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(54) **CHLORINE DIOXIDE RELEASING
COMPOSITE ARTICLE**

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(57) **ABSTRACT**

A composite article that includes a ClO₂-producing material integrated into an organic matrix and methods of using the same are described. The organic matrix of the composite article is formable at a temperature under about 150° C., permits contact between an activating stimulus (e.g., water vapor and/or electromagnetic energy) and the ClO₂-producing material when the composite article is exposed to the activating stimulus, and is permeable to ClO₂.

CHLORINE DIOXIDE RELEASING COMPOSITE ARTICLE

FIELD OF THE INVENTION

[0001] This invention relates to a device which will produce chlorine dioxide gas when exposed to an activating stimulus such as ambient humidity or light, and methods of using the same.

BACKGROUND OF THE INVENTION

[0002] The prior art discloses a variety of powdered compositions that produce ClO_2 gas under a variety of conditions. Included in these are materials for the controlled sustained release of ClO_2 (CSR materials), which release ClO_2 when exposed to water vapor. Also included are materials disclosed by which produce ClO_2 when exposed to light.

[0003] It is desirable for ease of use and disposal for such materials to be contained or packaged in a manner that contains the powder in a porous pouch (i.e., a sachet) or for it to be extruded into a polymer matrix film, such as polyethylene. In this manner the user is protected from direct contact with the powder, and spent powder may be more readily removed from the area that was treated.

[0004] Unfortunately, sachets are relatively bulky and expensive to fabricate, and in small sizes are very light and difficult to handle. As a result, the cost of packaging powders in small sachets (less than about 2 grams in size) is often impractically high.

[0005] Extruded polymer sheet material can be relatively less expensive to produce in small sizes, because the sheet may be produced in a large economical size, and then smaller size pieces may be inexpensively cut from the larger sheet. However, due to the low decomposition temperature of the chlorite anion that is incorporated into all ClO_2 producing materials, the extrusion temperature of ClO_2 -releasing polymer sheet must be no higher than about 150-160° C. If the temperature is above that, then the amount of chlorite that is lost by decomposition during extrusion can be unacceptably high. This has limited the choice of polymer matrices to those comprising a substantial amount of relatively low melting, low density polyethylene. But polyethylene is an undesirable matrix material because it is not highly permeable to water vapor used to initiate the release of chlorine dioxide from most chlorine dioxide-releasing materials. Plus the extrusion temperature of polyethylene is about 150 degrees C., so it is right on the borderline where decomposition of chlorite anion can occur. Since chlorite decomposition can lead to explosive oxidation of the polyethylene, such extruded sheet materials typically contain lower concentrations of chlorite anion than many powdered versions. Lower chlorite content, in turn, limits their maximum yield of ClO_2 .

SUMMARY OF THE INVENTION

[0006] Generally, the invention relates to composite articles comprising a material capable of producing ClO_2 upon exposure to an activating stimulus that is integrated into an organic matrix, and methods of using the article. The organic matrix is formable at a temperature below about 150° C., preferably below about 135° C., and most preferably below about 110° C. When the composite article is exposed to an activating stimulus, such as water or light, the organic

matrix permits at least some contact between the ClO_2 -producing material and the activating stimulus, which in turn causes the material to generate ClO_2 . The organic matrix is also permeable to ClO_2 so as to allow at least a portion of ClO_2 generated by the ClO_2 -producing material to escape the composite article. Preferably the article is stable during storage prior to exposure to the stimulus.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0007] The invention relates to a composite article comprising a ClO_2 -producing material integrated into an organic matrix, and methods of using the same.

[0008] The ClO_2 -producing material is any material or combination of materials that is capable of generating ClO_2 upon exposure to some activating stimulus. The activating stimulus may be water vapor, electromagnetic energy, or any other trigger that effects the formation of ClO_2 by the ClO_2 -producing material. Typically, ClO_2 -producing materials comprise a chlorite-containing compound, such as sodium chlorite, and an acidifying agent. Examples of ClO_2 -producing materials are described in U.S. Pat. Nos. 6,294,108 and WO 03/056951 A2, both incorporated herein by reference.

[0009] The organic matrix contains at least one organic material and: a) is formable at temperatures below about 150° C., preferably below about 135° C., more preferably below about 110° C.; b) permits at least some contact between an activating stimulus and the ClO_2 -producing material when the composite article is exposed to the activating stimulus so as to enable generation of ClO_2 ; and c) is permeable to ClO_2 . The low temperature formability of the organic matrix is compatible with temperature-sensitive ClO_2 -producing materials. When exposed to an activating stimulus, the organic matrix allows the activating stimulus to contact an integrated ClO_2 -producing material, and permits the resulting ClO_2 to escape into the space surrounding the article.

[0010] One class of materials that may be suitable for the organic matrix is low melting molecular solids. In particular, low melting hydrophilic molecular solids. Examples of low melting molecular solid materials are polyethylene glycol wax (such as that sold under the trade name CARBOWAX by the Dow Chemical Co.), mixtures of polyethylene glycol wax with paraffin wax, stearic acid, and mixtures of polyethylene glycol wax with stearic acid. An organic matrix comprising only paraffin wax as the organic material is preferably used with a humidity-activated ClO_2 -releasing material and with a pore former incorporated into the formulation to facilitate humidity intrusion.

[0011] Another class of materials suitable for the organic matrix are low melting thermoformable or thermosetting functionalized polymers, such as EVA (ethylene vinyl acetate). These are commonly used in the formulation of hot melt glue products that soften and flow (i.e. can be extruded) at relatively low temperatures. Other hot melt glue type formulations are also satisfactory for this purpose. If ClO_2 release is to be initiated by exposure to light, it is preferred that the matrix material be effectively transparent to the light.

[0012] The composite article may be formed by combining the ClO_2 -releasing material(s) with the organic matrix material(s), heating to a temperature that is below 150° C. to soften or melt the matrix material(s), and extruding the mixture into

rods, sheet, pellets, or the like. Alternatively, the matrix material(s) may be heated to a temperature below 150° C. and softened/melted prior to combination with the ClO₂-producing material.

[0013] Alternatively, the composite article may be formed by casting a mixture into a mold and cooling; by coating a mixture on a flat surface to form a thin sheet (such as by the doctor blade process); or by passing a mixture through the nip space between two rollers to form a sheet. Likewise, any of several other methods known to those in the art may be used to form an article.

[0014] The composite article may contain other constituents that provide desired characteristics. For example, fibrous material may be added to the composite to increase stiffness and strength, or plasticizers may be added to increase flexibility. Pore formers, such as silica gel and diatomaceous earth, may be added to increase the porosity of the article. Increased porosity could facilitate the passage of water vapor into, and/or ClO₂ out of, the article. Coloring and fragrances may be added to enhance aesthetics. Desiccants may be added to limit water exposure during storage.

[0015] The composite article may be used wherever ClO₂ would be desired and exposure to an activating stimulus would occur. Some specific applications include: food shelf-life extension, microbial deterioration protection of good (e.g., shoes) during transportation and/or storage, microbial-resistant packaging, deodorizing devices, and deodorizing coatings.

[0016] A non-limiting example of a preferred embodiment will now be described.

EXAMPLE

[0017] Thirteen point three (13.3) grams of chlorine dioxide releasing powder similar to that described in example 7 of U.S. Pat. No. 6,294,108 was mixed into 20 grams of melted

polyethylene glycol wax (CARBOWAX 4000 brand) at a temperature below 100° C. Five point three (5.3) grams of that mixture was poured into a small aluminum dish to produce a disk approximately 2 inches in diameter and 1/8 inch thick. This disk was tested for the release of chlorine dioxide at 80% relative humidity using the test method described in U.S. Pat. No. 6,294,108, and it produced 5 ppm of ClO₂ at about 20 hours.

What is claimed is:

1. A composite article comprising a ClO₂-producing material integrated into an organic matrix, wherein the ClO₂-producing material releases ClO₂ when contacted by an activating stimulus, and wherein the organic matrix:

- a) is formable at a temperature below about 150° C.;
- b) permits at least some contact between the activating stimulus and the ClO₂-producing material when the composite article is exposed to the activating stimulus; and
- c) is permeable to ClO₂.

2. The composite article of claim 1, wherein the organic matrix is formable at a temperature below about 135° C.

3. The composite article of claim 1, wherein the organic matrix is formable at a temperature below about 110° C.

4. The composite article of claim 1, wherein the activating stimulus is water vapor.

5. The composite article of claim 1, wherein the activating stimulus is electromagnetic energy.

6. A method of producing chlorine dioxide, comprising exposing the composite article of claim 1 to an activating stimulus.

7. The method of claim 6, wherein the activating stimulus is water vapor.

8. The method of claim 7, wherein the activating stimulus is electromagnetic energy.

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