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(54) ELECTRON PARAMAGNETIC RESONANCE DOSIMETER, METHODS OF MANUFACTURE, AND METHODS OF USE

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(57) **ABSTRACT**

A dosimeter for EPR dosimetry systems includes a carbonated hydroxyapatite cement formed by mixing a cement powder and a cement liquid in a ratio of a range of about 0.5 to 5.0 powder-to-liquid ratio. The cement powder includes one or more calcium phosphate compounds and one or more carbonate compounds. The cement liquid includes a sodium phosphate solution. The cement, when irradiated by a radiation source, is capable of producing a measurable signal as a spectrally clean EPR spectrum. Furthermore, the measurable signal is proportional to the received radiation dose.

12 Claims, 5 Drawing Sheets





FIG. 1



FIG. 3









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ELECTRON PARAMAGNETIC RESONANCE DOSIMETER, METHODS OF MANUFACTURE, AND METHODS OF USE

RELATED APPLICATIONS

This patent application claims priority to provisional patent application 62/133,018 filed Mar. 13, 2015, entitled "Electron Paramagnetic Dosimeter, Dosimetry Reference, Methods of Manufacture, and Methods of Use,". The disclosure of this provisional application is incorporated by reference.

BACKGROUND

Certain materials, when exposed to ionizing radiation, can be stimulated to emit a measurable signal that may be used to estimate the received radiation dose. Certain of these materials may be incorporated into a dosimeter that is worn or carried by an individual to measure the individual's ²⁰ exposure. A thermoluminescent dosimeter (TLD) is an example. To be effective in monitoring radiation exposure, the TLD must be worn or carried by the individual during periods of possible radiation exposure. For medical/industrial applications of ionizing radiation, dosimeters are used ²⁵ to assess the quality of the treatment or process.

Dosimetry systems and techniques exist that exploit radiation-induced signals emanating from biological materials. In some of these techniques, the signals may be measured in viva Examples of such techniques include electron para-³⁰ magnetic resonance (EPR) dosimetry, which may be used to measure signals in teeth, fingernails, toenails, bone and hair. These techniques hold out the promise for screening (i.e., as part of a triage effort), at a point-of-care facility, large populations groups that may have been exposed to ionizing ³⁵ radiation.

EPR dosimetry is based on the following: (1) ionizing radiation generates unpaired electrons (e.g., free radicals) in proportion to the absorbed dose; (2) EPR dosimetry can selectively and sensitively detect and determine the number ⁴⁰ of unpaired electrons; and (3) the unpaired electrons can persist in some tissues, such as teeth and nails, with enough stability so as to be measured by EPR dosimetry weeks to years after radiation exposure.

SUMMARY

A dosimeter for EPR dosimetry systems includes a carbonated hydroxyapatite cement formed by mixing a cement powder and a cement liquid in a ratio of a range of about 0.5 ⁵⁰ to 5.0 powder-to-liquid ratio. The cement powder comprises one or more calcium phosphate compounds and one or more carbonate compounds. The cement liquid comprises a phosphate solution. The cement, when irradiated by a radiation source, is capable of producing a measurable signal com-⁵⁵ prising a spectrally clean EPR spectrum. Furthermore, the measurable signal is proportional to the received radiation dose.

DESCRIPTION OF THE DRAWINGS

The Detailed Description refers to the following Figures, in which like numerals refer to like items, and in which:

FIG. **1** is a simplified block diagram of an example EPR dosimetry system; 65

FIG. **2** illustrates examples of carbonated hydroxyapatite cement samples for the EPR dosimetry system of FIG. **1**;

FIG. **3** illustrates XRD patterns of carbonated hydroxyapatite samples with different carbonate content;

FIG. **4** illustrates FTIR patterns of carbonated hydroxyapatite cement samples with 3% and 10% carbonate contents:

FIG. **5** illustrates an EPR spectrum of carbonated a hydroxyapatite cement sample with 3% carbonate content;

FIG. **6** illustrates an example use of EPR dosimetry using a carbonated hydroxyapatite dosimeter; and

FIG. 7 illustrates carbonated hydroxyapatite used as a reference source for EPR dosimetry.

DETAILED DESCRIPTION

Disclosed herein a dosimeter that uses a novel material to capture ionizing radiation and provide for reliable measurement of received dose. Also disclosed are methods of manufacture and methods of use. The dosimeter is based on the following concepts developed by the inventors to this application:

- A carbonated hydroxyapatite cement (CHC) may serve as an inexpensive, easily formed material for the dosimeter.
- For a given crystallinity of the CHC material, the EPR signal produced by a given irradiation dose increases with increasing carbonate content in the apatite.
- For a given carbonate content, the EPR signal produced by a given irradiation dose decreases with decreasing crystallinity of the CHC material.
- For a given crystallinity and carbonate content, the EPR signal increases with the absorbed radiation dose.
- The crystallinity of CHC decreases with increasing carbonate content.
- For a given carbonate content, the crystallinity increases, within certain limits, with increasing calcium substitution by sodium.

Starting with these hypotheses, the inventors developed several self-hardening cement compositions, and subjected the compositions to various tests, described herein, to prove these hypotheses.

In the course of this analysis and testing, the inventors discovered other surprising and unexpected properties and 45 hence uses for the cement compositions. These other properties and uses are disclosed herein.

In the course of the investigations, the inventors discovered that certain of these cement compositions could function well as an EPR dosimeter. More specifically, and in a herein described embodiment, the EPR dosimeter is based on the surprising discovery that a special synthetic carbonated hydroxyapatite cement (CHC) material in the form of a hardened mass of any desired dimension may, when exposed to certain ionizing radiation, produce a EPR signal. These materials are pure CHC without any binders. The materials may be in the shape of a cylinder, disc, block, plate, or film. Further, the CHC samples are chemically stable and have adequate mechanical strength and surface integrity to be used for any EPR dosimetry system.

In addition, the CHC compositions may have the potential to be used with other than photon irradiation, including irradiation from neutron sources.

The novel CHC precursor compositions include cement powder that consists of one or more calcium phosphate compounds selected from a group that includes monocalcium phosphate anhydrous, monocalcium phosphate monohydrate, dicalcium phosphate anhydrous, dicalcium phos20

phate dihydrate, amorphous calcium phosphate, α -tricalcium phosphate, β -tricalcium phosphate, and tetracalcium phosphate.

The compositions further include one or more soluble carbonate compounds (such as sodium carbonate, sodium ⁵ bicarbonate, potassium carbonate, potassium bicarbonate, ammonium carbonate) or sparingly soluble carbonate compounds (such as calcium carbonate, iron carbonate, magnesium carbonate, and zinc carbonate).

Optionally, the cement powder also may include one or 10 more of the following;

- Sparingly soluble calcium compounds (such as calcium lactate, calcium sulfate, calcium oxide, and calcium hydroxide).
- Sparingly soluble phosphate compounds (such as iron ¹⁵ phosphate, magnesium phosphate, zinc phosphate).
- Soluble phosphate compounds (such as sodium phosphate and potassium phosphate).
- One or more water reducing agents such as sodium citrate and citric acid.
- Median particle sizes of each of the cement powder components should be in the range of 0.1 to $150 \ \mu m$.
- Cement liquid in an aqueous phosphate solution with total phosphate concentration in the range of about 0.005 to 2.5 mol/L. The liquid may further contain gelling ²⁵ agents such as cellulose and a water reducing agent such as citrate.

Samples of the cement compositions were prepared according to the following:

- The cement powder and liquid were mixed with a powder/ ³⁰ liquid ratio in the range of about 0.5 to 5 to produce a uniform paste.
- The paste was then placed in a mold of desired shape and dimensions.
- After one day, the hardened sample was removed from the ³⁵ mold. The demolded sample was immersed in a physiological-like fluid for 5 days to allow the cement setting reaction to complete. Optionally, the formed sample can be fired to produce a ceramic material with enhanced properties. 40

A fully set CHC sample is an impure hydroxyapatite with a low to medium crystallinity compared to pure hydroxyapatite (NIST standard reference material). The material contains a structurally incorporated carbonate content in the range of 0.05 to 12 mass %. The material also may contain ⁴⁵ structurally incorporated non-calcium metallic cations (such as Na⁺) and acid phosphate anion, HPO₄²⁻.

Example 1

In Example 1, a cement powder consisted of tetracalcium phosphate, dicalcium phosphate, and sodium bicarbonate to allow the CHC product to contain 3% by weight of carbonate. The cement liquid was 0.5 mol/L Na₂HPO₄ solution. Cement paste with a powder/liquid ratio of 3 was prepared 55 and placed in a mold to produce discs (6 mm D×3 mm H). The hardened discs were analyzed by XRD and FTIR for phase composition and carbonate contents, respectively. The CHC discs were then gamma-ray irradiated to 10 kGy (10,000 Gy) with a NIST-calibrated Co-60 source and their 60 EPR characteristics were determined.

XRD showed that the only phase present in hardened CHC samples was low crystalline HA. FTIR analysis revealed carbonate bands at 1413 cm^{-1} and 1455 cm^{-1} indicating that the HA contained type-b carbonate similar to 65 the carbonate in apatitic biomaterials. After gamma-ray irradiation, the CHC discs showed reproducible EPR sig-

nals. The 3% carbonate samples exhibited a spectrally perfect example of the radical.

Example 2

In Example 2, the materials were as described in example 1, except that the carbonate content was increased to 10% by weight. The materials were formed into hardened discs and the discs were subjected to the same testing as described for Example 1. The 10% carbonate sample also produced EPR signals. However, the signals are not spectrally clean (FIG. 5 illustrates a spectrally clean EPR signal), making the material less suitable for use as high accuracy dosimeters or dosimeter reference sources.

The following table illustrates additional potential components of a carbonated hydroxyapatite cement.

TABLE

Cement Powder	Expected Product	Cement Liquid
$Ca_4(PO_4)_2O + CaHPO_4 + NaHCO_3$	$Ca_{5-x}Na_x(PO_4)_{3-x}$ (CO ₃) ₂ OH	Na_2HPO_4 solution
5	$\operatorname{Ca}_{5-x}\operatorname{H}_{x}(\operatorname{PO}_{4})_{3-x}(\operatorname{CO}_{3})_{x}\operatorname{OH}$	$\rm K_2HPO_4$ solution
3CaHPO ₄ + 2CaCO ₃ + NaF	$Ca_{5-x}Na_x(PO_4)_{3-x}$ $(CO_3)_xOH_{1-\nu}F_{\nu}$	${\rm Na_2HPO_4}$ solution
3CaHPO ₄ + 2CaCO ₃ + KF	$\begin{array}{c} (Ca_{5-x}H_{x}(PO_{4})_{3-x}) \\ (CO_{3})_{x}OH_{1-y}F_{y} \end{array}$	$\rm K_2 HPO_4$ solution

Rather than forming a cement (i.e., CHC), the carbonated hydroxyapatite powder, as noted herein, may be fired or sintered to form a hardened mass, which in turn, may serve as a component of an EPR dosimeter or as a EPR reference source.

FIG. 1 is a simplified diagram of an example CH-based EPR dosimetry system. In FIG. 1, EPR dosimetry system 10 includes EPR dosimeter 20, dosimeter reader 30, and reference source 40. The EPR dosimeter 20 includes carbonated hydroxyapatite cement (CHC) material 22 that receives a radiation dose and, when read in an appropriate dosimeter reader produces a measurable signal such as those shown in FIG. 4. As disclosed herein, the CHC material 22 is a carbonated hydroxyapatite cement formulated as described in Examples 1 and 2. The CHC material 22 may be enclosed in structure or housing 24 that protects the material and that allows the dosimeter 20 to be effectively attached to object 50 whose cumulative radiation dose is to be monitored and measured. For example, the structure 24 may include a clip 26 that enables the dosimeter 20 to be attached to the 50 clothing of a human subject. FIG. 6, described later, illustrates other structures for enclosing, protecting, and attaching an EPR dosimeter to an object whose cumulative radiation dose is to be monitored.

FIG. 2 illustrates an example of carbonated hydroxyapatite cement reference source samples for the EPR dosimetry system of FIG. 1. In FIG. 2, three different CHC references sources are shown. A first disc has a diameter of 6 mm and a thickness 2 mm; a second disc has a diameter of 6 mm and a thickness of 4 mm; and a third disc has a diameter of 6 mm and a thickness of 12 mm.

FIG. 3 illustrates XRD patterns of carbonated hydroxyapatite samples with different carbonate content. In FIG. 3, XRD patterns are shown for a CH powder produced, for example, by precipitation (the lowest curve in FIG. 3) and, respectively, a CHC sample with 10% carbonate, a CHC sample with 3% carbonate, and a CHC sample with 0% carbonate. The XRD patterns show that all the CHC samples and the CH powder contain low crystalline hydroxyapatite with no unreacted cement or other impurities.

FIG. 4 illustrates FTIR patterns that show that the CHC samples were hydroxyapatite that contained two levels of type-b carbonate similar to apatitic biominerals.

FIG. 5 illustrates an EPR spectrum of a carbonated hydroxyapatite cement reference source sample with 3% carbonate content. As can be seen, the CHC with 3% carbonate produced a spectrally clean example of the radical. The spectrum is free of paramagnetic impurities that 10 were observed in CH powder.

The herein disclosed carbonated hydroxyapatite cements may be used in a dosimeter for the measurement of ionizing radiation absorbed dose. In this situation, the dosimeters may be uniformly mass-produced in a size and shape and 15 shipped to an end user, unirradiated. The dosimeters may be packaged (for example, in a blister pack) and may each be provided a unique identification, such as a bar code or other optical or radiofrequency readout device. The dosimeters may incorporate the herein disclosed cement compositions 20 in a variety of shapes and sizes to address a specific measurement need. Though not a requirement, the addition of a binder may be employed to fabricate a dosimeter of a desired shape for use in a specific application. Such shapes include cylinders (see, for example, FIG. 2), films (either 25 rigid or flexible), or a custom shape or coating to accommodate a specific need.

In an embodiment, such dosimeters may be issued to individuals to serve as personal dosimeters (see FIG. 1).

In another embodiment, such dosimeters may be attached 30 to containers of raw materials (e.g., shrink-wrap films) and/or finished products (e.g., foods or medical devices) that are to receive a high radiation dose with the intent of achieving a desirable effect (e.g., destruction of toxins/ microorganisms, or modification of the material's physical 35 of ionizing radiation in a target material. properties). After such exposure, the dosimeters are removed and processed using an EPR spectroscopy system to verify the article or package to be irradiated did in fact receive an absorbed radiation dose within the targeted range. As a more specific example, the packaged and identified dosimeters 40 may be attached to containers on a conveyor system that moves the containers past an irradiation source that could be a radioisotope (e.g., Co-60) or an electron beam accelerator of energies between 50 keV and 10 MeV.

FIG. 6 illustrates an exemplary embodiment of the herein 45 disclosed carbonated hydroxyapatite cement (CHC) used as a dosimeter. In FIG. 6, system 600 includes transfer assembly 611, which is used to move packages 601 past radiation source 630. One or more of the packages 601 may have affixed thereon, CHC dosimeter 621, which is packaged in 50 blister pack 620. The CHC dosimeter may be supported on a substrate. The substrate may be imprinted with identification device 623. The identification device may be a barcode, for example.

In another embodiment, by incorporation of sensitizers, 55 the cement compositions may be adapted for a specific dose range (high range for industrial applications; low range for personal dosimetry) or a specific type of ionizing radiation (e.g., neutron radiation). In addition, the cement compositions may incorporate paramagnetic reference materials to 60 improve the accuracy and precision of the absorbed dose measurement.

EPR Biodosimetry with Irradiated CHC as a Reference Source

A large scale radiation event such as a reactor accident or 65 explosion of a nuclear device has the potential to expose a large population to ionizing radiation. Some members of this

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population may be minimally exposed and need little if any medical treatment; others may receive a larger exposure, and may require medical treatment; still others may have received so large a dose that medical treatment may not sufficient. Medical emergency response personnel may conduct a triage operation in an effort to identify and adequately treat the maximum number of exposed personnel. Unfortunately, since the population members likely are not being monitored with supplied individual dosimetry, current triage methods may rely on clinical procedures, which may not be able to handle the throughput necessary to assess the entire population. For example, clinical methods may require sample analysis at a remote facility, which in turn may require sample transport and later matching of sample results with the individuals. Alternately, or in addition to clinical analysis, triage methods may rely on field analysis that accesses certain symptoms. These field methods may be very inaccurate. Thus, current triage methods cannot be effectively employed when perhaps many thousands of persons must be evaluated and medical decisions made quickly.

An alternative to current triage methods involves use of biodosimetry. Biodosimetry does not rely on an individual carrying or being in close proximity to a dosimeter. Rather, biodosimetry relies on the fact that certain portions of the human body, when exposed to certain ionizing radiation, can give off a measurable signal that indicates such exposure. Determining or estimating radiation exposure in the case of biodosimetry may rely on electron paramagnetic resonance (EPR). Such resonance provides signal that may be read by a suitable EPR spectrometer.

EPR spectroscopy is a non-destructive technique that may be used to detect and quantify unpaired electrons (e.g., free radicals). The unpaired electrons result from the absorption

Thus, to determine if an individual has been exposed to ionizing radiation, a device or system such as an EPR spectrometer-based system may be used, in vivo. For example, to determine if a person was exposed to ionizing radiation, as indicated by production of free radicals in the person's teeth, the system may include resonators that are attached to a tooth. The resonators are coupled to a magnet system that effectively encompasses the subject's head.

Dose determination using electron paramagnetic resonance (EPR) spectroscopy of human tooth enamel (EPR biodosimetry) is an established technique for dose reconstruction in radiation accidents during photon irradiation. This technology is based on the fact that ionizing radiation generates unpaired electrons proportional to dose and that, in tooth enamel, these unpaired electron species are extremely stable, persisting for thousands of years. To use this technology, the EPR biodosimeter needs to be calibrated using a set of references that exhibit known and reproducible EPR signals in the desired range. Although tooth enamel is capable of exhibiting stable EPR signals proportional to the ionization irradiation dose, it is not an ideal reference tool for numerous reasons including its non-uniform chemical composition, variable physical properties, and unknown radiation history.

One aspect of EPR dosimetry that remains unresolved is the development and deployment of suitable reference sources for EPR dosimetry readers (i.e., EPR spectrometers). If available, such reference sources could be used to verify proper operation of the EPR spectrometers. To improve EPR dosimetry, especially to improve the integrity of a field-deployed EPR biodosimetry system that determines exposure to population members, disclosed herein is

a EPR reference source, method of manufacture, and method of use. To develop such a reference, we began with the hypotheses that:

FIG. 7 is a block diagram of an alternate EPR dosimetry system. In FIG. 7, EPR dosimetry system 700 includes ⁵ dosimeter reader 710, which in turn includes power supply 711, EPR electronics 713, user interface 715, processor 717, and measurement unit 719. The measurement unit 719 may include a resonator (not shown) that contacts one or more teeth of patient 730. The measurement unit 719 includes a ¹⁰ magnet coil section 718 which provides the required magnetic field to induce an EPR signal.

Also shown in FIG. 7 is a reference source 720, which is used to confirm proper operation of the system 710.

In operation, the EPR system **710** may be field-deployed ¹⁵ to perform triage operations following a large scale radiation event. FIG. **7** illustrates one possible configuration of an EPR measurement unit **719**. In this configuration the patient's head may be surrounded by, or merely adjacent a set of magnet coils that induce the magnetic field necessary ²⁰ to generate an EPR signal.

The reference source **720** is used to perform an initial check of the system **710**, and may thereafter be used to periodically confirm proper operation of the system **710**. The reference source **720** may have a form dictated by the system **710**. For example, the reference source **720** may have any of 25 the forms shown in FIG. **2**.

Prior to shipment to the operator of system **710**, the reference source **720** may be irradiated. For example, a certified laboratory may irradiate the reference source **720** using a Co-60 source. After such irradiation, and prior to $_{30}$ shipment, the reference source **720** may be tested in the laboratory to verify that it provides the desired EPR signal.

Disclosed above are methods (self-setting cement, sintering) for producing the carbonated hydroxyapatite (CH) crystalline structure used in an example EPR dosimeter. Other methods, including use of other starting components, also may produce a satisfactory crystalline structure for an EPR dosimeter. In particular, methods that result in substantially complete CH formation may be used to produce a satisfactory crystalline structure. In particular, U.S. Pat. No. 5,525,148, incorporated herein by reference, discloses methods for forming a hardened CH mass,

In addition to the self-setting cement forming processes described above, a satisfactory carbonate-substituted hydroxyapatite material may be formed by non-cement processes such as those disclosed in the following, which are 45 hereby incorporated by reference:

- L. G. Ellies, D. G. A. Nelson, J. D. B. Featherstone (1988): Crystallographic structure and surface morphology of sintered carbonated apatites. Journal of Biomedical Materials Research, Volume 22, Issue 6, pages 541-553.
- Iain R. Gibson and William Bonfield (2002): Novel synthesis and characterization of an AB-type carbonate-substituted hydroxyapatite. Journal of Biomedical Materials Research, Volume 59, Issue 4, pages 697-708.
- T. S Sampath Kumara, b, I Manjubalaa, J Gunasekarana (2000): Synthesis of carbonated calcium phosphate ceramics using microwave irradiation. Biomaterials, Volume 21, Issue 16, August 2000, Pages 1623-1629.
- 4. J. P. Lafona, E. Championa, D. Bernache-Assollantb (2008): Processing of AB-type carbonated hydroxyapatite Ca10-x(PO4)6-x(CO3)x(OH)2-x-2y(CO3)y ceramics with controlled composition. Journal of the European Ceramic Society, Volume 28, Issue 1, Pages 139-147.
- Michael E. Fleet, Xi Liu (2007): Coupled substitution of type A and B carbonate in sodium-bearing apatite. Biomaterials, Volume 28, Issue 6, Pages 916-926.

We claim:

1. A dosimeter for EPR dosimetry systems, comprising: a carbonated hydroxyapatite cement formed by mixing in a ratio of a range of about 0.5 to 5.0 powder-to-liquid

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- ratio: a cement powder comprising one or more calcium
- phosphate compounds,
- one or more carbonate compounds, and
- a cement liquid comprising a disodium phosphate solution to form a hardened mass; and
- the hardened mass, when irradiated by a radiation source, capable of producing a spectrally clean EPR spectrum, wherein the carbonate content is in a range of about 3% by weight to about 10% by weight of the hardened mass.

2. The dosimeter of claim **1**, wherein the radiation source is one of a gamma radiation emitter and an electron beam accelerator.

3. The dosimeter of claim 1, wherein the one or more calcium phosphate compounds are selected from a group consisting of monocalcium phosphate anhydrous, monocalcium phosphate monohydrate, dicalcium phosphate anhydrous, dicalcium phosphate dihydrate, amorphous calcium phosphate, α -tricalcium phosphate, and β -tricalcium phosphate.

4. The dosimeter of claim 1, wherein the one or more carbonate compounds are selected from a group consisting of sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, and ammonium carbonate.

5. The dosimeter of claim **1**, wherein the one or more carbonate compounds are selected from a group consisting of calcium carbonate, iron carbonate, magnesium carbonate, and zinc carbonate.

6. The dosimeter of claim 1, wherein the cement liquid has a total phosphate concentration in a range of about 0.005 mol/L to about 2.5 mol/L.

7. The dosimeter of claim 1, wherein the cement liquid comprises:

- a gelling agent; and
- a water reducing agent.

8. The dosimeter of claim 1, wherein the powder/liquid ratio is approximately 3.

9. The dosimeter of claim **1**, further comprising sensitizers that adapt the hardened mass for a specific range of radiation dose.

10. An EPR dosimeter, comprising:

- a carbonated hydroxyapatite material, comprising: a cement powder wherein the cement powder comprises one or more calcium phosphate compounds and one or more carbonate compounds, and
 - a cement liquid, wherein the cement powder and cement liquid are combined in a powder-to-liquid ratio of about 0.5 to about 5.0;
- a dosimeter housing, wherein the material when hardened, when irradiated is capable of generating a spectrally clean EPR spectrum, and wherein the carbonate content is in a range of about 3% by weight to about 10% by weight of the carbonated hydroxyapatite material when hardened.

11. The EPR dosimeter of claim 10, wherein the cement liquid comprises a phosphate solution.

12. The EPR dosimeter of claim **10**, wherein the cement liquid comprises:

a gelling agent; and

a water reducing agent.

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