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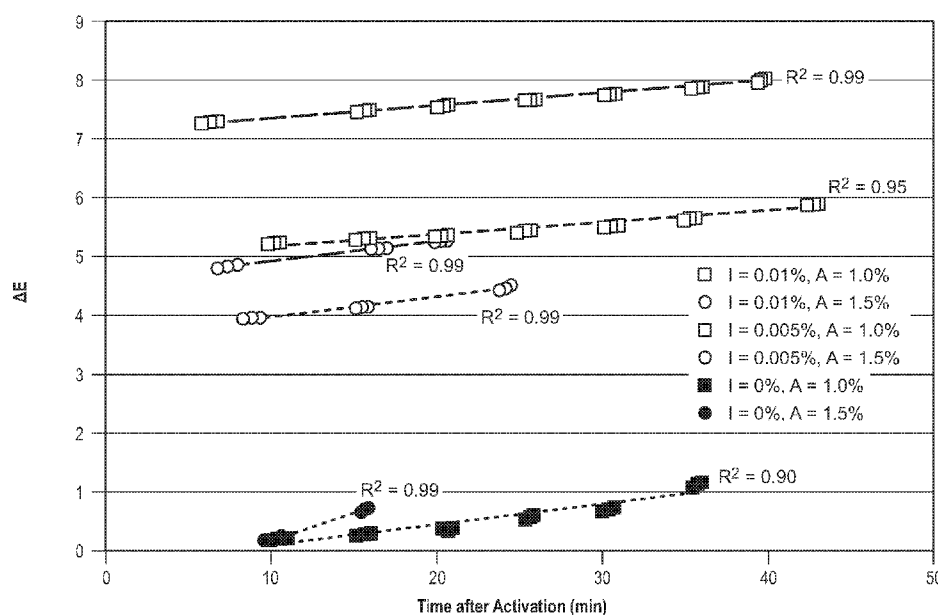


Fig. 4

(57) **Abstract:** A building construction product comprising a calcium compound and an indicator which comprises a reversible chelator of calcium ions, wherein the building construction product has a first color when the building construction product comprises water, wherein the first color is dependent on the presence of calcium ions in solution in the building construction product; and wherein the building construction product has a second color when the building construction product has solidified. Further aspects include methods of monitoring setting and drying reactions of building construction products, including setting-type joint compounds, drying-type joint compounds and plasters, where the building construction products comprise a calcium compound and an indicator which comprises a reversible chelator of calcium ions.



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JOINT COMPOUNDS AND PLASTERS WITH A COMPLEXOMETRIC DYE AND METHODS

TECHNICAL FIELD

This disclosure relates to building construction products including joint compounds, coatings, paints, gypsum slurries and plasters comprising an indicator,
5 and methods for making, storing and applying these products.

BACKGROUND

Joint compounds are commonly used in various construction projects, including for building a wall partition, ceiling and other assemblies. One of the applications for a joint compound is to fill in a seam between two gypsum panels
10 from which a wall is constructed. A great variety of other applications includes patching wall defects and cracks.

Two types of joint compounds are known: a setting-type joint compound and a drying-type joint compound. Often, a setting-type joint compound comprises calcium sulfate hemihydrate (also known as plaster of Paris or calcined
15 gypsum). The setting-type joint compounds set via a setting reaction in which calcium sulfate hemihydrate hydrates into calcium sulfate dihydrate (gypsum). This results in hardening of the setting-type joint compound. Setting-type joint compounds include those described in US Patents 4,661,161, 5,746,822, 6,805,741 and 9,174,881, which are incorporated herein by reference.

20 A setting-type joint compound can be formulated as a dry powder which is mixed with water prior to its application. Adding water to the dry powder initiates conversion of calcined gypsum into gypsum, which triggers setting and hardening of the joint compound.

A setting-type joint compound can be also formulated as a wet setting-
25 type joint compound in the ready-mixed state. Examples of such compounds are

provided in US patent 9,174,881. Such compounds are already pre-mixed with water, yet they can be stored on a shelf for a period of time without setting and hardening. In order to inhibit the setting reaction during storage and transportation, the wet ready-mixed setting-type joint compounds contain a retarder which is a
5 chelator that binds calcium ions and prevents a re-hydration reaction of calcined gypsum. An activator is then added to a ready-mixed setting-type joint compound in order to release the calcium ions and initiate a setting reaction.

Various activators are known, including zinc sulfate, iron sulfate and aluminum sulfate, as provided in US Patent 5,746,822, also incorporated herein by
10 reference.

Unlike setting-type joint compounds, drying-type joint compounds are not formulated with calcined gypsum. Drying-type joint compounds solidify when water evaporates and the compounds transition from an aqueous state into a solid compound. Many drying-type joint compounds comprise calcium carbonate. Drying-
15 type joint compounds include those provided in US Patent 6,476,099, 6,545,066 and 9,328,023, the disclosures of which are incorporated herein by reference.

Plaster, which can be formulated with calcined gypsum and water, is a building material which may be used as a protective and/or decorative coating on walls, ceilings or other structures to form a smooth hard surface when plaster paste
20 sets and hardens. Plaster formulations include those provided by US Patent 2,082,887, which is incorporated herein by reference.

Various coatings, including primer coatings, formulated with gypsum and/or calcium carbonate are also available on the market. Examples of coatings include those provided in US Patent 6,663,979, which is incorporated herein by
25 reference. A water-based gypsum slurry is used for making wallboard and other types of gypsum panels and tiles. Examples of gypsum panels include those provided in US Patent 8,323,785, incorporated herein by reference.

After an application of a setting-type joint compound, an operator may benefit from an indicator and/or test that allows the operator to determine accurately
30 whether the applied product has fully set. This may prevent a mistake of subsequent application before the previously applied product had fully set. Setting indicators

may be also useful in plasters, coatings and gypsum, slurries. With products such as drying-type joint compounds, an operator needs an indicator/test that determines accurately whether the drying joint compound has fully dried.

US Patent 6,531,528 provides a ready to use patch and repair product
5 that includes a color change indicator such as phenolphthalein (red) and thymolphthalein (blue). The compounds are pH indicators which change their color dependent on changes in pH.

Yet, accurate indicators are still needed which would not necessarily depend on a pH of a setting or drying product because not all products can be
10 accurately monitored, based on changes in pH.

SUMMARY

These and some other needs are addressed at least in part by this disclosure which provides a building construction product comprising an indicator. The building construction product has a first color when the product comprises water, the first color being dependent on the presence of metal ions in solution in the product. The product has a second color when the product has solidified. The building construction product may comprise at least one calcium compound. In these products, the indicator may comprise at least one reversible chelator of calcium ions. The building construction product may be a gypsum slurry, plaster, drying-type joint compound, setting-type joint compound, ready-mixed setting-type joint compound, coating, primer coating, or a paint. The indicator may comprise calconcarboxylic acid, its salt and/or derivative. The indicator may comprise calconcarboxylic acid coated on a carrier.

The building construction product may be a ready-mixed setting-type joint compound which comprises a retarder and the indicator may comprise calconcarboxylic acid. The building construction product may be a drying-type joint compound. The building construction product may be a drying-type joint compound which comprises a calcium compound and the indicator which comprises calconcarboxylic acid. The building construction product may be a ready-mixed drying-type joint compound which comprises a calcium compound and the indicator

may comprise calconcarboxylic acid. The building construction product may be a drying-type joint compound which comprises a calcium carbonate and the indicator which comprises calconcarboxylic acid. The building construction product may comprise metal ions including, but not limited to, ionic calcium, ionic magnesium, ionic aluminum, ionic ferrous, ionic ferric, ionic cuprous, ionic cupric, ionic bismuth, and/or ionic zinc. In the building construction products, the indicator may be present in an amount from 0.001% to 0.5% by weight of the building construction product, including water.

Further aspects of this disclosure provide a method of applying a building construction product which comprises a calcium compound and water to a substrate. The method comprises mixing the building construction product with an indicator which comprises a reversible chelator of calcium ions, and thereby
5 obtaining a mixture of the building construction product comprising the indicator, wherein the mixture develops a first color, and wherein the development of the first color is dependent on the presence of metal ions, which may be calcium ions; and then applying the mixture to the substrate, and wherein a change from the first color to a second color is indicative of the mixture dryness.

10 This method may be performed with a setting-type joint compound, drying-type joint compound, plaster, coating, primer coating, gypsum slurry or paint. In some applications of the method, the building construction product is a setting-type joint compound, plaster or gypsum slurry and the indicator comprises a reversible chelator of calcium ions. The building construction product may be a
15 setting-type joint compound, plaster or gypsum slurry and the indicator may comprise calconcarboxylic acid. The method may be performed with a ready-mixed setting-type joint compound which comprises a retarder, and the indicator may be mixed with the ready-mixed setting-type joint compound during at least one of the following time periods: (a) prior to application and (b) at the time of application. The
20 method may further comprise mixing the ready-mixed setting-type joint compound with at least one activator at the time of application. The method may be performed with a drying-type joint compound which comprises a calcium compound and the indicator which comprises a reversible chelator of calcium ions. The method may be

performed with a ready-mixed drying-type joint compound which comprises a calcium compound and the indicator which comprises calconcarboxylic acid, its derivative and/or salt.

Further aspects of this disclosure include a method for monitoring a ready-mixed setting-type joint compound, the method comprising formulating the ready-mixed setting-type joint compound with at least one indicator which comprises a reversible chelator of calcium ions, and monitoring the compound for a change in color, wherein the change in color is indicative of premature activation of a setting reaction.

This disclosure also provides an accessory product comprising an indicator which comprises a reversible chelator of calcium ions and optionally further comprising a solvent, wherein the accessory product is provided in a package which may be a container or a pouch, and wherein an amount of the indicator is dosed per the package. In preferred embodiments, the accessory product comprises calconcarboxylic acid coated on a carrier.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 are graphs of L^* value as a function of time for a setting-type joint compound in a ready-mixed state with varying amounts of an indicator and activator.

Fig. 2 are graphs of A^* value as a function of time for a setting-type joint compound in a ready-mixed state with varying amounts of an indicator and activator.

Fig. 3 are graphs of B^* value as a function of time for a setting-type joint compound in a ready-mixed state with varying amounts of an indicator and activator.

Fig. 4 are ΔE calculated after addition of an activator as a function of time for a setting-type joint compound in a ready-mixed state with varying amounts of an indicator and activator.

DETAILED DESCRIPTION

This disclosure provides building construction products including joint compounds, coatings, paints, gypsum slurries and plasters, which comprise an indicator. The product has a first color in the presence of water. The product changes its color once the product has hardened. Thus, the indicator monitors a setting reaction in a product which sets by rehydration of calcined gypsum. The indicator also monitors a drying reaction of a drying product comprising metal ions.

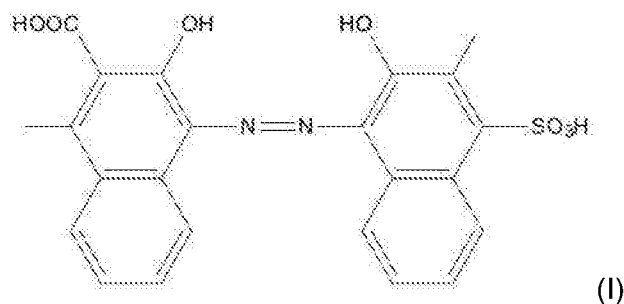
The indicator is a complexometric (i.e. ionochromic) dye which changes its color based on the presence or absence of free metal ions such as calcium ions in a setting or drying product.

The term "indicator" is used in this disclosure broadly, and includes a complexometric (i.e. ionochromic) dye which changes its color depending on the amount of metal ions in a solution.

Ionochoromic dyes are analytical chemistry reagents employed in complexometric titrations to determine an ionic metal concentration in samples of interest. An ionochromic dye is an ionsensitive molecule which manifests abrupt chromic transitions by changes in color. The indicator may be an ionochromic dye which changes its color dependent on the presence and concentration of at least one from ionic calcium, ionic magnesium, ionic aluminum, ionic iron (ferrous and/or ferric), ionic copper (cuprous and/or cupric), ionic bismuth, or ionic zinc. A preferred indication is an ionochromic dye which changes its color dependent on the presence and concentration of ionic calcium.

A particularly preferred indicator is a reagent comprising calconcarboxylic acid and/or its salt and/or its derivative. Suitable salts of calconcarboxylic acid include sodium salt of calconcarboxylic acid.

Calconcarboxylic acid is also referred to as the Patton-Reeder indicator (CAS ID Number 3737-95-6). It has the following structural formula (I):



Calconcarboxylic acid is a dark purple to almost black powder that is sparingly soluble in water. It may be mixed with sodium sulfate and is used in conjunction with EDTA in calcium titration experiments under alkaline conditions. Calconcarboxylic acid appears red in aqueous calcium solutions and blue otherwise.

- 5 Calconcarboxylic acid is a weak and reversible chelator of ionic calcium. Calconcarboxylic acid may be used to measure the ionic calcium concentration of aqueous solutions and solid samples. In some embodiments, solid samples must be first solubilized in an alkaline solution to produce a color change with a chelator.

- Other suitable indicators include complexometric compounds which
 10 complex with at least one metal ion in a colorimetric reaction which produces a detectable change in color. In the products of this disclosure, the presence of calcium ions and/or other metal ions is detected with the indicator.

- Suitable indicators which are used together with or instead of calconcarboxylic acid, its salts and derivatives include reagents listed in Table 1,
 15 their salts and derivatives. Any indicator in Table 1 may be used in combination with any other indicator in addition or instead of the compound with formula (I).

Table 1.

Indicator	CAS ID Number	Other Names	Manufacturer
Alizarin	72-48-0	Mordant Red	Sigma Aldrich

		11 and Turkey Red	
Arsenazo III	1668-00-4		Sigma Aldrich
ERIOCHROME ^R Blue Black R	2538-85-4	Mordant Black 17	LabChem
ERIOCHROME ^R Black T	1787-61-7	Mordant Black 11 and Solochrome Black	Sigma Aldrich
ERIOCHROME ^R Red B	3618-63-1		Fisher Chemical
Murexide	3051-09-0	ammonium purpurate	Sigma Aldrich
CALMAGITE ^R	3147-14-6		Sigma Aldrich
Hydroxynaphthol Blue	63451-35-4		Fisher Chemical
SPADNS	23647-14-5		ACROS Organics
Calcichrome	3810-39-7		Pfaltz & Bauer
MAGON	523-67-1		TCI America
Magneson	74-39-5	azo violet	Alfa Aesar
Phenazo	3687-26-1		Angene International
Catechol-violet	115-41-3		Sigma Aldrich
Thymol blue	76-61-9		Fisher Chemical
Curcumin	458-37-7		Sigma Aldrich
Fast Sulphon Black F	3682-47-1		ACROS Organics
Xylenol orange	1611-35-4		TCI America
Xylenol orange tetrasodium salt	3618-43-7		Sigma Aldrich
Calcein	1461-15-0	Fluorexon	MP Biomedicals
Calcein blue	54375-47-2		Sigma Aldrich
Zincon	135-52-4		Angene International
Zincon sodium salt	62625-22-3		Sigma Aldrich
Phthalein purple	2411-89-4		Sigma Aldrich

At least one of the indicators may be included in the formulation of a drying-type joint compound or any other building construction product which comprises metal ions when wet and which hardens by drying. The drying-type joint compound may comprise a calcium compound which may be calcium carbonate, calcium oxide, calcium sulfate and/or minerals such as gypsum and/or limestone.

In alternative, at least one of the indicators may be added as an accessory product (added before application) to a drying-type joint compound at the time of application and once the joint compound is premixed with water. A particularly preferred formulation for these drying-type joint compounds comprises calconcarboxylic acid as an indicator and at least one calcium compound. A particularly preferred accessory product for these drying-type joint compounds also comprises calconcarboxylic acid as an indicator.

As the applied joint compound comprising a calcium compound dries and a concentration of free calcium ions decreases, the joint compound changes its color. The indicator provides a visual notification to an end user that the applied joint compound is sufficiently dry, and it is prudent to proceed with additional finishing steps. The described formulation serves as manifest, visual indicator of joint compound dryness to both a contractor and amateur end user to facilitate proper finishing and painting of indoor spaces in commercial and residential construction.

One aspect of this disclosure provides a drying-type joint compound which comprises a calcium compound which may be calcium carbonate and a dryness indicator which is an ionochromic dye that detects calcium ions. In addition to or instead of a calcium compound, the drying-type joint compound may comprise a magnesium compound which may be magnesium hydroxide and/or magnesium salts and a dryness indicator which is an ionochromic dye that detects magnesium. In these embodiments comprising a magnesium compound, the ionochromic dye is used which is sensitive to aqueous magnesium.

The drying-type joint compound which comprises at least one ionochromic dye indicator which detects calcium and/or magnesium ions has a first color when mixed with water and is wet. The drying-type joint compound changes to a second color after the drying joint compound has dried. The second color may simply be a decrease or increase in the intensity of the first color. For example, a first color may be purple or red, while the second color may be blue in some embodiments or light purple in other embodiments. The first color and its intensity and the second color and its intensity depend on the amount and chemical structure of the indicator as well as on a concentration of a metal ion to be detected.

Any of the ionochromic dyes that complex with calcium ions may be used as a dryness indicator in these drying-type joint compounds or any other drying building construction products. This includes indicators which are listed in Table 1 and which complex with calcium ions. In some embodiments, at least one of the following indicators or their salts and/or derivatives may be used: calconcarboxylic acid, alizarin, Arsenazo III; phthalein purple and the like, and any combination thereof. A particularly preferred dryness indicator is a reagent which comprises calconcarboxylic acid and/or its derivative and/or its salt. The indicators may be used in any amount sufficient to detect the presence of calcium ions in solution and produce a visible color change once the joint compound has dried. Typically, the indicator is used in an amount from about 0.001% to about 0.5% by weight of the joint compound, including water. In some embodiments, the indicator is used in a range from 1 ppm to 0.5% by weight of the joint compound, including water.

Drying-type joint compounds can be formulated as a dry powder mixture. The dryness indicator may be added to the powder before the powder is packaged for storage and transportation. In these dry mixtures, the dryness indicator also serves as an indicator that the compound stays dry during storage and transportation. Once the joint compound is to be used, it is mixed with water and this produces a visible color change of the joint compound paste. Once the joint compound has dried the color fades away and/or changes to a second color. This provides a visual indication to a user that the applied joint compound has dried.

Drying-type joint compounds can be also formulated as a ready-mixed paste formulation with water. The dryness indicator may be added to the ready-mixed formulation in an amount sufficient to achieve an acceptable first color in the ready-mixed paste. Once the drying-type compound is applied and dries, the first color either fades away and/or changes to a second color. In this application, the dryness indicator also serves as an indicator that a ready-mixed joint compound has not prematurely partially dried during storage and/or transportation.

In further aspects, the dryness indicator may be formulated as an accessory product which is added to a drying-type joint compound at the time of application. A change in color alerts an end user that the drying-type joint compound

has dried. This is beneficial for determining whether the applied drying-type joint compound has dried completely. This also alerts the end user if the drying-type joint compound has dried partially in a pail before the drying-type joint compound has been applied.

5 A particularly preferred drying-type joint compound comprising a dryness indicator is a drying-type joint compound which comprises calconcarboxylic acid and/or its derivative and/or its salt. Sodium sulfate may be added to this formulation.

10 A particularly preferred accessory dryness indicator product (added before application) for a drying-type joint compound is a reagent which comprises calconcarboxylic acid and/or its derivative and/or its salt. The reagent may also comprise sodium sulfate.

The dryness indicators may be used with any of drying-type joint compounds, dry powder or ready-mixed.

15 A suitable drying-type joint compound may comprise calcium carbonate and/or any other calcium compound including, but not limited to, calcium oxide, calcium hydroxide, calcium bicarbonate, calcium hypochloride, calcium silicate, calcium nitrate, and calcium chloride. Calcium carbonate may have the highest weight fraction of any ingredient in the joint compound. Calcium carbonate may be
20 present in a form of limestone and/or as any other mineral.

While calcium carbonate has a low-water solubility, a joint compound mixed with water still contains some ionic calcium, while a dry joint compound does not. Other components in the drying-type joint compound may include rheological modifiers, typically cellulosic derivatives, adhesives such as natural or synthetic
25 latexes, water swelling clay minerals such as attapulgite, kaolin, talc, or mica; and binders such as starch derivatives and/or polymeric binders for cohesive properties. Suitable drying-type joint compound formulations are provided in US Patents 6,476,099, 6,545,066 and 9,328,023, incorporated herein by reference.

30 A wet joint compound paste which comprises a dryness indicator comprising calconcarboxylic acid appears purple or red in color, depending on the indicator concentration and grade, and calcium ion concentration, in the presence of

aqueous calcium. After the joint compound has dried, its color changes to blue. Calconcarboxylic-acid concentrations sufficient to achieve an acceptable color change to an end user may be in a range from 1 ppm to 0.1% by weight of the total joint compound, water included.

5 In some embodiments, the color of the joint compound comprising calconcarboxylic acid transitions from lavender to pale sky blue as the joint compound dries. In other embodiments, the color of the joint compound transitions from purple to blue as the joint compound dries. In yet other embodiments, the color of the joint compound transitions from blue to pale sky blue as the joint compound
10 dries.

Setting-type joint compounds possess manifold advantages over drying-type joint compounds in certain applications which require rapid setting, deep fill in patch and repair, and application at lower temperatures.

Setting-type joint compounds and plasters contain calcium sulfate
15 hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), which rapidly rehydrates to gypsum in the presence of water. This hydration reaction is the driver for the setting action in setting-type joint compounds, plasters and other products formulated with calcium sulfate hemihydrate and water, including a gypsum slurry. A typical setting-type joint compound may also comprise any of the following: a filler, rheological modifier,
20 binder, stabilizer and a biocide. Suitable setting-type joint compound formulations are provided in US Patents 4,661,161, 5,746,822, 6,805,741 and 9,174,881, which are incorporated herein by reference.

This disclosure provides a setting product which sets via rehydration of calcium sulfate hemihydrate into gypsum in the presence of water. The setting
25 product comprises a setting indicator which comprises an ionochromic dye which is a reversible chelator of calcium ions. The setting indicator may be pre-mixed with the setting product during formulation or the setting indicator may be used as an accessory product which is added to the setting product at the time the setting product is mixed with water and/or activator for application. The setting product may
30 be a setting-type joint compound comprising calcium sulfate hemihydrate. All types

of setting-type joint compounds are contemplated, including a powder setting-type joint compound and a ready-mixed setting-type joint compound.

The setting product may be a gypsum slurry, including gypsum slurries prepared by mixing calcium sulfate hemihydrate, water and other compounds in order to make a gypsum product such as wallboard, gypsum panels and/or tiles. The setting product may be a plaster, primer coating, or coating.

A setting indicator may comprise calconcarboxylic acid, its derivative or salt. A setting indicator may be any of ionochromic dyes that complex with calcium and listed in Table 1. A setting indicator may be one of the following ionochromic dyes or their salts and/or derivatives: calconcarboxylic acid, alizarin, arsenazo III; ERIOCHROM^R Blue Black R, xylene orange, calcein, calcein green, calcein blue, zincon, phthalein purple and the like, and any combination thereof. The setting indicator may be used in any concentration sufficient to impart a first color to a setting product in the presence of calcium ions. The first color fades away or is changed to a second color once the setting product has set.

Typically, the setting indicator is used in an amount from about 0.001% to about 0.5% by weight total, including water. For example, if the total weight of a product including water is 100 g, from 0.001g to 0.5g of the setting indicator may be used. In some embodiments, the indicator is used in a range from 1 ppm to 0.5% by weight total, including water.

A preferred setting indicator comprises, consists essentially of, consists of calconcarboxylic acid, its salts and derivatives. A particularly preferred setting indicator is calconcarboxylic acid.

Contemplated setting-type joint compounds include ready-mixed setting-type joint compounds. These compounds are pre-mixed with water and comprise at least one retarder which blocks a setting reaction by reversibly binding calcium until a setting activator is added during application. A retarder may be a proteinaceous retarder, a low molecular weight polyacrylate and/or non-calcium bearing phosphate. Typically, a retarder is a strong chelating agent such as tetrapotassium pyrophosphate (TKPP), tetrasodium pyrophosphate (TSPP), sodium citrate, among others. Other suitable retarders in this group include zinc

hexametaphosphate, potassium tripolyphosphate, sodium tripolyphosphate, mono-ammonium phosphate, monobasic potassium phosphate and any mixtures thereof.

A setting activator which is also referred interchangeably as an accelerator is added to a ready-mixed setting-type joint compound at the time of use
5 in order to trigger a setting reaction of calcium sulfate hemihydrate. This allows calcium sulfate hemihydrate to rehydrate and the compound to harden.

Suitable activators include zinc compounds, in particularly zinc sulfate and/or any of zinc sulfate hydrates; aluminum compounds, including aluminum salts such as aluminum sulfate, aluminum ammonium sulfate, and aluminum potassium
10 sulfate; and any combinations thereof. A setting time can be modulated by varying an amount of accelerator added. Suitable activators and inhibitors are provided in US Patent 5,746,822, incorporated herein by reference.

A setting indicator is incorporated into a setting-type joint compound or plaster formulation, with a color transition indicating the onset of the setting action.

15 In the presence of sufficient amounts of retarder, the calcium cation is chelated, and the ionochromic dye exhibits first color. Upon addition of a sufficient amount of activator, the first color changes abruptly into a second color. As the setting-type compound, gypsum slurry or plaster rehydrates and hardens, the second color intensity gradually diminishes.

20 Changes in color in a setting-type joint compound, plaster or any other gypsum setting product which comprise a setting indicator serves as a visual cue to the end user, e.g. the contractor or homeowner, of an onset of the setting action. Furthermore, it indicates that sufficient amounts of a retarder or activator have been incorporated into the product. Additionally, the color intensity after addition of an
25 activator may function as an estimate of setting or workability time also known as an open time which is the time until the product has hardened and no longer may be applied.

A setting indicator may be incorporated into a setting-type joint compound or plaster formulation in the presence of a retarder. The weight fraction of
30 the setting indicator ranges from 0.001% -1% on a dry basis of the compound total.

Before addition of any accelerator, a ready-mixed setting-type compound or plaster is of a first color, e.g. blue if a reagent comprising calconcarboxylic acid is used as a setting indicator. If an activator is added in an amount sufficient to induce a setting action, the first color of the joint compound or plaster changes abruptly to a second color, e.g. into red or purple with calconcarboxylic acid as an indicator. As the setting-type compound or plaster sets or undergoes drying to completion, the second color becomes gradually lighter or it changes to a third color, e.g. light pink with calconcarboxylic acid. Thus, a setting indicator may be used to monitor an open time during setting, completion of a setting reaction and cure, as well as to monitor a ready-mixed joint compound during storage and transportation for premature onset of setting.

If an activator is not added in an optimum amount to trigger a setting reaction sufficiently, the first color will not transition completely into the second color. This may be used as a rapid and accurate method for optimization of a setting reaction during application of a joint compound.

The color intensity may be more robust with more accelerator, serving as a method to qualify a setting time, i.e. a second color in a setting-type joint compound that sets in 10 minutes appears more intense, i.e. darker red if calconcarboxylic acid is used as an indication, than a setting-type joint compound that sets in 20 minutes.

While some ready-mixed setting-type joint compounds are formulated with a setting indicator during manufacturing, other applications include a ready-mixed setting-type joint compound to which a setting indicator is added at the same time when a setting reaction is triggered with an activator.

A setting-type joint compound, plaster or a gypsum slurry is prepared by mixing together calcined gypsum and water. Any of these formulations may also comprise one or more from the following components: a dispenser, surfactant, defoamer, binder, filler, biocide, retarder, activator, stabilizer. Some of these components may be first mixed with water and then mixed with dry ingredients including calcined gypsum. In some embodiments, the setting indicator is incorporated into water together with a dispersant and defoamer. In other

embodiments, the setting indicator is incorporated immediately after water, a binder, retarder and biocide, but before addition of the remainder of dry ingredients. In further embodiments, the setting indicator may be added after all other ingredients have been mixed. The setting indicator may be used in formulation with or without
5 defoamer, dispersant and with or without an activator.

An indicator either of a drying or setting reaction may be formulated as an accessory product which is added to a product such as a drying-type joint compound, a setting-type joint compound, a plaster, a coating, a primer coating or a gypsum slurry at the time of application.

10 An accessory product comprising an indicator may be provided in a separate package. The amount of the indicator may be dosed such that no additional measurements are needed during mixing with a joint compound. The package may be of any shape. It may be a container, a pre-filled syringe and/or bottle. A flexible bag or pouch is particularly preferred. If a package may provide the
15 indicator in predetermined dosages. The package may comprise several compartments, each compartment containing a predetermined dosage of the indicator. A predetermined dosage may be calculated as the dosage needed to produce a color change in a particular volume of a joint compound (i.e. one gallon, including water) or any other product for monitoring a setting or drying reaction of
20 which the indicator is to be used.

During application of an accessory product comprising the indicator, a user may easily use one or several dosages of the indicator, depending on the amount of a product to be monitored.

The indicator in the package may be formulated as a powder or as a
25 paste pre-mixed with a solvent which may be water or an organic solvent. Other components in the accessory product may include a stabilizer and/or a carrier.

The indicator such as calconcarboxylic acid may be premixed with a carrier in a solution. The mixture is then allowed to evaporate, producing a carrier coated with the indicator. Suitable carriers include any calcium compound, talc,
30 sodium salt, e.g. sodium chloride or sodium sulfate, and/or magnesium salt. Calcium carbonate and gypsum are particularly preferred compounds. A carrier may be a

filler (i.e. talc or mica) commonly used in a gypsum product. These indicator formulations which comprise a mixture of an indicator with a carrier may be used either as an accessory product or they may be also used in any other applications in order to improve mixing of an indicator with a joint compound or any other product a setting or drying reaction of which is to be monitored with an indicator.

Various methods may be used in order to detect changes in color of a product. Some indicators such as based on calconcarboxylic acid, its derivative or salt produce a change in color which is easily detected by a human eye. Other formulations may comprise an indicator which is a fluorescent dye which is to be detected with a UV lamp or some other equipment.

Color differences in the formulations of the present disclosure may be also measured more precisely by the $L^*a^*b^*$ method. This method employs a colorimeter such as for example ColorQUEST[®] from HunterLab. The $L^*a^*b^*$ method allows for the detection of even slight differences between two colors. In the $L^*a^*b^*$ method, color difference is defined as a numerical comparison of a sample's color to a standard. Three different coordinates are used:

L^* indicates lightness (black/white), with $L^* = 100$ being pure white and $L^* = 0$ being pure black;

a^* is the red/green coordinate, with $a^* = -100$ being perfectly green, and $a^* = 100$ being perfectly red, and

b^* is the yellow/blue coordinate, with $b^* = 100$ being perfectly yellow and $b^* = -100$ being perfectly blue.

All measurements are conducted against standards provided with a colorimeter for each coordinate.

Each of two samples are measured for L^* , a^* and b^* . Delta E is then calculated as follows:

$$\Delta E = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2}$$

Delta E represents a difference in color between the first sample and a second sample. Most humans can easily detect a color change between two colors if delta E between these two colors is 3 or higher. An experienced user is able to detect a change in color which is as low as 0.5-1.

5

Example 1.

A lightweight ready-mixed drying-type joint compound which comprised calcium carbonate was formulated with calconcarboxylic acid in the amount of 0.01% by weight of the joint compound, including water. The color of the compound was blue/lavender. The color changed to sky blue once the compound dried.

The color of the compound when wet and dry was also examined by the L*a*b* method. The wet state color was measured at the time of application. The dry state color was measured more than 24 hours after the application. The results are reported in Table 2 below:

Table 2.

	L*	A*	B*
Wet	69.0	-5.2	-4.2
Dry	72.9	-2.7	-1.7
Delta E	5.3		

Example 2.

A setting reaction was studied in a ready-mixed setting-type joint compound with various amounts of an indicator (calconcarboxylic acid) and activator. The compound comprised calcined gypsum with inhibitor. The indicator was added to the compound in an amount in the range from 0.005% to 0.010% by weight of the composition total, including water. The color of the compound was blue. An

activator (a mixture of zinc sulfate and alum) was then added in an amount in the range from 1.0% to 1.5% by weight of the composition total, including water. Once the activator was added, the color of the compound changed to red/pink. Once the compound was fully set, the color faded to light pink.

5 The color of the compounds when wet and set was also examined by the L*a*b* method. The results are reported in Figs. 1 – 4.

Fig. 1 is a scatterplot of L* values versus time (in minutes) after the activator has been added.

10 Fig. 2 is a scatterplot of a* values versus time (in minutes) after the activator has been added.

Fig. 3 is a scatterplot of b* values versus time (in minutes) after the activator has been added.

15 Fig. 4 reports delta E values calculated after the addition of an activator as a function of time for a setting-type joint compound with varying amounts of indicator and activator.

Example 3.

In order to produce an indicator coated on a carrier, 1 g of calconcarboxylic acid was mixed with 99 g of talc or sodium chloride, and water.

20 The mixture was boiled, and water was allowed to evaporate. The resulting solid product was calconcarboxylic acid coated on a carrier. A mortar or pestle was used to grind the resulting solid product into fine powder.

CLAIMS

1. A building construction product comprising a calcium compound and an indicator, wherein the indicator comprises a reversible chelator of calcium ions, wherein the building construction product has a first color when the building construction product comprises water, wherein the first color is dependent on the presence of calcium ions in solution in the building construction product; and wherein the building construction product has a second color when the building construction product has solidified.

2. The building construction product of claim 1, wherein the building construction product is a gypsum slurry, plaster, drying-type joint compound, setting-type joint compound, ready-mixed setting-type joint compound, coating, primer coating, or a paint.

3. The building construction product of claim 1, wherein the indicator comprises calconcarboxylic acid, its derivative, and/or its salt.

4. The building construction product of claim 1, wherein the indicator comprises calconcarboxylic acid coated on a carrier.

5. The building construction product of claim 1, wherein the indicator is present in an amount from 0.001% to 0.5% by weight of the building construction product, including water.

6. A method of applying a building construction product which comprises a calcium compound and water to a substrate, the method comprises: mixing the building construction product with an indicator which comprises a reversible chelator of calcium ions, and thereby obtaining a mixture of the building construction product comprising the indicator, wherein the mixture develops a first color, and wherein the

development of the first color is dependent on the presence of calcium ions; and
applying the mixture to a substrate, and wherein a change from the first color to a second color is indicative of the mixture dryness.

7. The method of claim 6, wherein the building construction product is a setting-type joint compound, drying-type joint compound, plaster, coating, primer coating, gypsum slurry or paint.

8. The method of claim 6, wherein the indicator comprises calconcarboxylic acid, its derivative and/or salt.

9. The method of claim 6, wherein the building construction product is a ready-mixed setting-type joint compound which comprises a retarder and wherein the method further comprises a step of mixing the ready-mixed setting-type joint compound with at least one activator at the time of application to the substrate.

10. A method for monitoring a ready-mixed setting-type joint compound which comprises at least one retarder, the method comprising formulating the ready-mixed setting-type joint compound with at least one indicator which comprises a reversible chelator of calcium ions and monitoring the ready-mixed setting-type joint compound for a change in color, wherein the change in color is indicative of premature activation of a setting reaction.

Scatterplot of L* vs Time (min)

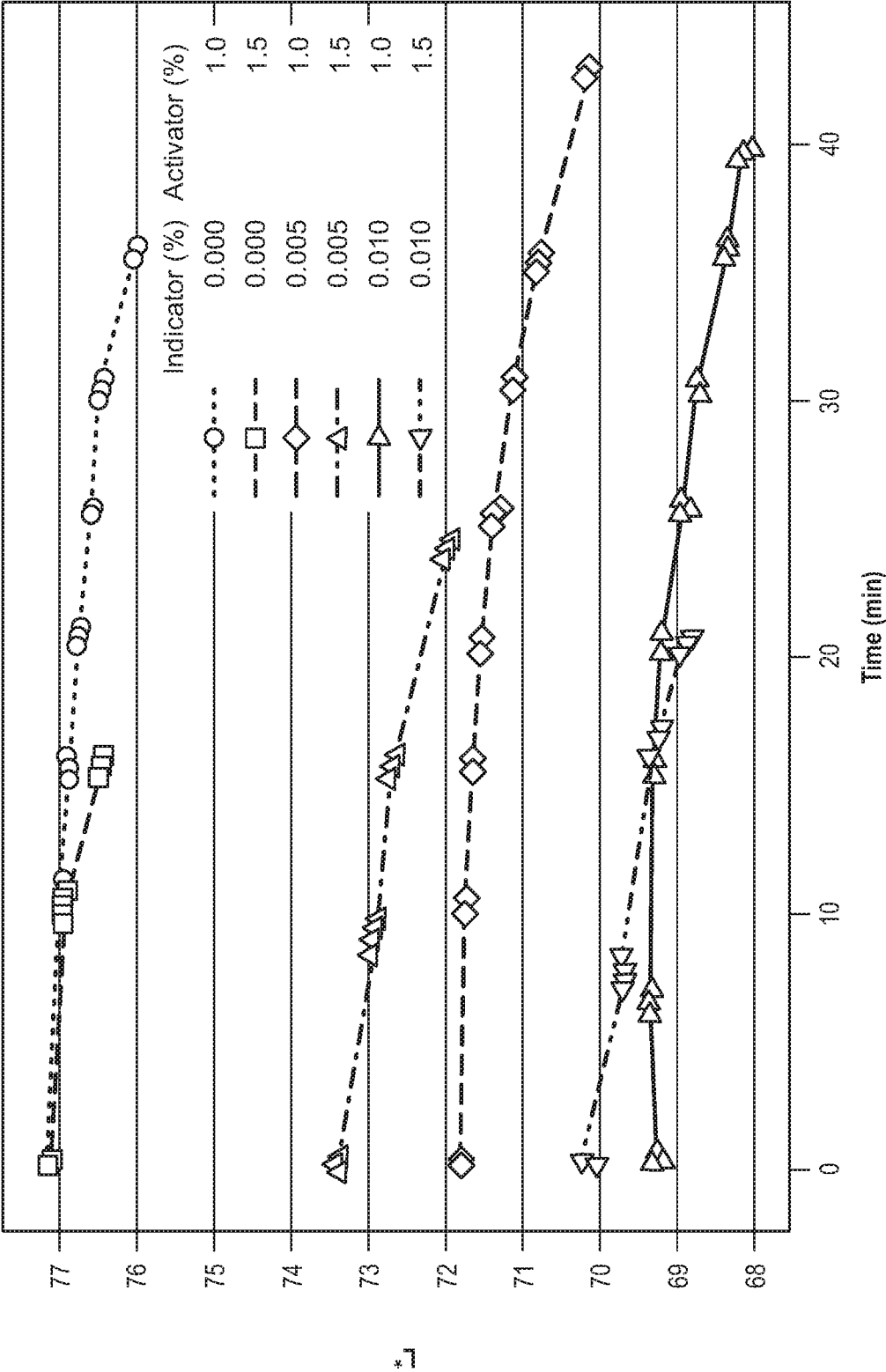


Fig. 1

Scatterplot of a* vs Time (min)

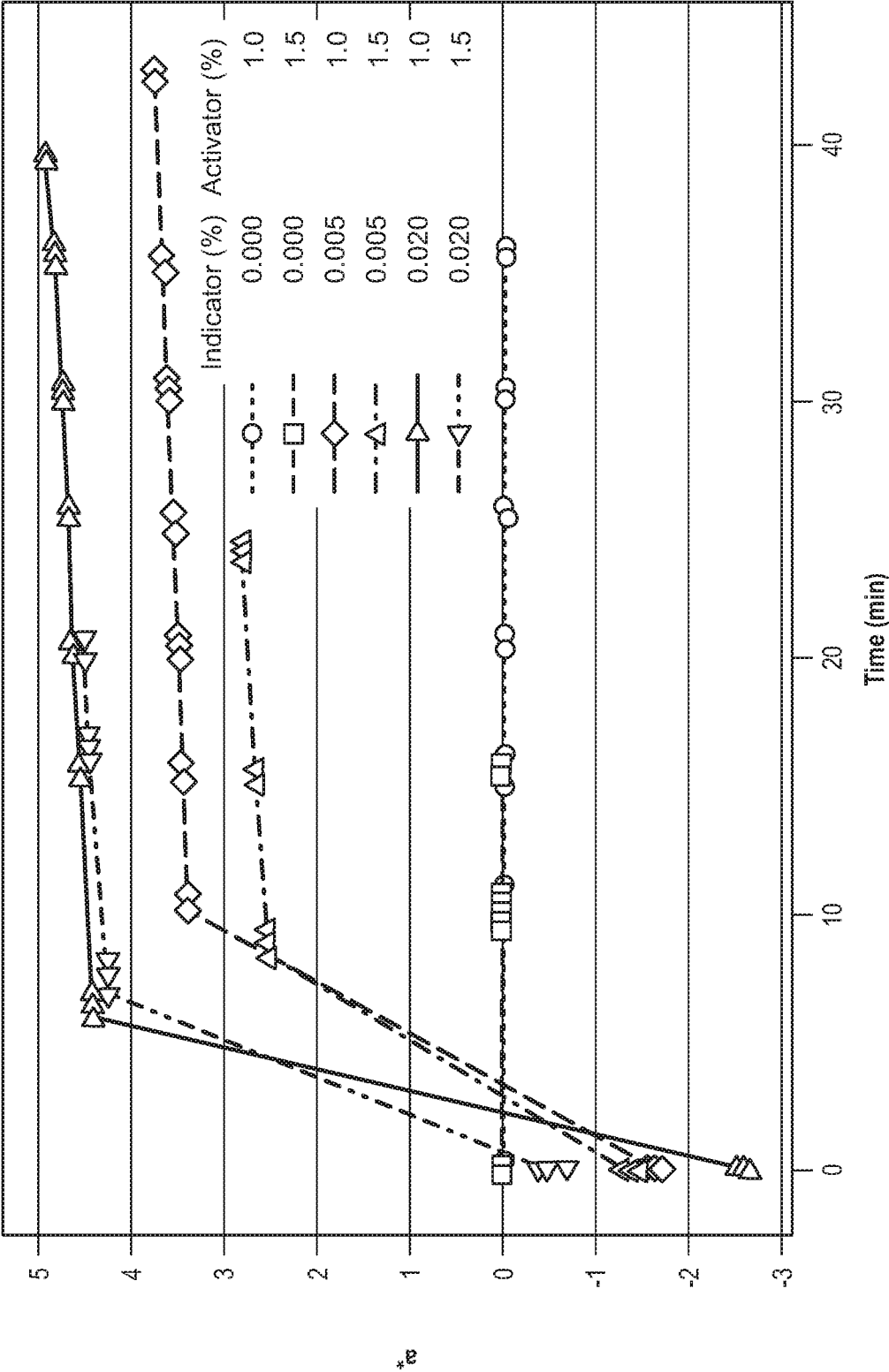


Fig. 2

Scatterplot of b^* vs Time (min)

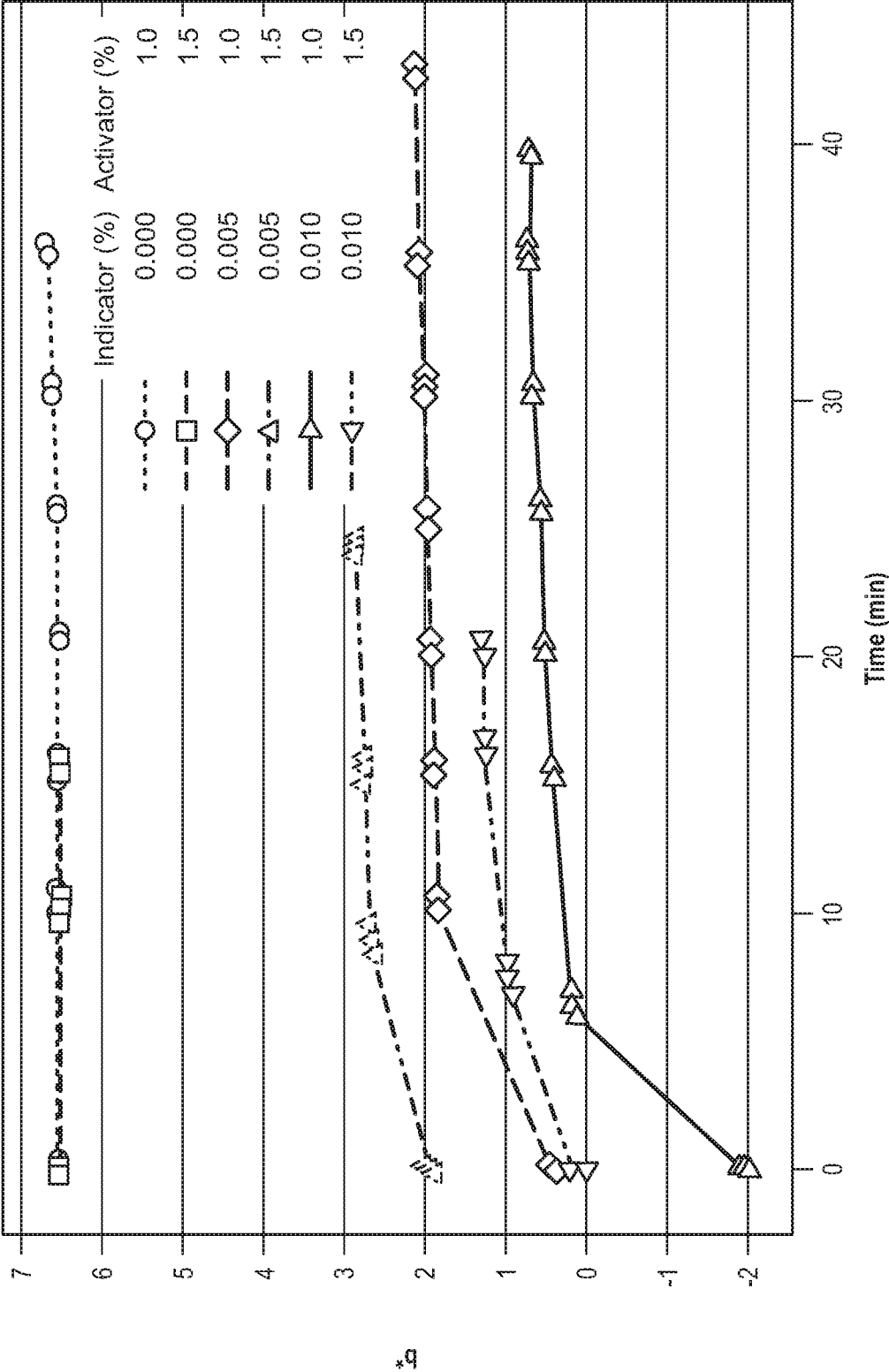


Fig. 3

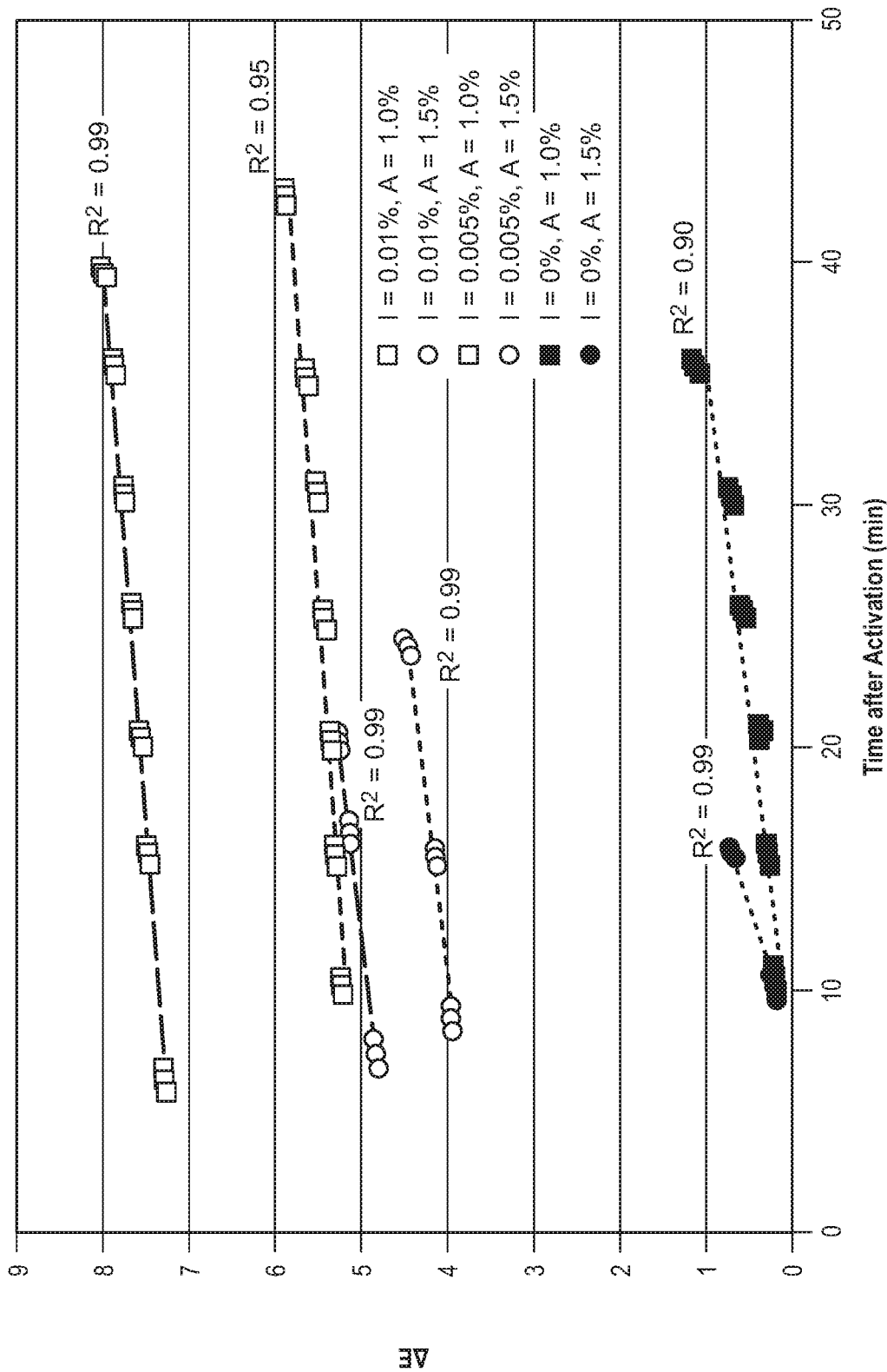


Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/012139

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N31/22 C04B28/14
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)
C04B G01N

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

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"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

11 March 2019

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/012139

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 2008/003672 A1 (BEISSIER [FR]; PFLANZ FREDERIC [FR]) 10 January 2008 (2008-01-10) page 1, lines 4-22 page 2, line 8 - page 4, line 29 page 5, lines 12-19 page 7, line 3 - page 12, line 3 page 18, lines 24-30 page 12, line 8 - page 18, line 30; claims 1-20; examples 1-2; tables 1-3 -----	1-10
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