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(54) Title: BIS(GLYOXIME)-TRANSITION METAL COLORIMETRIC MOISTURE INDICATORS

(57) Abstract: Colorimetric moisture-indicating sensors comprising a solid polymeric support and a bis(glyoxime)-transition metal complex bound to the solid polymeric support are described. The solid polymeric support is a strong acid cation exchange resin. These colorimetric moisture-indicating compositions and sensors can be used to detect moisture. In some embodiments, detecting moisture comprises the sequential steps of (1) providing a colorimetric moisture-indicating sensor comprising a solid polymeric support and a bis(glyoxime)-transition metal complex bound to the support, and (2) exposing the composition to a moist atmosphere. A method of making a colorimetric moisture-indicating sensor comprising the sequential steps of (1) adsorbing transition metal ions onto a solid polymeric support, and (2) complexing a bis(glyoxime) to the adsorbed transition metal ions is also provided.

BIS(GLYOXIME)-TRANSITION METAL COLORIMETRIC MOISTURE INDICATORS

Field

The present disclosure relates to colorimetric moisture indicators that include moisture-indicating compositions comprising bis(glyoxime)-transition metal complexes bound to solid polymeric supports.

Background

Moisture indicators are used, for example, to determine the amount of moisture or humidity in the vicinity of the indicator. Colorimetric indicators change color upon exposure to moisture or humidity. Current commercialized colorimetric moisture indicators are based on cobalt-containing compounds (e.g., $CoCl_2$). Alternatives to cobalt compounds are currently being pursued due to the potential adverse environmental impact and expense of cobalt. Other compositions, such as gel supports that include iron (II), iron (III), or copper chloride salts have also been used as moisture indicators, but these indicators do not show strong absorptions in the visible electromagnetic spectrum and the moisture-indicating color change is often difficult to detect.

Summary

There is a need for economic colorimetric moisture indicators that are not based on cobalt. There is also a need for colorimetric moisture indicators that have a highly visible color change, and that can change qualitatively and/or quantitatively with a change in humidity.

In one aspect of the present disclosure, a colorimetric relative humidity indicating sensor is provided that comprises a solid polymeric support and a bis(glyoxime)-transition metal complex bound to the solid polymeric support. The solid polymeric support is a strong acid cation exchange resin.

In another aspect of the present disclosure, a method of detecting moisture is provided comprising the sequential steps of (1) providing a colorimetric moisture-indicating sensor comprising a solid polymeric support and a bis(glyoxime)-transition metal complex bound to the solid polymeric support, and (2) exposing the colorimetric moisture-indicating sensor to a moist atmosphere. The solid polymeric support is a strong acid cation exchange resin.

Finally, in another aspect, a method of making a colorimetric moisture-indicating sensor is provided comprising the sequential steps of (1) adsorbing transition metal ions onto a solid polymeric support, and (2) complexing a bis(glyoxime) to the adsorbed transition metal ions to form a bis(glyoxime)-transition metal complex. The solid polymeric support is a strong acid cation exchange resin.

The sensors and methods herein can provide highly visible color change correlating to the amount of moisture in the vicinity of the sensors and can provide qualitative and/or quantitative indications of the amount of moisture in the vicinity of the sensors.

The above summary is not intended to describe each disclosed embodiment of every implementation of the present invention. The details of one or more embodiments of the invention are also set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description and from the claims.

Detailed Description

Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings disclosed herein. The use of numerical ranges by endpoints includes all numbers within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5) and any range within that range.

As used herein:

"Bis(glyoxime)-transition metal complex" refers to a complex that has two glyoxime moieties complexed to a transition metal; as described further herein, the glyoxime moieties may have alkyl or other groups substituted for hydrogen at the ortho positions.

"Glyoxime" refers to vicinal dioximes of substituted or unsubstituted orthoketones;

"Hue" ranges in value from 0 to 360 (including all numbers in between), and refers to the degree to which a stimulus can be described as similar to or different from stimuli that are described as red, green, and blue and can be calculated using known mathematical techniques described further herein.

"Humidity" and "moisture" are used interchangeably.

"Color intensity change" refers to the difference observed between two color states and in some embodiments can be expressed as difference in Hue.

"Visible spectroscopic reflection" refers to measurements of reflections that are typically in the near UV-visible region of the electromagnetic spectrum—from about 350 nm to about 830 nm; it is understood that the actual reflection spectrum of a particular composition may be influenced by solvent, solvation, interference of thin surface coatings, and other environmental parameters such as temperature.

"Optical spectrum" refers to the spectrum of reflected and/or transmitted electromagnetic radiation in the near visible and visible wavelengths from and/or through an object. In some cases, the change in optical spectrum is a visible color change.

"Transition metal" refers to any element or elements having atomic numbers from 21-30, 39-48, 72-80, and 104-112. Exemplary transition metals include zirconium, titanium, rhodium, iridium, platinum, palladium, gold, nickel, copper, and combinations thereof.

Unless otherwise specified, as used herein, all relative humidity values refer to relative humidity as measured at room temperature (between 22 °C and 28 °C).

Current commercially available humidity indicators rely on inorganic salts such as cobalt (II) chloride to provide visual indication by color intensity change upon exposure to various levels of relative humidity. Recently, cobalt (II) chloride has come under regulatory scrutiny due to environmental concerns. Another problem with the use of cobalt salts for humidity indication is that the color intensity change (for example, blue to pink for cobalt (II) chloride) can be difficult to ascertain, and hence it can be difficult to determine the humidity exposure level.

Compositions that include a solid polymeric support and a bis(glyoxime)-transition metal complex bound to the support can be a useful alternative to cobalt (II) chloride for colorimetric moisture or humidity determination. Depending upon composition, humidity sensors based on bis(glyoxime)-transition metal complex bound to a solid polymeric support can be constructed which can quantitatively determine the humidity level of the atmosphere to which the sensor is exposed. Such humidity sensors can also be constructed to provide reversible or irreversible humidity indication.

Provided herein are colorimetric moisture-indicating compositions and sensors comprising bis(glyoxime)-transition metal complexes bound to solid polymeric supports. The solid polymeric support is a strong acid cation exchange resin.

The compositions and sensors can provide highly visible color change correlating to the amount of moisture in the vicinity of the sensors and can provide qualitative and/or quantitative detection of the amount of moisture in the vicinity of the sensors.

The solid polymeric supports used in the compositions, sensors, and methods described herein generally include supports that allow bonding of bis(glyoxime)-transition metal complexes. By bonding it is meant that there is an attractive interaction between the bis(glyoxime)-transition metal complex and the solid polymeric support. The attractive interaction can include covalent bonds, ionic bonds, dative bonds, metallic bonds, hydrogen bonds, van der Waals forces, electrostatic forces, chemisorption, physisorption, or any other interaction that attracts the bis(glyoxime)-transition metal complex to the solid polymeric support. For example, when a bis(glyoxime)-transition metal complex that is insoluble in water or slightly soluble in water is bound to a solid polymeric support, it is typically not removed by successive or continuous rinsing with water. In some embodiments, the attractive interaction includes hydrogen bonds, ionic bonds, or a combination thereof.

In some embodiments, compositions and sensors are provided that include solid organic polymeric supports. In general, hydrophilic polymers that have the ability to bind transition metal ions and their bis(glyoxime) complexes may be used, such as those with functional groups such as sulfonates, phosphonates, and carboxylates. However, it has surprisingly been found that compositions or sensors with solid polymeric supports based on a strong acid cation exchange resin produce unexpectedly good results. Colorimetric moisture-indicating compositions or sensors based on a strong acid cation exchange resin show unexpectedly clear color differentiation at different environmental moisture levels.

The solid polymeric support included in the colorimetric moisture-indicating compositions and sensors is a strong acid cation exchange resin. As used herein, the term "strong acid" refers to an acidic group that dissociates completely in water. Strong acids typically have a pKa less than 4 or 5. The strong acid cation exchange resins typically have ionic groups such as sulfonic acid groups ($-SO_3H$), phosphonic acid groups ($-PO_3H_2$), or salts thereof. When present as a salt, the sulfonic acid groups are present as sulfonate anions and the phosphonic acid groups are present as phosphonate anions. Suitable salts often have cations selected from an alkali metal ion (e.g., sodium ion, lithium ion, or potassium ion), an alkaline earth metal ion (e.g., calcium or magnesium), an ammonium ion, or an ammonium ion substituted with one or more alkyl groups, aryl groups, or combinations thereof.

The cation exchange resins are typically crosslinked polymeric materials prepared from various ethylenically unsaturated monomers. The polymeric materials are usually based mainly on styrene, derivatives of styrene (e.g., alpha-methyl styrene), (meth)acrylates, or combinations thereof. The polymeric materials are typically crosslinked to provide the needed amount of rigidity. The cation exchange resins can be in the form of beads, films, fibers, or any other desired form.

In some embodiments, the cation exchange resins are polymeric materials prepared from styrene or derivatives of styrene. Divinyl benzene is commonly used as a crosslinker. The acidic groups can be introduced during the polymerization process by the inclusion of a monomer having an acidic group. Suitable monomers with an acidic group include, for example, 4-stryrene sulfonic acid, vinylsulfonic aicd, or a salt thereof in the monomer mixture. Alternatively, the acidic group can be introduced after the polymerization process by treating the polymeric material with a sulfonating agent.

In other embodiments, the cation exchange resins are based on polymeric materials prepared from (meth)acrylate monomers. Monomers with multiple (meth)acryloyl groups can be used as a crosslinker. The acidic group can be introduced during the polymerization process by the inclusion of a monomer having a sulfonic acid group (e.g., N-acrylamidomethanesulfonic acid, 2-acrylamidoethanesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, and 2-methacrylamido-2-methylpropanesulfonic acid, or a salt thereof) or by inclusion of a monomer having a phosphonic acid group (e.g., 2-acrylamidoethylphosphonic acid and 3-methacrylamidopropylphosphonic acid, or a salt thereof) Suitable (meth)acrylate-based strong cation exchange resins are further described in U.S. Patents 7,098,253 (Rasmussen et al.), 7,683,100 (Rasmussen et al.), and 7,674,835 (Rasmussen et al.).

Strong acid cation exchange resins are commercially available from multiple suppliers. Examples include the cation exchange resins commercially available from Dow Chemical (Midland, MI) under the trade designation AMBERLYST (e.g., AMBERLYST 15, AMBERLYST 35, AMBERLYST 40, and

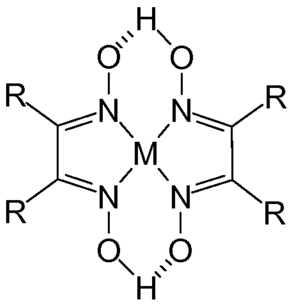
AMBERLYST 70), under the trade designation DOWEX (e.g., DOWEX MARATHON and DOWEX MONOSPHERE), under the trade designation AMBERJET (e.g., AMBERJET 1000H), and under the trade designation AMBERLITE (e.g., AMBERLITE IR120H).

The strong acid cation exchange resin can be a gel-type resin or macroporous (i.e., macroreticular) resin. As used herein, the term “macroporous” refers to particles that have a permanent porous structure even in the dry state. Although the resins can swell when contacted with a solvent, swelling is not needed to allow access to the interior of the particles through the porous structure. In contrast, gel-type resins do not have a permanent porous structure in the dry state but must be swollen by a suitable solvent to allow access to the interior of the particles. In many embodiments, the strong acid cation exchange resins are macroporous. Macroporous resins tend to have a higher crosslinking density compared to gel-type resins.

The ion exchange capacity of the cation exchange resins if often at least 0.2 equivalents per liter, at least 0.5 equivalent per liter, at least 1 equivalents per liter, or at least 2 equivalents per liter. The capacity is often up to 10 equivalents per liter, up to 8 equivalents per liter, or up to 5 equivalents per liter. The capacity can be, for example, in a range of 0.1 to 10 equivalents per liter, in a range of 0.5 to 10 equivalents per liter, or in a range of 0.5 to 5 equivalents per liter. High capacity is often desired to adsorb more of the transition metal ion that is part of the bis(glyoxime)-transition metal complex onto the cation exchange resin.

In some embodiments the solid polymeric supports may comprise beads, pellets, spheres, granules, extrudates, tablets, nanoparticles, fibers, rods, needles, wovens, or nonwovens. In some embodiments, the solid polymeric support may be in film form, such as coatings and free-standing films.

Compositions and sensors are provided herein with bis(glyoxime)-transition metal complexes, bound to the solid polymeric supports. The bis(glyoxime)-transition metal complex includes two glyoxime moieties that form a complex with transition metals. The bis(glyoxime)-transition metal complex generally has the structure of Formula (I):



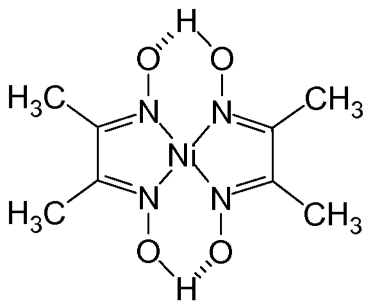
(I)

wherein:

M is a transition metal; and

R is independently selected from the groups comprising alkyl, such as ethyl and methyl; aryl, such as phenyl; thioaryl, such as thiophenyl; and a heterocyclic group, such as piperidine and morpholine.

Common glyoxime moieties include dialkylglyoximes such as, for example, dimethylglyoxime and diethylglyoxime. Common glyoximes that may also be useful in the provided compositions include diphenylglyoxime and bis(thiophenyl)glyoxime. Additionally, morpholine and piperidine have been reacted with anti-chloroglyoxime to give morpholineglyoxime and piperidineglyoxime. Since the transition metal ion complexes with the heteroatoms of the glyoxime species (nitrogen and oxygen, for example) it is contemplated that other substituents on the glyoxime molecule may be useful compositions if they do not interfere with the ability of the two glyoxime moieties to complex with a transition metal ion. When complexed, the bis(glyoxime)-transition metal complex typically has a square planar configuration. In some embodiments, the bis(glyoxime)-transition metal complex can include ions of rhodium, iridium, platinum, palladium, gold, nickel or copper which are well known by those of ordinary skill in the art to form square planar coordination complexes with glyoxime moieties like dimethylglyoxime. An exemplary bis(glyoxime)-transition metal complex for use in the moisture-indicating media is nickel dimethylglyoxime. A structure of an exemplary nickel bis(dimethylglyoxime) complex, bis-(dimethylglyoximato) nickel (II), is shown in Formula (II) below:



(II)

The colorimetric moisture-indicating compositions may be made into a multimedia construction in combination with other media and/or containment devices. Exemplary multimedia constructions can include loose-packed indicator constructions (e.g., particles or fibers contained in a vial, packed in a tube, or wrapped in a flexible fabric), loose, non-packed indicator constructions (e.g., physically entangled moisture-indicating media in a fibrous web, such as particle-loaded webs), multilayer constructions (e.g., indicator films on or between additional material layers which may have varying degrees of fluid permeability, or indicator particles or fibers sandwiched between containment layers), or partially embedded or encapsulated constructions (e.g., particles or fibers partially embedded in a polymer, such as an adhesive-coated film or fiber; composites, such as an articulated bulk shape, film, or fiber). In some embodiments, moisture-indicating media particles or fibers may also be contained in a porous matrix. In some embodiments, the colorimetric moisture-indicating composition may be dispersed or dissolved in a solvent.

In some embodiments, the colorimetric moisture-indicating compositions can be attached to, deposited on, physically entangled in, and/or embedded in secondary supports. The secondary supports can be one dimensional (e.g., fiber), two dimensional (e.g., planar substrates such as paper, glass, or polymer films), and three dimensional (e.g., fiber network, sponge structures). The colorimetric moisture-indicating compositions can be attached to the secondary supports by physical adsorption of the mixture to the secondary supports or using adhesives (such as pressure sensitive adhesives) or binding polymers (such as polyvinyl alcohol). In some embodiments, the colorimetric moisture-indicating composition can be deposited on backing material or carrier material to create moisture-indicating sensors in the form of cards and tapes according to conventional methods known in the art. Exemplary backing materials and carrier materials include those made of paper, kraft papers, polyethylene, polypropylene, polyester or composites of any of these materials. In some embodiments, the side of the backing materials and carrier materials opposite the deposited colorimetric moisture-indicating composition can be coated with release agents such as fluorochemicals or silicones. Exemplary tapes may comprise acrylic, urethane, and silicone polymers. In some embodiments, the sensor is structured such that the colorimetric moisture-indicating composition is in fluid communication with the surrounding environment.

In some embodiments, the colorimetric moisture-indicating compositions can be inserted between two secondary supports. In such cases, one of the secondary supports may be visibly transparent enough to allow visual observation the color change of indicators. At least one of the secondary supports should allow the transfer of humidity to the colorimetric moisture-indicating composition. In some embodiments, both of the secondary supports are impermeable to particles.

In some embodiments, the colorimetric moisture-indicating compositions can be contained within transparent or semi-transparent vials or containers that have caps. The caps may optionally comprise filtering layers that are impermeable to particles, but that allow the transfer of humidity across the filters.

The color of the colorimetric moisture-indicating compositions and sensors described herein may be observed visually with the human eye, or with the assistance of measuring devices such as a spectrophotometer or a colorimeter. The amount of moisture to which the colorimetric moisture-sensor is exposed can be measured spectroscopically, for example, by reflection. Since the provided colorimetric moisture-indicating compositions are solid, the change in color can be measured by reflecting light off of the surface of the solid and measuring the loss of intensity from wavelengths absorbed by the surface. In some embodiments, the absorbance at a given wavelength can be measured using an optics spectroscopy system that is configured for reflection spectroscopy. An exemplary optics spectroscopy system suitable for this measurement is Model Jaz-EL350, available from Ocean Optics, Dunedin, FL. Typically, a spectrum from a white piece of paper or white powders can be used as a reference spectrum when measuring reflection intensity.

In some embodiments, the visible spectroscopic reflection intensity in the wavelength range of 460 nm to 560 nm and color can be expressed as the Hue. Hue may be quantitatively related to the level of moisture in the environment within which the colorimetric moisture-indicating composition or sensor is located, and may be determined by converting a measured reflection spectrum to Hue using known mathematical techniques as described further herein.

In some embodiments, the color, Hue, reflection spectrum, or transmission spectrum of the colorimetric moisture-indicating composition is quantitatively related to the level of moisture (humidity or relative humidity) in the environment in which the colorimetric moisture-indicating composition or sensor is located. By quantitatively it is meant that the reflection intensity in the wavelength range of 460 nm to 560 nm and the Hue number, expressed by color, has a one-to-one correlation to the amount of humidity or relative humidity. The environment within which the colorimetric moisture-indicating composition or sensor is located can be an area or volume surrounding the colorimetric moisture-indicating composition or sensor, including, for example, the area, volume, and/or atmosphere in contact with the colorimetric moisture-indicating composition or sensor. In some embodiments, the color, Hue, reflection spectrum, or transmission spectrum of the colorimetric moisture-indicating composition or sensor is directly related to the level of moisture (humidity or relative humidity) in an environment. By directly related, it is meant that the property gives information about the level of moisture in the environment within which the colorimetric moisture-indicating composition or sensor is located. This information may be approximate, or may be quantitatively related to the level of moisture in the environment within which the colorimetric moisture-indicating composition or sensor is located. In some embodiments where color is visually observed to determine the level of moisture, the colorimetric moisture-indicating composition or sensor will exhibit a distinct color change with varying moisture conditions. For example, the colorimetric moisture-indicating composition or sensor may exhibit two different colors at two different levels of relative humidity, such as appearing green at a relative humidity of 30% and appearing pink at a relative humidity of 70% at 25 °C.

The colorimetric moisture-indicating compositions or sensors can be used in any environment or space, including both enclosed spaces or volumes and unenclosed spaces or volumes. Exemplary environments include enclosed containers, packaging, rooms, etc. In some embodiments, the conditions of temperature and pressure within the environment will be homogeneous. In some embodiments, the conditions of temperature and pressure within the environment will not be homogeneous.

In some embodiments, the colorimetric moisture-indicating composition or sensor quantitatively changes color, Hue, reflection spectrum, or transmission spectrum at relative humidities ranging from about 40% to about 80% relative humidity at 25°C. In some embodiments, the colorimetric moisture-indicating composition quantitatively changes color, reflection spectrum, or transmission spectrum at relative humidities ranging from about 50% to about 70% relative humidity at 25°C. In some embodiments, the colorimetric moisture-indicating composition quantitatively changes color, reflection spectrum, or transmission spectrum at relative humidities ranging from about 55% to about 65% relative humidity at 25°C.

In some embodiments, the colorimetric moisture-indicating compositions or sensors can be irreversible. By irreversible, it is meant that when the composition is exposed to one set of humidity conditions it has an original value associated with a specific optical spectrum (or Hue, or color). When the set of humidity conditions is changed, the composition changes color to give a different, second value associated with a specific optical spectrum (or Hue, or color). And, when the composition is returned to the initial set of humidity conditions, the optical spectrum (or Hue, or color) does not return to the original optical spectrum (or Hue, or color).

In some embodiments, the colorimetric moisture-indicating compositions can be reversible. By reversible it is meant that when the composition is exposed to one set of humidity conditions it has an original value associated with a specific optical spectrum (or Hue, or color). When the set of humidity conditions is changed, the composition changes color to give a different, second value associated with a specific optical spectrum (or Hue, or color); and, finally, when the composition is returned to the initial set of humidity conditions, the composition changes again, resulting in a third value associated with a specific optical spectrum (or Hue, or color). That resulting third value returns to approximately the original value. In some embodiments, the moisture-indicating compositions will exhibit complete reversibility. Such reversible moisture-indicating compositions substantially return to the original value of the specific optical spectrum (or Hue, or color) when re-exposed to the initial set of humidity conditions. Thus, for completely reversible colorimetric moisture-indicating compositions, the third value of the specific optical spectrum (or Hue, or color) is substantially equivalent to the original value of the specific optical spectrum (or Hue, or color). In other embodiments, the colorimetric moisture-indicating compositions will exhibit partial reversibility, i.e., when the composition is returned to the initial set of humidity conditions, the resulting third value of the specific optical spectrum (or Hue, or color) is closer to the original value than to the second value.

In some embodiments, the color changes are easily detectable with the human eye. In these embodiments, the human eye can detect the difference between the original value and the second value of the color (or Hue), as well as the difference between the second value and the third value of the color (or Hue). Thus, in some embodiments the difference between the original Hue number and the second Hue number, or the difference between the second Hue number and the third Hue number is at least 15, in some embodiments at least 30, and in some embodiments at least 60. In some color ranges, such as between Hue numbers of 0 and 60, or Hue numbers of 300 and 360, smaller differences in Hue are detectable. In other color ranges, such as between Hue numbers of 60 and 300, only larger differences in Hue number may be detectable. It is not necessary that the difference between the original value and the third value of the color (or Hue), if any, is detectable by the human eye.

Also provided is a method of detecting moisture. This method comprises the sequential steps of (1) providing a colorimetric moisture-indicating sensor comprising a solid polymeric support and a bis(glyoxime)-transition metal complex bound to the support, and (2) exposing the sensor to a moist atmosphere. The method can further comprise the step of (3) determining the level of moisture in the environment surrounding the sensor based on the color of the sensor. Determining the level of moisture can comprise visually observing the color of the sensor or measuring the visible reflection or transmission spectra of the sensor, as described above.

Also provided is a method of making a colorimetric moisture-indicating sensor. This method comprises the sequential steps of (1) adsorbing transition metal ions onto a solid polymeric support; and (2) complexing a bis(glyoxime) to the adsorbed transition metal ions.

Following are exemplary embodiments of a bis(glyoxime)-transition metal complexes and moisture indicators made therewith according to aspects of the present invention.

Embodiment 1 is a colorimetric moisture-indicating sensor comprising a colorimetric moisture-indicating composition comprising a solid polymeric support, and a bis(glyoxime)-transition metal complex bound to the solid polymeric support, wherein the solid polymeric support is a strong acid cation exchange resin.

.Embodiment 2 is a colorimetric moisture-indicating sensor according to embodiment 1, wherein the sensor has an optical spectrum that changes quantitatively according to the relative humidity within an environment within which the sensor is placed.

Embodiment 3 is a colorimetric moisture-indicating sensor of any of the preceding embodiments, wherein the optical spectrum of the sensor changes reversibly according to the relative humidity within the environment within which the sensor is placed.

Embodiment 4 is a colorimetric moisture-indicating sensor according to any of the preceding embodiments, wherein the transition metal in the bis(glyoxime)-transition metal complex comprises rhodium, iridium, platinum, palladium, gold, nickel, copper, or a combination thereof.

Embodiment 5 is a colorimetric moisture-indicating sensor according to any of the preceding embodiments, wherein the solid polymeric support is prepared from a monomer comprising styrene, derivative of styrene, or(meth)acrylate.

Embodiment 6 is a colorimetric moisture-indicating sensor according to any of the preceding embodiments, wherein the solid polymeric support has sulfonic acid groups.

Embodiment 7 is a colorimetric moisture-indicating sensor according to any of the preceding embodiments, wherein an amount of moisture in contact with the sensor is determined by observing a color of the sensor or by measuring a visible spectroscopic reflection spectrum of the sensor.

Embodiment 8 is a colorimetric moisture-indicating sensor according to any of the preceding embodiments, wherein the bis(glyoxime)-transition metal complex comprises nickel dimethylglyoxime.

Embodiment 9 is a method of detecting moisture comprising sequential steps of (1) providing a colorimetric moisture-indicating sensor comprising a solid polymeric support and a bis(glyoxime)-transition metal complex bound to the solid polymeric support, wherein the solid polymeric support is a strong acid cation exchange resin; and (2) exposing the colorimetric moisture-indicating sensor to a moist atmosphere.

Embodiment 10 is a method according to embodiment 9, further comprising the step of (3) determining a level of moisture in an environment surrounding the sensor based on a color of the sensor.

Embodiment 11 is a method according to any one of embodiments 10-11, wherein determining the level of moisture comprises visually observing the color of the sensor.

Embodiment 12 is a method according to any one of embodiments 10-11, wherein determining the level of moisture comprises measuring a visible reflection or transmission spectra of the sensor.

Embodiment 13 is a method according to any one of embodiments 10-12, wherein the transition metal in the bis(glyoxime)-transition metal complex comprises rhodium, iridium, platinum, palladium, gold, nickel, copper, or a combination thereof.

Embodiment 14 is a method according to any one of embodiments 10-13, wherein the bis(glyoxime)-transition metal complex comprises nickel dimethylglyoxime.

Embodiment 15 is a method according to any one of embodiments 10-14, wherein the solid polymeric support is prepared from a monomer comprising styrene, derivative of styrene, or (meth)acrylate.

Embodiment 16 is a method according to any one of embodiments 10-15, wherein the solid polymeric support has sulfonic acid groups.

Embodiment 17 is a method of making a colorimetric moisture-indicating sensor comprising sequential steps:

(1) adsorbing transition metal ions onto a solid polymeric support; and

(2) complexing a bis(glyoxime) to the adsorbed transition metal ions to form a bis(glyoxime)-transition metal complex;

wherein the solid polymeric support is a strong acid cation exchange resin.

Embodiment 18 is a method according to embodiment 17, wherein the transition metal in the bis(glyoxime)-transition metal complex comprises rhodium, iridium, platinum, palladium, gold, nickel, copper, or a combination thereof.

Embodiment 19 is a method according to any one of embodiments 17-18, wherein the bis(glyoxime)-transition metal complex comprises nickel dimethylglyoxime.

Embodiment 20 is a method according to any one of embodiments 17-19, wherein the solid polymeric support is prepared from a monomer comprising styrene, derivative of styrene, or a (meth)acrylate.

Embodiment 21 is a method according to any one of embodiments 17-20, wherein the solid polymeric support has sulfonic acid groups.

Examples

All percentages and ratios are by weight unless otherwise specified.

The moisture-indicating compositions are shown in these examples as: transition metal/(bis)glyoxime/solid polymeric support (e.g., Ni^{2+}/dimethylglyoxime/(sulfonated, strongly acidic) polymeric resin beads).

As used in these examples, each change in the level of relative humidity indicates a step change in 10% increments, unless specified otherwise.

Test Methods and Preparatory Methods

Humidity Controlled Air

A test assembly was used to humidify and deliver humidified air to a mixing chamber where it was mixed with dry air to provide humidified air controlled to the step changes in percent relative humidity (%RH) detailed in the examples. The controlled humidity air (%RH±1%) was delivered to a test chamber where a moisture indicator was tested.

Air was humidified in a 500 mL 3-neck water jacketed round-bottom flask controlled to 31.5°C with a heating/cooling circulator (Model 1160S from VWR). The flask contained around 250 mL of distilled water. Dry air was flowed through tubing from a flow meter into the inlet neck of the flask to evaporate water. The middle neck was fitted with a thermometer. The exit neck of the flask was connected by tubing to an inlet of a 3-neck flask that served as a mixing chamber. Additional dry air was flowed into the mixing chamber and mixed with the humid air to the desired relative humidity. The humidified air was then flowed into a test chamber. Gas flow regulators (Matheson, Basking Ridge, NJ) were used to control the flow of the air streams through the apparatus at about 7.5 liters/minute. TEFLON tubing was used throughout the system. The humidity and temperature were monitored and recorded with a humidity meter (iTHX-M Humidity Meter, Omega Engineering Inc., Stamford, CT).

The test chamber was prepared with two glass plates (approximately 7.5 cm x 10 cm) separated by two rubber sheets (approximately 7.5 cm x 10 cm x 0.7 cm) that had 2.5 cm x 7.5 cm cutouts in the center for forming a chamber. A 0.6 cm opening on the top glass plate at one end of the chamber was used to deliver controlled humidity air to the test chamber and air flowed out of a second 0.6 cm opening on the other end of chamber to the humidity meter.

Preparation of an Indicator Tape

The moisture-indicating compositions were tested and imaged in the form of an indicator tape. Approximately 20 mg of a moisture-indicating composition was placed on the center of a 1 cm x 9 cm rectangular piece of #1 Whatman filter paper. The moisture-indicating composition was covered by a 1 cm x 3 cm strip of clear adhesive tape (SCOTCH Premium Transparent Film Tape 600 Clear, 3M Company, St. Paul, MN) and the outer edges of the paper were sealed to the tape to encapsulate the moisture-indicating composition to form the indicator tape. The indicator tape was suspended across the opening on the top rubber sheet of the test chamber with the paper side facing the inside of the chamber and the tape side against the top glass plate. Controlled humidity air was flowed into the chamber as detailed above.

Example 1 – Ni^{2+}/dimethylglyoxime/(sulfonated, strongly acidic) Polymeric resin beads

AMBERLYST 15 Ion Exchange Resin (0.10 g, Sigma-Aldrich, St. Louis, MO) was immersed for 15 minutes in 3.25 g of 5 wt% aqueous solution of nickel acetate tetrahydrate (EM Science, Gibbstown, NJ) in a 10 mL glass vial. The beads were then washed with deionized water and the supernatant solution decanted at least 3 times until the supernatant solution was colorless. A basic dimethylglyoxime solution was prepared by mixing 0.12 g of dimethylglyoxime (Mallinckrodt; New York, NY), 11.54 g of 1M aqueous solution of potassium hydroxide (BDH/VWR International, West Chester, PA), and 28.34 g of deionized water. Then 4.93 g of dimethylglyoxime solution was added to the vial of beads and mixed for 60 seconds. The beads were then washed with deionized water and the supernatant solution decanted for at least 3 times until the supernatant was colorless. The wet, dark red beads were then transferred to a small glass Petri dish, and allowed to dry in an oven at 110°C in air for 66 hours. The dried beads had a dark green color. Example 1 shows an unexpectedly clear differentiation in color between the wet and dry states.

Comparative Example 1 – Ni^{2+}/dimethylglyoxime/(carboxylated, weakly acidic) Polymeric resin beads

AMBERLITE IRC-50 C.P. Ion Exchange Resin (0.35 g, Mallinckrodt Chemical Works, St. Louis, MO) was immersed for 15 minutes in 3.80 g of 5 wt% aqueous solution of nickel acetate tetrahydrate (EM Science, Gibbstown, NJ), followed by deionized water washing and decanting cycles (at least 3 times) in a small 10 mL glass vial until the supernatant solution was colorless. After final decanting, 2.51 g of basic dimethylglyoxime solution (Formulation: 0.12 g dimethylglyoxime (Mallinckrodt Chemical Works, New York, NY) + 11.54 g 1M aqueous solution of potassium hydroxide (BDH Chemicals, West Chester, PA) + 28.34 g deionized water) was added to the vial, and the mixture was mixed for 30 seconds before water washing/decant cycles were performed (at least 3 cycles) in small 10 mL glass vial until the supernatant solution was colorless. The wet, bright pink colored solids were then transferred to a small glass Petri dish, and allowed to dry in an oven at 110 °C for 66 hours in air. The dried solids had a red color. While a difference in color could be seen between the wet and dry states of Comparative Example 1, the color differentiation between the wet and dry states of Comparative Example 1 was much less apparent to the human eye than the color differentiation between the wet and dry states of Example 1.

Table 1
Materials for Examples 1-2

Example	Support	Support Type	Wet Color	Dry Color
1	AMBERLYST -15 Ion Exchange Resin	Polymeric (sulfonated, strongly acidic)	Dark Red	Dark green
CE1	AMBERLITE IRC-50 C.P. Ion Exchange Resin,	Polymeric (carboxylated, weakly acidic)	Bright Pink	Red

<u>Example 2 – Indicator Tape</u>

A moisture-indicating tape was prepared, tested, and imaged as described above with the moisture-indicating composition of Example 1. The tape was exposed to increasing humidity levels. The tape was held at each humidity level until the color change had stabilized and no color change was observed for at least 20 minutes. The indicator tape was exposed between 20 to 90 minutes. The temperature in the test chamber was 22.9±0.2°C

The tape changed color at 60~70% RH as shown in Table 2. Then, when the tape was exposed back to RH 0%, the color was changed back to dark green.

Table 2

Ex	Color at varying relative humidity levels								
	0%	10%	20%	30%	40%	50%	60%	70%	80%
2	Dark green	Dark green	Dark green	Dark green	Dark green	Dark green	Dark green-red	Dark red	Dark red

The Example 2 tape was also exposed to RH 0% and 80% alternatively and sequentially. After exposing the tape to RH 0% or 80% for 20 to 60 minutes, the color of indicator was observed. The color changed between dark green at RH 0% and dark red at RH 80% reversibly as shown in Table 3.

Table 3

Ex	Color at a series of relative humidity levels between 0 and 80%				
	1st cycle at RH 0%	1st cycle at RH 80%	2nd cycle at RH 0%	2nd cycle at RH 80%	3rd cycle at RH 0%
2	Dark green	Dark red	Dark green	Dark red	Dark green

What is claimed is:

1. A colorimetric moisture-indicating sensor comprising a colorimetric moisture-indicating composition comprising:

a solid polymeric support; and

a bis(glyoxime)-transition metal complex bound to the solid polymeric support,

wherein the solid polymeric support is a strong acid cation exchange resin.

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2. A colorimetric moisture-indicating sensor according to claim 1, wherein the sensor has an optical spectrum that changes quantitatively according to a relative humidity within an environment within which the sensor is placed.

3. A colorimetric moisture-indicating sensor according to any of the preceding claims, wherein the optical spectrum of the sensor changes reversibly according to the relative humidity within the environment within which the sensor is placed.

4. A colorimetric moisture-indicating sensor according to any of the preceding claims, wherein the transition metal in the bis(glyoxime)-transition metal complex comprises rhodium, iridium, platinum, palladium, gold, nickel, copper, or a combination thereof.

5. A colorimetric moisture-indicating sensor according to any of the preceding claims, wherein the solid polymeric support is prepared from a monomer comprising styrene, derivatives of styrene, or (meth)acrylate.

6. A colorimetric moisture-indicating sensor according to any of the preceding claims, wherein the solid polymeric support has sulfonic acid groups.

7. A colorimetric moisture-indicating sensor according to any of the preceding claims, wherein an amount of moisture in contact with the sensor is determined by observing a color of the sensor or by measuring a visible spectroscopic reflection spectrum of the sensor.

8. A colorimetric moisture-indicating sensor according to any of the preceding claims, wherein the bis(glyoxime)-transition metal complex comprises nickel dimethylglyoxime.

9. A method of detecting moisture comprising sequential steps:

(1) providing a colorimetric moisture-indicating sensor comprising:

a solid polymeric support; and

a bis(glyoxime)-transition metal complex bound to the solid polymeric support, wherein the solid polymeric support is a strong acid cation exchange resin; and

(2) exposing the colorimetric moisture-indicating sensor to a moist atmosphere.

10. A method according to claim 9, further comprising the step:

(3) determining a level of moisture in an environment surrounding the sensor based on a color of the sensor.

11. A method according to any one of claims 10-11, wherein determining the level of moisture comprises visually observing the color of the sensor.

12. A method according to any one of claims 10-11, wherein determining the level of moisture comprises measuring a visible reflection or transmission spectra of the sensor.

13. A method according to any one of claims 10-12, wherein the transition metal in the bis(glyoxime)-transition metal complex comprises rhodium, iridium, platinum, palladium, gold, nickel, copper, or a combination thereof.

14. A method according to any one of claims 10-13, wherein the bis(glyoxime)-transition metal complex comprises nickel dimethylglyoxime.

15. A method according to any one of claims 10-14, wherein the solid polymeric support is prepared from the group a monomer comprising styrene, derivatives of styrene, or (meth)acrylate.

16. A method according to any one of claims 10-15, wherein the solid polymeric support has sulfonic acid groups.

17. A method of making a colorimetric moisture-indicating sensor comprising sequential steps:

(1) adsorbing transition metal ions onto a solid polymeric support; and

(2) complexing a bis(glyoxime) to the adsorbed transition metal ions to form a bis(glyoxime)-transition metal complex;

wherein the solid polymeric support is a strong acid cation exchange resin.

18. A method according to claim 17, wherein the transition metal in the bis(glyoxime)-transition metal complex comprises rhodium, iridium, platinum, palladium, gold, nickel, copper, or a combination thereof.

19. A method according to any one of claims 17-18, wherein the bis(glyoxime)-transition metal complex comprises nickel dimethylglyoxime.

20. A method according to any one of claims 17-19, wherein the solid polymeric support is prepared from a monomer comprising styrene, derivatives of styrene, or (meth)acrylate.

21. A method according to any one of claims 17-20, wherein the solid polymeric support has sulfonic acid groups.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/065022

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N31/22 G01N21/78
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)
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, BIOSIS, EMBASE, FSTA, INSPEC, MEDLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	column 16, line 20 - column 17, line 3 table 1 claims 1-5 claims 11,24 -----	17-21
Y	WO 2004/099754 A2 (NORTHERN ILLINOIS UNIVERSITY [US]; LIN CHHIU-TSU [US]) 18 November 2004 (2004-11-18)	1-16
A	page 7, line 3 - page 8, line 3 page 10, lines 4-20 example 1 page 16, lines 19-32; table 1 claims 1-4 claim 8 -----	17-21
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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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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Michalitsch, Richard

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 2008/163673 A1 (ATTAR AMIR J [US] ET AL) 10 July 2008 (2008-07-10) example 1	17-21
E	WO 2012/154314 A1 (3M INNOVATIVE PROPERTIES CO [US]; HAJIME EVAN KOON LUN YUUJI [US]; KAN) 15 November 2012 (2012-11-15) the whole document	1-21

INTERNATIONAL SEARCH REPORT

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International application No
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