



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2681913 C 2014/01/07

(11)(21) **2 681 913**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 2008/02/11
(87) Date publication PCT/PCT Publication Date: 2008/09/04
(45) Date de délivrance/Issue Date: 2014/01/07
(85) Entrée phase nationale/National Entry: 2009/09/24
(86) N° demande PCT/PCT Application No.: US 2008/053542
(87) N° publication PCT/PCT Publication No.: 2008/106300
(30) Priorité/Priority: 2007/02/26 (US11/679,058)

(51) Cl.Int./Int.Cl. *C01G 23/00* (2006.01)

(72) Inventeur/Inventor:
TUCKER II, GARY D., US

(73) Propriétaire/Owner:
ENVONT LLC, US

(74) Agent: SMART & BIGGAR

(54) Titre : PROCESSUS DE FABRICATION DE MATERIAUX PHOTOCATALYTIQUES
(54) Title: PROCESS FOR MAKING PHOTOCATALYTIC MATERIALS

(57) **Abrégé/Abstract:**

A method of making amorphous metal peroxide solution includes mixing hydrogen peroxide and an amorphous metal hydroxide mixture to form a hydrogen peroxide and amorphous metal hydroxide mixture, and simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal hydroxide mixture for a period of time to form the amorphous metal peroxide solution.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
4 September 2008 (04.09.2008)

PCT

(10) International Publication Number
WO 2008/106300 A3

(51) International Patent Classification:
C01G 23/00 (2006.01)

(21) International Application Number:
PCT/US2008/053542

(22) International Filing Date:
11 February 2008 (11.02.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/679,058 26 February 2007 (26.02.2007) US

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:
US 11/679,058 (CON)
Filed on 26 February 2007 (26.02.2007)

(71) Applicant (for all designated States except US): ENVONT LLC [US/US]; 56335 Precision Drive, Chesterfield Township, Michigan 48051 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): TUCKER, Gary D. [US/US]; 61 Teresa Road, Manchester, Connecticut 06040 (US).

(74) Agents: HAYDEN, John F. et al.; Fish & Richardson P.C., P.O. Box 1022, Minneapolis, Minnesota 55440-1022 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:
7 May 2009

(54) Title: PROCESS FOR MAKING PHOTOCATALYTIC MATERIALS

(57) Abstract: A method of making amorphous metal peroxide solution includes mixing hydrogen peroxide and an amorphous metal hydroxide mixture to form a hydrogen peroxide and amorphous metal hydroxide mixture, and simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal hydroxide mixture for a period of time to form the amorphous metal peroxide solution.



WO 2008/106300 A3

54334-1

PROCESS FOR MAKING PHOTOCATALYTIC MATERIALS

TECHNICAL FIELD

This description relates to a process for making metal oxide solutions for
5 photocatalytic materials.

BACKGROUND

Photocatalytic coatings including a photocatalytically active oxide of a transition
metal (MO) or (MO₂) such as titanium oxide (TiO₂) or zirconium oxide (ZrO₂) can be used
10 for producing self-cleaning coatings on a surface such as a glass windows.

SUMMARY

In one general aspect, an amorphous metal peroxide solution is made by mixing
hydrogen peroxide and a prepared amorphous metal hydroxide mixture to form a hydrogen
15 peroxide and amorphous metal hydroxide mixture, and simultaneously heating and applying
pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal
hydroxide mixture for a period of time to form the amorphous metal peroxide solution.

Implementations can include one or more of the following features. For example, the
method can include preparing the amorphous metal hydroxide mixture. The amorphous
20 metal hydroxide mixture can be prepared by mixing aqueous ammonia to a salt solution of
the metal to form an amorphous metal hydroxide, and washing and separating the amorphous
metal hydroxide.

The method can include adding a wetting agent to the hydrogen peroxide and
amorphous metal hydroxide mixture prior to the simultaneous heating and application of
25 pressure to form a hydrogen peroxide/amorphous metal hydroxide/wetting agent mixture.

Simultaneously heating and applying pressure above atmospheric pressure can
include heating the hydrogen peroxide and amorphous metal hydroxide mixture to a
temperature between about 90° C and about 250° C.

The method can include agitating the hydrogen peroxide and amorphous metal
30 hydroxide mixture simultaneously with heating and applying pressure to the hydrogen
peroxide and amorphous metal hydroxide mixture.

The amorphous metal peroxide solution can be amorphous titanium peroxide solution, and the prepared amorphous metal hydroxide mixture can be a prepared amorphous titanium hydroxide mixture. Simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal hydroxide mixture for a period of time can include simultaneously heating to a temperature between about 90° C and about 250° C and applying pressure for about 1 ½ - 2 hours to form the amorphous titanium peroxide solution.

The method can include monitoring a temperature of the hydrogen peroxide and amorphous metal hydroxide mixture while simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal hydroxide mixture for a period of time. The method can include monitoring a pH level of the hydrogen peroxide and amorphous metal hydroxide mixture while simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal hydroxide mixture for a period of time.

In another general aspect, a method of making amorphous metal peroxide solution includes mixing hydrogen peroxide, a prepared amorphous metal hydroxide mixture, and a wetting agent to form a hydrogen peroxide/amorphous metal hydroxide/wetting agent mixture, and treating the hydrogen peroxide/amorphous metal hydroxide/wetting agent mixture to form the amorphous metal peroxide solution.

Implementations can include one or more of the following features. For example, treating the hydrogen peroxide/amorphous metal hydroxide/wetting agent mixture can include simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide/amorphous metal hydroxide/wetting agent mixture for a period of time to form the amorphous metal peroxide solution.

The method can include agitating the hydrogen peroxide/amorphous metal hydroxide/wetting agent mixture simultaneously with heating and applying pressure. The method can include preparing the amorphous metal hydroxide mixture.

The amorphous metal hydroxide mixture can be prepared by mixing aqueous ammonia to a salt solution of the metal to form an amorphous metal hydroxide, and washing and separating the amorphous metal hydroxide.

The amorphous metal peroxide solution can be amorphous titanium peroxide solution, and the prepared amorphous metal hydroxide mixture can be a prepared amorphous

titanium hydroxide mixture. Simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide/amorphous metal hydroxide/wetting agent mixture for a period of time to form the amorphous metal peroxide solution can include simultaneously heating to a temperature between about 90° C and about 250° C and applying pressure for about 1 ½ - 2 hours to form the amorphous titanium peroxide solution.

In another general aspect, a method of making anatase metal oxide solution includes preparing amorphous metal peroxide solution, and simultaneously heating and applying pressure above atmospheric pressure to the prepared amorphous metal peroxide solution for a period of time to form the anatase metal oxide solution.

Implementations can include one or more of the following features. For example, preparing the amorphous metal peroxide solution can be prepared by mixing hydrogen peroxide and a prepared amorphous metal hydroxide mixture to form a hydrogen peroxide and amorphous metal hydroxide mixture, and simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal hydroxide mixture for a period of time to form the amorphous metal peroxide solution.

The method can include preparing the amorphous metal hydroxide solution.

Preparing the amorphous metal peroxide solution can include preparing an amorphous metal hydroxide mixture, mixing hydrogen peroxide and the prepared amorphous metal hydroxide to form a hydrogen peroxide and amorphous metal hydroxide mixture, and treating the hydrogen peroxide and amorphous metal hydroxide mixture to form the amorphous metal peroxide solution. Treating the hydrogen peroxide and amorphous metal hydroxide mixture can include simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal hydroxide mixture for a period of time to form the amorphous metal peroxide solution. The method can also include adding a wetting agent to the hydrogen peroxide and amorphous metal hydroxide mixture prior to treating. Treating the hydrogen peroxide and amorphous metal hydroxide mixture can include simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal hydroxide mixture for a period of time to form the amorphous metal peroxide solution.

The amorphous metal peroxide solution can be an amorphous titanium peroxide solution, and the anatase metal oxide solution can be anatase titanium oxide solution.

Simultaneously heating and applying pressure above atmospheric pressure to the prepared amorphous titanium peroxide solution for a period of time to form the anatase titanium oxide solution can include heating the prepared amorphous titanium peroxide solution to a temperature between about 90° C and about 250° C under the applied pressure until the anatase titanium oxide solution is formed.

In another general aspect, a method of applying an anatase metal oxide solution to a substrate includes making an amorphous metal peroxide solution, forming an anatase metal oxide solution from the amorphous metal peroxide solution, and applying the anatase metal oxide solution to the substrate. The amorphous metal peroxide solution is made by simultaneously heating and applying pressure above atmospheric pressure to a hydrogen peroxide and amorphous metal hydroxide mixture for a period of time to form the amorphous metal peroxide solution.

Implementations can include one or more of the following features. For example, the anatase metal oxide solution can be applied to the substrate by applying the anatase metal oxide solution as a coating to a surface of the substrate. The anatase metal oxide solution can be applied to the substrate by integrating the anatase metal oxide solution within the substrate. Integrating the anatase metal oxide solution within the substrate can include dispersing the anatase metal oxide solution within the substrate such that the anatase metal oxide solution is distributed throughout the substrate.

The time it takes to produce the amorphous metal peroxide solution is reduced because the mixture of the hydrogen peroxide and the metal hydroxide is heated simultaneously with being pressurized. The reaction does not need to be kept cool and therefore does not need to be slowly and carefully warmed up to ensure that the pH rises slowly and stably enough from the cool temperature.

Similarly, the time it takes to produce the anatase metal oxide solution is reduced because the amorphous metal peroxide solution is heated simultaneously with being pressurized. Time can be reduced to about 3 hours.

Because the wetting agent is introduced to the amorphous metal hydroxide and hydrogen peroxide mixture prior to heating and pressurizing of the mixture, the amorphous metal peroxide solution is more homogenous and therefore provides a better film or coating former. Additionally, the amorphous metal peroxide solution produced in this manner (that is, with the early introduction of the wetting agent) does not need to be intermittently shaken

54334-1

or agitated after formation to maintain its homogeneity. Moreover, the amorphous metal peroxide solution can be applied as a thinner coating at 12 to 18 micron droplets at ranges from 100 nm and higher film thickness regardless of the spray apparatus and the spray application parameters. Moreover, a special apparatus is not needed to apply the amorphous metal peroxide solution to obtain a coating having a thickness of at least 100 nm.

Additionally, because the time needed to complete the reactions involved in forming the solutions is reduced, the cost for producing the amorphous metal peroxide solution and the anatase metal oxide solution is also reduced.

DETAILED DESCRIPTION

When a metal oxide such as anatase titanium oxide TiO_2 is illuminated by ultraviolet light having a wavelength below about 390 nm, electrons in the valence band are excited to the conduction band leaving behind positively-charged holes that are reactive with absorbed water vapor hydroxide ions, resulting in the formation of positively-charged hydroxyl radicals. The hydroxyl radicals are strong oxidizing radicals that can react with and strip electrons from the organic pollutants to produce simpler, non-offensive products such as CO_2 and H_2O . Because of these properties, anatase titanium oxide is used in photocatalytic coatings that are applied to surfaces to react with and decompose the organic pollutants deposited upon the surface from the environment under the effects of exposure to sunlight, and in particular, to ultraviolet radiation. The non-offensive products produced on the

54334-1

surface from the reaction with the anatase titanium oxide can re-enter the atmosphere or wash away under the effects of heat, wind, or rain.

In one aspect of the present invention a procedure (the first procedure) is performed for producing an anatase metal oxide solution.

5 The first procedure comprises the following steps:

- a) make amorphous metal peroxide solution;
- b) make anatase metal oxide solution; and
- c) apply anatase metal oxide solution to surface.

In one implementation, the anatase metal oxide solution is a titanium oxide
 10 TiO₂ mixture. Other types of metal oxide solution that can be produced using the procedure
 100 include, for example, ZrO₂, ZnO, SrTiO₃, CdS, CdO, CaP, InP, In₂O₃, CaAs, BaTiO₃,
 K₂NbO₃, Fe₂O₃, Ta₂O₅, WO₃, SnO₂, Bi₂O₃, NiO, Cu₂O, SiC, SiO₂, MoS₂, MoS₃, InPb, RuO₂,
 CeO₂, and the like. The anatase metal oxide solution can be a sol or a powder. The produced
 anatase metal oxide solution can be used as a photocatalytic material that can be applied as a
 15 coating to many different kinds of substrate surfaces and/or can be integrated within many
 different kinds of substrates. Integration within a substrate includes dispersion of the
 photocatalytic material within the substrate such that the photocatalytic material is distributed
 more or less evenly throughout the substrate. For example, if the substrate is cement, the
 photocatalytic material can be mixed into the dry cement before liquid is added to the cement.
 20 As another example, the photocatalytic material can be mixed into the molten material that
 will form glass prior to cooling so that the photocatalytic material is dispersed within the
 glass.

Examples of substrates include metals, glass, polymeric materials, textiles,
 building materials such as concrete and vinyl, ceramics, pigments and fillers, fiber materials,
 25 electronics, carbon, graphite, plastics, resin materials, inorganic materials, organic materials,
 wood, paper, waste, skin, hair, and in particular, substrates and surfaces such as surgical steel,

54334-1

stainless steel, medical devices, Delrin® acetal resin, Kevlar® brand fiber, polycarbonate, fiberglass, cement, and anodized aluminum.

Initially, an amorphous metal peroxide solution is prepared (first procedure, step a). The amorphous metal peroxide solution is a metal peroxide solution that is
5 amorphous (that is, non-crystalline). The amorphous metal peroxide solution is typically not photocatalytic, but is used as a precursor to produce the photocatalytic anatase metal oxide solution, as will be described later. The amorphous metal peroxide solution can be stored at room temperatures over a long time for use later, and the solution will not form the photocatalytic anatase metal oxide solution unless treated, as further discussed below. The
10 amorphous metal peroxide solution can be applied to a surface, and then later treated to form the photocatalytic anatase metal oxide solution. The anatase metal oxide solution is prepared using the amorphous metal peroxide solution (first procedure, step b). Next, the anatase metal oxide solution can be applied (by, for example, coating, spraying, or drying) to any suitable surface as a photocatalytically-active metal oxide (first procedure, step c). Each of these steps
15 is described in greater detail below with reference to a second, third and fourth procedure.

In a second aspect of the invention, in one implementation, a procedure (the second procedure) is performed for preparing the amorphous metal peroxide solution (first procedure, step a).

The second procedure comprises the following steps:

- 20 a) prepare amorphous metal hydroxide mixture;
- b) mix H_2O_2 and prepared amorphous metal hydroxide mixture;
- c) optionally add wetting agent to mixture;
- d) heat mixture under pressure for a period of time to form amorphous metal peroxide solution; and
- 25 e) allow amorphous metal peroxide solution to cool to room temperature.

54334-1

Initially in the second procedure an amorphous metal hydroxide mixture is prepared (second procedure, step a).

In a third aspect of the invention, a procedure (the third procedure) can be performed to prepare the amorphous metal hydroxide mixture.

5 The third procedure comprises the following steps:

a) mix aqueous ammonia with salt solution to form amorphous metal hydroxide mixture; and

b) wash and separate amorphous metal hydroxide mixture.

Initially, an alkali hydroxide (such as aqueous ammonia or sodium hydroxide) is added to an aqueous solution of a salt including the metal to form a metal hydroxide (third procedure, step a). Agitation can be applied during the mixing of the two components. For example, if the metal is titanium, then the salt solution can be titanium tetrachloride TiCl_4 (which can be purchased, for example, from Alfa Aesar) and the aqueous ammonia can be a solution of ammonium hydroxide NH_4OH (which can be purchased, for example, from Alfa Aesar). In this example, HCl (36-38%) is mixed into distilled or deionized water H_2O at a ratio of 1:10; TiCl_4 (98%) is mixed into the distilled or deionized $\text{H}_2\text{O}/\text{HCl}$ solution at a ratio of 1:25 to form a TiCl_4 dilution; NH_4OH (28-30%) is mixed into distilled or deionized H_2O at a ratio of 1:10 to form a NH_4OH dilution; and the TiCl_4 dilution is mixed into the NH_4OH dilution by volume of 7:1 for pH neutralization to form the titanium hydroxide $\text{Ti}(\text{OH})_4$. Neutralization is finished once the pH of the mixture is adjusted to 7.2-7.5. The pH of the mixture is adjusted by adjusting the relative amounts of components of the mixture and the pH can be checked, for example, with a pH meter. At this point, the amorphous metal hydroxide mixture can be allowed to stand for a while and any supernatant liquid can be discarded.

25 Next, the amorphous metal hydroxide mixture is washed (for example, by decantation or filtration) and separated from the chlorine ions in the mixture (third procedure, step b). The metal hydroxide mixture can be washed and separated by adding distilled water

54334-1

to the mixture, applying sufficient agitation to the mixture, allowing the mixture to stand, and discarding any supernatant liquid. Washing is repeated until little or no chlorine ions are detected in the supernatant liquid (for example, by using silver nitrate to measure levels of chlorine ions in the supernatant liquid or by using a chlorine ion probe). In some

- 5 implementations, washing can be repeated until the amount of chlorine ions in the supernatant liquid is less

54334-1

than about 5 parts per million (ppm). In some cases, the mixture also can be subjected to centrifugal dehydration.

Additionally, water can be re-added to the mixture at this step or at later steps in suitable amounts to adjust the density of the mixture (the density being related to the amount of solid dispersed within the water). The density of the mixture can be adjusted depending on the surface or substrate to which the solution will be applied. For example, for porous or absorbent surfaces or substrates such as concrete, the density of the mixture can be relatively higher and for non-porous or non-absorbent surfaces or substrates such as glass, the density of the mixture can be relatively lower. The density of the mixture can impact the response time of the photocatalytic reaction. As the density of the mixture goes up, the thickness of the film build goes up.

Referring again to the second procedure, next, hydrogen peroxide H_2O_2 (30%) is added at a ratio of 1:14 to the amorphous metal hydroxide mixture (second procedure, step b). A wetting agent or combination of agents can be added to the mixture at this time (second procedure, step c). The wetting agent can be used to alleviate the non-wettability or hydrophobic nature of the metal peroxide mixture that will be formed in the next step. In this way, a thinner film of the metal peroxide mixture can be applied to a surface. Thinner films have reduced yellow appearance and reduced moiré patterns, and reduced cure times. In one implementation in which the amorphous metal hydroxide mixture is a titanium hydroxide mixture, the wetting agent is a polyethylene oxide silane. In other implementations, the wetting agent can be isopropyl alcohol (IPA). The amount of wetting agent added to the mixture can be adjusted depending on the type of substrate or surface to which the ultimate solution will be applied and depending on the metal used in the solution. For example, as little as 0.005% (per volume of mixture) of wetting agent can be added to the mixture for applications in which the substrate or surface is highly water absorbent (for example, for concrete). As another example, as much as 0.03% (per volume of mixture) of wetting agent be added to the mixture for applications in which the substrate or surface that has a low surface tension or is highly water repellant (for example, for glass or polished metals).

Next, the mixture of the wetting agent, the hydrogen peroxide, and the metal hydroxide is heated simultaneously with being pressurized to a pressure that is above atmospheric pressure in combination with a suitable level of agitation for a suitable period of time until the amorphous metal peroxide solution is formed (second procedure, step d). Atmospheric

54334-1

pressure is the pressure at any point in the atmosphere local to the mixture due solely to the weight of the atmospheric gases above the mixture. The temperature at which the mixture is heated can depend on several factors, including the type of metal used in the mixture and constraints associated with manufacturing (for example, if the temperature needs to be
5 lowered due to manufacturing limitations, then the time can be increased by a suitable amount). For example, a mixture of titanium hydroxide and hydrogen peroxide having a volume of about 2 liters can be heated to between about 90°C to about 250°C for about 1½ to 2 hours at 10 to 100 pounds per square inch (psi). For larger volumes of the mixture, for example, as used in manufacturing, the pressure can be suitably higher, for example, up to
10 2500 psi.

The level of agitation can be any level that provides enough agitation to disassociate the ions of the mixture and form the amorphous metal peroxide mixture. For example, the level of agitation can be between about 500 to about 10,000 rotations per minute (rpm) depending on the volume of the mixture. In some implementations, the level of
15 agitation is between about 2500 to about 7000 rpm. During the heating and pressure application step, the mixture is monitored for temperature and pH levels to ensure that the mixture results in a completed solution in which the components (that is, the wetting agent, the hydrogen peroxide, and the metal hydroxide) are uniformly distributed throughout the mixture and to avoid forming a coagulated mixture.

20 After the amorphous metal peroxide solution is formed (second procedure, step d), it is allowed to cool to room temperature (second procedure, step e). The time to cool the solution can vary depending on the quantity of solution formed, the temperature at which the mixture was heated, and the metal used in the metal hydroxide. In some implementations, cooling can take between one to several hours.

25 The amorphous metal peroxide solution that is made (first procedure, step a) has about a 95-97% light transmissiveness. Thus, it appears clear to the human eye. Moreover, the density of the solution (that is, the amount of solid dispersed in solution) can be anywhere between 0.5 to about 2.0%, depending on the application in which the solution will be used.

54334-1

Referring again to the first procedure, after the amorphous metal peroxide solution is made (first procedure, step a), the anatase metal oxide solution is made from the amorphous metal peroxide solution (first procedure, step b). To make the anatase metal oxide solution, the amorphous metal peroxide solution is heated under a pressure that is above
5 atmospheric pressure for a period of time until anatase metal oxide solution is formed. Agitation can be applied to the solution during the heating and pressure application. In particular, as the metal peroxide solution is heated, the peroxide begins to break down and the metal oxide units are allowed to combine into their natural crystalline states. The levels of the temperature and pressure can be adjusted depending on the quantity of solution and the type
10 of metal in the solution. For example, 1-5 liters of amorphous titanium peroxide can be heated to between about 90°C to about 250°C under 10-100 psi of pressure for about 3 hours until anatase metal oxide solution is formed. As the amorphous titanium peroxide is heated under pressure, it turns a clear transparent and becomes crystallized to form the anatase metal oxide solution. Anatase particles of titanium oxide can be formed in the range of 1-7 nm.

15 For a density of about 1.2-1.5% anatase metal oxide, the anatase metal oxide solution can have a light transmissiveness of about 87-93% and the solution appears clear to the human eye, and the human eye would be unable to detect yellow within the solution. In some implementation, the density of the anatase metal oxide solution (that is, the amount of solid dispersed in solution) can be anywhere between 0.5 to about 2.0%, depending on the
20 application in which the solution will be used.

In a forth aspect of the invention, in another implementation, a procedure (the fourth procedure) can be performed for making the amorphous metal peroxide solution (at step of the first procedure).

The fourth procedure comprises the following steps:

- 25 a) prepare amorphous metal hydroxide mixture;
- b) mix H_2O_2 and prepared amorphous metal hydroxide mixture;
- c) add a wetting agent to the mixture;

54334-1

d) treat mixture for a period of time to form an amorphous metal peroxide solution; and

e) allow the amorphous metal peroxide solution to stabilize at room temperature.

5 Initially, an amorphous metal hydroxide is prepared (fourth procedure, step a) as is described in step a of the second procedure and as detailed in the third procedure. Next, hydrogen peroxide H_2O_2 (30%) is added at a ratio of 1:14 to the amorphous metal hydroxide mixture (fourth procedure, step b). A wetting agent or combination of agents is added to the mixture at this time (fourth procedure, step c). The wetting agent can be used to alleviate the
10 non-wettability or hydrophobic nature of the metal peroxide mixture that will be formed in the next step. In this way, a thinner film of the metal peroxide mixture can be applied to a surface. Thinner films have reduced yellow appearance and reduced moiré patterns, and reduced cure times. In one implementation in which the amorphous metal hydroxide mixture is a titanium hydroxide mixture, the wetting agent is a polyethylene oxide silane. In other implementations,
15 the wetting agent can be IPA. As discussed above, the amount of wetting agent added to the mixture can be adjusted depending on the type of substrate or surface to which the ultimate solution will be applied and depending on the metal used in the solution. For example, as little as 0.005% (per volume of mixture) of wetting agent can be added to the mixture for applications in which the substrate or surface is highly water absorbent (for example, for concrete). As
20 another example, as much as 0.03% (per volume of mixture) of wetting agent be added to the mixture for applications in which the substrate or surface that has a low surface tension or is highly water repellant (for example, for glass or polished metals).

Next, the mixture of the wetting agent, the hydrogen peroxide, and the metal hydroxide is treated for a period of time until amorphous metal peroxide solution is formed
25 (fourth procedure, step d). For example, one way to treat the mixture of the wetting agent, the hydrogen peroxide, and the metal hydroxide is to heat the mixture simultaneously with being pressurized to a pressure that is above atmospheric pressure in combination with a suitable level of agitation for a suitable period of time until the amorphous metal peroxide solution is formed, as described above with respect to step d of the second procedure. Another way to

54334-1

treat the mixture is to cool the mixture to 5°C for about 24 hours while applying agitation, as described in U.S. Patent No. 6,429,169.

- After the amorphous metal peroxide solution is formed (fourth procedure, step d), it is allowed to reach room temperature (fourth procedure, step e) by either cooling
- 5 down or heating up, depending on how the mixture was treated at step d, of the fourth procedure.

What is claimed is:

1. A method of making amorphous metal peroxide solution, the method comprising:
mixing hydrogen peroxide and an amorphous metal hydroxide mixture to form a
hydrogen peroxide and amorphous metal hydroxide mixture; and

5 simultaneously heating and applying pressure above atmospheric pressure to the
hydrogen peroxide and amorphous metal hydroxide mixture for a period of time to form the
amorphous metal peroxide solution.

2. The method of claim 1, further comprising preparing the amorphous metal
10 hydroxide mixture.

3. The method of claim 2, wherein preparing the amorphous metal hydroxide mixture
comprises:

mixing aqueous ammonia to a salt solution of the metal to form an amorphous metal
15 hydroxide; and

washing and separating the amorphous metal hydroxide.

4. The method of claim 1, further comprising adding a wetting agent to the hydrogen
peroxide and amorphous metal hydroxide mixture prior to the simultaneous heating and
20 application of pressure to form a hydrogen peroxide/amorphous metal hydroxide/wetting
agent mixture.

5. The method of claim 1, wherein simultaneously heating and applying pressure
above atmospheric pressure includes heating the hydrogen peroxide and amorphous metal
25 hydroxide mixture to a temperature between about 90° C and about 250° C.

6. The method of claim 1, further comprising agitating the hydrogen peroxide and
amorphous metal hydroxide mixture simultaneously with heating and applying pressure to
the hydrogen peroxide and amorphous metal hydroxide mixture.

7. The method of claim 1, wherein:

the amorphous metal peroxide solution is amorphous titanium peroxide solution;

54334-1

the amorphous metal hydroxide mixture is an amorphous titanium hydroxide mixture;
and

simultaneously heating and applying pressure above atmospheric pressure to the
hydrogen peroxide and amorphous metal hydroxide mixture for a period of time includes
5 simultaneously heating to a temperature between about 90° C and about 250° C and applying
pressure for about 1 ½ - 2 hours to form the amorphous titanium peroxide solution.

8. The method of claim 1, further comprising monitoring a temperature of the
hydrogen peroxide and amorphous metal hydroxide mixture while simultaneously heating
10 and applying pressure above atmospheric pressure to the hydrogen peroxide and amorphous
metal hydroxide mixture for a period of time.

9. The method of claim 1, further comprising monitoring a pH level of the hydrogen
peroxide and amorphous metal hydroxide mixture while simultaneously heating and applying
15 pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal
hydroxide mixture for a period of time.

10. A method of making amorphous metal peroxide solution, the method comprising:
20 mixing hydrogen peroxide, an amorphous metal hydroxide mixture, and a wetting
agent to form a hydrogen peroxide/amorphous metal hydroxide/wetting agent mixture; and
simultaneously heating and applying pressure above atmospheric pressure to the
hydrogen peroxide/amorphous metal hydroxide/wetting agent mixture to form the amorphous
25 metal peroxide solution.

11. The method of claim 10, further comprising agitating the hydrogen peroxide/amorphous
metal hydroxide/wetting agent mixture simultaneously with heating and applying pressure.

54334-1

12. The method of claim 10, further comprising preparing the amorphous metal hydroxide mixture.

5 13. The method of claim 12, wherein preparing the amorphous metal hydroxide mixture comprises:

 mixing aqueous ammonia to a salt solution of the metal to form an amorphous metal hydroxide; and

 washing and separating the amorphous metal hydroxide.

10 14. The method of claim 10, wherein:

 the amorphous metal peroxide solution is amorphous titanium peroxide solution;

 the amorphous metal hydroxide mixture is an amorphous titanium hydroxide mixture;

and

15 simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide/amorphous metal hydroxide/wetting agent mixture for a period of time to form the amorphous metal peroxide solution includes simultaneously heating to a temperature between about 90° C and about 250° C and applying pressure for about 1 ½ - 2 hours to form the amorphous titanium peroxide solution.

20 15. A method of making a photocatalytic anatase metal oxide solution, the method comprising:

 preparing amorphous metal peroxide solution; and

25 simultaneously heating and applying pressure above atmospheric pressure to the prepared amorphous metal peroxide solution for a period of time to form the anatase metal oxide solution.

 16. The method of claim 15, wherein preparing the amorphous metal peroxide solution comprises:

30 mixing hydrogen peroxide and a prepared amorphous metal hydroxide mixture to form a hydrogen peroxide and amorphous metal hydroxide mixture; and

54334-1

simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal hydroxide mixture for a period of time to form the amorphous metal peroxide solution.

5 17. The method of claim 16, further comprising preparing the amorphous metal hydroxide solution.

18. The method of claim 15, wherein preparing the amorphous metal peroxide solution comprises:

10 preparing an amorphous metal hydroxide mixture;
 mixing hydrogen peroxide and the prepared amorphous metal hydroxide to form a hydrogen peroxide and amorphous metal hydroxide mixture; and
 treating the hydrogen peroxide and amorphous metal hydroxide mixture to form the amorphous metal peroxide solution.

15 19. The method of claim 18, wherein treating the hydrogen peroxide and amorphous metal hydroxide mixture comprises simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal hydroxide mixture for a period of time to form the amorphous metal peroxide solution.

20 20. The method of claim 18, further comprising adding a wetting agent to the hydrogen peroxide and amorphous metal hydroxide mixture prior to treating.

21. The method of claim 20, wherein treating the hydrogen peroxide and amorphous metal hydroxide mixture comprises simultaneously heating and applying pressure above atmospheric pressure to the hydrogen peroxide and amorphous metal hydroxide mixture for a period of time to form the amorphous metal peroxide solution.

22. The method of claim 15, wherein:
30 the amorphous metal peroxide solution is an amorphous titanium peroxide solution,
 and
 the anatase metal oxide solution is anatase titanium oxide solution.

54334-1

23. The method of claim 22, wherein simultaneously heating and applying pressure above atmospheric pressure to the prepared amorphous titanium peroxide solution for a period of time to form the anatase titanium oxide solution comprises heating the prepared amorphous titanium peroxide solution to a temperature between about 90° C and about 250° C under the applied pressure until the anatase titanium oxide solution is formed.

24. A method of applying a photocatalytic anatase metal oxide solution to a substrate, the method comprising:

10 making an amorphous metal peroxide solution including simultaneously heating and applying pressure above atmospheric pressure to a hydrogen peroxide and amorphous metal hydroxide mixture for a period of time to form the amorphous metal peroxide solution, forming a photocatalytic anatase metal oxide solution from the amorphous metal peroxide solution, and

15 applying the photocatalytic anatase metal oxide solution to the substrate.

25. The method of claim 24, wherein applying the photocatalytic anatase metal oxide solution to the substrate includes applying the photocatalytic anatase metal oxide solution as a coating to a surface of the substrate.

20

26. The method of claim 24, wherein applying the photocatalytic anatase metal oxide solution to the substrate includes integrating the photocatalytic anatase metal oxide solution within the substrate.

25 27. The method of claim 26, wherein integrating the photocatalytic anatase metal oxide solution within the substrate includes dispersing the photocatalytic anatase metal oxide solution within the substrate such that the anatase metal oxide solution is distributed throughout the substrate.