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**SILICATE-CONTAINING POWDERS PROVIDING
CONTROLLED, SUSTAINED GAS RELEASE**

Background of the Invention

The present invention relates generally to a
5 particle, a powder incorporating such particles for
providing sustained release of a gas, and a product such
as a film or coating which incorporates the powder for
sustained gas release. The invention particularly
relates to a silicate particle containing anions capable
10 of reacting with a hydronium ion to generate a gas, and a
powder containing such silicate particles for retarding,
controlling, killing or preventing microbiological
contamination (e.g., bacteria, fungi, viruses, mold
spores, algae, and protozoa), deodorizing, enhancing
15 freshness, and/or retarding, preventing or controlling
chemotaxis by release of a gas or a combination of gases,
such as chlorine dioxide, sulfur dioxide, nitrogen
dioxide, nitric oxide, nitrous oxide, carbon dioxide,
hydrogen sulfide, hydrocyanic acid, dichlorine monoxide,
20 or chlorine.

Chlorine dioxide (ClO_2) is a superior oxidizing agent
widely used as a bleach, disinfectant, fumigant or
deodorizer. It can penetrate the cell wall or membrane
and cytoplasm of mold spores, bacteria and other
25 microbiological contaminants at concentrations below one
part per million and destroy them.

The incorporation of chlorine dioxide or sodium
chlorite in food packaging has prompted studies to
determine whether residual levels of such preservatives
30 result in a significant genetic or carcinogenic hazard to
humans. Meier et al. studied the effect of subchronic
and acute oral administration of chlorine, chlorine
dioxide, sodium chlorite and sodium chlorate on the
induction of chromosomal aberrations and spermhead
35 abnormalities in mice [Environ. Mutagenesis, 7, 201



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sodium chlorite. A polyalcohol humectant and water are encapsulated with the polyanhydride or polyacid in a nylon coating. After sodium chlorite is diffused into the capsule through the nylon wall, an impermeable polystyrene layer is coacervated around the nylon capsule. Solvents are required for reaction and application of the capsules. The capsules can be coated onto surfaces to release chlorine dioxide. Although the capsules are said to provide biocidal action for several days to months, chlorine dioxide release begins immediately after the capsules are prepared. The batchwise process used to prepare the capsules also involves numerous chemical reactions and physical processes, some of which involve environmental disposal problems.

Powders that release chlorine dioxide as soon as they are prepared have been formed by mixing acid solids and chlorite solids. Lovely, U.S. Patent No. 3,591,515 describes a chlorite-containing powder that releases chlorine dioxide upon being admixed with an acid-containing powder. Hartshorn, U.S. Patent No. 4,104,190 describes solid mixtures of sodium chlorite and citric, adipic or malic acid that are compressed to form tablets. Mason et al., U.S. Patent Nos. 4,547,381 and 4,689,169 disclose mixtures of powdered sodium chlorite, acid and inert diluent that release chlorine dioxide without exposing the mixtures to ambient moisture. Tice et al., U.S. Patent No. 4,585,482 describe solid admixtures of sodium chlorite and polylactic acid.

Klatte et al., U.S. Patent Nos. 5,567,405 and 5,573,743, describe zeolite crystals impregnated with sodium chlorite, an acid, sodium sulfite, or sodium bisulfite by immersing the zeolite in an aqueous solution to adsorb anions onto its surface. Chlorine dioxide is said to be generated by passing a fluid containing oxygen

Wellinghoff et al. U.S. Patent No. 5,639,295 describes a method for maximizing chlorine dioxide release from an amine-containing composite by omitting the chlorite source until the composite is applied to a surface. After application, the composite is exposed to chlorine dioxide gas that either reacts with the amine to form iminium chlorite in situ or reacts with the amine to provide chlorite anions. The composite is then activated in the presence of moisture to release chlorine dioxide. The composite can be exposed to elevated temperatures during processing, storage and application before reaction to form iminium chlorite because the hydrophilic material does not contain iminium chlorite or any chlorite anions that could decompose at such temperatures. The method also precludes premature release of chlorine dioxide from the composite.

Barenberg et al. U.S. patent application no. 08/724,907 and Wellinghoff et al. U.S. patent application no. 08/858,860 describe numerous methods of using composites such as those disclosed by Wellinghoff et al. to retard bacterial, fungal, and viral contamination and growth of molds on food, produce, meat, and other materials and to deodorize materials such as textiles and storage spaces.

Wellinghoff et al. U.S. patent application serial no. 08/651,876 describes transparent compositions that provide sustained release of chlorine dioxide.

Wellinghoff et al. U.S. patent application serial no. 08/858,859 discloses powders containing a hydrophilic core, a hydrophobic layer on an outer surface of the hydrophilic core, and particles in contact with the hydrophobic layer. The hydrophobic layer contains an acid releasing agent. The particles contain an anhydrous material capable of binding with water. The core, the particles, and the hydrophobic layer are substantially free of water, and the core is capable of generating and

provision of such a powder that is free-flowing and can be easily blended with other ingredients prior to application; the provision of such a powder that can penetrate porous surfaces; the provision of such a powder or percolation network that increases the release rate of chlorine dioxide or other gas in response to increased levels of temperature and humidity, which promote mold and bacteria growth, so that the gas release does not start until a critical humidity is achieved whose value is determined by the structure of the powder; the provision of such a powder or percolation network that, except for the anions therein for generating the biocidal gas, only contains substances approved for human exposure; the provision of such a powder or percolation network that is odorless; the provision of a process for preparing a powder which requires few reactions or physical processes to provide sustained release of chlorine dioxide or other biocidal gases; the provision of such a process which allows for high temperature processing and application of the powder without thermal decomposition thereof; the provision of such a process which utilizes relatively inexpensive starting materials to minimize applications cost; and the provision of such a process which reduces manufacturing hazards and disposal requirements as compared to most conventional processes for preparing chlorine dioxide releasing powders.

The present invention is directed to a particle containing anions dissolved in an amorphous, paracrystalline or crystalline solid solution. The anions are capable of reacting with hydronium ions to generate a gas.

The particles are prepared by a process including the steps of admixing an amorphous, paracrystalline or crystalline material, a solvent, and a chlorite, bisulfite, sulfite, hydrosulfide, nitrite, hypochlorite,

and a second layer between the core and the first layer. The second layer contains a silicate. The core and the first and second layers are substantially free of water. The second layer is substantially water-insoluble, and
5 the core is capable of generating and releasing a gas after hydrolysis of the acid releasing agent.

The present invention is also directed to a powder for sustained release of a gas, wherein the powder includes a core containing a silicate and anions that are
10 capable of reacting with hydronium ions to generate a gas, and a layer on the outer surface of the core. The layer contains an acid releasing agent and a silicate. The core and the layer are substantially free of water, the layer is substantially water-insoluble, and the core
15 is capable of generating and releasing a gas after hydrolysis of the acid releasing agent.

Another aspect of the invention is directed to a composition comprising a hydrophobic phase and a hydrophilic phase containing a percolation agent and a
20 gas-generating agent, such as any of the powders described above. The composition is a co-continuous network or a discontinuous network which contains passages formed by the percolation agent. The passages are capable of transmitting moisture to the gas-
25 generating material to generate and release a gas.

The powders are prepared by admixing particles containing a silicate and anions that are capable of reacting with hydronium ions to generate a gas with a solvent to form a slurry, admixing a zinc, magnesium,
30 calcium, aluminum or other monovalent, divalent or multivalent salt and an acid releasing agent with the slurry to form a solids-containing suspension, and forming a powder from the solids-containing suspension. The powder is substantially free of water and capable of
35 generating and releasing the gas after hydrolysis of the acid releasing agent.

hydrophobic material to form a melt, and cooling the melt to form the composition. The composition is a continuous network or a discontinuous network which contains passages formed by the percolation agent. The passages are capable of transmitting moisture to the gas-generating material to generate and release a gas.

Another embodiment of the invention is directed to a method of retarding, killing, preventing or controlling microbiological contamination on a surface of a material, within the material or in the atmosphere surrounding the material, by exposing a surface of a material to the powder, and exposing the surface to moisture to generate and release a biocidal gas from the powder into the atmosphere surrounding the surface.

The invention is also directed to a method of retarding, killing, preventing or controlling microbiological contamination on a surface of a material, within the material or in the atmosphere surrounding the material, by placing a material adjacent the powder, and exposing the powder to moisture to release a biocidal gas from the powder into the atmosphere surrounding the material.

The invention is also directed to a method of retarding, preventing or controlling biochemical decomposition on a surface of a material or within the material by exposing a surface of a material to a powder of the invention, and exposing the surface to moisture to generate and release a biochemical decomposition-inhibiting gas from the powder into the atmosphere surrounding the surface.

Another embodiment of the invention is directed to a method of retarding, preventing or controlling biochemical decomposition on a surface of a material or within the material by placing the material adjacent a powder of the invention, and exposing the powder to moisture to release a biochemical decomposition-

The invention is also directed to a method of retarding, preventing or controlling chemotactic attraction of an organism to a material, by placing a material adjacent the powder, and exposing the powder to
5 moisture to release an odor-masking or odor-neutralizing gas from the powder into the atmosphere surrounding the material.

Other objects and advantages of the invention will be apparent from the following detailed description.
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Brief Description of the Drawings

FIGs. 1a-10b are schematics of particles for providing sustained release of a gas;

FIGs. 11-13 are photomicrographs of silicate
15 particles and powders of the present invention;

FIGs. 14 and 15 are plots of chlorine dioxide concentration and humidity as a function of time for a powder composition;

FIG. 16 is a plot of chlorine dioxide concentration, temperature and humidity as a function of time for a
20 powder composition;

FIG. 17 is a plot of an x-ray diffraction pattern for a powder composition;

FIG. 18 is an exaggerated cross-sectional view of a
25 film composed of a co-continuous network; and

FIG. 19 is an exaggerated cross-sectional view of a film composed of a discontinuous network.

Detailed Description of the Preferred Embodiments

In accordance with the present invention, it has
30 been discovered that anions such as chlorite which are used to generate a gas can be stabilized against thermal decomposition by dispersing the anions in a particle containing an amorphous, paracrystalline or crystalline solid solution via a spray drying process. When the
35 particle is dried to a moisture level of up to about 10

Particles of the Invention

In one embodiment of the invention, a particle is comprised of anions dissolved within an amorphous, paracrystalline or crystalline solid solution. The anions are capable of reacting with hydronium ions to generate a gas. The particle contains one or more phases, which may be amorphous, paracrystalline or crystalline, with the anions dissolved in one or more of the phases. In these phases, the dissolved anions are either randomly distributed (e.g., a solid solution), or distributed in an ordered crystalline lattice in which the anions are substantially prevented from being neighbors. The anions can be an interstitial component of an alloy or other crystalline solid solution, or can be dissolved in a glass or other amorphous or paracrystalline solid solution. A paracrystalline solid solution is generally a material having one or more phases that exhibit some characteristics of a crystalline state as demonstrated, for example, by broadening of the reflections in the x-ray diffraction pattern. The amorphous, paracrystalline or crystalline material is not a zeolite or other material which must be heated at a temperature that would destroy the anions in order to dissolve the anions in the material. Preferably, the particle is comprised of a substantially amorphous silicate. For purposes of the present invention, the term "substantially amorphous" is defined as including no more than 20% crystalline inclusions, preferably no more than 10%, and more preferably no more than 2%.

The silicate particle is preferably in the form of a substantially amorphous silicate matrix in which the anions are uniformly dispersed and encapsulated. The silicate particles generally range in size between about 0.1 and about 1,000 microns depending upon the intended end use, and can be made of any size possible via any solid forming process, but preferably via spray drying.

decompose at a temperature above the decomposition temperature of sodium chlorite, enabling high temperature processing of the particles or powders containing the particles.

5 Preferably, each silicate particle comprises between about 3 wt.% and about 95 wt.% silicate, between about 1 wt.% and about 30 wt.% anions capable of reacting to generate a gas, and up to about 95 wt.% inert core. More preferably, the silicate particle comprises between about
10 4 wt.% and about 95 wt.% silicate, between about 1 wt.% and about 15 wt.% anions capable of reacting to generate a gas, and up to about 95 wt.% inert core.

 The silicate particle is substantially free of water to minimize diffusion of the anions into solution when
15 further processing the particle, such as when the particles are added to an aqueous slurry containing an acid releasing agent to form a powder for sustained release of a gas. For purposes of the present invention, the silicate particle is substantially free of water if
20 the amount of water in the silicate particle does not provide a pathway for transmission of anions from the particle into a solvent. Preferably, each of the silicate particles includes up to about 10 wt.%, preferably up to about 5 wt.% water without providing
25 such a pathway for diffusion from the particle to the solvent.

 Any silicate that is soluble in water or a water solution of a water miscible organic material, such as an alcohol, acetone or dimethylformamide, can be used in the
30 silicate particles of the invention. Suitable silicates include sodium silicate, sodium metasilicate, sodium sesquisilicate, sodium orthosilicate, borosilicates, and aluminosilicates. The ratio of silicon measured as SiO_2 to alkali metal cation measured as M_2O in the silicate
35 particles, wherein M is selected from the group consisting of sodium and potassium, is between about 2.5

ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal cyanide, an alkaline-earth metal cyanide, or a cyanide salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine. Preferred salts include sodium, potassium, calcium, lithium or ammonium salts of a chlorite, bisulfite, sulfite, sulfide, hydrosulfide, bicarbonate, carbonate, hypochlorite, nitrite, or cyanide. Commercially available forms of chlorite and other salts suitable for use, such as Textone (Vulcan Corp.), can contain additional salts and additives such as tin compounds to catalyze conversion to a gas.

The silicate particles optionally contain a base or a filler. The base controls release of gas from the particle by reacting with hydronium ions that diffuse into the particle from an acid releasing layer or interdiffuse into the anion-rich areas of the particle to form a salt. When the base is depleted, excess hydronium ions then react with the anions within the particle to form a gas. The filler controls release of a gas by creating a barrier to diffusion of hydronium ions. The amount of base or filler within the core can be adjusted to alter the time period before gas is released from the particle. For example, the concentration of the base or filler can be increased if a longer delay of gas release is desired. The silicate particle preferably includes a base or filler if chlorite anions are present in the particle to stabilize the chlorite during preparation of the particle or a powder containing the particle.

Any base that reacts with a hydronium ion or any filler can be incorporated in the silicate particle. Suitable bases or fillers include, but are not limited to, an alkali metal bicarbonate such as lithium, sodium, or potassium bicarbonate, an alkali metal carbonate such as lithium, sodium or potassium carbonate, an alkaline-

releasing layer and, optionally, coatings or anhydrous particles that can delay or control generation and release of a gas. A powder including a particle as part of an interpenetrating network is shown in FIGs. 9a-10b.

5 These powders include an interpenetrating network containing a silicate, anions and an acid releasing agent and, optionally, coatings or anhydrous particles that can delay generation and release of a gas. A powder comprised of a single phase solid solution or

10 interpenetrating network can also be prepared without incorporating the particles.

Powders of Coated Silicate Particles

In one embodiment of the invention as shown in FIG. 1a, a powder is comprised of a plurality of particles 10 including a core 12 having an acid releasing layer 14 on

15 an outer surface 16 of the core. The core 12 comprises a particle as described above. The layer 14 includes a silicate and an acid releasing agent. Preferably, the core contains a substantially amorphous silicate, and the

20 silicate in the layer 14 is substantially water-insoluble. Although the layer 14 is preferably continuous and substantially uniform, a particle 10 having a discontinuous layer 14 of variable thickness provides acceptable, sustained release of a gas.

25 FIG. 2a illustrates a more preferred embodiment of the invention wherein a layer 18 containing a substantially water-insoluble silicate is between the core 12 and an acid releasing layer 20, forming a particle 22. The layer 18 minimizes diffusion of the

30 anions into the solution used to prepare the powder, to minimize loss of anions needed to generate a gas. The layer 20 contains an acid releasing agent. Although the layers 18 and 20 are preferably continuous and substantially uniform, a particle 22 having discontinuous

invention for a variety of end uses, including deodorization, freshness enhancement, chemotaxis control, delay or prevention such as reduction of insect infestation, biochemical decomposition control, reduction or prevention, respiration control, and control, delay, destruction or prevention of the growth of microorganisms such as bacteria, molds, fungi, algae, protozoa, and viruses on materials. Although the powders generally provide sustained release of a gas, the powders can be formulated so that gas is released during less than one day if desired for a particular end use.

The powders of the invention can also be prepared to further delay generation of the gas as illustrated in FIGs. 3a-8b. In FIG. 3a, the particle 10 as shown in FIG. 1a is surrounded by a layer 30 containing a hydrophobic, water-soluble, water-degradable or water-swella-
ble material to form a particle 32. In FIG. 4a, the particle 22 of FIG. 2a is surrounded by a layer 30 containing a hydrophobic, water-soluble, water-degradable or water-swella-
ble material to form a particle 34. When the particle 32 or 34 coated with a water-soluble or water-degradable material is exposed to moisture, the water dissolves or degrades the material for a period of up to six months, preferably from several hours to one month, before water contacts the acid releasing agent. When the particle 32 or 34 coated with a water-swella-
ble material is exposed to moisture, the water diffuses into the material and causes the material to expand for a period of up to six months, preferably from several hours to one month, before water contacts the acid releasing agent. Coating the particles 10 or 22 with a hydrophobic material also prolongs the diffusion of water into the acid releasing layer for a period of up to six months, preferably from several hours to one month. Gas release does not occur until enough moisture is transmitted by the hydrophobic layer 30 to provide a pathway for

30 are preferably continuous and substantially uniform, a particle 40 or 44 having discontinuous layers 14 and 30 of variable thickness provides acceptable, sustained release of a gas.

5 FIG. 6a illustrates a particle 46 in which the layer 30 containing the hydrophobic, water-soluble, water-degradable or water-swella-
ble material contacts the outer surface 48 of the layer 18 containing a substantially water-insoluble silicate. The acid releasing layer 20
10 contacts an outer surface 42 of the layer 30 such that the layer 30 separates the coated core from the acid releasing layer 20 and delays diffusion of hydronium ions into the core. In FIG. 6b, the particle 46 of FIG. 6a is contacted with the particles 24 to form a particle 50.
15 The acid releasing layer 20 contains an acid releasing agent, and the particles 24 contain an anhydrous material capable of binding with water. When the acid releasing layer 20 is exposed to moisture, the acid releasing agent is hydrolyzed, releasing acid and hydronium ions which
20 diffuse from the acid releasing layer 20 to the layer 30. The hydronium ions do not diffuse into the layer 18 until enough hydronium ions or moisture are present in the layer 30 to provide a pathway for interdiffusion between the layer 30 and the layer 18. The layer 30 controls the
25 release of gas by prolonging diffusion of hydronium ions into the layer 18 to delay their reaction with anions within the core as described above. Although the layers 18, 20 and 30 are preferably continuous and substantially uniform, a particle 46 or 50 having discontinuous layers
30 18, 20 and 30 of variable thickness provides acceptable, sustained release of a gas.

 In another embodiment illustrated in FIG. 7a, the particle 40 as shown in FIG. 5a is surrounded by an outer layer 30 containing a hydrophobic, water-soluble, water-degradable or water-swella-
35 ble material to form a particle 52. The outer layer 30 controls gas release by delaying

powder. For purposes of the present invention, the layers 14, 18, 20 and 30, and the particles 24 are substantially free of water if the amount of water in the powder does not provide a pathway for transmission of hydronium ions from the layer 14 or 20 to the core 12. Preferably, each of the layers 14, 18, 20 and 30, and the total particles 24 embedded in the outer layer of the particles 10, 22, 32, 34, 36, 38, 40, 44, 46, 50, 52, 54, 56 or 58 can include up to about 10 wt.% water and, more preferably up to about 5 wt.% water, without providing such a pathway for interdiffusion between the core 12 and the acid releasing layer 14 or 20. Insubstantial amounts of water can hydrolyze a portion of the acid releasing agent to produce acid and hydronium ions within the acid-releasing layer. The hydronium ions, however, do not diffuse into the core until enough water is present for transport of hydronium ions.

The powders of the invention can include coatings (i.e., additional layers) between the core 12 and the layers 14 or 20 or between the layers 14 or 20 and the outer surface of the powder so long as the coatings do not completely prevent the diffusion of hydronium ions from the acid-releasing layer 14 or 20 to the core 12 or diffusion of gas from the powder. Although discontinuous layers are acceptable, the additional layers are preferably continuous and substantially uniform. The powders preferably are about 0.1 microns to about 1 millimeter in size.

Powders including an Interpenetrating Network

In another embodiment of the invention as shown in FIG. 9a, a powder is comprised of a plurality of particles 60 containing an interpenetrating network 62. The interpenetrating network contains an amorphous, paracrystalline or crystalline solid solution, anions that are capable of reacting with hydronium ions to

reaction proceeds to completion, or hydronium ions, counterions, acid and water when the reaction is in equilibrium. The hydronium ions diffuse through the interpenetrating network until they contact and react
5 with anions to generate a gas. The gas diffuses out of the particle 60 or 64 into the surrounding atmosphere for a period of up to about six months to affect materials situated near the powder. Powders that release at least about 1.0×10^{-6} gram gas/cm³ for a period of at least one
10 day, one week, one month or six months can be formulated by the processes of the present invention for a variety of end uses, as described herein. Although the powders generally provide sustained release of a gas, the powders can be formulated so that gas is released during less
15 than one day if desired for a particular end use.

The powder can also be prepared to further delay generation of the gas. The particle 60 can be surrounded by a layer 30 containing a hydrophobic, water-soluble, water-degradable or water-swellable material to form a
20 particle 66 as shown in FIG. 10a. When the particle 60 coated with a water-soluble or water-degradable material is exposed to moisture, the water dissolves or degrades the material for a period of up to six months, preferably from several hours to one month, before water contacts
25 the acid releasing agent. When the particle 60 coated with a water-swellable material is exposed to moisture, the water diffuses into the material and causes the material to expand for a period of up to six months, preferably from several hours to one month, before water
30 contacts the acid releasing agent. Coating the particle 60 with a hydrophobic material also prolongs the diffusion of water into the interpenetrating network for a period of up to six months, preferably from several hours to one month. Gas release does not occur until
35 enough moisture is transmitted by the hydrophobic layer 30 to provide a pathway for interdiffusion between the

water-soluble silicate, anions that are capable of reacting with hydronium ions to generate a gas, and an acid releasing agent.

5 The powder can also include particles containing an anhydrous material which contact an outer surface of the particle or are embedded in the particle. The anhydrous material is capable of binding with water.

10 When the powder is exposed to ambient moisture or otherwise contacted with water, the water diffuses into the single phase. If the powder includes the anhydrous particles, the water binds to the anhydrous particles on the outer surface of the powder before diffusing into the single phase. The acid releasing agent within the single phase is either an acid, a substance that can be
15 hydrolyzed to an acid (i.e., a substance that reacts with the water that diffuses into the single phase to form an acid), or a mixture thereof. In either case, the acid in the single phase dissolves in the water that diffuses into the powder, forming hydronium ions and a counterion.
20 The reaction products of this hydrolysis reaction are hydronium ions and counterions when the reaction proceeds to completion, or hydronium ions, counterions, acid and water when the reaction is in equilibrium. The hydronium ions diffuse through the single phase until they contact
25 and react with anions to generate a gas. The gas diffuses out of the powder into the surrounding atmosphere for a period of up to about six months to affect materials situated near the powder. Powders that release at least about 1.0×10^{-6} gram gas/cm³ for a
30 period of at least one day, one week, one month or six months can be formulated by the processes of the present invention for a variety of end uses, as described herein. Although the powders generally provide sustained release of a gas, the powders can be formulated so that gas is
35 released during less than one day if desired for a particular end use.

therein, changing the powder microstructure, substituting alternative hydrophobic materials, anhydrous particles or zinc, magnesium, calcium, aluminum or other monovalent, divalent or multivalent salts, changing the method of processing the powder, or changing the order of addition of ingredients in preparing the powder.

Relative Proportions

Preferably, the powder of FIG. 1a or 1b comprises between about 10 wt.% and about 30 wt.% core, between about 30 wt.% and about 90 wt.% acid releasing layer 14, and up to about 60 wt.% of the particles 24. More preferably, the powder comprises between about 15 wt.% and about 25 wt.% core, between about 50 wt.% and about 85 wt.% acid releasing layer, and up to about 35 wt.% of the particles. In addition to the acid releasing agent, the acid releasing layer 14 may also include between about 2 wt.% and about 20 wt.% substantially insoluble silicate, preferably between about 2 wt.% and about 15 wt.%, and more preferably, between about 2 wt.% and about 10 wt.%.

Preferably, the powder of FIG. 2a or 2b comprises between about 10 wt.% and about 30 wt.% core, between about 2 wt.% and about 70 wt.% silicate-containing layer 18, between about 20 wt.% and about 88 wt.% acid releasing layer 20, and up to about 60 wt.% of the particles 24. More preferably, the powder comprises between about 15 wt.% and about 25 wt.% core, between about 2 wt.% and about 65 wt.% silicate-containing layer 18, between about 25 wt.% and about 80 wt.% acid releasing layer, and up to about 50 wt.% of the particles.

The powders of FIGs. 3a-8b preferably comprise between about 10 wt.% and about 30 wt.% core, between about 2 wt.% and about 70 wt.% silicate-containing layer 18, between about 20 wt.% and about 88 wt.% acid

about 25 wt.% core, between about 25 wt.% and about 35 wt.% acid releasing layer 14, between about 15 wt.% and about 40 wt.% of the particles 24, and between about 10 wt.% and about 35 wt.% hydrophobic, water-soluble, water-degradable or water-swella-
5 ble material in each of the layers 30. The powder of FIG. 8a preferably contains between about 15 wt.% and about 25 wt.% core, between about 2 wt.% and about 10 wt.% silicate-containing layer 18, between about 25 wt.% and about 35 wt.% acid
10 releasing layer 20, and between about 10 wt.% and about 45 wt.% hydrophobic, water-soluble, water-degradable or water-swella- ble material in each of the layers 30. The powder of FIG. 8b preferably comprises between about 15 wt.% and about 25 wt.% core, between about 2 wt.% and
15 about 10 wt.% silicate-containing layer 18, between about 25 wt.% and about 35 wt.% acid releasing layer 20, between about 15 wt.% and about 40 wt.% of the particles 24, and between about 10 wt.% and about 30 wt.%
hydrophobic, water-soluble, water-degradable or water-swella-
20 ble material in each of the layers 30.

When the acid releasing layer contains an inorganic acid releasing agent, the acid releasing layer preferably comprises between about 30 wt.% and 100 wt.% acid
25 releasing agent and up to about 70 wt.% of inert salts such as a sulfate salt.

When the acid releasing layer contains an organic acid releasing agent, the acid releasing layer preferably comprises between about 50 wt.% and 100 wt.% acid
30 releasing agent, up to about 50 wt.% diluent and up to about 20 wt.% dispersant, and, more preferably, between about 35 wt.% and about 65 wt.% acid releasing agent, between about 35 wt.% and about 45 wt.% diluent and
between about 2 wt.% and about 12 wt.% dispersant.

When the powder includes one hydrophobic, water-soluble, water-degradable or water-swella-
35 ble layer 30, the layer 30 preferably contains between about 10 wt.%

comprised of a water-insoluble silicate. More preferably, the powder 60 or 64 comprises between about 40 and 100 wt.% of an interpenetrating network, up to about 50 wt.% hydrophobic, water-soluble, water-degradable or water-swella-
5 ble material, and up to about 50 wt.% of the particles 24.

Preferably, the powder prepared from the single-phase particles comprises between about 30 and 100 wt.% of a single phase comprised of a silicate, an acid
10 releasing agent, and anions capable of reacting to generate a gas, up to about 50 wt.% hydrophobic, water-soluble, water-degradable or water-swella-
ble material, and up to about 60 wt.% of the anhydrous particles. More preferably, the powder comprises between about 40 and 100
15 wt.% of the single phase, up to about 50 wt.% hydrophobic, water-soluble, water-degradable or water-swella-
ble material, and up to about 50 wt.% of the anhydrous particles.

When the powder 60 or 64 or the powder prepared from the single phase particles includes a hydrophobic, water-soluble, water-degradable or water-swella-
20 ble layer 30, the layer 30 preferably contains between about 10 wt.% and 100 wt.% hydrophobic, water-soluble, water-degradable or water-swella-
ble material, up to about 80 wt.% diluent and up to about 20 wt.% dispersant, and, more preferably,
25 between about 40 wt.% and about 90 wt.% hydrophobic, water-soluble, water-degradable or water-swella-
ble material, between about 2 wt.% and about 50 wt.% diluent and between about 2 wt.% and about 15 wt.% dispersant.

30 Gas Generated and Released

The gas released by the powder will depend upon the anions within the core. Any gas that is formed by reaction of a hydronium ion and an anion can be generated and released by the powder. The gas is preferably
35 chlorine dioxide, sulfur dioxide, hydrogen sulfide,

cycles where aluminum or iron powder is used to selectively scrub chlorine from a mixture of chlorine and chlorine dioxide. The powders are also useful in modified atmosphere packaging by placing the powder within a package and sealing the package to create a sulfur dioxide atmosphere within the package.

Hydrogen sulfide is released from a core containing hydrosulfide or sulfide anions. Acceptable sources of hydrosulfide anions include alkali metal hydrosulfides such as sodium hydrosulfide or potassium hydrosulfide, alkaline-earth metal hydrosulfides such as calcium hydrosulfide, or hydrosulfide salts of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine. Acceptable sources of sulfide anions include alkali metal sulfides such as sodium sulfide or potassium sulfide, alkaline-earth metal sulfides such as calcium sulfide, or sulfide salts of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine. Hydrogen sulfide gas-releasing powders can be used as a reducing agent or a sulfur source in the manufacture of chemicals, and as a polymerization inhibitor.

Chlorine gas and dichlorine monoxide are released from a core containing hypochlorite anions. Acceptable sources of hypochlorite anions include alkali metal hypochlorites such as sodium hypochlorite, alkaline-earth metal hypochlorites such as calcium hypochlorite, or hypochlorite salts of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine. Chlorine gas-releasing powders can be used in processing meat, fish and produce and as an insecticide. Dichlorine monoxide releasing powders can be used as a biocide.

Hydrocyanic acid is released from a core if it contains a source of cyanide anions. Suitable sources of cyanide anions include alkali metal cyanides such as

powders can be used to improve biocompatibility of biomaterials and for modified atmosphere packaging.

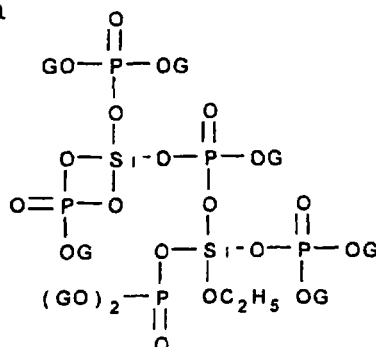
In some instances, powders containing two or more different anions are effective in controlling release of a gas. The powder, for example, can be prepared from silicate particles prepared by admixing a chlorite salt and a bisulfite salt with a solvent and a silicate to form a solution, and spray drying the solution to form the particle. If chlorine dioxide and sulfur dioxide are released in preparing the silicate particles or the powder, the sulfur dioxide reduces the chlorine dioxide to chlorite, controlling release of chlorine dioxide. The presence of bisulfite anions in the silicate particles also delays chlorine dioxide release from the silicate particles or the powder during storage to avoid reaction of chlorine dioxide with powder additives such as fragrances. Powders containing two or more different anions can also release two or more different gases at different rates for different purposes. For example, a powder containing bisulfite and chlorite anions may release sulfur dioxide for food preservation and chlorine dioxide for deodorization, freshness enhancement, control of chemotaxis, or control of microorganisms.

Components

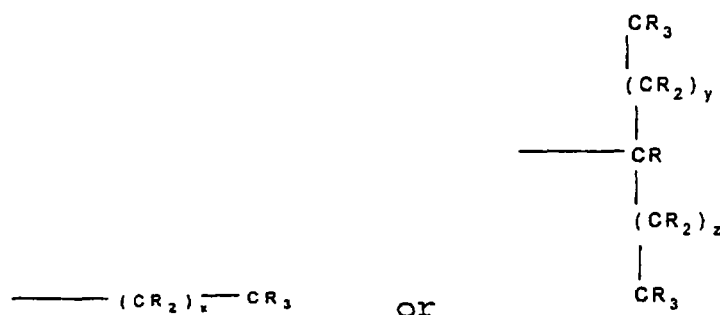
Acid Releasing Agents

Any acid releasing agent that is capable of being hydrolyzed by ambient moisture and adhered onto a particle, incorporated in a coating to be applied to a particle, incorporated into an interpenetrating network containing anions and an amorphous, paracrystalline or crystalline solid solution, or incorporated into a single phase amorphous, paracrystalline or crystalline solid solution containing anions is acceptable for purposes of the present invention. Preferably, the acid releasing agent does not react with the core or solid solution in

agents. Preferred phosphosilicic anhydrides of esters have the formula

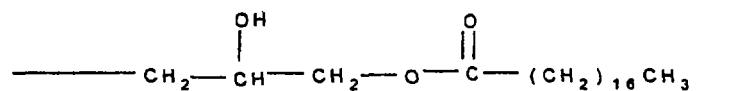


wherein G is a carboxylic acid ester of a polyhydric
 5 alcohol and a C₄ to C₂₇ hydrocarbon, which has the formula

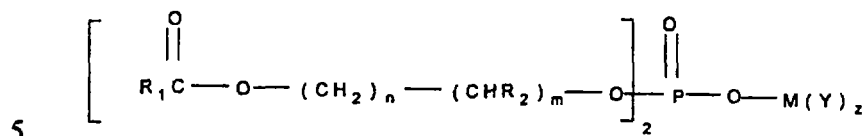
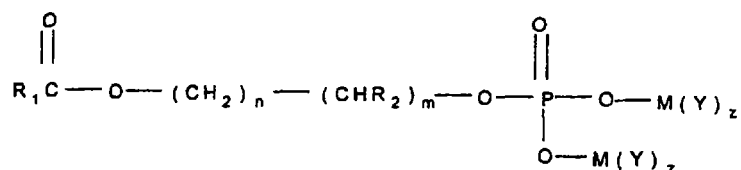


wherein each R is individually selected from hydrogen,
 hydroxy, alkyl, alkenyl, or -OC(O)R'; R' is a C₄ to C₂₇,
 10 alkyl or C₄ to C₂₇ alkenyl; x is an integer from 1 to 30;
 y is an integer from 0 to 30; and z is an integer from 0
 to 30. Particularly preferred phosphosilicic anhydrides
 of polyol based esters include alkylene glycol fatty acid
 ester acid releasing waxes such as propylene glycol

wherein G has the formula

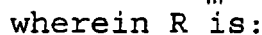


Other preferred acid releasing agents have the formulae:

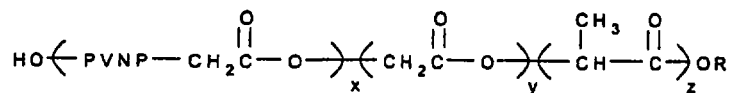


wherein M(Y)_z is an oligomeric radical in which Y is a portion of a multifunctional oxide structure and M is a group IIIA, IVA, or IVB element such as titanium, aluminum, tin, or silicon;; R_1 is an alkyl group; R_2 is methyl, ethyl, propyl, a methyl amido, or an ethyl amido group; m is 0, 1, 2 or 3; n is 0, 1, 2 or 3; and z is 2 or 3.

Acid anhydrides are also preferred acid releasing agents and include organic acid anhydrides, mixed organic acid anhydrides, homopolymers of an organic acid anhydride or a mixed inorganic acid anhydride, and copolymers of an organic acid anhydride or a mixed inorganic acid anhydride with a monomer containing a double bond. Preferred mixed inorganic acid anhydrides contain a phosphorus-oxygen-silicon bond. Preferred



10



have the formula $(\text{NaPO}_3)_n$, wherein n is 3 to 10 for cyclic molecules and n is 3 to 50 for polyphosphate chains.

The preferred phosphosilicic anhydride acid releasing waxes are generally prepared by melting a
5 carboxylic acid ester of a polyhydric alcohol, admixing phosphorus pentoxide into the melt, then admixing a silicate or silane into the melt, and cooling to solidify the resulting acid releasing wax. The carboxylic acid ester of a polyhydric alcohol is preferably a glycerol
10 ester or glycol ester including, for example, an alkylene glycol carboxylate such as propylene glycol monostearate, glycerol monostearate, or glycerol distearate. Propylene glycol monostearate is most preferred because it does not foam excessively or obstruct nozzles or other fluid
15 transport equipment when preparing the acid releasing wax, or the powders or when incorporating the powders into polymer films or other materials as end products. A substance that is capable of reacting with the silicate or silane to form P-O-Si or C(O)-O-Si bonds in the acid
20 releasing wax can be substituted for phosphorus pentoxide, such as monostearyl diethylphosphate. A process for preparing a phosphosilicic anhydride acid releasing wax using monostearyl diethylphosphate can be performed with reference to Ralph Iler, "Chemistry of
25 Silica: Solubility, Polymerization, Colloid and Surface Properties in Biochemistry," J. Wiley & Sons, N.Y., p. 297 (1979). Preferred silicates or silanes include tetraalkoxy silanes such as tetraethyl orthosilicate, and monoalkoxy silanes. The process of preparing the acid
30 releasing waxes is described in copending Wellinghoff et al. U.S. patent application nos. 08/858,860, filed May 19, 1997 entitled "Compositions for Sustained Release of a Gas," and 08/921,357, filed August 29, 1997 entitled "Powders Providing Controlled Sustained Release of a
35 Gas," which are incorporated herein by reference.

than 220°C, and include amides of carboxylates such as amide isostearates, polyvinyl acetates, polyvinyl alcohols, polyvinylpyrrolidone copolymers, polymers of alkylene oxides such as polyglycols, polyols, 5 polyalkylene glycols (e.g., polyethylene glycols, polypropylene glycols, polybutylene glycols), alkoxypolyalkylene glycols such as methoxypolyethylene glycols, trifunctional polyethylene glycols, poly(ethylene-propylene)glycols, metallic, oligomeric or 10 copolymeric olefinic carboxylic acids and/or fatty acids, polyethers, and metal carboxylates such as zinc isostearate, and derivatives (e.g., carboxylic acids such as fatty acids), blends and copolymers thereof. Some acid releasing agents, such as sodium polyphosphate, also 15 act as a dispersant. Dispersants having a melting point greater than 50°C are preferably admixed with the silicate particles before being admixed with the acid releasing agent. Suitable polyvinylpyrrolidone copolymers include copolymers of polyvinylpyrrolidone and 20 hexadecane such as Ganex V-216, and copolymers of polyvinylpyrrolidone and eicosene such as Ganex V-220, which are commercially available from GAF Corp.

**Hydrophobic, Water-Soluble,
Water-Degradable or Water-Swellable Materials**

25 The hydrophobic material of layer 30 is any hydrophobic material that can be applied to the core 12, the layer 14, 18 or 20 or the particle 60 and solidified to form a layer on the core 12, the layer 14, 18 or 20 or the particle 60. Suitable hydrophobic materials are the 30 diluents described above.

Any water-soluble, water-degradable or water-swellable material that can be applied to the core 12, the layer 14, 18 or 20 or the particle 60 and solidified to form a layer on the core 12, the layer 14, 18 or 20 or 35 the particle 60 can be used in the layer 30. Suitable

Anhydrous Particles

The particles 24 embedded in the outer layer of the powder 26, 28, 36, 38, 44, 50, 54, 58 or 64 contain an anhydrous material capable of binding with water. The
5 particles act as moisture scavengers to minimize premature hydrolysis of the acid releasing agent. Suitable anhydrous materials include sodium sulfate, calcium sulfate, calcium carbonate, magnesium sulfate, calcium chloride, moisture-depleted silica gel, alumina,
10 zeolites, clays such as bentonite and kaolin, potassium permanganate, molecular sieves and oxygen-scavenging materials. The anhydrous particles are commercially available from numerous sources. The anhydrous particles are preferably between about 0.1 and about 300 microns in
15 diameter.

The powder may also include conventional ingredients such as fragrances and flow enhancers such as sugars, talc and micronized polymers.

Process for Preparing Particles

20 The particles of the present invention are prepared by admixing an amorphous, paracrystalline or crystalline material, a solvent, a chlorite, bisulfite, sulfite, sulfide, hydrosulfide, nitrite, hypochlorite, or cyanide salt, and optionally, an inert core, to form a solution
25 or suspension, and forming particles containing an amorphous, paracrystalline or crystalline solid solution from the solution or the suspension.

The silicate particles of the present invention are prepared by admixing a silicate, a solvent, a chlorite,
30 bisulfite, sulfite, sulfide, bicarbonate, carbonate, hydrosulfide, nitrite, hypochlorite, or cyanide salt, and optionally, an inert core, to form a solution or a suspension, and forming the particles from the solution or the suspension.

temperature, flow direction in the dryer, or the type of nozzle or atomizer used in the spray drying process, or by changing the composition of the feed materials, such as the particle size, solids concentration, viscosity, surface tension or temperature of the feed solution.

The crystallinity of the silicate particles is altered by changing the silicate used in preparing the particles.

Any silicate that is soluble in water or a water solution of a water miscible organic material can be used in preparing the silicate particles of the invention. Suitable silicates include sodium silicate, sodium metasilicate, sodium sesquisilicate, sodium orthosilicate, borosilicates and aluminosilicates.

Commercially available forms of such silicates suitable for use generally include sodium and potassium cations. The ratio of silicon measured as SiO_2 to alkali metal cation measured as M_2O in the silicate particles, wherein M is selected from the group consisting of sodium and potassium, is between about 2.5 and about 3.5, preferably between about 3.0 and about 3.5, most preferably about 3.2.

Suitable salts used in preparing the silicate particles include an alkali metal chlorite, an alkaline-earth metal chlorite, a chlorite salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal bisulfite, an alkaline-earth metal bisulfite, a bisulfite salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal sulfite, an alkaline-earth metal sulfite, a sulfite salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal sulfide, an alkaline-earth metal sulfide, a sulfide salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary

form a gas. The filler controls release of a gas by creating a barrier to diffusion of hydronium ions. The amount of base or filler within the core can be adjusted to alter the time period before gas is released from the particle. For example, the concentration of the base or filler can be increased if a longer delay of gas release is desired. The silicate particle preferably includes a base or filler if chlorite anions are present in the particle to stabilize the chlorite during preparation of the particle or a powder containing the particle.

Any base that reacts with a hydronium ion or any filler can be incorporated in the silicate particle. Suitable bases or fillers include, but are not limited to, an alkali metal bicarbonate such as lithium, sodium, or potassium bicarbonate, an alkali metal carbonate such as lithium, sodium or potassium carbonate, an alkaline-earth metal bicarbonate, an alkaline-earth metal carbonate such as magnesium or calcium carbonate, a bicarbonate salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine such as ammonium bicarbonate, a carbonate salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal hydroxide such as lithium, sodium or potassium hydroxide, an alkaline-earth metal hydroxide such as calcium or magnesium hydroxide, a hydroxide salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine such as ammonium hydroxide, an alkali metal phosphate such as dibasic or tribasic phosphate salts, an alkaline-earth metal phosphate such as bicalcium or tricalcium phosphate, a phosphate salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal sulfate such as sodium or potassium sulfate, an alkaline-earth metal sulfate such as calcium or magnesium sulfate, a sulfate salt of a transition metal ion, a protonated

When preparing the slurry, ultrasonic mixing, high-shear mixing, or any conventional homogenizing method can be used to slurry the silicate particles. The solvent used to form the slurry is any liquid in which the zinc, magnesium, calcium, aluminum or other monovalent,
5 divalent or multivalent salt is soluble, such as water or a water solution of a water miscible organic material such as an alcohol, acetone or dimethylformamide.

The zinc, magnesium, calcium, aluminum or other
10 monovalent, divalent or multivalent salt and acid releasing agent can be added to the slurry simultaneously, or sequentially (i.e., addition of the zinc, magnesium, calcium, aluminum or other monovalent, divalent or multivalent salt before the acid releasing
15 agent) to form the solids-containing suspension. When addition is simultaneous, a layer 14 containing an insoluble silicate and an acid releasing agent is formed as shown in FIG. 1a, or an interpenetrating network containing an insoluble silicate is formed as shown in
20 FIG. 9a. When the zinc, magnesium, calcium, aluminum or other monovalent, divalent or multivalent salt is added to the slurry before the acid releasing agent, a layer 18 containing an insoluble silicate is formed around the core, or an interpenetrating network containing an
25 insoluble silicate is formed as shown in FIG. 9a. An acid releasing layer 20 adheres to an outer surface of the layer 18 to form the powder 22 as shown in FIG. 2a. The silicate in the layer 14 or 18 or the interpenetrating network is formed by reaction of the
30 zinc, magnesium, calcium, aluminum or other monovalent, divalent or multivalent salt with the silicate in the silicate particles, and is substantially insoluble in the solvent but permeable to water and hydronium ions.

Any soluble zinc, magnesium, calcium, aluminum or
35 other monovalent, divalent or multivalent salt that will react with the silicate in the silicate particles to form

particles 32, 34 or 60 and sintering or by hot spray coating the powder with anhydrous particles suspended in an emulsifier.

5 A powder of particles 40 as shown in FIG. 5a is generally prepared by admixing the core particles with a liquid containing a hydrophobic, water-soluble, water-degradable or water-swella-
ble material to form a slurry, separating coated core particles from the slurry, drying the coated core particles, admixing the coated core
10 particles with a solution containing a zinc, magnesium, calcium, aluminum or other monovalent, divalent or multivalent salt and an acid releasing agent to form a solids-containing suspension, and forming the powder from the solids-containing suspension. A powder of the
15 particles 44 as shown in FIG. 5b can be prepared by admixing anhydrous particles with the powder and sintering or by hot spray coating the powder with anhydrous particles suspended in an emulsifier.

A powder of particles 46 as shown in FIG. 6a is
20 generally prepared by admixing the core particles with a silicate solution to form a dispersion, separating encapsulated core particles from the dispersion, drying the encapsulated core particles, admixing the encapsulated core particles with a liquid containing a
25 hydrophobic, water-soluble, water-degradable or water-swella-
ble material to form a slurry, separating coated core particles from the slurry, drying the coated core particles, admixing the coated core particles with a solution containing an acid releasing agent to form a
30 solids-containing suspension, and forming the powder from the solids-containing suspension. A powder of the particles 50 as shown in FIG. 6b can be prepared by admixing anhydrous particles with the powder and sintering or by hot spray coating the powder with
35 anhydrous particles suspended in an emulsifier.

the product, and fragmenting the product to form the powder. A powder of particles 22 is formed by admixing the core particles with silicate-containing particles, sintering to form encapsulated core particles, admixing
5 the encapsulated core particles with acid releasing particles to form a mixture, sintering the mixture to form a product, cooling the product, and fragmenting the product to form the powder. A powder of the particles 26 or 28 can be prepared by admixing anhydrous particles
10 with the product and sintering before cooling. The acid releasing particles or the liquid containing the acid releasing agent can include a dispersant as described above to prevent agglomeration of the core particles.

A powder of the particles 32 or 34 as shown in FIGs. 3a and 4a can be made by preparing the particles 10 or 22 as described above and then admixing the particles 10 or 22 with a liquid containing a hydrophobic, water-soluble, water-degradable or water-swella-
15 ble material to form a coated product, cooling the coated product, and fragmenting the coated product to form the powder. A powder of particles 36 or 38 as shown in FIGs. 3b and 4b can be prepared by admixing anhydrous particles with the coated product before cooling.
20

A powder of particles 32 or 34 can also be formed by admixing the particles 10 or 22 with particles containing a hydrophobic, water-soluble, water-degradable or water-swella-
25 ble material to form a mixture, sintering the mixture to form a product, cooling the product, and fragmenting the product to form the powder. A powder of the particles 36 or 38 can be prepared by admixing
30 anhydrous particles with the product and sintering before cooling.

A powder of particles 40 as shown in FIG. 5a can also be prepared by admixing the core particles with
35 particles containing a hydrophobic, water-soluble, water-degradable or water-swella-
ble material to form a first

46 with a liquid containing a hydrophobic, water-soluble, water-degradable or water-swella-
ble material to form a coated product, cooling the coated product, and
fragmenting the coated product to form the powder. A
5 powder of particles 54 or 58 as shown in FIGs. 7b and 8b
can be prepared by admixing anhydrous particles with the
coated product before cooling.

A powder of particles 52 or 56 can also be formed by
admixing the particles 40 or 46 with particles containing
10 a hydrophobic, water-soluble, water-degradable or water-
swella-ble material to form a mixture, sintering the
mixture to form a product, cooling the product, and
fragmenting the product to form the powder. A powder of
the particles 54 or 58 can be prepared by admixing
15 anhydrous particles with the product and sintering before
cooling.

The powders of the invention can be prepared by the
methods described above or by any conventional coating
process, such as fluidization. In a fluidization method,
20 the coating material is aerosolized by passing the
material through small diameter nozzles into the chamber
of the fluidized bed where it can impinge upon the
fluidized core particles. Upon contact with the
fluidized core particles, the powder is formed as the
25 coating material solidifies. The particles can then be
packaged in a dry sealed container. The particles can
also be micronized to reduce their particle size and form
a finer powder before being packaged. The powders of the
invention can also be prepared using mechanical blending,
30 mechanical-fluidized blending and other known powder
preparation methods.

The anhydrous particles, silicate, and other
ingredients can be manufactured by conventional processes
and packaged in dry sealed containers, or can be
35 purchased from various sources. The particles and other

**Molded, Thermal-Formed or Extrusion-Formed
Products Incorporating Powders of the Invention**

It has been discovered that the powders of the present invention can be incorporated into injection-
5 molded, compression-molded, thermal-formed, or extrusion-
formed products by contacting the powder with a percolation agent to form a percolation network within the product. The percolation network provides passages for transmission of moisture from the atmosphere
10 surrounding the product to the gas-generating material within the network, increasing the amount of gas that can be generated during use of the product as compared to products formed without a percolation agent. Products formed without a percolation agent are generally more
15 moisture impermeable and release less gas because less moisture is transmitted to the gas-generating material.

For purposes of the present invention, a "percolation network" is a material comprised of two or more phases in which at least one hydrophobic phase is
20 topologically continuous from one free surface to another. The percolation network can be a co-continuous network, a discontinuous network, or a subsurface network. A "co-continuous network" is a percolation network in which all phases are topologically continuous
25 from one free surface to another. A "discontinuous network" is a percolation network in which only the hydrophobic phase(s) is topologically continuous from one free surface to another. A "subsurface network" is a percolation network having a surface tension of less than
30 72 dynes/cm (i.e., hydrophobic surfaces) due to the formation of a skin or coating on its surfaces during processing. A subsurface network can be treated via corona discharge to add hydroxyl groups to one or more hydrophobic surfaces of the network, converting the
35 hydrophobic surface to a hydrophilic surface.

polyvinyl chloride is selected as the hydrophobic material. A hydrophobic plasticizer is also preferably included when a polyolefin is used. When a hydrophobic plasticizer is included, it can phase separate with the hydrophilic phase to form a discontinuous network having hydrophobic phases that are topologically continuous from one free surface to another.

The hydrophilic phase contains the percolation agent and the gas-generating material. The percolation agent is any hydrophilic material that, when in direct contact with a gas-generating material, forms a percolation network with the hydrophobic phase but does not cause premature activation of the gas-generating material to release a gas. For example, ethylene glycol and glycerin cannot be used as percolation agents because they activate the gas-generating material as moisture does. Until the present invention, it was believed that all hydrophilic percolation agents would cause such premature activation of the gas-generating material. However, it has been discovered that many hydrophilic materials can perform as percolation agents without activating the gas-generating agent. Suitable percolation agents include organic humectants such as polyalkylene glycols (e.g., polyethylene glycol, polypropylene glycol), ethylene vinyl alcohol, polyvinyl alcohol, vinylpyrrolidone, N-methyl pyrrolidone, polyvinylpyrrolidone, polysaccharides (e.g., polysaccharides composed of glucose, fructose and alcohols thereof and mannitol) and derivatives, copolymers or combinations thereof, inorganic humectants such as alkali metal and alkaline earth metal salts (e.g., magnesium sulfate, sodium sulfate, calcium chloride), super absorbent acrylates, super absorbent starches, super absorbent resins, antistatic agents, and processing aids such as plasticizers, lubricants, and foaming agents (e.g., surfactants).

polymer. Any hydrophilic material that forms a solution with the anions and counterions and the acid releasing polymer is acceptable, such as an amide, an amine, or a polyhydric alcohol.

5 Yet another suitable gas-releasing powder includes a hydrophilic core, a hydrophobic layer on an outer surface of the hydrophilic core, and particles in contact with the hydrophobic layer. The hydrophobic layer contains an acid releasing agent as described above and may contain
10 microcrystalline wax, paraffin wax, synthetic wax, or a polymer such as atactic polypropylene, polyolefin, or polyester, or polymer blends, multicomponent polymers such as copolymers or terpolymers, or polymer alloys thereof. The particles contain an anhydrous material
15 capable of binding with water, such as sodium sulfate, calcium sulfate, ferrous sulfate, magnesium sulfate, calcium chloride, moisture-depleted silica gel, alumina, zeolites, clays such as bentonite and kaolin, potassium permanganate, molecular sieves and oxygen-scavenging
20 salts. The core, the particles, and the hydrophobic layer are substantially free of water, and the core is capable of generating and releasing a gas after hydrolysis of the acid releasing agent. The hydrophilic core of the powder contains a salt composed of anions,
25 which react with hydronium ions to form the gas, and counterions.

Conventional film forming additives can be added to the hydrophobic and hydrophilic materials as needed. Such additives include crosslinking agents, UV
30 stabilizers, flame retardants, emulsifiers and compatibilizers.

The percolation networks of the present invention preferably contain between about 0.05 wt.% and about 50 wt.% percolation agent, between about 0.25 wt.% and about
35 70 wt.% gas-generating material, between about 20 wt.% and about 99.7 wt.% hydrophobic material, and up to about

material, and hydrophobic material ingredients can be mixed together in a mixer, such as a Henschel mixer, and fed to an extruder or molding apparatus operated at a temperature not exceeding about 200°C to form a melt.

5 The melt can be cast-extruded as a film, formed into pellets using dry air cooling on a vibrating conveyer, or formed into a desired shape by conventional injection-molding, thermal-forming, or compression-molding methods. A hydrophobic plasticizer can optionally be added to the
10 powder mixture to reduce the viscosity of the melt and increase the mixing compatibility of the hydrophobic material and the percolation agent. The percolation agent is miscible with the hydrophobic material when the melt is formed, but separates to form a hydrophilic phase
15 as the melt solidifies, resulting in fine, capillary-like passages containing the gas-generating material throughout the percolation network.

In a preferred embodiment, powders of the percolation agent and the gas-generating material are
20 blended together before the hydrophobic powder is introduced to ensure intimate contact between the percolation agent and the gas-generating material. The composition is prepared by admixing the percolation agent and the gas-generating material to form a powdered
25 mixture, admixing the powdered mixture with the hydrophobic material to form a blend, heating the blend to form a melt, and cooling the melt to form the composition, which is a co-continuous network or a discontinuous network containing passages formed by the
30 percolation agent. The passages are capable of transmitting moisture to the gas-generating material to generate and release a gas.

In another preferred embodiment, powders of the percolation agent and the gas-generating material are
35 mixed together and added to a molten hydrophobic material. The composition is prepared by admixing the

surface to moisture to generate and release a biochemical decomposition-inhibiting gas from the powder into the atmosphere surrounding the surface. In an alternative embodiment, biochemical decomposition is retarded, prevented or controlled on a surface of a material or within the material by placing the material adjacent a powder of the invention, and exposing the powder to moisture to release a biochemical decomposition-inhibiting gas from the powder into the atmosphere surrounding the material. The material is preferably produce such as fruits or vegetables, or other food. The food is preferably stored or transported in modified atmosphere packaging to extend the shelf life of the food by retarding, preventing or controlling biochemical decomposition or microbiological contamination.

The gas-releasing powders can also be used to control respiration of a material by exposing a surface of a material to a powder of the invention, and exposing the surface to moisture to generate and release a respiration-controlling gas from the powder into the atmosphere surrounding the surface. In an alternative embodiment, respiration of a material is controlled by placing the material adjacent a powder of the invention, and exposing the powder to moisture to release a respiration-controlling gas from the powder into the atmosphere surrounding the material. The material is preferably fruits, vegetables, flowers, or other plants. Control of respiration of foods and flowers is generally accomplished by storing and transporting the food or flowers in modified atmosphere packaging or selective gas permeable packaging.

The gas-releasing powders can also be used to deodorize a surface of a material or the atmosphere surrounding the material or enhance freshness of the material by exposing a surface of a material to a powder of the invention, and exposing the surface to moisture to

packet, sachet bag, "tea bag" or other gas-permeable container of the powder can be included in a storage container to provide a chlorine dioxide microatmosphere upon activation. The chlorine dioxide-releasing powder
5 can also be impregnated into a paper or polymeric material (e.g., a shower mat, shoe liners, inserts or insoles, bandage material, a meat cutting board, a food wrapper, a food packaging tray, or a seed packet); incorporated into a wax or polymeric coating applied to
10 paperboard containers or other surfaces; incorporated into films such as packaging films; formed into porous parts to sterilize water; admixed with a material to create a microatmosphere of chlorine dioxide about the material (e.g., soil); or admixed with other powders to
15 kill microorganisms, enhance freshness or deodorize (e.g., foot powders, bath powders, powders used in treating jock itch, powders for treating soft surfaces such as carpet powders, desiccants for moisture removal).

The powders can also be admixed with binders or
20 other conventional tabletting materials to form tablets that can be dissolved in water at the point of use to release chlorine dioxide for flower preservation, surface disinfection, sterilization of medical devices, or use as a mouthwash.

25 In addition to deodorization to neutralize malodors, the powders can be used to retard, prevent or control chemotaxis (i.e., the attraction of a living organism to a chemical substance). For example, odors from food can attract insects to the food. When the food is adjacent a
30 powder of the invention that releases an odor-masking gas, the odor released from food is indistinct or imperceptible to the insects. The powders of the invention can also be used to release an odor-neutralizing gas so that the odor released from food is
35 reduced or eliminated and insects are not attracted to the food.

The silicate particles prepared by this process are illustrated in FIG. 11, which shows generally spherical silicate particles of variable size.

5 **Example 2: Three Step Powder Preparation Process**

25 kg of the silicate particles of Example 1 were slurried into 100 liters of a 50% magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) aqueous solution. 100 liters of a 30% sodium polyphosphate ($(\text{NaPO}_3)_x$) aqueous solution was then added with vigorous stirring. The resulting slurry was immediately spray dried in a commercial spray drying unit. The inlet temperature was set at 350°C , the outlet temperature was maintained at 150°C , the feed solution flow rate was 100 ml/min, and the atomizing gas was delivered at a ratio of 60:1 to the feed solution. The drying air was conveyed at a rate of 200 kg air/hour. The product was somewhat moist (4-8% water) and was further dried immediately to below 1% water in a vacuum oven ($100^\circ\text{C}/30$ in. Hg vacuum) and stored in a dry atmosphere.

Example 3: Two Step Powder Preparation Process

25 kg of the silicate particles of Example 1 were slurried into 200 liters of an aqueous solution containing 25% magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and 15% sodium polyphosphate ($(\text{NaPO}_3)_x$) with vigorous stirring. The resulting slurry was immediately spray dried in a commercial spray drying unit. The inlet temperature was set at 350°C , the outlet temperature was maintained at 150°C , the feed solution flow rate was 100 ml/min, and the atomizing gas was delivered at a ratio of 60:1 to the feed solution. The drying air was conveyed at a rate of 200 kg air/hour. The product was somewhat moist (4-8% water) and was further dried immediately to below 1% water in a vacuum oven ($100^\circ\text{C}/30$ in. Hg vacuum) and stored in a dry atmosphere.

available from Astor Wax Corp., Doraville, Ga.). The blended wax was melted at about 195 °C and coated onto Xerox® printer paper using a Waxmaster coater. The coated paper was then exposed to humidity. Release of chlorine dioxide after exposure to moisture was demonstrated using a chlorine test strip. After a few hours, no gas release was observed. However, the paper turned green after about 12 hours, indicating the slow release of chlorine dioxide from the coating.

Example 6: Percolation Network Preparation Process

The powder of Example 3 was blended with sodium sulfate (1:1 volume ratio) and dried. The blend was mixed with melted Gulf paraffin wax or melted Astor 3040L microcrystalline wax in volume ratios of blend to wax of 1:3 and 1:4. The 1:3 material released chlorine dioxide after exposure to moisture as demonstrated using a chlorine test strip. The 1:4 material did not release chlorine dioxide, which indicated that a percolation network containing an inorganic salt as a humectant may require more than 10 wt.% of the humectant in the network to activate the gas-generating material.

U.S. Patent Nos. 5,360,609, 5,631,300, 5,639,295, 5,650,446, 5,668,185, 5,695,814, 5,705,092, and 5,707,739, and U.S. patent application serial nos. 08/016,904, 08/724,907, 08/858,859, 08/858,860, and 08/924,684 are incorporated herein by reference in their entirety.

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof have been shown by way of example in the drawings and have been described herein in detail. It should be understood, however, that it is not intended to limit the invention to the particular form disclosed, but on the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit

WE CLAIM:

1. A particle comprising anions dissolved in an amorphous, paracrystalline or crystalline solid solution, the anions being capable of reacting with hydronium ions to generate a gas.
2. Silicate particles prepared by a process comprising the steps of admixing a silicate, a solvent, and a chlorite, bisulfite, sulfite, sulfide, hydrosulfide, nitrite, hypochlorite, or cyanide salt to form a
5 solution, and forming silicate particles containing an amorphous, paracrystalline or crystalline solid solution from the solution.
3. A silicate particle comprising anions dispersed throughout substantially amorphous silicate, the anions being capable of reacting with hydronium ions to generate a gas.
4. A process for preparing particles comprising the steps of admixing an amorphous, paracrystalline or crystalline material, a solvent, and a chlorite, bisulfite, sulfite, sulfide, hydrosulfide, nitrite,
5 hypochlorite, or cyanide salt to form a solution, and forming particles containing an amorphous, paracrystalline or crystalline solid solution from the solution.
5. A process for preparing silicate particles comprising the steps of admixing a silicate, a solvent, and a chlorite, bisulfite, sulfite, sulfide, hydrosulfide, nitrite, hypochlorite, or cyanide salt to
5 form a solution, and forming substantially amorphous silicate particles from the solution.

5 a layer on the outer surface of the core, the layer containing an acid releasing agent and a silicate;

 the core and the layer being substantially free of water, the layer being substantially water-insoluble, and the core being capable of generating and releasing a gas after hydrolysis of the acid releasing agent.

10. A process for preparing a powder providing sustained release of a gas, the process comprising:

 admixing particles containing a silicate and anions that are capable of reacting with hydronium ions to

5 generate a gas with a solvent to form a slurry;

 admixing a zinc, magnesium, calcium, aluminum or other monovalent, divalent or multivalent salt and an acid releasing agent with the slurry to form a solids-containing suspension;

10 and forming a powder from the solids-containing suspension, the powder being substantially free of water and capable of generating and releasing the gas after hydrolysis of the acid releasing agent.

11. A process for preparing a powder providing sustained release of a gas, the process comprising admixing a zinc, magnesium, calcium, aluminum or other monovalent, divalent or multivalent salt, an acid releasing agent,

5 and particles containing a silicate and anions that are capable of reacting with hydronium ions to generate a gas with a solvent to form a solids-containing suspension, and forming a powder from the solids-containing

10 suspension, the powder being substantially free of water and capable of generating and releasing the gas after hydrolysis of the acid releasing agent.

16. A method of retarding, preventing or controlling biochemical decomposition on a surface of a material or within the material comprising placing the material adjacent a powder of any one of claims 6 to 9, and
5 exposing the powder to moisture to release a biochemical decomposition-inhibiting gas from the powder into the atmosphere surrounding the material.

17. A method of controlling respiration of a material comprising exposing a surface of a material to a powder of any one of claims 6 to 9, and exposing the surface to moisture to generate and release a respiration-
5 controlling gas from the powder into the atmosphere surrounding the surface.

18. A method of controlling respiration of a material comprising placing the material adjacent a powder of any one of claims 6 to 9, and exposing the powder to moisture to release a respiration-controlling gas from the powder
5 into the atmosphere surrounding the material.

19. A method of deodorizing a surface of a material or the atmosphere surrounding the material or enhance freshness of the material, comprising exposing a surface of a material to a powder of any one of claims 6 to 9,
5 and exposing the surface to moisture to generate and release a deodorizing gas from the powder into the atmosphere surrounding the surface.

20. A method of deodorizing a surface of a material or the atmosphere surrounding the material or enhance freshness of the material, comprising placing a material adjacent a powder of any one of claims 6 to 9, and
5 exposing the powder to moisture to release a deodorizing gas from the powder into the atmosphere surrounding the material.

5 admixing the powdered mixture with a hydrophobic
material to form a blend;
heating the blend to form a melt; and
 cooling the melt to form the composition, the
composition being a co-continuous network or a
10 discontinuous network which contains passages formed by
the percolation agent, the passages being capable of
transmitting moisture to the gas-generating material to
generate and release a gas.

26. A process for preparing a composition providing
sustained release of a gas, the process comprising:
 admixing a percolation agent and a gas-generating
material to form a powdered mixture;
5 admixing the powdered mixture with a melted
hydrophobic material to form a melt; and
 cooling the melt to form the composition, the
composition being a co-continuous network or a
discontinuous network which contains passages formed by
10 the percolation agent, the passages being capable of
transmitting moisture to the gas-generating material to
generate and release a gas.

27. The particle of claim 1 or 3 wherein the particle is
hollow or solid, and substantially spherical.

28. The particle of claim 1 or 3 wherein the particle
includes an inert core.

29. The particle of claim 2 wherein the particles are
substantially amorphous.

30. The particles of claim 2 wherein the particles are
formed from the solution by spray drying the solution.

sulfonate salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal borate, an alkaline-earth metal borate, and a borate salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine.

35. The particles of claim 2 wherein the salt is an alkali metal chlorite, an alkaline-earth metal chlorite, a chlorite salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal bisulfite, an alkaline-earth metal bisulfite, a bisulfite salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal sulfite, an alkaline-earth metal sulfite, a sulfite salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal sulfide, an alkaline-earth metal sulfide, a sulfide salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal hydrosulfide, an alkaline-earth metal hydrosulfide, a hydrosulfide salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal nitrite, an alkaline-earth metal nitrite, a nitrite salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal hypochlorite, an alkaline-earth metal hypochlorite, a hypochlorite salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal cyanide, an alkaline-earth metal cyanide, or a cyanide salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine.

44. The powder of any one of claims 7, 8 or 9 wherein the acid releasing agent is a phosphate.

45. The powder of claim 44 wherein the phosphate is selected from the group consisting of tetraalkyl ammonium polyphosphates, monobasic potassium phosphate, potassium polymetaphosphate, a sodium metaphosphate, a sodium
5 polyphosphate, potassium tripolyphosphate, sodium-potassium phosphate, borophosphates, aluminophosphates, silicophosphates, and salts containing a hydrolyzable metal cation.

46. The powder of any one of claims 7, 8 or 9 wherein the acid releasing agent is an acid releasing wax, an acid releasing polymer, or an acid releasing oligomer.

47. The powder of any one of claims 7, 8 or 9 wherein the acid releasing agent includes a carboxylic acid, an ester, an anhydride, an acyl halide, phosphoric acid, a phosphate ester, a trialkylsilyl phosphate ester, a
5 dialkyl phosphate, sulfonic acid, a sulfonic acid ester, a sulfonic acid chloride, a phosphosilicic anhydride, or a phosphosilicate.

48. The powder of any one of claims 7, 8 or 9 wherein the interpenetrating network includes a microcrystalline wax, a paraffin wax, a synthetic wax, a polymer or an oligomer.

49. The powder of any one of claims 7, 8 or 9 further including a hydrophobic, water-soluble, water-degradable or water-swellaable layer on an outer surface of the interpenetrating network, the first layer or the layer,
5 the hydrophobic, water-soluble, water-degradable or water-swellaable layer being substantially free of water.

54. The powder of claim 49 further including particles in contact with the hydrophobic, water-soluble, water-degradable or water-swellaable layer, the particles being substantially free of water and containing an anhydrous material capable of binding with water.

55. The powder of any one of claims 7, 8 or 9 wherein at least about 1.0×10^{-6} gram gas/cm³ is released from the powder for a period of at least one week after hydrolysis of the acid releasing agent.

56. The powder of claim 49 wherein the hydrophobic, water-soluble, water-degradable or water-swellaable layer is continuous.

57. The powder of any one of claims 8 or 9 wherein the core is substantially amorphous.

58. The powder of any one of claims 8 or 9 wherein the core further includes an inert particle having the silicate and anions on an outer surface thereof.

59. The powder of any one of claims 8 or 9 wherein the silicate in the core is soluble in water or a water solution of a water miscible organic material.

60. The powder of claim 59 wherein the silicate in the core is selected from the group consisting of sodium silicate, sodium metasilicate, sodium sesquisilicate, sodium orthosilicate, borosilicates and aluminosilicates.

61. The powder of any one of claims 8 or 9 wherein the silicate in the second layer or in the layer is selected from the group consisting of magnesium silicate, magnesium trisilicate, calcium metasilicate, aluminum silicate, or zinc silicate.

5 form a solution containing the particles, and forming the particles from the solution.

71. The process of claim 70 wherein the silicate is selected from the group consisting of an alkali metal silicate, an alkaline-earth metal silicate, and a silicate salt of a transition metal ion, a protonated
5 primary, secondary or tertiary amine, or a quaternary amine.

10 72. The process of claim 70 wherein the particles contain a sodium, potassium, calcium, lithium or ammonium salt of a chlorite, bisulfite, sulfite, sulfide, hydrosulfide, nitrite, hypochlorite, or cyanide.

73. The process of claim 70 wherein a base is admixed with the silicate, the solvent and the salt to form the solution, the base being selected from the group consisting of an alkali metal bicarbonate, an alkali
5 metal carbonate, an alkaline-earth metal bicarbonate, an alkaline-earth metal carbonate, a bicarbonate salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, a carbonate salt of a transition metal ion, a protonated primary,
10 secondary or tertiary amine, or a quaternary amine, an alkali metal hydroxide, an alkaline-earth metal hydroxide, an hydroxide salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal phosphate, an alkaline-
15 earth metal phosphate, a phosphate salt of a transition metal ion, a protonated primary, secondary or tertiary amine, or a quaternary amine, an alkali metal sulfate, an alkaline-earth metal sulfate, a sulfate salt of a transition metal ion, a protonated primary, secondary or
20 tertiary amine, or a quaternary amine, an alkali metal sulfonate, an alkaline-earth metal sulfonate, or a

75. The process of any one of claims 10 or 11 wherein the powder is admixed with a hydrophobic material, a water-soluble material, a water-degradable material, or a water-swellable material, cooled, and fragmented to delay
5 release of the gas from the powder.

76. The process of claim 70 wherein the salt is a sodium, potassium, calcium, lithium or ammonium salt of a chlorite, bisulfite, sulfite, sulfide, hydrosulfide, nitrite, hypochlorite, or cyanide.

77. The process of any one of claims 10 or 11 wherein a dispersant, a hydrophobic material, a water-soluble material, a water-degradable material, or a water-swellable material is admixed with the acid releasing
5 agent before the acid releasing agent is admixed with the particles.

78. The process of any one of claims 10 or 11 wherein the powder is admixed with particles containing an anhydrous material capable of binding with water, sintered and cooled, the particles being substantially
5 free of water.

79. The process of claim 11 wherein the powder is admixed with a hydrophobic material, a water-soluble material, a water-degradable material, or a water-swellable material, cooled, and fragmented to delay
5 release of the gas from the powder.

80. The process of claim 79 wherein the powder is admixed with particles containing an anhydrous material capable of binding with water before it is cooled, the particles being substantially free of water.