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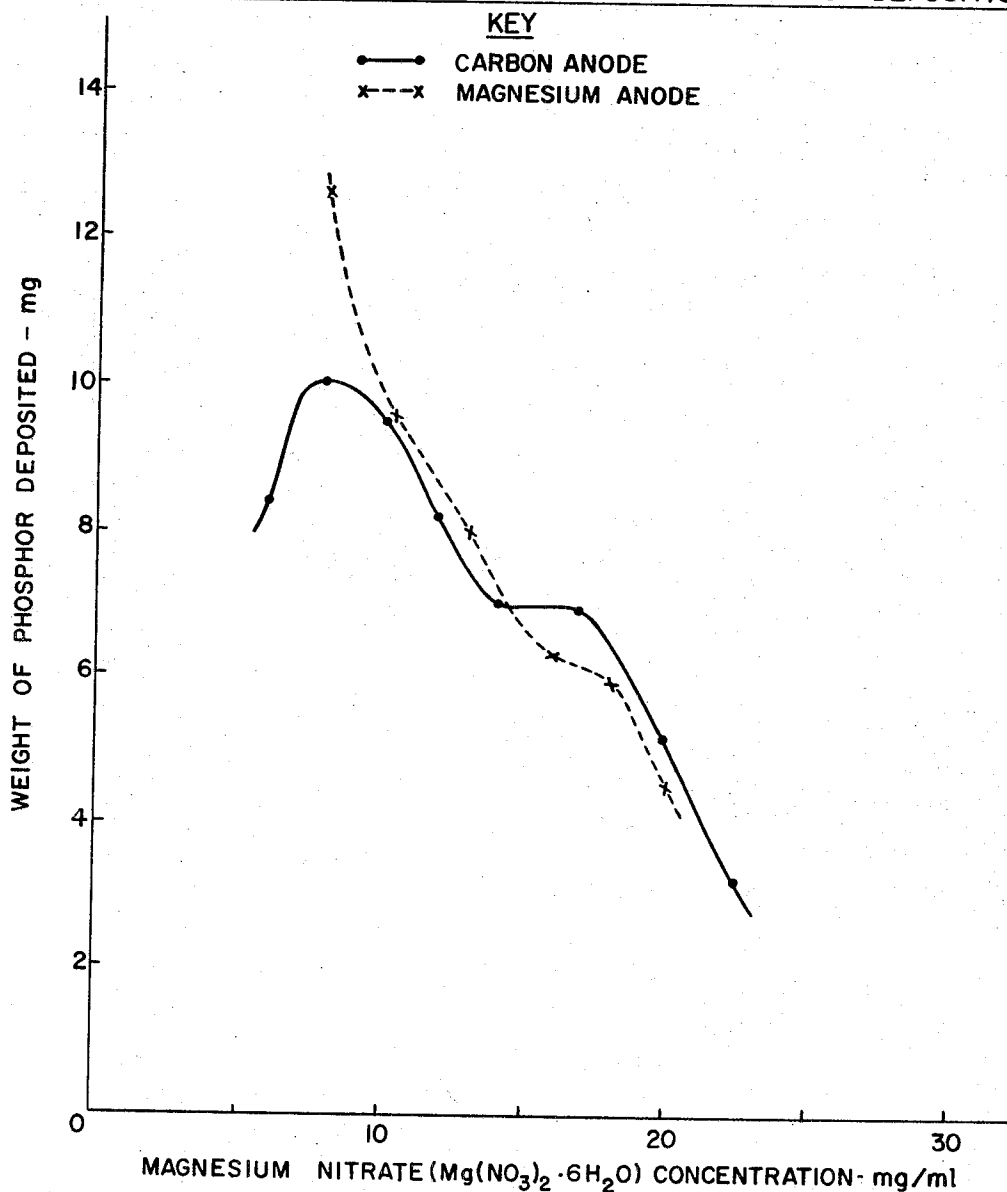
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PROCESS FOR COATING A METAL

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EFFECT OF MAGNESIUM NITRATE CONCENTRATION ON PHOSPHOR DEPOSITION



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3,551,306

PROCESS FOR COATING A METAL

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ABSTRACT OF THE DISCLOSURE

A novel electrodeposition process is disclosed for the preparation of thin adherent films of various oxides or hydroxides. Formation of these films is achieved by electrolyzing a quiescent solution of a soluble salt of the corresponding metal in an organic solvent miscible with water containing from about 0.01% to about 1% volume water, and having an electrolyte concentration in the order of 0.5–25 mg./ml. The novel process of this invention may be used in conjunction with cataphoretic deposition of luminescent materials to prepare a film of these materials cemented to the substrate surface with the metal oxide or hydroxide. Metal oxide or hydroxide films of various colors may be formed by providing for the presence of a color forming compound capable of reacting with these metal oxides or hydroxides to yield highly colored precipitates.

Methods of forming electrodeposited luminescent coatings have been extensively studied in the art. In one type of process which has received attention from various experimenters, an electric-field-responsive luminescent material is dispersed in a suitable solvent. For example, the solvent might consist of in the order of 90% to 95% alcohol, the balance being water. An electrolyte is then added to charge and disperse the particles of phosphor and render them amenable to deposition by a cataphoretic process. Such a technique is described in U.S. Pat. No. 2,851,408 to Cerulli. As described by Cerulli, after the electrolyte charging agent has been added, the dispersion is agitated and subjected to the influence of an electric field to bring about deposition of the suspended luminous material. However, under the deposition conditions described in the Cerulli patent, electrolyte is deposited concurrently with the luminescent material. This can be, and ordinarily is, leached out from the cataphoretically deposited film after suitable film thicknesses develop.

It is known, as disclosed, for example, in British Pat. No. 963,539, that under suitable conditions metal oxide film, such as magnesium oxide film, may be deposited by electrolyzing aqueous solutions of the corresponding salts. In the aforementioned British patent, this phenomenon has been utilized as a basis for forming images of magnesium oxide on photoconductive layers which can be subsequently developed as a visible image by means of color-forming compounds such as phenolphthalein, malachite green, etc. It has not, however, been recognized heretofore that such metal oxide films can be deposited from essentially anhydrous media such as encountered in electrophoretic deposition processes of the type described in the above-mentioned Cerulli patent.

In accordance with the present invention, it has now been discovered that a film of an alkaline earth oxide or hydroxide, or other related metal oxide or hydroxide can be formed on a surface by electrolyzing an essentially anhydrous solution of a salt of that metal in a water-miscible organic solvent. While the solution which is electrolyzed is conveniently described as "essentially anhydrous," the solution, in fact, contains minor quantities

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of water in the order of 0.01% to 1% by volume. Suitable electrolyte concentration is in the order of 0.0005 to 0.025 gm./ml. The resulting film is found to be tightly adherent and, if made from a suitable non-conductive metal oxide or hydroxide, is sufficiently impervious to provide exceptional insulating properties.

The metal oxide or hydroxide films formed in accordance with the present invention have numerous uses. Firstly, as already suggested, because of the dense adherent nature of the film, the process of the present invention provides a suitable method for the preparation of insulating metal oxide or hydroxide films. In another application, by providing for the presence of suitable color-forming compounds, such as pH indicators or dyestuffs in the solution which is electrolyzed, films of various colors may be deposited. This may be employed not only for decorative purposes (for example, in the color coding of insulated wires), but also for the purpose of forming color images where the cathodic substrate employed in electrolyzing is a photoconductive material which has been exposed to a light image. When employed in conjunction with electrophoretic deposition of luminescent materials, the film formed by the process of the present invention provides exceptionally strong bonding of the luminescent material to the substrate on which it is applied.

In the preferred embodiment of this invention the organic solvent includes a cathodic depolarizing agent. The presence of a cathodic depolarizing agent is desirable to avoid formation of bubbles of nascent hydrogen on and in the vicinity of the cathode which tend to interfere with the uniformity of the deposited film. Suitable cathodic depolarizers include solvents such as ketones and aldehydes, as well as reducing agents such as various sugar and dyestuffs. Ketones, and especially acetone, are particularly desirable since the materials are also suitable as solvents. A typical solvent system incorporating the preferred embodiment of the present invention would be composed of 74% acetone, 25% isopropyl alcohol and 1% water.

Suitable salts from which electrodeposited films can be formed in the practice of the present invention include magnesium chloride, magnesium nitrate, aluminum nitrate, calcium nitrate, strontium nitrate, zinc nitrate, zinc chloride, copper nitrate, copper chloride, gallium nitrate, cobalt chloride, silver nitrate, copper sulfate, gold chloride, manganese chloride, barium nitrate, barium chloride, barium acetate, lithium bromide, lithium nitrate, cesium nitrate, and aluminum chloride. It is preferable to use non-reducible salts to avoid electroplating of the metal during the deposition of the metal oxide or hydroxide.

In connection with the foregoing, it should be noted that while a wide range of metal oxides or hydroxides may be formed when the present invention is used in the electrophoretic deposition of luminescent phosphor films, other considerations must also be taken into account in selecting suitable electrolytes.

The preferred anions for the electrolyte are the nitrates, chlorides, and, to the a lesser extent, the bromides. Nitrates and chlorides of magnesium, aluminum and lithium give good depositions; the sulfates of these and other metals perform relatively poorly in the electro-deposition of phosphors.

For purposes of forming a dispersion of the phosphorescent material to be electrophoretically deposited, the individual particles of the phosphor must be given a positive charge so that they will migrate to the negative cathode. Salts of metals such as magnesium are effective to charge many phosphorescent materials because the metal ion is adsorbed onto the surface of the phosphor giving it a positive charge surrounded by a negatively charged ionic double-layer of the anion of the adsorbed metal ion.

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When the present invention is employed in the cathophoretic deposition of phosphorescent materials, any electric-field-responsive luminescent particles which can be positively charged for deposition at a cathode can be employed. Phosphor materials which may be deposited include, but are not limited to, silicates such as calcium magnesium silicate, zinc silicate, calcium silicate, magnesium silicate; phosphates such as zinc phosphate; sulfides such as zinc sulfide and zinc cadmium sulfide; fluorides such as zinc magnesium fluoride; chlorides such as potassium chloride; tungstates such as calcium tungstate, and oxides such as zinc oxide. The concentration of phosphor should be in the order of 0.01 to 0.1 gms./cc. At higher concentrations mechanical agitation is necessary to maintain the phosphor in suspension. Since the present invention requires that the solution which is electrolyzed be quiescent, the concentration of phosphor suspensions must be accordingly limited.

The cell conditions in the practice of the present invention are typical of those found in electrophoretic processes. Typically, the potential difference between the anode and the cathode is in the order of 10 to 500 volts. A current density of 1 to 50 milliamperes/cm.² is usually employed.

The present invention may be further understood by reference to the following examples and figure which graphically illustrate some of the results obtained in the practice of this invention.

EXAMPLE 1

In order to compare the efficacy of various added electrolytes and various nonaqueous liquid suspending media for promoting cathophoretic deposition and various phosphors, the following test procedure was employed.

The deposition cell consisted of an unstirred vessel of 300 ml. capacity which was provided with a stainless steel frame supporting a one-inch diameter test blank in a vertical position. The test blanks were either conductive glass or stainless steel. These blanks, one of which was used as the cathode in each experiment, were cleaned ultrasonically with acetone and weighed before each experiment. Facing the blank electrode and separated from it by a distance of $\frac{3}{4}$ inch was a row of three $\frac{1}{4}$ inch carbon rods held in a vertical position. Obviously other suitable inert anode materials may be employed such as platinum, gold, lead, etc. These rods were the anode in each experiment. A variable DC power supply capable of providing potentials of up to 500 volts and currents of up to 250 milliamperes was used to cause deposition.

In a typical operation, 250 mg. of phosphor powder was added to 250 cc. of the fluid-suspending medium in which the electrolyte under test had previously been dissolved. The phosphor was allowed to equilibrate with the liquid medium by stirring for 5 minutes and the resulting suspension was then poured into the test cell. Sufficient potential was immediately applied to yield a current of 10 milliamperes and deposition was allowed to proceed for 5 minutes at 25° C. without stirring. The test cathode was then withdrawn, dried and weighed. The appearance of the deposited layer was examined and noted.

Employing the foregoing procedure, a series of experiments were performed in which the solvent was 99% isopropyl alcohol and 1% water. Various proportions of magnesium nitrate were dissolved in the solvent system. After the magnesium nitrate had been dissolved, 250 mg. of a calcium magnesium silicate phosphor powder were dispersed into 250 cc. of the suspending medium. The magnesium nitrate charged the particles of added phosphor so that a stable suspension resulted. The suspension was thereupon placed in an electrophoretic cell and subjected to the influence of an electric field. The results are shown as Curve No. 1 of the figure wherein the vertical axis is the weight of phosphor deposited on the test cathode and the horizontal axis is the concentration of the magnesium nitrate·6H₂O electrolyte in mg./ml. suspension.

As will be apparent from an examination of Curve No.

1, optimum results are obtained when the concentration of added electrolyte is approximately 8 mg./ml. in a suspension containing 1 mg./ml. of phosphorescent powder. The optimum results are believed attributable to the occurrence of optimum charging of the calcium magnesium silicate phosphor. Thus, if less magnesium nitrate is added, optimum charging is not attained; and if more is used, the amount of phosphor deposited also decreases because the increase in conductivity tends to favor electrolysis over electrophoretic deposition.

Example 1 may be repeated with similar results substituting calcium, barium or aluminum for the magnesium nitrate referred to in Example 1. The nitrate and chloride salts of these materials gave uniformly good results.

EXAMPLE 2

Example 1 was repeated, this time substituting a magnesium anode for the carbon anode. The results are shown as Curve No. 2 of the figure. As will be apparent, more efficient deposition was obtained, especially at lower concentrations of electrolyte. This is believed due to the replacement in the electrolytic solution of the magnesium ions lost through deposition of magnesium hydroxide at the cathode.

EXAMPLE 3

To a solvent mixture containing 150 ml. acetone, 48 ml. isopropyl alcohol and 2 ml. distilled water was added 200 mg. phenolphthalein and 100 mg. magnesium nitrate (Mg(NO₃)₂·6H₂O). After stirring, the resulting clear, water-white solution was poured into a suitable electrolytic cell which was provided with a carbon rod anode. An aluminum foil cathode of approximately 1 square inch area was then placed in the electrolyte at a distance of approximately 1 inch from the anode. The anode and the cathode were then connected to a source of direct current. At a voltage of 100 volts, approximately 25 ma. of current passed through the cell and during a period of 1 minute at 25° C. a bright, transparent, bluish-red deposit formed on the cathode, principally on the side facing the anode. This coating was approximately .0001 inch thick and presumably consisted of a mixture of magnesium hydroxide and the magnesium salt of phenolphthalein. It was well adherent. When the aluminum foil was sharply bent, the coating remained on the metal. It resisted washing with water, acetone, isopropyl alcohol and toluene, and it had a high electrical resistance.

During the formation of this coating, there was no apparent liberation of gases at either the anode or the cathode.

When this example was repeated using an electrolyte consisting of 200 mg. phenolphthalein and 100 mg. magnesium nitrate dissolved in a solvent mixture consisting of 50 ml. isopropyl alcohol and 150 ml. distilled water, a brightly colored adherent coating was not formed. With this electrolyte the conductivity was much higher, only 25 volts being required to produce a current flow of 25 ma. There was much gassing and a transient formation of bluish-red color in the electrolyte near the cathode. When the cathode was removed from the cell and washed with water, no colored coating remained.

This illustrates the advantageous use of substantially nonaqueous electrolytes in this coating process.

EXAMPLE 4

Example 3 was repeated except that the colored coating was deposited onto a sheet nickel cathode at a voltage of 50 volts and a current of 12.5 ma. during a period of 1 minute.

EXAMPLE 5

Example 3 was repeated except that the colored coating was deposited onto a sheet stainless steel cathode at a voltage of 25 volts and a current of 7.5 ma. during a period of 3 minutes.

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EXAMPLE 6

A small coil of No. 20 gauge aluminum wire was placed in the electrolyte described in Example 3. When connected as the cathode to a 100 volt DC supply while 25 ma. current flowed through the cell, the coil was coated with a purple, electrically-insulating layer within 2 minutes.

EXAMPLE 7

To 200 ml. of the solvent mixture described in Example 3 was added 100 mg. of calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 300 mg. of phenolphthalein. When the resulting clear solution was electrolyzed with a voltage of 100 volt DC and a current of 20 ma. using a carbon rod anode and an aluminum foil cathode of 1 square inch area, the cathode was coated with a purple, electrically-insulating layer within 30 seconds at room temperature. This coating resisted acetone and alcohol but was slowly washed away by running water.

EXAMPLE 8

100 mg. of strontium nitrate $\text{Sr}(\text{NO}_3)_2$ was dissolved in 2 ml. distilled water and a solution of 200 mg. of phenolphthalein in 198 ml. isopropanol was then added with stirring. The resulting solution was used as the electrolyte in an electrolytic cell as described in Example 3. Upon the passage of 10 ma. current at a voltage of 450 volts DC for 1 minute, a bluish-red coating was formed on the aluminum foil cathode. No gassing was observed during this deposition.

EXAMPLE 9

A clear yellow solution of 100 mg. of magnesium nitrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 50 mg. of fluorescein in 1 ml. distilled water and 199 ml. isopropyl alcohol was electrolyzed at 200 volts DC with a current flow of 15 ma., using a $\frac{1}{4}$ inch carbon rod immersed 1 inch into the electrolyte as the anode and an aluminum foil cathode having an area of 1 square inch. Within 2 minutes a transparent yellow, electrically-insulating coating had formed on the portion of the aluminum foil which was immersed in the electrolyte.

EXAMPLE 10

Example 3 was repeated except that 50 mg. phenol red was used in place of 200 mg. phenolphthalein. The voltage was 50 volts and the current 15 ma. With an electrolysis time of 1 minute, a dark red coating was formed on the aluminum foil cathode.

EXAMPLE 11

An electrolyte solution was prepared by dissolving 50 mg. bromothymol blue and 100 mg. magnesium nitrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 2 ml. water, 50 ml. methyl ethyl ketone and 148 ml. of isopropyl alcohol. With a carbon rod anode, as described in Examples 3 and 9, and a 1 square inch aluminum cathode, 20 ma. current was passed at a voltage of 200 volts for a period of 5 minutes. A translucent, pale blue, insulating layer 0.1 mil thick was formed on the cathode.

EXAMPLE 12

To 20 ml. of the solvent mixture described in Example 3 was added 100 mg. bromothymol blue and 100 mg. magnesium nitrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The resulting bright yellow solution was subjected to electrolysis. A carbon rod was used as the anode and sheet aluminum of 2 square inches area as the cathode. With an electrode spacing of 2 cm., a current of 20 ma. and a voltage of 50 volts, a bright blue coating was formed on the cathode within 45 seconds. This was washed with acetone and allowed to dry in air. This decorative deposit was found to be a poor conductor of electricity.

EXAMPLE 13

An electrolyte solution was prepared as follows: 100 mg. of magnesium nitrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 100 mg. of phenolphthalein were dissolved in 2 ml. water and 198

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ml. isopropanol. A carbon rod anode was placed in this electrolyte. As the cathode, a sheet of aluminum foil coated with a zinc oxide-resin dispersion was used. An optical image was projected onto this cathode and 100 volts DC were supplied to the anode and cathode. Within 30 seconds a brilliant reddish purple image formed on the light struck areas of the zinc oxide (photoconducting) coated foil. This colored negative print was withdrawn from the electrolytic cell, washed with isopropanol and dried.

EXAMPLE 14

Example 13 was repeated except that thymolphthalein was used in place of phenolphthalein. A blue negative image print was obtained.

EXAMPLE 15

A reddish purple negative print was prepared as in Example 13. After washing with isopropanol, but before drying, it was placed in the electrolyte described in Example 14, reexposed in the same image areas and a blue negative image was superimposed on the original reddish purple image. The resulting compound negative image was purplish blue.

EXAMPLE 16

A solution of 100 mg. magnesium nitrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 50 mg. of "Magneson" (4-(p-nitrophenylazo)-resorcinol) in 2 ml. water and 198 ml. isopropanol was electrolyzed using a carbon anode and a sheet aluminum cathode. With a voltage of 100 volts DC and a current of 25 ma. per square inch of cathode area, a light blue coating formed on the cathode during a period of three minutes. After washing with isopropanol, this coating turned yellow upon drying.

EXAMPLE 17

Example 16 was repeated except that aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was used in place of magnesium nitrate and 1,2,5,8 - tetrahydroxyanthraquinone (quinizarin) was used in place of "Magneson." A bluish red coating of the aluminum hydroxide-quinizarin complex was obtained on the cathode.

EXAMPLE 18

When Example 17 was repeated using "Aluminon" in place of quinizarin, a reddish-orange coating was obtained on the cathode.

We claim:

1. In a process for forming an adhering film of a metal oxide or hydroxide on a surface, the step of electrolyzing a solution, in a solvent substantially free of suspended material, of a salt selected from the group consisting of the chlorides, bromides, acetates and nitrates of calcium, magnesium, aluminum, zinc, copper, cobalt, gallium, manganese, barium, lithium, cesium, silver and gold, said solvent being an organic solvent miscible in water and water, said solution containing from about 0.01% to about 1.0% by volume water, and from 0.05 to about 25 mg./ml. of said salt, the electrolysis of said solution being effected while said solution is quiescent in an electrolytic cell having an anode and a cathode, said cathode being the surface on which said metal oxide or hydroxide film is to be formed, the potential difference between said anode and said cathode being from about 10 to about 500 volts and the current density at said cathode being from about 1 to about 50 milliamperes/cm.² for a period of time to develop a metal oxide or hydroxide coating on said cathode.

2. In a process for forming an adhering film of a metal oxide or hydroxide on a surface, the step of electrolyzing a solution, in a solvent substantially free of suspended material, of a salt selected from the group consisting of the chlorides, bromides, acetates and nitrates of calcium, magnesium, aluminum, zinc, copper, cobalt, gallium, manganese, barium, lithium, cesium, silver and gold, said

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solvent being an organic solvent miscible in water and water, said solution containing from about 0.01% to about 1.0% by volume water, from about 0.5 to about 25 mg./ml. of said salt and an effective amount of a color-forming compound which will react with said metal oxide or hydroxide during the precipitation thereof to yield a colored precipitate, the electrolysis of said solution being effected while said solution is quiescent in an electrolytic cell having an anode and a cathode, said cathode being the surface on which said metal oxide or hydroxide film is to be formed, the potential difference between said anode and said cathode being from about 10 to about 500 volts and the current density at said cathode being from about 1 to about 50 milliamperes/cm.² for a period of time to develop a metal oxide or hydroxide coating on said cathode.

3. A method according to claim 2 wherein said solution contains a cathodic depolarizing agent.

4. A method according to claim 3 wherein said organic solvent consists essentially of from about 0.01% to about 1% by volume water, and about 25% by volume isopropanol, the balance thereof being acetone.

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5. A process according to claim 3 wherein said color-forming compound is selected from a group consisting of phenolphthalein, bromthymol blue, thymolphthalein, 4-(p-nitrophenyl-azo)-resorcinol and quinalizarin.

6. A process according to claim 3 wherein said salt is selected from the group consisting of magnesium nitrate, magnesium chloride, aluminum nitrate, aluminum chloride, calcium nitrate, calcium chloride, strontium nitrate, strontium chloride, zinc nitrate, zinc chloride, barium nitrate, barium chloride, lithium nitrate and lithium chloride.

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