2SO_4)	39.69
Total SO_4	47.69
Fe_2O_3 and Al_2O_3	.34
H_2O (105° C. overnight)	11.56
Cl_2	None

Chromic sulphate as pointed out above, is particularly useful in making impression materials specifically for dental impression work. Other chromic salts may be employed but toxic materials such as chromic fluoride are desirably not used in compositions for dental purposes.

Lead salts, particularly those having solubilities in the range of about 0.1 to 1% may be used. Any slightly soluble lead salts may be employed. Such said lead salts when used, should be capable of setting the carboxy alkyl cellulose or should be capable of being utilized with materials which will give the desired setting in the composition. Lead monosilicate (85% PbO, 15% SiO_2) alone will usually not set carboxy methyl cellulose but acid may be incorporated, as for example, in the form of acid salts to get the desired results so long as an insoluble lead salt is not formed. Thus potassium acid tartrate or potassum acid phthalate desirably in small amounts may be used to obtain setting of the carboxy methyl cellulose for example, with lead monosilicate. Aluminum silicofluoride and zinc nitrate may also be employed with the lead monosilicate to produce setting. Lead chloride $PbCl_2$ is particularly useful in making materials for dental impression work and the soluble sulphates such as potassium sulphate are good retarders for use in such compositions containing lead salts.

As fillers, any substantially water-insoluble powder may be employed so long as it does not exhibit excessive basicity. Because of the amphoteric character of aluminum hydroxide, fillers of high basicity are desirably avoided. Non-basic fillers such as silica, barium sulfate, silicates and the like, may be employed. Calcium carbonate may be utilized because of its low solubility. Other fillers that may be employed include the various calcium carbonates in their heavy or light forms, clays, diatomaceous earth, chalk, bentonite, mica, asbestos, volcanic ash, hard waxes and the like.

Magnesium carbonates are generally too basic to be used as fillers, but this depends in part on the setting agent employed in the impression material. For example, with some grades of chromic sulphate as illustrated below, magnesium carbonate may be used.

Such filler usually makes up the bulk of the composition and has some influence on the final physical properties of the gel, influences the setting time somewhat, the working properties of the paste, and the fineness of the impression. Some fillers may exert a particular property of value in some cases, as for example, the use of volcanic ash to give smoothness and to improve hardness. Where the higher proportions of basic aluminum acetate are employed, the amount of filler used may be considerably reduced and as much as one-half of such filler replaced by the utilization of the higher proportions of the basic aluminum acetates for example. Very heavy fillers such as lead silicate may be used in quantities considerably more than the lighter fillers.

The over-all proportions of the components utilized should be capable of giving the desired gel structure when the composition is set from a paste with water. For example, with 1 part by weight of 2000 viscosity carboxy methyl cellulose there may be employed from 0.7 to 5 parts by weight of setting agent such as basic aluminum acetate dependent in part on the acetate content as explained above, and from 7 to 12 parts by weight of a fairly light filler such as diatomaceous earth, whereas when a very heavy filler such as lead silicate is used, the weight of filler may be up to 30 parts by weight and higher. As noted above, where a high proportion of setting agent such as aluminum acetate is used such as 5 parts by weight to 1 part by weight of the carboxy methyl cellulose, this may replace as much as one-half of the filler, particularly the lighter fillers. Where lower viscosity carboxy alkyl celluloses are employed, as for example, in the 500 to 700 viscosity grades, the heavier fillers like lead silicate are preferably used and increased in amount, and desirably a greater amount of the carboxy alkyl cellulose is employed. The materials referred to above are mixed with water for use and this may vary, enough water being employed to form a "putty" satisfactory for taking dental or other impressions. In general with compositions of the character set forth above, the amount of water will usually be from 11 to 17 parts by weight with about 12 parts by weight preferred, to 5 parts of powder.

The following examples illustrate the invention, parts being by weight unless otherwise indicated.

Example 1

	Parts
Diatomaceous silica	5
Basic aluminum acetate	5
Sodium carboxymethyl cellulose (2000 visc)	1

Example 2

	Parts
Diatomaceous silica	5
Calcium carbonate	5
Sodium carboxymethyl cellulose (2000 visc)	1
Basic aluminum acetate	1

Example 3

A commercial basic aluminum acetate which had an aluminum oxide content of 33.4% was heated 42 hours at 140° C. to remove a little acetic acid and then exposed to the air for several weeks to allow it to gain some moisture and to reach a nearly constant weight.

	Parts
Above aluminum acetate	1
Sodium carboxymethyl cellulose (2000 visc)	1
China clay	5
Diatomaceous silica	5

Example 4

Like Example 3 except that 1 part of sodium carboxyethyl cellulose is used in place of sodium carboxymethyl cellulose.

Example 5

	Parts
Diatomaceous silica ("Celite HSC")	10
$CaCO_3$	6
Chromic sulfate ("Tanolin R")	2.5
NH_4Cl	1
Sodium carboxymethyl cellulose (2000 visc)	2

Such composition may be utilized in the ratio of 6 parts of the stated powder to 12½ parts of water.

Example 6

	Parts
Celite	5
$CaCO_3$	3
Sodium carboxymethyl cellulose (2000 visc at 1%)	1
$PbCl_2$	1.25

5 parts of this powder may be used with 12½ parts of water containing a small amount of trisodium phosphate (such as 0.45 g. in 112.5 cc.) and gives a very strong impression.

Example 7

	Parts
Celite	5
$CaCO_3$	3
$PbCl_2$	1.6
Sodium carboxymethyl cellulose (2000 visc)	1

5 grams of this powder may be used with 12 cc. of 1% potassium sulfate solution.

Having thus set forth my invention, I claim:

1. An impression material containing a water-soluble salt of a carboxy alkyl cellulose in a mixture with a setting agent of a salt of a metal forming a gel with the carboxy alkyl cellulose, in proportions to give a gel structure when set from a paste with water.

2. An impression material as set forth in claim 1, in which the setting agent is aluminum acetate.

3. An impression material as set forth in claim 1, in which the setting agent is basic aluminum acetate.

4. An impression material as set forth in claim 1, in which the setting agent is basic aluminum acetate of aluminum oxide content of 33.4% heat treated at 140° C. for 42 hours.

5. An impression material as set forth in claim 1, in which the setting agent is chromic sulphate.

6. An impression material as set forth in claim 1, in which the setting agent is a slightly soluble salt of lead.

7. An impression material as set forth in claim 1, including a retarder and a filler.

8. An impression material as set forth in claim 1, including an accelerator and a filler.

9. An impression material as set forth in claim 1, in which the cellulose derivative is carboxy methyl cellulose.

10. An impression material as set forth in claim 1, in which the cellulose material is carboxy ethyl cellulose.

11. An impression material as set forth in claim 1, in which the cellulose is in the form of the sodium salt of carboxy methyl cellulose.

12. An impression material as set forth in claim 1, in which the viscosity of the cellulose derivative is from 500 to 2000 C. P. S.

13. An impression material as set forth in claim 1, in which the setting agent is basic aluminum acetate of aluminum oxide content of 33.4% heat treated at 140° C. for 42 hours, and the cellulose material is the sodium salt of carboxy methyl cellulose.

14. An impression material as set forth in claim 1, in which the setting agent is chromic sulphate and the cellulose material is the sodium salt of carboxy methyl cellulose.

15. An impression material as set forth in claim 1, in which the setting agent is a slightly soluble salt of lead and the cellulose material is the sodium salt of carboxy methyl cellulose.

16. An impression material as set forth in claim 1, in which the composition includes a retarder and filler and the cellulose material is the sodium salt of carboxy methyl cellulose.

17. An impression material as set forth in claim 1, in which the cellulose material is the sodium salt of carboxy methyl cellulose of viscosity from 500 to 2000 C. P. S.

18. As an article of manufacture, a shaped dental impression from a carboxyl alkyl cellulose gel.

19. An impression material containing in parts by weight, 1 part sodium carboxy methyl cellulose of 2000 viscosity, .7 to 5 parts basic aluminum acetate, 3.5 to 30 parts filler, and from 11 to 17 parts water.

20. An impression material containing in parts by weight, 1 part sodium carboxy methyl cellulose of 2000 viscosity, .7 to 1.5 parts lead chloride, 3.5 to 30 parts filler, and from 11 to 17 parts water.

21. As an article of manufacture, a shaped impression from a carboxy alkyl cellulose gel containing a setting agent of a salt of a metal forming a gel with the carboxy alkyl cellulose.

22. As an article of manufacture, a shaped impression from a carboxy alkyl cellulose gel containing basic aluminum acetate.

23. As an article of manufacture, a shaped impression from a composition containing a carboxy methyl cellulose and a setting agent of a salt of a metal forming a gel with said carboxy methyl cellulose.

24. As an article of manufacture, a shaped dental impression from a carboxy methyl cellulose gel the sodium salt of which carboxy methyl cellulose has a viscosity from 500 to 2000 C. P. S.

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