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(54) Title: HIGHLY ACIDIC METALATED ORGANIC ACID

(57) Abstract: A highly acidic metalated organic acid composition and its preparation. The acidic composition can be prepared by mixing a monovalent or polyvalent cation and an organic acid in the presence of a strong oxyacid, wherein the resultant acidic composition is less corrosive to a ferrous metal than a solution of a mineral acid having the same acidic pH value as that of the acidic composition, and where in the acid composition is more biocidal than a mixture of the organic acid and metal salt of the organic acid which the mixture has the same acid normality value as that of the acidic composition. The acidic composition can be prepared by mixing at least one regenerating acid, at least one metal base, and at least one organic acid, wherein the amount of the regenerating acid is in excess of the equivalent amount of the metal base.



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HIGHLY ACIDIC METALATED ORGANIC ACIDBACKGROUND

This invention relates to a highly acidic metalated organic acid and its preparation.

5 Organic acids and alcohols have been used throughout recorded history as ingredients to decontaminate and preserve food and other biological materials. The pickling process using acetic acid is the food preservation method most familiar to the
10 public. Large numbers of other organic acids have also been used in food processing. The addition of an organic acid to foodstuffs is called acidulation. Acidulated foods are defined in the Code of Federal Regulations (21 CFR) as any consumable food product
15 with a pH of less than 4.6 and produced to comply with current Good Manufacturing Practices ("cGMP") for food and food additives. These products have cost and taste advantages over heat-treated foods. Acidulated foods give a better taste of "freshness"
20 than those that have been heat treated.

 Another common method of food preservation and preparation utilizes heat followed by drying, packaging or canning to prevent contamination. Heat-treated foods retain qualities of freshly prepared
25 food but, nevertheless, give the canned food taste. As energy cost continues to rise, the percentage of production cost due to energy may make some food preparation and/or production costs prohibitive. Additionally, new packaging and other regulatory
30 costs will certainly drive up the cost of food..

Newer methods of food preservation include the addition of non-pathogenic bacteria to prevent spoilage and irradiation with ionizing radiation for preservation. Each of these methods has cost, quality and food safety issues associated with implementation. Acidulation of food with mineral and/or organic acids remains the least costly and most effective method of food preservation.

In the late 80's and early 90's, researchers in Japan developed strong ionized water ("SIW") as disinfectants. The SIW was established as water with pH 2.7 or less, having an oxidation-reduction potential of 1,000 mv or more, and chlorine concentration of 0.8 ppm or more. The SIW is prepared by electrolysis of water.

Electrolysis of tap water has also been used to produce "strong acid water" and "strong alkali water" both of which were claimed to have antiseptic properties.

U.S. Patent Number 5,830,838 to Wurzbarger, et al. describes a solution for cleaning metal surfaces. The solution is prepared by mixing calcium hydroxide and potassium hydroxide with equivalent sulfuric acid in water then passing the solution through a 10 micron filter. The resulting concentrate can be diluted depending on the degree of surface oxidation of the metal to be treated.

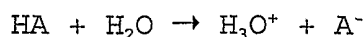
U.S. Patent Number 5,895,782 to Overton, et al. describes a solution for cleaning metal surfaces particularly non-ferrous alloys such as copper, brass and high strength aluminum alloys. The solution is prepared by mixing $\text{Ca}(\text{OH})_2$ and KOH with equivalent sulfuric acid in water then passing the solution

through a 10 micron filter. The resulting concentrate can be used full strength or diluted depending on the degree of surface oxidation of the metal to be treated.

5 International Publication WO 94/09798 describes a pharmaceutical composition for treatment of disease, injury and other disorders. The pharmaceutical composition comprises a complex of a calcium-containing component and a sulfate-containing
10 component in a pharmaceutically acceptable carrier. The reference teaches the isolation from natural materials, such as peat, the inorganic compositions. The inorganic preparations comprise an alkaline, aqueous or organic, or mixture thereof, extract of
15 peat. Peat is extracted with aqueous solutions, organic solutions or water-miscible organic solvents at temperature from below room temperature up to the boiling point of the solvents. The preferred extracting solvents are those having a pH of at least
20 9. Biologically active constituents of fractionated peat preparations were identified as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), $\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (syngenite, also referred to as the double salt of gypsum) and $\text{K}_3\text{Na}(\text{SO}_4)_2$ (apthitalite) by X-ray powder diffraction analysis.
25 The reference also describes the synthesis of syngenite.

Chemists describe and measure the ability of a substance to donate protons $[\text{H}^+]$ to a chemical reaction as the pKa of that substance where

30



Although a hydronium ion is usually represented by H_3O^+ , its true formula is not certain, and best represented as $H^+(H_2O)_n$. The aggregate could be $H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$, or even larger.

5 Hydrated hydronium ion has the ability to donate protons $[H^+]$. The donation of a proton is usually an intermediate step in any acid hydrolysis reaction. Acids are usually the chemical reagents used to donate protons in an aqueous solution.

10 A strong acid is used to neutralize and remove the lime, or quicklime, from bricks and mortar. A strong acid, such as hydrochloric acid, also known as muriatic acid, is also used to clean hard water spots on shower stalls, windows, glass, toilets, urinals,
15 mirrors and other surfaces. Hydrochloric acid is used to de-scale water towers and heat exchangers and to adjust the pH of waste water effluent. A full strength mineral acid, such as hydrochloric acid, is extremely corrosive to many substances, including
20 metals. In addition, hydrochloric acid at a low pH of 0.5 or so can burn a sensitive human skin in a very short period of time. The acid is also very harmful in that it emits fumes irritating to the mucous membrane. If left near other chemicals, like
25 bleach, hydrochloric acid will interact with them, even through a typical plastic bottle.

It is thus desirable to be able to have a source of "acidity," or H_3O^+ , without these unwanted disadvantages and be able to reduce environmental and
30 safety hazards associated with acid hydrolysis. Preferably, this source of "acidity" should be able to prevent re-contamination following decontamination, not induce bacterial resistance, not

alter the taste, color or smell of treated foodstuffs, not create any odor, effective in water in a wide range of temperatures, relatively free of danger when overdosed, can be neutralized after use, 5 not carcinogenic or mutagenic, non-toxic, almost harmless in water and the environment, environmentally friendly, and can be stored for a long period of time without decomposition or turning into hazardous compound.

10 The control of microbial growth is necessary in many practical situations, and significant advances in agriculture, medicine and food science have been made through study of this area of microbiology. "Control of growth" means to prevent growth of 15 microorganisms. This control is effected in one of two basic ways: (1) By killing microorganisms; or (2) by inhibiting the growth of microorganisms. Control of growth usually involves the use of physical or chemical agents which either kill or 20 prevent the growth of microorganisms. Agents which kill cells are called "cidal" agents; agents which inhibit the growth of cells, but without killing them, are referred to as "static" agents. Thus the term "bactericidal" refers to killing bacteria and 25 "bacteriostatic" refers to inhibiting the growth of bacterial cells. A "bactericide" kills bacteria, a "fungicide" kills fungi. "Sterilization" is the complete destruction or elimination of all viable organisms in or on an object being sterilized. The 30 object is either sterile or not, there are no degrees of sterilization. Sterilization procedures involve the use of heat, radiation or chemicals, or physical removal of microorganisms.

Microorganisms tend to colonize and replicate on different surfaces resulting in adherent heterogenous microbial accumulations termed "biofilms." Biofilms may form on surfaces of food substances, feed
5 substances, processing equipment and instrumentations. The microorganisms in the biofilms may include bacteria, fungi, viruses, and protozoans. Since food safety is a national priority, any product that can help by solving a multitude of problems
10 associated with food production is desirable. Removal and control of biofilms which harbor dangerous microbial contamination is a sanitation goal that needs to be achieved. It is also desirable to be able to safely decontaminate water and
15 nutriment by lowering pH to levels where contaminants would react and organisms cannot live.

Current sanitizing, disinfectant and pesticide products on the market for these uses contain
residues of chlorine, ammonia, organic iodine, metal
20 salts and other deleterious residues. It is desirable to have a way that would preclude these residues by promoting acid hydrolysis without the presence of deleterious chemicals. Additionally, this method should generate few hazardous volatile gases.
25 Importantly, it is highly desirable to have a composition that can control the growth of, and kill, microorganisms and, at the same time, destroy the products, generated by, or associated with, the microorganisms.

SUMMARY

The present invention involves a highly acidic metalated organic acid composition and its preparation. One embodiment of the present invention pertains to an acidic composition having an acidic pH value and an acid normality value. The acidic composition is prepared by mixing a monovalent or polyvalent cation and an organic acid in the presence of a strong oxyacid, wherein the resultant acidic composition is less corrosive to a ferrous metal than a solution of a mineral acid having the same acidic pH value as that of the acidic composition, and wherein the acid composition is more biocidal than a mixture of the organic acid and a metal salt of the organic acid which mixture has the same acid normality value as that of the acidic composition. The acidic composition can be prepared by mixing at least one regenerating acid, at least one metal base, and at least one organic acid, wherein the amount of the regenerating acid is in excess of the equivalent amount of the metal base. One aspect of the present invention pertains to method of preparing the highly acidic metalated organic acid.

DETAILED DESCRIPTION

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One aspect of the present invention pertains to a composition of a highly acidic metalated organic acid ("HAMO"). The composition may have a suspension of very fine particles, and it has a monovalent or a

polyvalent cation, an organic acid, and an anion of a
regenerating acid, such as the anion of a strong
oxyacid. The term "highly acid" means the pH is in
the acidic region, below at least about 4. HAMO of
5 the present invention is less corrosive to a ferrous
metal than a solution of a mineral acid having the
same acidic pH value as that of the acidic
composition. HAMO is also more biocidal than a
mixture of the organic acid and a metal salt of the
10 organic acid which mixture having the same acid
normality value as that of the acidic composition.

Broadly, one way HAMO can be prepared is by
mixing the following ingredients: (1) at least one
regenerating acid; (2) at least one metal base; and
15 (3) at least one organic acid, wherein the equivalent
amount of the regenerating acid is in excess of the
equivalent amount of the metal base. The equivalent
amount of the metal base should be about equal to
that of the organic acid. Instead of using a metal
20 base and an organic acid, a metal salt of the organic
acid can be used in place of the metal base and the
organic acid. The insoluble solid is removed by any
conventional method, such as sedimentation,
filtration, or centrifugation.

25 Generally, HAMO can be prepared by blending or
mixing the necessary ingredients in at least the
following manners:

1. Regenerating acid + (metal base + organic
acid);
- 30 2. Regenerating acid + (metal base + salt of
organic acid);

3. (Regenerating acid + salt of organic acid)
+ base; and
4. Regenerating acid + salt of organic acid.

The parenthesis in the above scheme denotes
5 "pre-mixing" the two ingredients recited in the
parenthesis. Normally, the regenerating acid is
added last to generate the HAMO. Although each of
the reagents is listed as a single reagent,
optionally, more than one single reagent, such as
10 more than one regenerating acid or organic acid, can
be used in the current invention. The number of
equivalents of the regenerating acid must be larger
than the number of equivalents of the metal base, or
those of the metal salt of the organic acid. When
15 the organic acid is an amino acid, which, by
definition contains at least one amino group, then
the number of equivalents of the regenerating acid
must be larger than the total number of equivalents
of the metal base, or metal salt of the organic acid,
20 and the "base" amino group of the amino acid. Thus,
the resultant highly acidic metalated organic acid is
different from, and not, a buffer.

As used herein, a regenerating acid is an acid
that will "re-generate" the organic acid from its
25 salt. Examples of a regenerating acid include a
strong binary acid, a strong oxyacid, and others. A
binary acid is an acid in which protons are directly
bound to a central atom, that is (central atom)-H.
Examples of a binary acid include HF, HCl, HBr, HI,
30 H₂S and HN₃. An oxyacid is an acid in which the
acidic protons are bound to oxygen, which in turn is

bound to a central atom, that is (central atom)-O-H. Examples of oxyacid include acids having Cl, Br, Cr, As, Ge, Te, P, B, As, I, S, Se, Sn, Te, N, Mo, W, or Mn as the central atom. Some examples include H₂SO₄,
5 HNO₃, H₂SeO₄, HClO₄, H₃PO₄, and HMnO₄. Some of the acids (e.g. HMnO₄) cannot actually be isolated as such, but occur only in the form of their dilute solutions, anions, and salts. A "strong oxyacid" is an oxyacid which at a concentration of 1 molar in water gives a
10 concentration of H₃O⁺ greater than about 0.8 molar.

The regenerating acid can also be an acidic solution of sparingly-soluble Group IIA complexes ("AGIIS"). AGIIS can be prepared by mixing or
blending materials given in one of the following
15 scheme with good reproducibility:

- (1) H₂SO₄ and Ca(OH)₂;
- (2) H₂SO₄, Ca(OH)₂, and CaCO₃;
- (3) H₂SO₄, Ca(OH)₂, CaCO₃, and CO₂ (gas);
- (4) H₂SO₄ and CaCO₃;
- 20 (5) H₂SO₄, CaCO₃, and Ca(OH)₂;
- (6) H₂SO₄, CaCO₃, and CO₂ (gas);
- (7) H₂SO₄ and CaSO₄;
- (8) H₂SO₄, Ca(OH)₂, and CaSO₄;
- (9) H₂SO₄, CaSO₄, and CaCO₃;
- 25 (10) H₂SO₄, CaSO₄, CaCO₃, and Ca(OH)₂;
- (11) H₂SO₄, CaSO₄, CaCO₃, and CO₂ (gas); and
- (12) H₂SO₄, CaSO₄, CaCO₃, CO₂ (gas), and Ca(OH)₂.

Thus, preferably, AGIIS is prepared by mixing
30 calcium hydroxide with concentrated sulfuric acid, with or without an optional Group IIA salt of a dibasic acid (such as calcium sulfate) added to the sulfuric acid. The optional calcium sulfate can be

added to the concentrated sulfuric acid prior to the introduction of calcium hydroxide into the blending mixture. The addition of calcium sulfate to the concentrated sulfuric acid appears to reduce the amount of calcium hydroxide needed for the preparation of AGIIS. Other optional reagents include calcium carbonate and gaseous carbon dioxide being bubbled into the mixture. Regardless of the use of any optional reagents, it was found that the use of calcium hydroxide is desirable.

One preferred method of preparing AGIIS can be described briefly as: Concentrated sulfuric acid is added to chilled water (8°-12°C) in the mixing vessel, then, with stirring, calcium sulfate is added to the acid in chilled water to give a mixture. Temperature control is paramount to this process. To this stirred mixture is then added a slurry of calcium hydroxide in water. The solid formed from the mixture is then removed. This method involves the use of sulfuric acid, calcium sulfate, and calcium hydroxide, and it has several unexpected advantages. Firstly, this mixing is not violent and is not exceedingly exothermic. Besides being easy to control and easy to reproduce, this mixing uses ingredients each of which has been reviewed by the U.S. Food and Drug Administration ("U.S. FDA") and determined to be "generally recognized as safe" ("GRAS"). As such, each of these ingredients can be added directly to food, subject, of course, to certain limitations. Under proper concentration, each of these ingredients can be used as processing aids and in food contact applications. Their use is

limited only by product suitability and Good Manufacturing Practices ("GMP").

The sulfuric acid used in the preparation of AGIIS or for this invention is usually 95-98% FCC Grade (about 35-37 N). Concentration of sulfuric acid used to generate AGIIS can range from about 0.05 M to about 18 M (about 0.1 N to about 36 N), preferably from about 1 M to about 5 M. It is application specific. The term "M" used denotes molar or moles per liter.

In the preparation of AGIIS, normally, a slurry of finely ground calcium hydroxide suspended in water (about 50% of W/V) is the preferred way of introducing the calcium hydroxide, in increments, into a stirred solution of sulfuric acid, with or without the presence of calcium sulfate. Ordinarily, the mixing is carried out below 40°C, preferably below room temperature, and more preferably below 10°C. The time to add calcium hydroxide can range from about 1 hour to about 4 hours. The agitation speed can vary from about 600 to about 700 rpm, or higher. After mixing, the mixture is filtered through a 5 micron filter. The filtrate is then allowed to sit overnight and the fine sediment is removed by decantation.

The calcium hydroxide used for AGIIS or for this invention is usually FCC Grade of about 98% purity. For every mole of concentrated acid, such as sulfuric acid, the amount, in moles, of calcium hydroxide used is application specific and ranges from about 0.1 to about 1.

The calcium carbonate is normally FCC Grade having a purity of about 98%. When used with calcium

hydroxide as described above for the preparation of AGIIS, for every mole of a concentrated acid, such as sulfuric acid, the amount, in moles, of calcium carbonate ranges from about 0.001 to about 0.2, depending on the amount of calcium hydroxide used.

The optional carbon dioxide in the preparation of AGIIS is usually bubbled into the slurry containing calcium hydroxide at a speed of from about 1 to about 3 pounds pressure. The carbon dioxide is bubbled into the slurry for a period of from about 1 to about 3 hours. The slurry is then added to the mixing vessel containing the concentrated sulfuric acid.

Another optional ingredient in the preparation of AGIIS is calcium sulfate, a Group IIA salt of a dibasic acid. Normally, dihydrated calcium sulfate is used. As used in this application, the phrase "calcium sulfate," or the formula " CaSO_4 ," means either anhydrous or hydrated calcium sulfate. The purity of calcium sulfate (dihydrate) used is usually 95-98% FCC Grade. The amount of calcium sulfate, in moles per liter of concentrated sulfuric acid ranges from about 0.005 to about 0.15, preferably from about 0.007 to about 0.07, and more preferably from about 0.007 to about 0.04. It is application specific.

An organic acid is an acidic compounds containing carbon. It includes carboxylic acid, amino acid, acidic vitamin, sulfonic acid, phosphonic acid, and others. A carboxylic acid is an organic compound containing an $-\text{COOH}$ group, i.e., a carbonyl attached to a hydroxyl group. A carboxylic acid can be a mono-carboxylic acid, a di-carboxylic acid, or a tri-carboxylic acid. A mono-carboxylic acid can be

represented by a general formula of $R^1\text{-COOH}$, wherein R^1 can be: H; $C_1\text{-}C_4$ saturated alkyl; $C_2\text{-}C_5$ unsaturated alkyl with 2 or less double bonds; or $C_2\text{-}C_5$ unsaturated alkyl with 2 or less triple bonds;

5 $\text{CH}_3\text{CH(OH)}$; $\text{HOCH}_2(\text{CHOH})_4$; or $\text{R}_2\text{CH(NH}_2)$, wherein R_2 is H, $C_1\text{-}C_4$ saturated alkyl, $\text{C}_6\text{H}_5\text{CH}_2$, $p\text{-HO-C}_6\text{H}_4\text{CH}_2$, $\text{H}_2\text{N(CH}_2)_4$, HOCH_2 , or CH_3CHOH . A di-carboxylic acid can be represented by a general formula of $\text{HOOC-R}^3\text{-COOH}$, wherein R^3 can be: $(\text{CH}_2)_m$, in which m can be 1-3;

10 $(\text{CH}=\text{CH})$; $\text{CH}_2\text{CH(OH)H(OH)C-CH(OH)}$; or $(\text{CH}_2)_p\text{CH(NH}_2)$, in which p is 2 or 3. A tri-carboxylic acid can be represented by a general formula of $\text{HOOCR}^4(\text{COOH})\text{COOH}$, wherein R^4 can be: $\text{CH}_2\text{C(OH)CH}_2$; or CH_2CHCH_2 . Although some amino acids have been included in the general

15 category of mono-carboxylic acid, it is known in the art that amino acids include: alanine; arginine; aspartic acid (asparagine); cysteine (cystine); glutamic acid (glutamine); glycine; histidine; hydroxylysine; hydroxyproline; isoleucine; leucine;

20 lycine; methionine; phenylalanine; proline; serine; threonine; tryptophan; tyrosine; valine; aminoadipic acid; diaminobutyric; ornithine; pipercolic acid; sarcosine; and thiiodothyronine (thyroxine).

The metal base can be in the form of an OH^- ,

25 CO_3^- , HCO_3^- , or O^- salt. The metal can be a monovalent metal, a polyvalent metal, all transition and rare earth elements, Sn, Pb, or Bi. Examples of monovalent metals include elements in Group IA. The polyvalent metals can be a divalent metal or a

30 trivalent metal. Examples of divalent metals include elements in Group IIA, except Be; and examples of trivalent metals include elements in Group IIIA, except B. Preferably the metal is Mn, Mg, Ca,

Fe(II), Cu(II), Zn(II), Ce, Ni, Pd, Cr, Ti, Zr, Co, Al, Sn, Pb, Bi, V(III), Cd, Hg, Pt, Hf, and other first-row lanthanides, except Pm. More preferably, the metal is Mg, Ca, Fe(II), Cu(II), Zn, Cr, or Co.

5 Salts of an organic acid as used in this application include the salts of the metals, discussed above, salts of the organic acids, also discussed above, and others.

The term "biocidal" means destruction of a biological contaminant. A "biological contaminant" is defined as a biological organism, or the product of biological organism, such as toxin, or both, all of which contaminate the environment and useful products. This biological contaminant results in making the environment or product hazardous.

15 Biological contaminants, such as bacteria, fungi, mold, mildew, spores, and viruses have potentially reactive substances in their cell wall/membranes; however, they hide in cells (viruses and some bacteria) and/or secrete biofilms (most bacteria, fungi, mold and mildew) to protect them from the environment.

Bacteria form or elaborate intracellular or extracellular toxins. Toxin is a noxious or poisonous substances that: (1) are an integral part of the bacteria; (2) are an extracellular product (exotoxin) of the bacteria; or (3) represent a combination or the two situations, formed or elaborated during the metabolism and growth of bacteria. Toxins are, in general, relatively complex antigenic molecules and the chemical compositions are usually not known. The harmful effects of bacteria come not only from the bacteria themselves, but also

from the toxins produced by bacteria. Toxins produced by bacteria are just as, if not more, hazardous to the product than the bacteria themselves. Ordinary disinfectants, such as

5 quaternary ammonium compounds, will kill bacteria but may have no effect on bacterial toxins and endotoxins. In fact, many disinfectants actually contribute to the endotoxins problems by causing their release from the bacteria. The bacterial

10 toxins and endotoxins can cause serious adverse effects in human and animals. Endotoxins are a major cause of contamination in food products, in the production of pharmaceuticals, medical devices, and other medical products.

15 The outer covering, i.e. epidermis, of animals and cuticle of plants resist the growth and/or entry of the above microorganisms into the interior of the complex organism. One of the microbial growth prevention methods used by plants and animals is the

20 maintenance of a surface pH or secretion of a coating that is not conducive to the attachment and propagation of micro-organisms. After a plant product is harvested or an animal product processed, these products lose the ability to resist the

25 infestation of micro-organisms.

The composition of the present invention was found to be a "preservative." The composition is minimally corrosive; however, it can create an environment where destructive micro-organisms cannot

30 live and propagate, thus prolonging the shelf-life of the product. As is known in the art, formic acid is not as corrosive to a ferrous metal as is a mineral acid, such as hydrochloric acid. Yet, formic acid

solution is more corrosive to a galvanized roofing nail than is a solution of HAMO. In one experiment, after 48 hours of air-drying, a galvanized roofing nail, which had been dipped for 20 minutes at room
5 temperature in a solution of formic acid with a pH of 1.5, showed obvious, visible corrosion. Yet, under similar conditions, no such obvious, visible corrosion was observed for a galvanized roofing nail having been dipped in a solution of HAMO (prepared
10 from lactic acid, calcium hydroxide and regenerated with phosphoric acid) at a pH of 1.44.

The utility of the method of preservation demonstrated herein is that additional chemicals do not have to be added to the food or other substance
15 to be preserved because the inherent low pH of the mixture is preservative. Since preservative chemicals do not have to be added to the food substance, taste is improved and residues are avoided. Organoleptic testing of a number of freshly
20 preserved and previously preserved food stuffs have revealed the addition of composition improves taste and eliminates preservative flavors. The term "organoleptic" means making an impression based upon
25 senses of an organ or the whole organism.

The composition of the present invention was found to be biocidal. The composition was found to be biocidal to E.coli, and other bacteria.

The following examples are provided to further illustrate this invention and the manner in which it
30 may be carried out. It will be understood, however, that the specific details given in the examples have been chosen for purposes of illustration only and not be construed as limiting the invention. Unless

otherwise defined, the amount of each ingredient or component of the present invention is based on the weight percent of the final composition.

Example 1

5 Preparation of 1.2-1.5 N AGIIS ($H_2SO_4/Ca(OH)_2$)

An amount of 1055 ml (19.2 moles, after purity adjustment and taking into account the amount of acid neutralized by base) of concentrated sulfuric acid (FCC Grade, 95-98% purity) was slowly added with
10 stirring, to 16.868 L of RO/DI water in each of mixing flasks a, b, c, e, and f. The amount of water had been adjusted to allow for the volume of acid and the calcium hydroxide slurry. The mixture in each flask was mixed thoroughly. Each of the mixing
15 flasks was chilled in an ice bath and the temperature of the mixture in the reaction flask was about 8-12°C. The mixture was continuously stirred at a rate of about 700 rpm.

Separately, a slurry was made by adding RO/DI
20 water to 4 kg of calcium hydroxide (FCC Grade, 98% purity) making a final volume of 8 L. The mole ratio of calcium hydroxide to concentrated sulfuric acid was from about 0.45 to about 1. The slurry was a 50% (W/V) mixture of calcium hydroxide in water. The
25 slurry was mixed well with a high-shear-force mixer until the slurry appeared uniform. The slurry was then chilled to about 8-12°C in an ice bath and continuous stirred at about 700 rpm.

To each of the mixing flasks was added 150 ml of
30 the calcium hydroxide slurry every 20 minutes until 1.276 L (i.e. 638 g dry weight, 8.61 moles, of

calcium hydroxide) of the slurry had been added to each reaction vessel. The addition was again accompanied by thorough mixing at about 700 rpm.

5 After the completion of the addition of the calcium hydroxide to the mixture in each mixing vessel, the mixture was filtered through a 5-micron filter.

The filtrate was allowed to sit for 12 hours, the clear solution was decanted to discard any precipitate formed. The resulting product was AGIIS
10 having an acid normality of 1.2-1.5. Analysis showed: Ca, 715 ppm (600 ppm - 800 ppm); SO₄, 45,700 ppm (40,000 ppm - 55,000 ppm).

Example 2

15 Preparation of 2 N AGIIS (H₂SO₄/Ca(OH)₂/CaSO₄)

For the preparation of 1 L of 2 N AGIIS, an amount of 79.54 ml (1.44 moles, after purity adjustment and taking into account the amount of acid to be neutralized by base) of concentrated sulfuric
20 acid (FCC Grade, 95-98% purity) was slowly added, with stirring, to 853.93 ml of RO/DI water in a 2 L mixing flask. Five grams of calcium sulfate (FCC Grade, 95% purity) were then added slowly and with stirring to the mixing flask. The mixture was mixed
25 thoroughly. At this point, the mixture would usually exhibit an acid normality of 2.88. The mixing flask was chilled in an ice bath and the temperature of the mixture in the reaction flask was about 8-12°C. The mixture was continuously stirred
30 at a rate of about 700 rpm.

Separately, a slurry was made by adding 49.89 ml of RO/DI water to 33.26 g (0.44 mole, after purity adjustment) of calcium hydroxide (FCC Grace, 98% purity) making a final volume of 66.53 ml. The mole ratio of calcium hydroxide to concentrated sulfuric acid was from about 0.44 to about 1. The slurry was mixed well with a high-shear-force mixer until the slurry appeared uniform. The slurry was then chilled to about 8-12°C in an ice bath and continuously stirred at about 700 rpm.

The slurry was then slowly added over a period of 2-3 hours to the mixture, still chilled in an ice bath and being stirred at about 700 rpm.

After the completion of the addition of slurry to the mixture, the product was filtered through a 5-micron filter. It was normal to observe a 20% loss in volume of the mixture due to the retention of the solution by the salt and removal of the salt.

The filtrate was allowed to sit for 12 hours, the clear solution was decanted to discard any precipitate formed. The resulting product was AGIIS having an acid normality of 2.

Example 3

Preparation of 12 N AGIIS ($H_2SO_4/Ca(OH)_2/CaSO_4$)

For the preparation of 1 L of 12 N AGIIS, an amount of 434.17 ml (7.86 moles, after purity adjustment and taking into account amount of acid neutralized by base) of concentrated sulfuric acid (FCC Grade, 95-98% purity) was slowly added, with stirring, to 284.60 ml of RO/DI water in a 2 L mixing

flask. Three grams of calcium sulfate (FCC Grade, 95% purity) were then added slowly and with stirring to the mixing flask. The mixture was mixed thoroughly. The mixing flask was chilled in an ice bath and the temperature of the mixture in the mixing flask was about 8-12°C. The ingredients were continuously stirred at a rate of about 700 rpm.

Separately, a slurry was made by adding 210.92 ml of RO/DI water to 140.61 g (1.86 moles, after purity adjustment) of calcium hydroxide (FCC Grade, 98% purity) making a final volume of 281.23 ml. The mole ratio of calcium hydroxide to concentrated sulfuric acid was about 0.31. The slurry was mixed well with a high-shear-force mixer until the slurry appeared uniform. The slurry was then chilled to about 8-12°C in an ice bath and continuous stirred at about 700 rpm.

The slurry was then slowly added over a period of 2-3 hours to the mixture, still chilled in an ice bath and being stirred at about 700 rpm.

After the completion of the addition of slurry to the mixture, the product was filtered through a 5-micron filter. It was normal to observe a 20% loss in volume of the mixture due to the retention of the solution by the salt and removal of the salt.

The filtrate was allow to sit for 12 hours, the clear solution was decanted to discard any precipitate formed. The resulting product was AGIIS having an acid normality of 12.

Example 4

General Method for the Preparation of HAMO

For a 1 L final volume of HAMO, n moles of organic acid (n is from about 0.01 to about 15) is suspended or dissolved in 2n moles of DI water. To this mixture is then added monovalent, divalent or trivalent metal base (hydroxide, oxide, carbonate or bicarbonate, or combination thereof) as the dry solid or as a slurry in DI water in the ratio of 1.0 equivalent weights of base per equivalent weight of acid. The addition is accomplished as quickly as possible. To the resultant mixture is added a quantity of regenerating acid sufficient to ensure complete regeneration of the organic acid from its metal salt, but a quantity not greater than 18 moles/L. Preferably, the addition of the regenerating acid is accomplished as quickly as possible without permitting the mixture temperature to rise above 80°C. After the mixing is complete, usually from about 0.5 hour to about 1 hour. the undissolved solids are removed by filtration through a 5-micron filter or by centrifugation.

Example 5

Formation of a HAMO from Maleic Acid, CalciumHydroxide, and Sulfuric Acid

To a mixture of maleic acid (1 kg, 8.61 moles) and RO-DI water (1 L), solid calcium hydroxide (335 g, 4.52 moles) was added in 50-g portions with stirring. After the addition of the calcium

hydroxide was complete, RO-DI water (500 mL) was added. To the resulting mixture, concentrated sulfuric acid (238 mL) was added in 25-mL aliquots at a rate that maintained the reaction temperature below 85°C. The resultant mixture was centrifuged at 15000 rpm for 25 minutes to provide the HAMO as supernatant, pH of 0.5 - 1.0. Analysis showed: Ca, 12,900 ppm; SO₄ 159,000 ppm.

Example 6

10 Formation of a HAMO from Gluconic Acid, Calcium Hydroxide, and Sulfuric Acid

To a stirred mixture of gluconic acid (50%, 1 kg, 2.55 moles) and water (200 mL) was added 97 g (1.3 moles) of solid calcium hydroxide. After the mixing was complete, concentrated sulfuric acid (76 mL) was added as rapidly as possible while keeping the reaction temperature below 85°C. The final mixture was centrifuged at 15,000 rpm for 25 minutes to give the HAMO as supernatant, pH of 1.0. Analysis showed: Ca, 1,210 ppm; SO₄, 11,600 ppm.

Example 7

15 Formation of a HAMO from Succinic Acid, Calcium Hydroxide, and Phosphoric Acid

25 Solid calcium hydroxide (320 g, 4.23 moles) was added in 50-g portions to a stirred mixture of succinic acid (1 kg, 8.47 moles) and RO-DI water (1200 mL). Concentrated phosphoric acid (529 mL,

4.75 moles) was added in 50-mL aliquots as rapidly as possible while maintaining the temperature below 85°C. The final product had a pH of 1.5. Analysis showed: Ca, 26,700 ppm; PO₄, 250,000 ppm.

5

Example 8

Formation of a HAMO from Acetic Acid, Calcium Carbonate, and Sulfuric Acid

1. Preparation of Calcium Acetate. One liter (17.48 moles) of acetic acid was added to an eight-liter container, and one liter of water was added. Calcium carbonate powder (874 g, 8.74 mole, 99+%) was added in 100-g portions over 2.5 hours with agitation until the solution was neutral to pH paper. Water was added as needed to maintain fluidity in the mixture during the neutralization.

2. Formation of the HAMO. Water was added to the calcium acetate formed in step 1 to bring the total volume to 3 gallons. To this solution, 17.48 moles of 95-98% sulfuric acid was added. The mixture was mixed well, and the mixing allowed to proceed without cooling. After the mixing was complete, the mixture was filtered through a 5 micron filter to give the HAMO, pH was 1.15. Analysis showed: Ca, 17,000 ppm; PO₄, 158,000 ppm.

In smaller scale preparations, it was more convenient to free the HAMO from undissolved solids by centrifugation.

Example 9

Formation of a HAMO from Lactic Acid, Calcium Carbonate, and Sulfuric Acid

1. Preparation of Calcium Lactate. One liter (11.25 mole) of 85% lactic acid was added to a five-liter container, and one liter of water was added. Calcium carbonate powder (874 g, 8.74 mole, 99+%) was added in 100-g portions over 2.5 hours with agitation until the solution was neutral to pH paper. Water was added as needed to maintain fluidity in the mixture during the neutralization.

2. Formation of the HAMO. Water was added to the calcium lactate formed in step 1 to bring the total volume to 5 gallons. To this solution, 11.25 moles of 95-98% sulfuric acid was added. The mixture was mixed well, and the mixing was allowed to proceed without cooling. After the mixing was complete, the mixture was filtered through a 5 micron filter to give the HAMO, pH of less than 1.0.

In smaller scale preparations, it was more convenient to free the HAMO from undissolved solids by centrifugation.

20

Example 10

Formation of a HAMO from Gluconic Acid, Ferrous Hydroxide, and Phosphoric Acid

Ferrous hydroxide was prepared by the reaction between 646 grams of ferrous sulfate and 224 grams of sodium hydroxide in RO-DI water to give a final volume of 2730 mL. The suspension of ferrous hydroxide obtained in this way was allowed to settle, the supernatant was removed by decantation, and the solid was washed three times with water by suspending in a total volume of 2730 mL, allowing the solid to settle, and decanting the supernatant.

The ferrous hydroxide was suspended in RO-DI water to give a total volume of 500 mL, and this mixture was added to a mixture of gluconic acid (50%, 1 kg, 2.55 moles) and RO-DI water (100 mL).
5 Concentrated phosphoric acid (100 mL) and sucrose (35 g) were added sequentially to this mixture. The final material did not require filtration or centrifugation, pH of 1.0. Analysis showed: Fe, 12,800 ppm; Na, 7,450 ppm; PO₄, 90,600 ppm; SO₄,
10 15,800 ppm.

Example 11

Formation of a HAMO from Butyric Acid, Magnesium Hydroxide, and Phosphoric Acid

To a mixture of butyric acid (500 mL, 5.4 moles) and RO-DI water (500 mL) was added solid magnesium hydroxide (163.6 g, 2.73 moles) in 25-g portions. To the resulting mixture was added concentrated phosphoric acid (180 mL) in 50-mL aliquots. The final solution had a pH of 1.0. Analysis showed:
20 Mg, 390 ppm; PO₄, 1,560 ppm.

Example 12

Formation of a HAMO from Maleic Acid, Magnesium Hydroxide, and Phosphoric Acid

Solid magnesium hydroxide (300 g, 97.5%, 5.02 moles) was added in 50-g portions to stirred solution of maleic acid (1 kg, 8.53 moles) in RO-DI water (1,500 mL). At the end of the addition, the pH of the mixture was 5.0. Concentrated phosphoric acid (338 mL, .85-90%) was added in 25-mL aliquots. No

precipitate was observed during the acidification step. The final pH of the HAMO solution was 1.0. Analysis showed: Mg, 19,500 ppm; PO₄, 287,000 ppm.

Example 13

5 Formation of a HAMO from Succinic Acid, Magnesium Hydroxide, and AGIIS

Solid magnesium hydroxide (101 g, 1.16 moles) was added in two equal portions to a stirred
10 suspension of succinic acid (400 g, 3.39 moles) in RO-DI water (1 L). After the reaction was complete, AGIIS (607 mL, 5.58 N) was added in 50-mL aliquots at a rate that maintained the reaction temperature below
15 85°C. The solution was centrifuged at 15,000 rpm for about 25 minutes. The pH of the HAMO was 1.0 - 1.5. Analysis showed: Mg, 24,100 ppm; SO₄, 115,000 ppm.

Example 14

20 Formation of a HAMO from Calcium Hydroxide, a Mixture of Acetic, Lactic and Propionic Acids, and Sulfuric Acid

Lactic acid (6 moles), propionic acid (6 moles), and acetic acid (6 moles) were added to a 5-gallon container and RO-DI water (1L) was added. Solid calcium hydroxide (678 g, 9 moles) was added slowly
25 to this mixture with stirring. To this mixture was added 9 M sulfuric acid (1L, 9 moles H₂SO₄), and water (3L) as necessary to keep the mixture mobile. The resultant mixture was filtered through a 5-micron

filter. The pH of the HAMO was 0.6. Analysis showed: Ca, 205 ppm; SO₄, 23,900 ppm.

Example 15

5 Formation of a HAMO from Calcium Hydroxide, a Mixture of Formic, Lactic and Propionic Acids, and AGIIS

Lactic acid (6 moles), propionic acid (6 moles), and formic acid (6 moles) were added to a 5-gallon container and a saturated solution of calcium sulfate (1L) was added. Solid calcium hydroxide (680 g, 9
10 moles) was added to this mixture in 100-g portions with stirring. During the addition, the reaction temperature rose to 85°C. To this mixture was added 9 M sulfuric acid (950 mL, 8.55 moles H₂SO₄), AGIIS (1.2 N, 250 mL, 0.15 moles acid), and water (1L).
15 The resultant mixture was filtered through a 5-micron filter. The final HAMO had a pH of 1.0. Analysis showed: Ca, 215 ppm; SO₄, 17,000 ppm.

Example 16

20 Formation of a HAMO from Calcium Propionate and Sulfuric Acid

RO-DI water (2 L) was placed in an 8-L container and calcium propionate (5.36 moles) was added. The mixture was stirred, and an additional 2.5 L of RO-DI
25 water was added to complete dissolution of the salt. Concentrated sulfuric acid (300 mL, 5.62 moles) was added, and the mixture stirred until the reaction was complete. The resultant mixture was filtered through

a 5-micron filter. The pH of the HAMO was 1.5.
Analysis showed Ca, 987 ppm; SO₄, 2,580 ppm.

Example 17

5 Formation of a HAMO from Calcium Lactate and AGIIS

To a mixture of 5.60 N AGIIS (1 L) and RO-DI
water (1 L) was added solid calcium lactate
pentahydrate (2.79 moles). The resultant mixture was
allowed to stir without cooling until the mixing was
10 complete. The final mixture was filtered through a
5-micron filter. The pH of the HAMO was 2.5 - 3.0.
Analysis showed: Ca, 2,550 ppm; SO₄, 1,090 ppm.

Example 18

Physical Properties of Selected HAMO's

	Description	pH	Ca (ppm) $\times 10^3$	SO ₄ (ppm) $\times 10^3$	Mg (ppm) $\times 10^3$	PO ₄ (ppm) $\times 10^3$	Other
5	Lactic acid HAMO neutralized with CaCO ₃ and regenerated with sulfuric acid	1.0					Slight yellow tint, Sour/ citrus taste
10							
15	Acetic acid HAMO neutralized with CaCO ₃ and regenerated with sulfuric acid	<0.0					
20							
25	Lactic acid HAMO from Ca Lactate and regenerated with 5.6 N AGIIS	2.5- 3.0					Slight yellow tint
30	Lactic acid HAMO from CaCO ₃ Lactate and regenerated with 5.6 N AGIIS	<0.0	2.55	1.09			Slight yellow tint
35							

5	Propionic acid HAMO neutralized with Ca(OH) ₂ and regenerated with sulfuric acid	1.5	0.917	2.55			
10 15	Formic Acid HAMO neutralized with Ca(OH) ₂ and regenerated with sulfuric acid	1.0-1.5	0.163	3.07			
20 25	Lactic acid HAMO neutralized with Ca(OH) ₂ and regenerated with phosphoric acid		44.6			329	Pickles iron and prohibits rust
30 35	Formic acid HAMO neutralized with Ca(OH) ₂ and regenerated with phosphoric acid	1.0-1.5	22.6			156	
40 45	Propionic acid, formic acid, lactic acid HAMO neutralized with Ca(OH) ₂ and regenerated with sulfuric acid	1.0	0.215	17			

5	Propionic acid, lactic acid HAMO neutralized with $\text{Ca}(\text{OH})_2$ and regenerated with sulfuric acid	0.6	0.205	23.9			
10							
15	Gluconic acid HAMO neutralized with $\text{Ca}(\text{OH})_2$ and regenerated with sulfuric acid	1.0	1.21	11.6			Sugar odor
20							
25	Gluconic acid HAMO neutralized with $\text{Fe}(\text{OH})_2$ and regenerated with phosphoric acid	1.0	1.28 (Fe)	15.8		90.6	The solution had a faint metallic odor and taste
30							
35	Acetic acid HAMO neutralized with CaCO_3 and regenerated with sulfuric acid	<0.0					
40							
45	Acetic acid HAMO from Ca acetate and regenerated with phosphoric acid	2.0-2.5	17			158	

5	Maleic acid HAMO neutralized with Ca(OH) ₂ and regenerated with sulfuric acid	0.5- 1.0	12.9	15.9			
10 15	Maleic acid HAMO neutralized with Ca(OH) ₂ and regenerated with phosphoric acid	1.0- 1.5					
20 25	Maleic acid HAMO neutralized with Mg(OH) ₂ and regenerated with sulfuric acid	0.5		163	34.9		
30 35	Maleic acid HAMO neutralized with Mg(OH) ₂ and regenerated with phosphoric acid	1.0			19.5	287	
40 45	Lactic acid, propionic acid, acetic acid HAMO neutralized with Ca(OH) ₂ and regenerated with 10 N AGIIS	<<0.0					

5	Butyric acid HAMO neutralized with Ca(OH) ₂ and regenerated with phosphoric acid		0.589			7.16	
10	Butyric acid HAMO neutralized with Ca(OH) ₂ and regenerated with phosphoric acid				0.390	1.56	
15							
20	Succinic acid HAMO neutralized with Ca(OH) ₂ and regenerated with phosphoric acid	1.5	26.7			250	
25							
30	Succinic acid HAMO neutralized with Ca(OH) ₂ and regenerated with sulfuric acid	0.5-1.0	0.500	31			
35							
40	Succinic acid HAMO neutralized with Ca(OH) ₂ and regenerated with 5.58 N AGIIS	1.0-1.5	0.443	23.5			
45							

5	Succinic acid HAMO neutralized with $Mg(OH)_2$ and regenerated with 5.58 N AGIIS	1.0-1.5		115	24.1		
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Example 19

Formation of a HAMO from Glycine, Calcium Hydroxide and Sulfuric Acid

Glycine (37.55 g, 0.5 moles) was suspended in DI
5 water (100 mL) and solid calcium hydroxide (18.55 g,
0.25 moles) was added to the vigorously stirred
suspension. The mixture was allowed to stir at room
temperature for 30 minutes, and was then diluted to a
volume of 350 mL with DI water. Concentrated
10 sulfuric acid (27 mL, 55.6 g, 0.56 moles) was added
as rapidly as possible without causing the mixture to
rise above 85°C. The final mixture was allowed to
stir for 30 minutes, and was then diluted to a final
volume of 500 mL with DI water, and stirred a further
15 1 hour. The mixture was filtered through a medium-
porosity glass sinter to give the HAMO.

Example 20

Formation of a HAMO from Glutamic Acid, Calcium Hydroxide and Sulfuric Acid

20 Glutamic Acid (58.88 g, 0.4 moles) was suspended
in DI water (100 mL) and solid calcium hydroxide
(27.6 g, 0.4 moles) was added to the vigorously
stirred suspension. The reaction mixture became
noticeably warm. The mixture was allowed to stir at
25 room temperature for 45 minutes, and was then diluted
to a volume of approximately 350 mL with DI water.
Concentrated sulfuric acid (28 mL, 57.5 g, 0.57
moles) was added as rapidly as possible without
causing the mixture to rise above 85°C. The final
30 mixture was allowed to stir for 30 minutes, and was

then diluted to a final volume of 500 mL with DI water, and stirred a further 1 hour. The mixture was filtered through a medium-porosity glass sinter to give the HAMO. Analysis showed: Ca, 646 ppm; SO₄,
5 5,120 ppm.

Example 21

Formation of a HAMO from Glutamic Acid, Basic Copper(II) Carbonate and Phosphoric Acid

10 Glutamic Acid (58.88 g, 0.4 moles) was suspended in DI water (100 mL) and solid basic copper carbonate (55.2 g, 0.25 moles of CuCO₃•Cu(OH)₂) was added to the vigorously stirred suspension. The mixture became extremely viscous and slow effervescence was
15 observed. The mixture was stirred at ambient temperature for 24 hours to complete the reaction. Concentrated phosphoric acid (53.6 g, 86.5%, 0.47 moles) was added to the vigorously stirred mixture in a single aliquot, and the mixture was stirred for 24
20 hours. Constant stirring was required to prevent the mixture from setting solid. Filtration of the mixture through a medium porosity sintered glass funnel provided the HAMO as a deep blue solution.

Example 22

25 Formation of a HAMO from Glutamic Acid, Basic Cobalt(II) Carbonate and Phosphoric Acid

Glutamic Acid (58.3 g, 0.4 moles) was suspended in DI water (200 mL) and solid basic cobalt carbonate (81.35 g, 0.16 moles of 2CoCO₃•3Co(OH)₂) was added to
30 the vigorously stirred suspension. The mixture

became viscous and slow effervescence was observed. The mixture was stirred at ambient temperature for 24 hours to complete the reaction. Concentrated phosphoric acid (53.6 g, 86.5%, 0.47 moles) was added
5 to the vigorously stirred mixture in a single aliquot, and the mixture was stirred for 24 hours. Constant stirring was required to prevent the mixture from setting solid. Filtration of the mixture through a medium porosity sintered glass funnel
10 provided the HAMO as a pink solution.

Example 23

General Method for the Formation of an Amino Acid HAMO Using 1.2 M Sulfuric Acid as Regenerating Acid

A solution of dilute sulfuric acid approximately
15 1.2 M in sulfuric acid was prepared by weighing 111.64 g of concentrated (96-98%) sulfuric acid and diluting with water to 1000.0 mL.

The amino acid or its hydrochloride salt (0.025-
0.1 mole) was weighed into an Erlenmeyer flask and
20 approximately 10 mole equivalents of water was added. Solid calcium hydroxide (7.40 g, 0.10 mol) was added to the flask and the mixture was stirred at room temperature for 30 minutes to ensure complete reaction. The dilute sulfuric acid (84.0 mL, 0.10
25 moles H_2SO_4) was then added to the mixture. The mixture was filtered through a medium-porosity glass frit to give the HAMO. The total acid content of the HAMO was determined by titration against standard tris-(hydroxymethyl)aminomethane ("THAM").

HAMOs Prepared From Amino Acids by This Method

	<u>Amino Acid</u>	<u>Moles of Amino Acid</u>	<u>[H₃O⁺] in HAMO*</u>
	L-glutamine	0.10	0.133 M ¹
	L-phenylalanine	0.05	0.185 M ²
5	L-asparagine	0.10	0.070 M ³
	L-histidine•HCl	0.10	0.57 M
	L-glutamic acid	0.10	0.124 M ⁴
	L-aspartic acid	0.10	0.170 M ⁵
	L-lysine.HCl	0.10	0.56 M ⁶
10	L-leucine	0.10	0.173 M ⁷
	L-alanine	0.10	0.099 M ⁸
	L-isoleucine	0.02	0.351 M ⁹
	L-serine	0.025	0.274 M

15 *Molarity

1. Ca, 844 ppm ; SO₄, 3,120 ppm.
2. Ca, 390 ppm ; SO₄, 13,900 ppm.
3. Ca, 625 ppm ; SO₄, 3,120 ppm.
4. Ca, 646 ppm ; SO₄, 5,120 ppm.
- 20 5. Ca, 1,290 ppm ; SO₄, 3,850 ppm.
6. Ca, 1,910 ppm ; SO₄, 7,560 ppm.
7. Ca, 329 ppm ; SO₄, 315,000 ppm.
8. Ca, 1,230 ppm ; SO₄, 4,480 ppm.
- 25 9. Ca, 749 ppm ; SO₄, 314,000 ppm.

HAMOs Prepared With Amino Acids and Metal Bases*

	<u>Amino Acid</u>	<u>Metal Base</u>	<u>Regenerating Acid</u>
5	L-glutamine	Ca(OH) ₂	H ₂ SO ₄
	L-phenylalanine	Ca(OH) ₂	H ₂ SO ₄
	L-asparagine	Ca(OH) ₂	H ₂ SO ₄
	L-histidine•HCl	Ca(OH) ₂	H ₂ SO ₄
	L-glutamic acid	Ca(OH) ₂	H ₂ SO ₄
10	L-aspartic acid	Ca(OH) ₂	H ₂ SO ₄
	L-lysine•HCl	Ca(OH) ₂	H ₂ SO ₄
	L-leucine	Ca(OH) ₂	H ₂ SO ₄
	L-alanine	Ca(OH) ₂	H ₂ SO ₄
	L-isoleucine	Ca(OH) ₂	H ₂ SO ₄
15	L-serine	Ca(OH) ₂	H ₂ SO ₄
	glycine	Ca(OH) ₂	H ₂ SO ₄
	L-glutamic acid	CuCO ₃ •Cu(OH) ₂	H ₃ PO ₄
	L-glutamic acid	2CoCO ₃ •3Co(OH) ₂	H ₃ PO ₄
20	L-glutamic acid	MnCO ₃	H ₃ PO ₄

*Each of the product has a pH of lower than about 3.

Example 24**Using HAMO to Decontaminate Apples**

Each apple in this experiment was immersed in an E.coli O157:H7 culture containing 8.8×10^8 /ml for 5 minutes, and then air-dried at room temperature for about 24 hours. In one group, a volume of 300 ml of HAMO (prepared from acetic acid using phosphoric acid as the regenerating acid. The pH of the HAMO was 1.13) was used to decontaminate E.coli O157:H7-contaminated apples for 1 minute with shaking. In another group, the control group, each of the contaminated-apple was treated with 300 ml of sterilized saline. After treatment, each apple was homogenized. A comparison of plate-counts between treated and control group was made. The saline treated apple had 5.37×10^5 /g (5.32×10^7 /apple) survival of E.coli O157:H7; while the HAMO treated apple had 4.4×10^1 /ml (4.39×10^3 /apple) survival of E.coli O157:H7. Each of the treated and untreated apple weighed about 99 g.

Example 25**Using HAMO to Prolong the Shelf-Life of Sausages**

Half a pack of non-preserved sausages was dipped in HAMO (prepared from propionic acid using AGIIS as the regenerating acid. The pH of the HAMO was 1.51) for about 0.5 minute, and then packed into a zip-lock bag. The bag was then left at room temperature for 72 hours. In parallel, the other half pack of the sausage was dipped in the same amount of autoclaved de-ionized water. After 72 hours at room

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temperature, the control group of sausage was rotten; while the HAMO treated group was still fresh. The HAMO treated sausages had over 9-logs reductions in total bacterial counts compare with control group
5 (i.e. from 9.55×10^9 /sausage for the control to an amount that was undetectable in the treated sausage).

Example 26

"Sanitizing" Chopping Board With HAMO

Two small chopping board were inoculated with
10 5ml of E.coli O157:H7 culture (3.55×10^8 /ml). The board were then air-dried overnight. One board was then soaked for 5 minutes with 10 ml of HAMO (prepared from acetic acid using phosphoric acid as the regenerating acid. pH of the HAMO was 1.13).
15 The board was then wiped 3 times with sterile gauze, each gauze was then soaked in 20 ml of saline solution in a stomacher bag and the bag was stomached at high speed for 2 minutes. Then the serial dilution was performed to determine the bacterial
20 survival.. A parallel control was performed using 10 ml of de-ionized water to treat the chopping board. The result shows the water treated chopping board had a survival E.coli O157:H7 level of 3.96×10^5 / board, while the HAMO treated one had no E.coli O157:H7 that
25 could be detected.

Example 27

Prolonging Shelf-Life of Cheese With HAMO

A block of mild cheddar cheese (about 8 oz) was sprayed with a solution of HAMO (prepared from propionic acid and AGIIS, the pH value of the HAMO was 1.51). The treated cheese was then stored in a zip lock bag and kept at 4° C. A control block of mild cheddar cheese was stored under identical conditions. After 13 days, mold growth was observed on the control, whereas the treated cheese remained mold free for another 20 days.

What is claimed is:

1. An acidic composition having an acidic pH value and an acid normality value, the acidic composition comprising:
 - 5 a monovalent or polyvalent cation;
an organic acid; and
an anion of a strong oxyacid,
wherein the acidic composition is less
corrosive to a ferrous metal than is a solution of a
10 mineral acid having the same acidic pH value as that of
the acidic composition, and
wherein the acid composition is more biocidal
than a mixture of the organic acid and a metal salt of
the organic acid which mixture having the same acid
15 normality value as that of the acidic composition.
2. The acidic composition of claim 1, wherein
the monovalent cation comprises an ion of Group IA
element.
3. The acidic composition of claim 1, wherein
20 the polyvalent cation comprises an ion of a Group IIA
element, but not beryllium.
4. The acidic composition of claim 1, wherein
the polyvalent cation comprises an ion of a Group IIIA
element, but not boron.
- 25 5. The acidic composition of claim 1, wherein
the polyvalent cation comprises a metal of the first
transition series.
6. The acidic composition of claim 1, wherein

the polyvalent cation comprises an ion of magnesium, calcium, ferrous, copper, or zinc.

7. The acidic composition of claim 1, wherein the polyvalent cation comprises an ion of lead,
5 bismuth, or tin.

8. The acidic composition of claim 1, wherein the organic acid comprises a carboxylic acid or an acidic vitamin.

9. The acidic composition of claim 8, wherein
10 the acidic vitamin comprises vitamin C.

10. The acidic composition of claim 1, wherein the organic acid comprises a monocarboxylic acid, a dicarboxylic acid, or a tricarboxylic acid.

11. The acidic composition of claim 1, wherein
15 the organic acid comprises acetic acid, lactic acid, formic acid, or propionic acid.

12. The acidic composition of claim 1, wherein the organic acid comprises an amino acid.

13. The acidic composition of claim 12, wherein
20 the organic acid comprises glycine, valine, leucine, phenylalanine, lysine, serine, asparagine, glutamic acid, alanine, arginine, aspartic acid, cysteine, histidine, hydroxylysine, hydroxyproline, isoleucine, methionine, proline, threonine, tryptophan, tyrosine,
25 aminoadipic acid, diaminobutyric, ornithine, pepicollic acid, sarcosine or triiodothyronine.

14. An acidic composition prepared by mixing ingredients comprising:
- at least one regenerating acid having a first
5 number of equivalents;
 - at least one metal base having a second number of equivalents; and
 - at least one organic acid,
- 10 wherein the first number of equivalents of the regenerating acid is greater than that of the second number of equivalents of the metal base.
- 15 15. The acidic composition of claim 14, wherein the regenerating acid comprises a strong oxyacid of sulfur, phosphorus, nitrogen, chromium, or iodine.
16. The acidic composition of claim 14, wherein
15 the regenerating acid comprises a strong oxyacid of molybdenum, tungsten, or selenium.
17. The acidic composition of claim 14, wherein
20 the regenerating acid comprises sulfuric acid, phosphoric acid, or an acidic solution of sparingly-soluble Group IIA complexes.
18. The acidic composition of claim 17, wherein
25 the acidic sparingly-soluble Group IIA complex is prepared by mixing ingredients comprising a mineral acid and a Group IIA hydroxide, or a Group IIA salt of a dibasic acid, or a mixture thereof.
19. The acidic composition of claim 18, wherein the Group IIA hydroxide comprises calcium hydroxide,

the mineral acid comprises sulfuric acid, and the Group IIA salt of the dibasic acid comprises calcium sulfate.

20. The acidic composition of claim 14, wherein the metal base comprises a hydroxide, a carbonate, a bicarbonate, or an oxide of a metal.

21. The acidic composition of claim 14, wherein the metal base comprises a base of a Group IA element.

22. The acidic composition of claim 14, wherein the metal base comprises a base of a Group IIA element, but not beryllium.

23. The acidic composition of claim 14, wherein the metal base comprises a base of a Group IIIA element, but not boron.

24. The acidic composition of claim 14, wherein the metal base comprises a base of a metal of the first transition series.

25. The acidic composition of claim 14, wherein the metal base comprises a base of magnesium, calcium, ferrous, copper, or zinc.

26. The acidic composition of claim 14, wherein the metal base comprises a base of lead, bismuth, or tin.

27. The acidic composition of claim 14, wherein the organic acid comprises a carboxylic acid or an acidic vitamin.

28. The acidic composition of claim 27, wherein the acidic vitamin comprises vitamin C.

29. The acidic composition of claim 14, wherein the organic acid comprises a monocarboxylic acid, a dicarboxylic acid, or a tricarboxylic acid.

30. The acidic composition of claim 14, wherein the organic acid comprises acetic acid, lactic acid, formic acid, or propionic acid.

31. The acidic composition of claim 14, wherein the organic acid comprises an amino acid having an amino group, and wherein the number of equivalents of the regenerating acid is greater than the total number of equivalents of the metal base and the amino group of the amino acid.

32. The acidic composition of claim 31, wherein the organic acid comprises glycine, valine, leucine, phenylalanine, lysine, serine, asparagine, glutamic acid, alanine, arginine, aspartic acid, cysteine, histidine, hydroxylysine, hydroxyproline, isoleucine, methionine, proline, threonine, tryptophan, tyrosine, aminoadipic acid, diaminobutyric, ornithine, pepicollic acid, sarcosine or triiodothyronine.

33. An acidic composition prepared by mixing ingredients comprising:

at least one regenerating acid having a first number of equivalents; and

at least one metal salt of an organic acid having a second number of equivalents,

wherein the first number of equivalents of the regenerating acid is greater than the second number of equivalents of the metal salt of the organic acid.

34. The acidic composition of claim 33, wherein
5 the regenerating acid comprises a strong oxyacid of sulfur, phosphorus, nitrogen, chromium, or iodine.

35. The acidic composition of claim 33, wherein the regenerating acid comprises a strong oxyacid of molybdenum, tungsten, or selenium.

10 36. The acidic composition of claim 33, wherein the regenerating acid comprises sulfuric acid, phosphoric acid, or an acidic solution of sparingly-soluble Group IIA complexes.

15 37. The acidic composition of claim 36, wherein the acidic sparingly-soluble Group IIA complex is prepared by mixing ingredients comprising a mineral acid and a Group IIA hydroxide, or a Group IIA salt of a dibasic acid, or a mixture thereof.

20 38. The acidic composition of claim 36, wherein the Group IIA hydroxide comprises calcium hydroxide, the mineral acid comprises sulfuric acid, and the Group IIA salt of the dibasic acid comprises calcium sulfate.

25 39. The acidic composition of claim 36, wherein the metal salt of the organic acid comprises a salt of a Group IA element.

40. The acidic composition of claim 36, wherein

the metal salt of the organic acid comprises a salt of a Group IIA element, but not beryllium.

41. The acidic composition of claim 36, wherein the metal salt of the organic acid comprises a salt of a Group IIIA element, but not boron.

42. The acidic composition of claim 36, wherein the metal salt of the organic acid comprises a salt of a metal of the first transition series.

43. The acidic composition of claim 36, wherein the metal salt of the organic acid comprises a salt of magnesium, calcium, ferrous, copper, or zinc.

44. The acidic composition of claim 36, wherein the metal salt of the organic acid comprises a salt of lead, bismuth, or tin.

45. The acidic composition of claim 36, wherein the organic acid comprises a carboxylic acid or an acidic vitamin.

46. The acidic composition of claim 36, wherein the acidic vitamin comprises vitamin C.

47. The acidic composition of claim 36, wherein the organic acid comprises a monocarboxylic acid, a dicarboxylic acid, or a tricarboxylic acid.

48. The acidic composition of claim 36, wherein the organic acid comprises acetic acid, lactic acid, formic acid, or propionic acid.

49. The acidic composition of claim 36, wherein the organic acid comprises an amino acid having an amino group, wherein the total number of equivalents of the regenerating acid is greater than the total number
5 of equivalents of the metal salt of the organic acid and the total number of equivalents of amino groups from the amino acid.

50. The acidic composition of claim 49, wherein the organic acid comprises glycine, valine, leucine,
10 phenylalanine, lysine, serine, asparagine, glutamic acid, alanine, arginine, aspartic acid, cysteine, histidine, hydroxylysine, hydroxyproline, isoleucine, methionine, proline, threonine, tryptophan, tyrosine, aminoadipic acid, diaminobutyric, ornithine, pepicollic
15 acid, sarcosine or triiodothyronine.

51. An acidic composition prepared by mixing ingredients comprising:

at least one regenerating acid, wherein the regenerating acid comprises sulfuric acid, phosphoric
20 acid or an acidic solution of sparingly-soluble Group IIA complexes, and wherein the regenerating acid has a first number of equivalents;

at least one polyvalent base, wherein the polyvalent base is calcium hydroxide, calcium
25 carbonate, or magnesium hydroxide, and wherein the polyvalent base has a second number of equivalents; and

at least one organic acid, wherein the organic acid is acetic acid, lactic acid, formic acid
or propionic acid, and

30 wherein the first number of equivalents of the regenerating acid is greater than the second number

of equivalents of the polyvalent base.

52. The acidic composition of claim 51, wherein the acidic sparingly-soluble Group IIA complex is prepared by mixing ingredients comprising a mineral
5 acid and a Group IIA hydroxide, or a Group IIA salt of a dibasic acid, or a mixture thereof.

53. The acidic composition of claim 52, wherein the Group IIA hydroxide comprises calcium hydroxide, the mineral acid comprises sulfuric acid, and the Group
10 IIA salt of the dibasic acid comprises calcium sulfate.

54. An acidic composition prepared by mixing ingredients comprising:

at least one regenerating acid, wherein the regenerating acid comprises sulfuric acid, phosphoric
15 acid or an acidic solution of sparingly-soluble Group IIA complexes, and wherein the regenerating acid has a first number of equivalents;

at least one salt of an organic acid, wherein the salt is a calcium or magnesium salt of acetic acid,
20 lactic acid, formic acid or propionic acid, and wherein the salt of the organic acid has a second number of equivalents, and

wherein the first number of equivalents of the regenerating acid is greater than the second number
25 of equivalents of the salt or the organic acid.

55. The acidic composition of claim 54, wherein the acidic sparingly-soluble Group IIA complex is prepared by mixing ingredients comprising a mineral
30 acid and a Group IIA hydroxide, or a Group IIA salt of

a dibasic acid, or a mixture thereof.

56. The acidic composition of claim 55, wherein the Group IIA hydroxide comprises calcium hydroxide, the mineral acid comprises sulfuric acid, and the Group IIA salt of the dibasic acid comprises calcium sulfate.

57. A method of preparing an acidic composition, comprising:

dissolving or suspending an organic acid in water to give a solution or suspension of the organic acid;

adding a metal base to this solution or suspension of the organic acid to give a mixture;

adding to the mixture an amount of regenerating acid sufficient to ensure complete regeneration of the organic acid from its metal salt; and

removing the undissolved solid to give the acidic composition.

58. A method of preparing an acidic composition, comprising:

dissolving or suspending a monovalent, divalent or trivalent metal salt of an organic acid to give a solution or suspension of the salt of the organic acid;

adding to the solution or suspension of the salt of the organic acid an amount of regenerating acid sufficient to ensure complete regeneration of the organic from its metal salt; and

removing the undissolved solid to give the acidic composition.