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(54) Title: CURING MATERIAL FOR ALGINATE-BASED DENTAL IMPRESSION MATERIAL AND DENTAL IMPRESSION MATERIAL

(57) Abstract: To provide a curing material for alginate-based dental impression material, in which the change over time in curing time is small by controlling alteration while storing, using a hemihydrate of calcium sulfate, and a dental impression material including such. A curing material for alginate-based dental impression material is provided, including calcium sulfate hemihydrate and metal sulfate anhydride. In a preferred embodiment, the metal sulfate anhydride includes metal ions of 2 valence or more. In another embodiment, a dental impression material is provided including an alginate-based base material, and the curing material.



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CURING MATERIAL FOR ALGINATE-BASED DENTAL IMPRESSION MATERIAL AND DENTAL IMPRESSION MATERIAL

Technical Field

The present invention relates to a curing material for alginate-based dental impression material, and dental impression material.

Background

Conventionally, hydrocolloid impression material (for example, agar-based or alginate-based impression material) is widely used as dental impression material. For example, alginate-based impression material is prepared by mixing a paste base material including alginate and a paste curing material including a curing agent using an automixer.

Having an appropriate consistency, and adjusting the time necessary for extracting the impression (that is, curing time) to be in an appropriate range are desired in impression materials. Base materials and curing materials that are pastes have more favorable operability and reproducibility compared to, for example, when they are powder.

Patent Literature 1 describes a dental alginate impression material including (A) calcium sulfate, (B) metal salt in which ionization tendency is smaller than calcium, having solubility to 20°C water of 0.1 to 1.5 g/L, and (C) algic acid monovalent salt.

Patent Literature 2 describes a dental alginate impression composition that cures by mixing two types of paste, namely a main material paste having alginate, water, and a filling material as main components, and a curing material paste having calcium sulfate and a liquid component as main components, wherein one type or two or more types selected from carrageenan, pullulan, guar gum, xanthan gum, gellan gum, pectin, konjac glucomannan, xyloglucan, guar gum, gum arabic, locust bean gum are contained at 0.01 to 15 weight % in the main paste and polybutene is contained at 0.5 to 50 weight % in the curing material paste.

Patent Literature 3 describes a dental alginate impression material provided with a base material paste including (A) alginate and (B) water as the main components thereof, and a curing agent paste including (C) a gelling agent, (D) a water insoluble organic solvent, and (E) a moisturizing agent as the main components thereof.

PRIOR ART DOCUMENTS

Patent Literature 1: Japanese Unexamined Patent Application Publication No. 2014-156437

Patent Literature 2: Japanese Unexamined Patent Application Publication No. 2002-87922

Patent Literature 3: WO No. 2012/063618

Summary

In an alginate-based dental impression material, calcium sulfate hemihydrate, dihydrate, and the like are generally used as gelling agents in curing materials. Curing materials that include calcium sulfate hemihydrate as the gelling agent are advantageous in terms of being able to more favorably control the physical properties of a dental impression material after being cured, but calcium sulfate hemihydrate has the defect of it being easy to generate dihydrates by being hydrated (that is, cured) by moisture when storing the curing material. Due to this hydration reaction, when the surface area of calcium sulfate reduces due to the growth of acicular crystal of the calcium sulfate, the dissolving speed of calcium sulfate is reduced (that is, the calcium sulfate is deactivated). In a dental impression material obtained using a curing material in which this kind of alteration from a hemihydrate to a dihydrate has occurred, there are problems of the curing reaction between the base material and the curing material becoming slow, and the time necessary for curing becoming longer than conventional designs.

In light of the above, an object of the present invention is to provide a curing material for alginate-based dental impression material, in which the change over time in required curing time when preparing and using the dental impression material is small by controlling alteration while storing, using a hemihydrate of calcium sulfate, and a dental impression material including such.

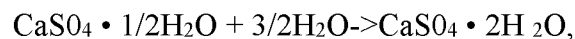
Detailed Description

Exemplary embodiments of the present invention will be described below, but the present invention is not limited to these embodiments.

One embodiment of the present invention provided is a curing material for alginate-based dental impression material, including calcium sulfate hemihydrate and

metal sulfate anhydride. Generally, alginate-based dental impression material includes alginate (for example, potassium alginate or sodium alginate) in the base material and calcium sulfate in the curing material as gelling materials, and when these are mixed, ion conversion (that is, linking) occurs between alginate and calcium sulfate, thereby forming calcium alginate. The alginate-based dental impression material is cured by this linked structure.

The curing reaction is affected by calcium ion derived from calcium sulfate. However, calcium sulfate dihydrate is formed by the calcium sulfate easily reacting with surrounding moisture while storing the curing material. For example, the calcium sulfate hemihydrate is hydrated in the following formula:



generating a dihydrate. Due to this hydration reaction, when the surface area of calcium sulfate reduces due to the growth of acicular crystal of the calcium sulfate, the dissolving speed of calcium sulfate is reduced (that is, the calcium sulfate is deactivated). Because of the above reason, it is thought that a curing delay (in other words, an increase in curing time) of the alginate-based dental material occurs when using a curing material after storing. Meanwhile, it is thought that the problem of dissolving reduction due to such a further hydration reaction in calcium sulfate dihydrate does not occur. It is reported that alginate impression material made up of only calcium sulfate dihydrate has higher water absorption swelling and shrinkage compared to alginate impression material containing calcium sulfate hemihydrate when immersing a gelled body that has an impression extracted in water. Therefore, calcium sulfate hemihydrate is more advantageous in terms of controlling physical properties after curing. Therefore, in one embodiment, the curing material includes at least calcium sulfate hemihydrate as the gelling agent.

In one embodiment, the gelling agent in the curing material may be substantially only calcium sulfate hemihydrate, or may further include additional compounds. Metal compound of 2 valence or more, for example, calcium sulfate dihydrate, calcium sulfate anhydride, magnesium sulfate, and the like are given as additional compounds. When the curing material includes an additional compound as a gelling agent in addition to calcium sulfate hemihydrate, in terms of realizing a favorable curing reaction of the

dental impression material, the total content ratio of gelling agent to 100 weight % of curing material is preferably approximately 30 weight % or more, approximately 35 weight % or more, or approximately 45 weight % or more, and in terms of preventing the curing speed of the dental impression material from becoming too fast, is preferably
5 approximately 70 weight % or less, approximately 65 weight % or less, or approximately 60 weight % or less.

In one embodiment, the curing material includes metal sulfate anhydride. Metal sulfate anhydride contributes to obtaining favorable storing stability while using calcium sulfate hemihydrate in the curing material. While it is not desirable to be bound by theory,
10 metal sulfate anhydride is easy to hydrate compared to calcium sulfate hemihydrate. Ease of hydration can be evaluated using, for example, hydration enthalpy as an indicator. Metal sulfate anhydride has the tendency to have a larger hydration enthalpy than calcium sulfate hemihydrate. By calcium sulfate hemihydrate and metal sulfate anhydride, which is easier to hydrate than this, coexisting in the curing material, the hydration reaction due to moisture in
15 the environment in the curing material being stored preferentially proceeds more in metal sulfate anhydride than in calcium sulfate hemihydrate, and it is thereby thought that the hydration reaction of calcium sulfate hemihydrate can be suppressed.

In a preferred embodiment, metal sulfate anhydride includes metal ions of 2 valence or more. Metal ions of 2 valence or more are advantageous because they tend to
20 more easily form hydrates compared to monovalent metal ions, and because of the valence thereof, contribution for one molecule of metal sulfate anhydride to suppressing hydration reaction of calcium sulfate hemihydrate is large.

In a preferred embodiment, in terms of being easier to hydrate compared to calcium sulfate hemihydrate (for example, hydration enthalpy being large) aluminum sulfate anhydride, potassium aluminum sulfate anhydride, and magnesium sulfate
25 anhydride can be given as examples of metal sulfate anhydride. In a preferred embodiment, metal sulfate anhydride includes one or more type selected from a group made up of aluminum sulfate anhydride, potassium aluminum sulfate anhydride, and magnesium sulfate anhydride, or is substantially made up of these. In a preferred
30 embodiment, metal sulfate anhydride includes one or more type selected from a group made up of aluminum sulfate anhydride and potassium aluminum sulfate anhydride, or is

substantially made up of these. In a preferred embodiment, the metal sulfate anhydride is aluminum sulfate anhydride.

In terms of calcium salt sometimes reducing curing performance of the curing material due to the curing reaction of calcium sulfate hemihydrate when the metal sulfate anhydride includes calcium salt, metal sulfate anhydride does not substantially include calcium salt in a preferred embodiment.

In a preferred embodiment, in terms of favorably obtaining a curing retardation suppressing effect, the mole ratio of metal sulfate anhydride to calcium sulfate hemihydrate is approximately $5 \times 10^{-4}/1$ or more, approximately $1 \times 10^{-3}/1$ or more, or approximately $5 \times 10^{-3}/1$ or more, and in terms of favorably obtaining functionality as a gelling agent of the calcium sulfate hemihydrate, is approximately $1 \times 10^{-1}/1$ or less, approximately $5 \times 10^{-2}/1$ or less, or approximately 1×10^{-2} or less.

In a preferred embodiment, in terms of favorably obtaining functionality as a gelling agent of the calcium sulfate hemihydrate, the content ratio of calcium sulfate hemihydrate to 100 weight % of curing material is approximately 0.1 weight % or more, approximately 1 weight % or more, or approximately 10 weight % or more, and in terms of preventing curing of the dental impression material that is too fast, and favorably securing operating time while extracting the impression, is approximately 70 weight % or less, approximately 65 weight % or less, or approximately 60 weight % or less.

In a preferred embodiment, in terms of obtaining a favorable curing retardation suppressing effect, the content ratio of metal sulfate anhydride to 100 weight % of curing material is approximately 0.1 weight % or more, approximately 0.5 weight % or more, or approximately 0.8 weight % or more, and in terms of favorably obtaining functionality as a gelling agent of the calcium sulfate hemihydrate, is approximately 5.0 weight % or less, approximately 3.0 weight % or less, or approximately 2.0 weight % or less.

In addition to the above, the curing material can include solvents, surfactants, surface modifiers, coloring agents, fillers, additional metal salts, and the like as additional components.

Hydrocarbons, alcohols, phenols, fatty acids or esters thereof, hydrophobic polymers, polyethers, and the like are given as solvents.

Aliphatic chain hydrocarbons such as hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, kerosene, 2, 7-dimethyloctane, 1-

octene; and alicyclic hydrocarbons such as cycloheptane and cyclononane are given as hydrocarbons. The hydrocarbon can be a hydrocarbon mixture such as liquid paraffin.

Saturated aliphatic alcohols such as 1-hexanol and 1-octanol; unsaturated aliphatic alcohols such as citronellol and oleyl alcohol; and aromatic alcohols such as benzyl alcohol; are given as alcohols. Cresols and the like are given as phenols.

Saturated fatty acids such as hexanoic acid and octanoic acid; unsaturated fatty acids such as oleic acid and linoleic acid; and fatty acid esters such as ethyl octanoate, dibutyl phthalate, oleic acid glyceride are given as fatty acids or esters thereof. Polysiloxanes are given as hydrophobic polymers.

Among these, liquid paraffin is preferable in terms of favorable hydrophobicity, simplicity of acquisition and handling, safety to organisms, and the like.

Linear or branched polyethers are given as polyethers, and polyalkylene glycol is preferable. Polyethylene glycol, polypropylene glycol, and the like are given as polyalkylene glycols, and among these, polyethylene glycol is preferable because it excels in hydrophilicity.

In a preferred embodiment, the amount of solvent in 100 weight % of curing material is approximately 10 weight % to approximately 50 weight %. In terms of favorably preparing viscosity of the curing material, this amount is preferably approximately 10 weight % or more, or approximately 20 weight % or more, and in terms of favorably securing a content ratio of other components of the curing material, it is preferably approximately 50 weight % or less, or approximately 40 weight % or less.

Anionic surfactants (for example, alkylsulfonates, alkylbenzenesulfonates, alkyl ether carboxylates, and the like), cationic surfactants (for example, alkylamine salts and quaternary ammonium salts, and the like), amphoteric surfactants (for example, amino carboxylate salt, and the like), and nonionic surfactants (for example, polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, polyoxyethylene-polyoxypropylene block polymers, polyoxyethylene glycerin fatty acid esters, polyoxyglycerin fatty acid esters, sorbitan fatty acid esters, sucrose esters, polyoxyethylene alkylamines, block polymers of polysiloxanes and polyoxyethylenes, and the like) are given as surfactants.

In a preferred embodiment, the amount of surfactant in 100 weight % of curing material is approximately 0.1 to approximately 10 weight %. In terms of preventing separation of a hydrophobic component and a hydrophilic component in the curing material

and obtaining favorable storing stability, this amount is preferably approximately 0.1 weight % or more, or approximately 0.5 weight % or more, and in terms of favorably securing the content ratio of other components of the curing material, is preferably approximately 10 weight % or less, or approximately 5 weight % or less.

5 The surface modifier has the function of making the surface of the impression material smoother, and making impression precision favorable. Inorganic fluoride compounds such as potassium titanium fluoride and potassium fluorosilicate, and metal oxides such as magnesium oxide and zinc oxide and the like are given as surface modifiers. Among these, titanium potassium fluoride is preferable because it improves
10 impression precision. In a preferred embodiment, in terms of obtaining favorable impression precision, the amount of surface modifier in 100 weight % of curing material is approximately 0.5 to approximately 30 weight %, approximately 1 to approximately 27 weight %, approximately 5 to approximately 24 weight %, or approximately 9 to approximately 18 weight %.

15 Red no. 226, red no. 3, blue no. 1, green no. 3 and the like are given as coloring agents. In a preferred embodiment, the amount of coloring agent in 100 weight % of curing material is approximately 0.01 to approximately 1.0 weight %.

 Diatomaceous earth, silica, alumina, and the like are given as fillers. In a preferred embodiment, the amount of filler in 100 weight % of curing material is approximately 1 to
20 approximately 40 weight %. In terms of making viscosity of the curing material higher and making the physical properties of the impression material favorable, this amount is preferably approximately 1 weight % or more, or approximately 2 weight % or more, and in terms of favorably securing a content ratio of other components of the curing material, it is preferably approximately 40 weight % or less, or approximately 20 weight % or less.

25 Furthermore, in terms of favorably securing operating time while extracting the impression, one or more selected from a group made up of alkali metal phosphate (for example, trisodium orthophosphate, tripotassium phosphate, sodium diphosphate, sodium tripolyphosphate, and the like), alkali metal oxalate (for example, sodium oxalate, potassium oxalate, and the like), and alkali metal carbonate (for example, sodium
30 carbonate, potassium carbonate, and the like) may also be used as an additional metal salt. Among these, sodium diphosphate decahydrate are preferable in terms of simplicity of

handling. In a preferred embodiment, the amount of additional metal salt in 100 weight % of curing material is approximately 0 to approximately 1.0 weight %.

In a preferred embodiment, the curing material includes calcium sulfate hemihydrate: approximately 45 weight % to approximately 55 weight %, and metal sulfate anhydride: approximately 0.5 weight % to approximately 3 weight %.

In a preferred embodiment, in addition to calcium sulfate hemihydrate and metal sulfate anhydride of the above content ratio, the curing material further includes one type or more of:

Solvent: approximately 25 weight % to approximately 35 weight %,

Surfactant: approximately 0.5 weight % to approximately 1.5 weight %,

Surface modifier: approximately 5 weight % to approximately 15 weight %,

Coloring agent: approximately 0.01 weight % to approximately 0.2 weight %, and

Filler: approximately 3 weight % to approximately 8 weight %.

Dental Impression Material

One embodiment of the present invention provides a dental impression material including the base alginate-based base material and the curing material according to the one embodiment of the present invention as described above. Various conventionally well-known compositions can be used as a base material of alginate-based dental impression material. In a typical embodiment, the base material includes a solvent and alginate (as a gelling agent).

Potassium salt and sodium salt of alginic acid are given as examples of alginate. In a preferred embodiment, the alginate is sodium alginate.

In a preferred embodiment, the amount of alginate in 100 weight % of base material is approximately 1 to approximately 10 weight %. In terms of giving favorable physical characteristics to the impression material, this amount is preferably approximately 1 weight % or more, approximately 2 weight % or more, or approximately 3 weight % or more, and is preferably approximately 10 weight % or less, approximately 8 weight % or less, or approximately 7 weight % or less.

In a preferred embodiment, the solvent is water. The water may be purified water, deionized water, or the like. In a preferred embodiment, the amount of water in 100 weight % of base material is approximately 50 to approximately 90 weight %. In

terms of preventing the base material viscosity from becoming too high, and making mixing the base material and curing agent, and applying the impression material (in other words, extracting the impression) easier, this amount is preferably approximately 50 weight % or more, approximately 55 weight % or more, or approximately 60 weight % or more, and in terms of preventing the base material viscosity from becoming too low, and making favorable physical properties of the impression material, this amount is preferably approximately 90 weight % or less, approximately 85 weight % or less, or approximately 80 weight % or less.

The base material may further include additional components in addition to the solvent and alginate. Fillers, surfactants, preservatives, curing retardants, perfumes or the like are given as additional components, and one or more of these may be used.

Those described above in regard to the curing agent can be appropriately used for fillers, surfactants, and curing retardants. In a preferred embodiment, the amount of filler in 100 weight % of base material is approximately 10 to approximately 30 weight %. In a preferred embodiment, the amount of surfactant in 100 weight % of base material is approximately 0.1 to approximately 5 weight %. In a preferred embodiment, the amount of curing retardant in 100 weight % of base material is approximately 0.1 to approximately 5 weight %.

Methyl parahydroxybenzoate, propyl paraoxybenzoate, or the like are given as preservatives. In a preferred embodiment, the amount of preservative in 100 weight % of base material is approximately 0.01 to approximately 1.0 weight %.

Peppermint flavor, apple flavor, or the like are given as perfumes. In a preferred embodiment, the amount of perfume in 100 weight % of base material is approximately 0.01 to approximately 1.0 weight %.

Manufacturing the Base Material, Curing Material, and Dental Impression Material

The base material and curing material can each be produced using, for example, a method for mixing compound ingredients in a well-known agitating mixer. A ball mill, a ribbon mixer, a co-kneader, an internal mixer, a screw kneader, a Henschel mixer, a universal mixer, a Loedige mixer, a butterfly mixer, and the like can be used as an agitating mixer. The dental impression material of the present invention can be supplied as a combination of a base material and a curing material produced as described above.

In a typical embodiment, the base material and curing material are each provided enclosed in a package, and an impression material paste is provided by mounting these packages to a well-known automatic mixer and automatically mixing the base material and the curing material in a prescribed ratio.

5

Examples

Exemplary embodiments of the present invention will be described below giving examples, but the present invention is not limited to these examples.

10 Preparation of Curing Material Paste and Base Material Paste

Each of the compound ingredients shown in table 1 (base material) and the compound ingredients shown in table 3 (curing material) are mixed at room temperature in the usual manner so that bubbles are not generated, thereby obtaining a uniform base material paste and a uniform curing material paste.

15 Measurement of Moisture Amount

Regarding the curing material in example 1, the moisture amount was measured at a measure temperature of 105°C using a heating and drying type moisture meter “A&D MX-50” (manufactured by A&D (Co.)) in a research lab having a temperature of 25.9°C and a relative humidity of 32%. The obtained moisture amount value was 0.44 weight %.

20

Evaluation while Curing

(1) Sample Preparation

In regard to the curing material paste described above, the curing material paste directly after preparation (referred to below as before aging) was inserted into a sample
25 bottle and sealed, and left for 1 week in an environment having a temperature of 60°C, thereby preparing a curing material paste after aging. The following tests (2) and (3) were carried out using the curing material paste before aging and after aging.

(2) Initial Curing Time (Gelling Time)

30 The base material paste described above and each curing material paste before aging and after aging in (1) above were mixed, and the initial curing time was evaluated conforming to JIS T6505. The results are shown in Table 3.

(3) Curing Time

The base material paste obtained as described above and each curing material paste before aging and after aging in (1) above were mixed, and poured into a rigid ring mold (Conforming to ISO21563: 2013, 7.1.1a). After starting mixing, a cylindrical polymethyl methacrylate test rod was pressed to the surface of the impression material (conforming to ISO21563: 2013, 7.2.1b). The curing time was made to be the time it took until a mark of the test rod was not made on the curing material. The results are shown in Table 3.

Table 1: Compounds of Base Material and Component Amount thereof

Compound Ingredient		Compound Amount (Weight Parts)
Solvent	Water	72.0
Curing retardant	Sodium pyrophosphate decahydrate	0.7
Perfume	Peppermint Flavor	0.0
	Applemint Flavor	0.1
Surfactant	Polyoxyethylene Sorbitan Monolaurate	0.4
Preservative	Methyl Parahydroxybenzoate	0.1
	Propyl Parahydroxybenzoate	0.1
Gelling Agent	Potassium Alginate	4.5
Filler	Diatomaceous Earth	18.2
	Silica	4.0

Table 2

Name of Compound	Molecular Weight (g/mol)	Hydration Enthalpy (crystal water) $\Delta_{\text{hyd}}H$ (kJ mol ⁻¹)	Remarks
Calcium Sulfate Hemihydrate	145.14	-18.1	Literature Value ⁽¹⁾
Aluminum Sulfate Anhydride	342.14	-155.9	Calculated Value ⁽³⁾
Potassium Aluminum Sulfate Anhydride	474.39	-162	Literature Value ⁽²⁾
Magnesium Sulfate Anhydride	120.37	-85.4	Literature Value ⁽¹⁾
Calcium Chloride Anhydride	110.98	-94.68	Literature Value ⁽¹⁾

⁽¹⁾ Chemical Society of Japan Vol. "Chemistry Handbook Basics Vol. II" Revised Edition 5, Maruzen, 2004

⁽²⁾ Yuuji Shibata, Kenjiro Kimura "Inorganic Chemistry Compendium X-1-1 Aluminum", Maruzen, 1975

⁽³⁾ The calculating method is as described below.

Aluminum sulfate hydrates are assumed as hexahydrate, and after calculating the hydration enthalpy of aluminum sulfate from the standard enthalpy of formation (-5312.634 (kJ/mol) of aluminum sulfate hexahydrate, -3441.8 (kJ/mol) of aluminum sulfate, and -285.83 (kJ/mol) of water (liquid)) described in the reference literature

5 (Eremin and group, "Calculation of the standard thermodynamic potentials of aluminum sulfates and basic aluminum sulfates", Russian Journal of Inorganic Chemistry, August 2015, Volume 60, Issue 8, pp 950-957), it was -155.854 (kJ/mol).

Table 3

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Reference Example 1	Reference Example 2
			2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
			1.1	1.1	1.1	1.1	1.1	1.1	1.05	1.05
	Surfactant									
			1.1	1.05	1.1	1.1	1.1	1.1	1.05	1.05
	Surface Modifier									
			4.2	4.19	4.2	4.2	4.2	4.2	4.19	4.19
			4.2	4.19	4.2	4.2	4.2	4.2	4.19	4.19
	Coloring Agent		0.1	0.05	0.1	0.1	0.1	0.1	0.05	0.05
Stabilizer			1.0	5	0.5	0.1	N/A	N/A	1.0	N/A
			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
			N/A	N/A	N/A	N/A	1.0	N/A	N/A	N/A
Gelling Agent			48.6	48.61	48.6	48.6	48.6	48.6	N/A	N/A
			N/A	N/A	N/A	N/A	N/A	N/A	48.61	48.61
Filler			5.2	5.24	5.2	5.2	5.2	5.2	5.24	5.24
Mole No. of Calcium Sulfate Hemihydrate in Curing Material			3.3×10^{-1}	3.3×10^{-1}	3.3×10^{-1}	3.3×10^{-1}	3.3×10^{-1}	N/A	N/A	N/A
			2.9×10^{-3}	1.5×10^{-2}	1.5×10^{-3}	2.9×10^{-4}	2.0×10^{-3}			
Mole No. of Metal Sulfate Anhydride in Curing Material								N/A	N/A	N/A

	Mole No. of Metal Sulfate Anhydride/Calcium Sulfate Hemihydrate	8.7×10 ⁻³	4.4×10 ⁻²	4.4×10 ⁻³	8.7×10 ⁻⁴	6.3×10 ⁻³	2.5×10 ⁻²		
Performance Evaluation	Base Material/Curing Material Amount(g)in Curing Time Measurement Test	Base Material 15/Curing Material 4.15							Base Material 15/Curing Material 2.00
	Before	Initial Curing Time (Seconds)	64	66	65	60	30	88	58
	Aging Test	Gelling Time (Seconds)	160	130	120	152	82	190	122
	After Aging Test	Initial Curing Time (Seconds)	70	72	97	90	56	183	60
		Gelling Time (Seconds)	170	130	190	230	138	503	152
	Retardation of Initial Curing Time (Seconds)		6	6	32	25	30	26	96
	Retardation of Gelling Time (Seconds)		10	0	70	70	78	56	313
	Hydration Enthalpy -(kJ/mol)(Same as Table 2)		-155.9	-155.9	-155.9	-162	-85.4	N/A	-155.9
									N/A

(1) Product Name "Tai Ace", Can be obtained by purchasing from TAIMEI CHEMICALS (Co., Ltd.)

(2) Can be obtained from TAIMEI CHEMICALS (Co., Ltd.)

(3) Product Name "Dry Magnesium Sulfate SSN-00", Can be obtained by purchasing from SANAKA KASEI KOGYO (Co., Ltd.)

As shown in Table 3, in examples 1 to 6, which use metal sulfate anhydride, the retardation of both the initial curing time and the curing time before and after aging, were significantly reduced compared to comparative example 1, which did not use metal sulfate anhydride. Furthermore, as understood from comparing example 1 and example 5,
5 aluminum sulfate anhydride has a more favorable curing retardation reducing effect when compared with potassium aluminum sulfate anhydride.

Note that reference examples 1 and 2 are examples that do not use calcium sulfate hemihydrate as the gelling agent, and only use calcium sulfate bihydrate. In these examples, curing is extremely fast compared to paste using calcium sulfate hemihydrate, and because the
10 curing time is controlled in an appropriate time, the weight ratio of curing material to base material is smaller compared to the examples and comparative examples.

Industrial Applicability

The curing material in the present invention is appropriately applied to alginate-based dental impression material.

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What is claimed is:

1. A curing material for alginate-based dental impression material, comprising: calcium sulfate hemihydrate and metal sulfate anhydride.

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2. The curing material according to claim 1, wherein the metal sulfate anhydride includes metal ions of 2 valence or more.

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3. The curing material according to claim 1 or 2, wherein the metal sulfate anhydride includes one or more type selected from a group made up of aluminum sulfate anhydride, potassium aluminum sulfate anhydride, and magnesium sulfate anhydride.

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4. The curing material according to any one of claims 1 to 3, wherein a mole ratio of the metal sulfate anhydride to the calcium sulfate hemihydrate is $5 \times 10^{-4}/1$ to $5 \times 10^{-2}/1$.

5. The curing material according to any one of claims 1 to 4, wherein a content ratio of the calcium sulfate hemihydrate to 100 weight % of the curing material is 0.1 to 70 weight %.

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6. The curing material according to any one of claims 1 to 5, wherein a content ratio of the metal sulfate anhydride to 100 weight % of the curing material is 0.025 weight % to 5.0 weight %.

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7. A dental impression material, comprising: an alginate-based base material, and the curing material according to any one of claims 1 to 6.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/022310

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K6/10 A61K6/06 C08L5/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, EMBASE, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP H11 209215 A (MITSUBISHI CHEM CORP) 3 August 1999 (1999-08-03) the whole document	1-7
X	US 6 379 458 B1 (IMMORDINO SALVATORE C [US] ET AL) 30 April 2002 (2002-04-30) claims 1-7	1,2
A	T.K.-C CHAN ET AL: "Effect of storage conditions on calcium sulphate hemihydrate-containing products", DENTAL MATERIALS, vol. 17, no. 2, 1 March 2001 (2001-03-01), pages 134-141, XP055477651, AMSTERDAM, NL ISSN: 0109-5641, DOI: 10.1016/S0109-5641(00)00052-X abstract	1-7
	- / - -	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

25 May 2018

Date of mailing of the international search report

01/06/2018

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/022310

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	EP 2 638 893 A1 (TOKUYAMA DENTAL CORP [JP]) 18 September 2013 (2013-09-18) cited in the application page 5, paragraph 25 - page 7, paragraph 46 claims 1-6 & WO 2012/063618 A1 (TOKUYAMA DENTAL CORP [JP]; NAGASAWA YUKO [JP]; MATSUSHIGE KOJI [JP]; G) 18 May 2012 (2012-05-18) -----	1-7
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Information on patent family members

International application No

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