Abstract:

Title: COMPOSITIONS AND USES THEREOF

(57) Abstract: A synthetic acid composition for replacing hydrochloric acid in industrial activities requiring large amounts of hydrochloric acid, said composition comprising: urea and hydrogen chloride in a molar ratio of not less than 0.1:1 and formic acid or a derivative thereof; optionally, a phosphonic acid derivative; a metal iodide or iodate; and an alcohol or derivative thereof can also be included.
SYNTHETIC ACID COMPOSITIONS AND USES THEREOF

FIELD OF THE INVENTION

This invention relates to compositions for use in performing various operations in industries including, but not limited to, pulp & paper, mining, dairy, ion exchange bed regeneration, manufacturing, food-brewery-sugar production and textiles manufacturing more specifically to synthetic acid compositions as alternatives to HCl (hydrochloric acid).

BACKGROUND OF THE INVENTION

Multiple industries work with HCl in large amounts and on a daily basis. One of the problems encountered with HCl (hydrochloric acid) is that it releases airborne toxins that can have serious side effects on plant and mill workers, as well as the environment in the surrounding area. For example, if hydrochloric acid is not properly filtered through air purification ducts and is released into the atmosphere, in its aerosol form hydrogen chloride gas is highly toxic and corrosive. So while the need for acids in industries will never diminish, the toxins released in the air by their application needs to be.

It is advantageous to have an alternative to HCl that does not create hydrogen chloride gas and has low rates of corrosion. Hydrochloric acid is corrosive to the eyes, skin, and mucous membranes. Acute (short-term) inhalation exposure may cause eye, nose, and respiratory tract irritation and inflammation and pulmonary edema in humans. Acute oral exposure may cause corrosion of the mucous membranes, esophagus, and stomach and dermal contact may produce severe burns, ulceration, and scarring in humans. Chronic (long-term) occupational exposure to hydrochloric acid has been reported to cause gastritis, chronic bronchitis, dermatitis, and photosensitization in workers. Prolonged exposure to low concentrations may also cause dental discoloration and erosion.

There are many different mineral and organic acids used to perform various functions in these industries. A common type of acid employed is hydrochloric acid (HCl), which is useful in, but not limited to, cleaning scale or to lower the pH of a fluid. Corrosion and fumes are the major concerns when HCl is applied in industry.
As an example, the total annual corrosion costs for the pulp, paper, and paperboard industry, as determined as a fraction of the maintenance cost, is estimated to be over $2.0 billion per year in the US alone. Therefore it is highly desirable to have a non-fuming product that has very low corrosion rates that can replace the harsh acids typically utilized.

Paper production consists of a series of processes and can be roughly divided according to the five major manufacturing steps: (1) pulp production, (2) pulp processing and chemical recovery, (3) pulp bleaching, (4) stock preparation, and (5) paper manufacturing. Each manufacturing step has its own corrosion problems related to the size and quality of the wood fibers, the amount of and temperature of the process water, the concentration of the treatment chemicals, and the materials used for machinery construction. Examples of corrosion affecting production are: (1) corrosion products polluting the paper; and (2) corrosion of rolls leading to scarring of the sheets of paper. Corrosion of components may also result in fractures or leaks in the machines, causing production loss and safety hazards. Table 1 sets out the main chemicals and amounts release in total and on average in the pulp and paper industry.

Table 1 - Top five highest amounts of toxics release inventory (TRI) chemicals released in 1995 by pulp and paper facilities

<table>
<thead>
<tr>
<th>CHEMICAL</th>
<th>TOTAL NUMBER OF RELEASES (in metric tons)</th>
<th>AVERAGE RELEASE FACILITY: PER (in metric tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>62,657</td>
<td>358</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>11,022</td>
<td>68</td>
</tr>
<tr>
<td>Ammonia</td>
<td>6,643</td>
<td>34</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>5,864</td>
<td>40</td>
</tr>
</tbody>
</table>

In industries demanding purity (e.g. food, pharmaceutical, drinking water), high-quality hydrochloric acid is used to control the pH of process water streams. In less demanding industry, technical quality hydrochloric acid suffices for the neutralization of waste streams and for swimming pool treatment. It is desirable to have a synthetic option to HC1 having very low levels of toxicity and corrosion and being non-fuming which can be safely handled and utilized in those industries.
Some major industrial uses of HCl include the food and dairy industry. In the food industry, hydrochloric acid is used in the manufacture of protein and starch. It is also used in demineralizing whey. Moreover, it is also extensively used in casein manufacturing, as well as the regeneration of ion exchange resins. Ion exchange resins are used to remove impurities in the production of corn syrups such as high-fructose corn syrup (HFCS). HFCS are widely used in the food industry but by far their largest use (upwards of 70%) is in the manufacturing of soft drinks. It is also used for hydrolyzing starch and proteins in the preparation of various food products. In the dairy industry acid cleaners remove or prevent accumulated mineral deposits or milkstone buildup. It is advantageous to have an alternative to harsh acids that is non-hazardous.

As part of water treatment processes, hydrochloric acid is widely used as an effective neutralization agent for alkaline (high pH) effluent.

HCl is also used in neutralizing alkaline soils in agricultural and landscaping applications. It is also commonly used in the manufacture of fertilizers.

HCl is also used as an efflorescence cleaner for retaining walls, driveways, brick and as a mortar cleaner. It is also used to etch concrete which is typically treated with phosphoric acid. Phosphoric acid is another strong acid which emits toxic fumes irritating the nasal passages, eyes and skin.

HCl is also used as cement cleaner, more specifically in the removal of cement based material from equipment or structures as well as in the treatment of boiler scale, as well as being a scale cleaner applicable to ships, submarines, offshore vessels, and evaporators.

HCl can also be used as a catalyst and solvent in organic syntheses, as a laboratory reagent, for refining ore in the production of tin and tantalum among other minerals.

In the mining industry, there is heavy reliance on the acid leaching of certain minerals from ore deposits, an economical method of recovering valuable minerals from otherwise inaccessible bodies of ore. HCl is thus widely used in this industry as well.

Moreover, HCl is also used extensively in steel pickling. Steel pickling of carbon, alloy and stainless steels is a process where the acid removes surface impurities on steel. Such
impurities include iron oxides and scale. The iron oxides are removed by contact with the acid which solubilizes the oxides. Steel pickling is a necessary step in further processing steel products into such items as: wires, coating of sheet and strip as well as tin mill products. Other than pickling operations, HCl can also be used to perform aluminum etching, metal galvanizing, soldering and metal cleaning as well as a number of other operations.

HCl is also used in several retail applications as a component in typical household cleaners for cleaning tiles and sinks etc.

HCL is also commonly employed in the photographic and rubber industries, electronics manufacturing, as well as the textile industry in which waste from textile industries is rarely neutral. Certain processes such as reactive dyeing require large quantities of alkali but pre-treatments and some washes can be acidic. It is therefore necessary to adjust the pH in the treatment process to make the wastewater neutral. This is particularly important if biological treatment is being used, as the microbes used in biological treatment require a pH in the range of 6-8 and will be killed by highly acidic or alkali wastewater. In PCETP, the wastewater is mostly alkali wastes (high pH). For this purpose, hydrochloric acid (HCl) is added to maintain the pH value from 7.5 to 7.8 to save the microbes used in biological treatment as well as to reduce the wastage of chemicals. Therefore, it is advantageous to have an alternative pH control mechanism that is non-hazardous.

Some of the major challenges faced in various industries include the following: general high levels of corrosion due to the use of acids. These corrosion problems are typically countered by the addition of corrosion inhibitors that are typically themselves sometimes toxic and harmful to humans, the environment and or even the equipment. Reactions between acids and various types of metals can vary greatly, but softer metals, such as aluminum, are very susceptible to severe corrosion causing immediate damage. Toxicity levels of acids applied (including multiple additives used to control corrosion, emulsions, compatibility with oils/liquids, iron controls, water wetting agents etc.). Hydrochloric acid produces hydrogen chloride gas which is toxic and corrosive to skin, eyes and metals. At levels above 50 ppm (parts per million), hydrogen chloride gas can be Immediately Dangerous to Life and Health (IDHL). At levels ranging from 1300-2000 ppm, death can occur in 2-3 minutes.
The inherent environmental dangers (organic sterility, poisoning of wildlife etc.) of the use of acids in the event of an unintended/accidental release into water aquifers or sources of water are devastating as they can cause significant pH reduction of such and can substantially increase the toxicity and could potentially cause a mass culling of aquatic species and potential poisoning of humans/livestock and wildlife exposed to/or drinking the water. An unintended surface release can also cause the release of a hydrogen chloride gas cloud, potentially endangering human and animal health. This is a common event at large storage sites when tanks split or leak or during a traffic accident involving an acid tanker. Typically, if near the public, large areas need to be evacuated post-event. Because of its acidic nature, hydrogen chloride gas is also corrosive, particularly in the presence of moisture.

The inability for acids and blends of such to biodegrade naturally without neutralizing the soil results in expensive cleanup-reclamation costs for the operator should an unintended release occur. Moreover, the toxic fumes produced by mineral & organic acids are harmful to humans/animals and are highly corrosive and/or explosive potentially blending exposure dangers for personnel exposed to handling harmful acids.

Another concern is the potential for spills on locations due to high corrosion levels of acids causing storage container failures and/or deployment equipment failures caused by high corrosion rates. Other concerns include: inconsistent strength or quality level of mineral & organic acids; potential supply issues based on industrial output levels; and ongoing risks to individuals handling acid containing containers.

Price fluctuations with typical mineral and organic acids based on industrial output causing end users an inability to establish long term costs in their respective budgets; severe reaction with dermal/eye tissue; major PPE requirements (personal protective equipment) for handling, such as on-site shower units; extremely high corrosion rates as temperature increases.

When used to treat scaling issues on surface due to precipitation of minerals, acids are exposed to humans and mechanical devices as well as expensive equipment causing increased risk for the operator and corrosion effects that damage equipment and create hazardous fumes. When mixed with bases or higher pH fluids, acids will create a large amount of thermal energy (exothermic reaction) causing potential safety concerns and equipment damage.
Typical organic and mineral acids used in a pH control situation can or will cause degradation of certain additives/systems requiring further chemicals to be added to counter these potentially negative effects. When using an acid to pickle steel, very careful attention must be paid to the process due to high levels of corrosion. Acids are very destructive to many typical elastomers found in various industries such as in water treatment/transfer pumps. It is advantageous to have an HCl alternative that preferably does no damage to elastomers.

Acids perform many critical functions in various industries and are considered indispensable to achieve a desired result. However, the associated dangers that come with using acids are expansive and risk mitigation through various control measures (whether they are chemically or mechanically engineered) are both costly and complex and/or time-consuming.

Eliminating or even simply reducing the negative effects of acids while maintaining their usefulness is a struggle for many industries. As the public demand for the use of cleaner/safer/greener products increases, companies are looking for alternatives that perform the required function without all or most of the drawbacks associated with the use of acids.

US patent no. 4,402,852 discloses compositions containing 5 to 75% of urea, 5 to 85% of sulfuric acid and from 5 to 75% of water. These compositions are said to have reduced corrosivity to carbon steels.

US patent no. 6,147,042 discloses compositions comprising a polyphosphoric acid-urea condensate or polymer which results from the reaction of orthophosphoric acid and urea used in the removal of etching residue containing organometal residues.

US patent no. 7,938,912 discloses compositions containing hydrochloric acid, urea, a complex substituted keto-amine-hydrochloride, an alcohol, an ethoxylate and a ketone for use to clean surfaces having cementitious compositions. US patent no. 8,430,971 and 8,580,047 disclose and claim compositions containing specific amounts of hydrochloric acid (55% by wt), urea (42% by wt), a complex substituted keto-amine-hydrochloride (0.067% by wt), propargyl alcohol (0.067% by wt), an ethoxylated nonylphenol (0.022% by wt), methyl vinyl ketone (0.022% by wt), acetone (0.0022% by wt), and acetophenone (0.0022% by wt).
US patent no. 5,672,279 discloses a composition containing urea hydrochloride prepared by mixing urea and hydrochloric acid. Urea hydrochloride is used to remove scale in hot water boilers and other industrial equipment such as papermaking equipment. Scale is caused by the presence of calcium carbonate which is poorly soluble in water and tends to accumulate on surfaces and affect equipment exposed to it.

US patent no. 3,779,935 discloses a composition for use in the inhibition of corrosion caused by the use of acids on ferrous metals. It is said that the essential components of the invention are at least one acetylenic alcohol which may have 3 to 10 carbon atoms, the quaternary ammonium compound and the formic acid compound all of which cooperate to reduce the corrosivity of corrosive acids. The alkanols perform the function of a solvent. The ethoxylated compounds function as a surfactant. The compositions disclosed do contain chemicals which are highly reactive and can cause skin irritation, serious eye irritation and respiratory irritation.

US patent no. 4,028,268 discloses compositions for use in the reduction of metal corrosion comprising be prepared by blending at least four unique specially selected components which interact together to provide metal corrosion inhibition, the components include custom-made specific quartemized cyclic nitrogen base, a specific acetylenic alcohol, a surface active agent and a formic acid derivative.

EP 276 879 discloses corrosion inhibitor compositions to be added to an aqueous acid. The compositions disclosed combine at least one iodide salt, at least one compound selected from the group of formic acid compounds, formic acid derivatives, and formate esters, together with at least one nitrogen compound or at least one oxygen-containing compound, as described in the patent. Tested compositions contained a mixture of 2-benzoyl-3-methoxy-1-propene and 2-benzoyl-1,3-dimethoxy-propane (PK), a quinolinium compound, namely naphthylmethylquinolinium chloride (NMQC1), potassium iodide, and formic acid. The NMQC1 was prepared by refluxing equimolar amounts of quinoline and chloromethylnaphthylene in methanol at 70 to 75°C for six hours.

Given the list of hazards related to human exposure it is desirable to prepare compositions which do not contain this chemical but which provide an adequate and preferably,
comparable, level of efficacy in synthetic acid compositions with respect to its effect on corrosion inhibition.

Synthetic acid compositions are mostly applicable in the cleaning industry. However, such compositions require the additional of a number of various chemical compounds which are dangerous in their undiluted states. The physical process to make such cleaning compositions involves multiple steps of mixing, blending and dilution. The present invention proposes the removal of certain chemicals used which would rationalize the process to make the compositions of the present invention and therefore render the manufacturing process safer from a production point of view. Moreover, it was discovered that the composition according to the present invention exhibits stability for operations at elevated temperature (above 65°C) and therefore makes them useful in various operations across several industries. Consequently, there is still a need for compositions for use in the various industries which can be used over a range of applications which can decrease a number of the associated dangers/issues typically associated with acid applications to the extent that these acid compositions are considered much safer for handling on worksites.

Consequently, there is still a need for alternative compositions to HCl for use in various industries which can be used over a range of applications which can decrease a number of the associated dangers/issues typically associated with applications requiring HCl to the extent that these compositions are considered much safer for handling on worksites.

The present invention answers the need for both a simpler manufacturing process and abridged synthetic acid compositions for use in high volume operations in various industrial settings where water usage and discharge in the environment is a concern.

**SUMMARY OF THE INVENTION**

Compositions according to the present invention have been developed for, but not limited to, pulp & paper, mining, dairy, ion exchange bed regeneration, manufacturing, food-brewery-sugar production and textiles manufacturing industries and associated applications, by targeting the problems of corrosion, logistics, storage, human/environmental exposure and equipment/liquid-product compatibilities.
It is an object of the present invention to provide a synthetic acid composition which can be used over a broad range of applications in these industries and which exhibit advantageous properties over HCl.

According to one aspect of the present invention, there is provided a synthetic acid composition which, upon proper use, results in a very low corrosion rate of various industry activities equipment.

According to another aspect of the present invention, there is provided a synthetic acid composition for use in various industries which is biodegradable.

According to a preferred embodiment of the present invention, there is provided a synthetic acid composition for use in industry which has a methodically spending (reacting) nature that is linear at higher temperature, non-fuming, non-toxic, high quality-consistent controlled.

According to a preferred embodiment of the present invention, there is provided a synthetic acid composition for use in industry which has a pH below 1.

According to a preferred embodiment of the present invention, there is provided a synthetic acid composition for use in industry which has minimal exothermic reactivity.

According to a preferred embodiment of the present invention, there is provided a synthetic acid composition for use in industry which is compatible with most existing industries additives and pump elastomers/seals.

According to a preferred embodiment of the present invention, there is provided a synthetic acid composition that has a very low evaporation rate.

According to a preferred embodiment of the present invention, there is provided a synthetic acid composition for use in industry which is reactive upon contact/application.

According to a preferred embodiment of the present invention, there is provided a synthetic acid composition for use in industry which provides an easily adjustable, methodical
and comprehensive reaction rate. In most industrial applications it is advantageous to have a more methodical reacting product as it will produce less potential for precipitation of minerals due to increased "free" room of a lower chloride fluid in the present invention.

According to an aspect of the present invention, there is provided a synthetic acid composition for use in the mining industry, the use being selected from, but not limited to, the group consisting of treating scale and adjusting pH levels in fluid systems.

According to another aspect of the present invention, there is provided a synthetic acid composition for use in the water treatment industry said use being selected from the group consisting of adjusting pH and neutralizing alkaline effluent.

According to another aspect of the present invention, there is provided a synthetic acid composition for use in the fertilizer/landscaping industry to adjust the pH level of a soil.

According to yet another aspect of the present invention, there is provided a synthetic acid composition for use to regenerate ion exchange beds.

According to an aspect of the present invention, there is provided a synthetic acid composition for use in the construction industry said use being selected from the group consisting of etching concrete and cleaning concrete of efflorescence.

According to an aspect of the present invention, there is provided a synthetic acid composition for use in the electrical generation industry, said use being selected from the group consisting of descaling pipelines and related equipment and descaling facilities.

According to another aspect of the present invention, there is provided a synthetic acid composition for use in the food and dairy industry, said use being selected from the group consisting of: manufacturing protein, manufacturing starch, demineralizing whey, manufacturing casein, milk stone removal and regenerating ion exchange resins.

According to a preferred embodiment of the present invention, there is provided a synthetic acid composition for use in the swimming pool industry to lower the pH of fluids.
According to an aspect of the present invention, there is provided a synthetic acid composition for use in the manufacturing industry to perform an operation selected from the group consisting of pickling steel and cleaning metal.

According to an aspect of the present invention, there is provided a synthetic acid composition for use in the retail industry as a low pH cleaning additive.

According to an aspect of the present invention, there is provided a synthetic acid which has a low rate of corrosion on aluminum.

Accordingly, the composition according to the present invention is intended to overcome many of the drawbacks found in the use of prior art compositions of HCl in various industries.

It is understood that other uses or applications within these industries can be accomplished with the compositions according to the present invention.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The description that follows, and the embodiments described therein, are provided by way of illustration of an example, or examples, of particular embodiments of the principles of the present invention. These examples are provided for the purposes of explanation, and not limitation, of those principles and of the invention.

According to an aspect of the invention, there is provided a synthetic acid composition comprising:

- urea & hydrogen chloride in a molar ratio of not less than 0.1:1; preferably in a molar ratio not less than 0.5:1, more preferably in a molar ratio not less than 1:1; and

- formic acid or a derivative thereof such as acetic acid, ethylformate and butyl formate are present in an amount ranging from 0.05 - 2.0 %, preferably in an amount of approximately 0.15%; formic acid is the preferred compound.

Optionally, a phosphonic acid or derivatives can be incorporated, preferably alkylphosphonic acid or derivatives thereof and more preferably amino tris methylene phosphonic acid and derivatives thereof. Also optionally, a metal iodide or iodates can be
incorporated, preferably cupric iodide, potassium iodide, sodium iodide or lithium iodide; and also optionally, an alcohol or derivatives thereof can be added, preferably alkynyl alcohol or derivatives thereof, more preferably propargyl alcohol (or a derivative of).

Urea is the main component in terms of volume and weight percent of the composition of the present invention, and consists basically of a carbonyl group connecting with nitrogen and hydrogen. When added to hydrochloric acid, there is a reaction that results in urea hydrochloride, which basically traps the chloride ion within the molecular structure. This reaction greatly reduces the hazardous effects of the hydrochloric acid on its own, such as the fuming effects, the hygroscopic effects, and the highly corrosive nature (the Cl⁻ ion will not readily bond with the Fe ion). The excess nitrogen can also act as a corrosion inhibitor at higher temperatures. Urea and hydrogen chloride in a molar ratio of not less than 0.1:1; preferably in a molar ratio not less than 0.5:1, and more preferably in a molar ratio not less than 0.8:1. However, this ratio can be increased depending on the application.

The urea (hydrochloride) also allows for a reduced rate of reaction when in the presence of carbonate-based materials. This again due to the stronger molecular bonds associated over what hydrochloric acid traditionally displays. Further, since the composition according to the present invention is mainly comprised of urea (which is naturally biodegradable), the product testing has shown that the urea hydrochloride will maintain the same biodegradability function, something that hydrochloric acid will not.

The use of formic acid as corrosion inhibitor has been known for decades. However, the high concentrations in which its use has been reported along with the compounds it has been intermixed with have not made it a desirable compound in many applications. Prior art compositions containing formic acid require the presence of quinoline containing compounds or derivatives thereof, which render their use, in an increasingly environmentally conscious world, quite restricted.

In the present invention, formic acid or a derivative thereof such as formic acid, acetic acid, ethylformate and butyl formate are present in an amount ranging from 0.05 - 2.0 %, preferably in an amount of approximately 0.15%. Formic acid is the preferred compound.
Phosphonic acids and derivatives such as amino tris methylene phosphonic acid (ATMP) have some value as scale inhibitors. In fact, ATMP is a chemical traditionally used as an oilfield scale inhibitor, it has been found, when used in combination with urea/HCl, to increase the corrosion inhibition. It has a good environmental profile, is readily available and reasonably priced.

Amino tris (methylene phosphonic acid) (ATMP) and its sodium salts are typically used in water treatment operations as scale inhibitors. They also find use as detergents and in cleaning applications, in paper, textile and photographic industries and in off-shore oil applications. Pure ATMP presents itself as a solid but it is generally obtained through process steps leading to a solution ranging from being colourless to having a pale yellow colour. ATMP acid and some of its sodium salts may cause corrosion to metals and may cause serious eye irritation to a varying degree dependent upon the pH/degree of neutralization.

ATMP must be handled with care when in its pure form or not in combination with certain other products. Typically, ATMP present in products intended for industrial use must be maintained in appropriate conditions in order to limit the exposure at a safe level to ensure human health and environment.

Amino tris (methylene phosphonic acid) and its sodium salts belong to the ATMP category in that all category members are various ionized forms of the acid. This category includes potassium and ammonium salts of that acid. The properties of the members of a category are usually consistent. Moreover, certain properties for a salt, in ecotoxicity studies, for example, can be directly appreciated by analogy to the properties of the parent acid. Amino tris (methylene phosphonic acid) may specifically be used as an intermediate for producing the phosphonates salts. The salt is used in situ (usually the case) or stored separately for further neutralization. One of the common uses of phosphonates is as scale inhibitors in the treatment of cooling and boiler water systems. In particular, for ATMP and its sodium salts are used in to prevent the formation of calcium carbonate scale.

Alcohols and derivatives thereof, such as alkyne alcohols and derivatives and preferably propargyl alcohol and derivatives thereof can be used as corrosion inhibitors. Propargyl alcohol itself is traditionally used as a corrosion inhibitor which works extremely well at low concentrations. It is a toxic/flammable chemical to handle as a concentrate, so care must be
taken during handling the concentrate. In the composition according to the present invention, the toxic effect does not negatively impact the safety of the composition.

Metal iodides or iodates such as potassium iodide, sodium iodide and cuprous iodide can potentially be used as corrosion inhibitor intensifier. In fact, potassium iodide is a metal iodide traditionally used as corrosion inhibitor intensifier, however it is expensive, but works extremely well. It is non-regulated and friendly to handle.

**Example 1 - Process to prepare a composition according to a preferred embodiment of the invention**

Start with a 50% by weight solution of pure urea liquor. Add a 36% by weight solution of hydrogen chloride while circulating until all reactions have completely ceased. The formic acid is then added. Circulation is maintained until all products have been solubilized. Additional products can then be added as required. Table 2 lists the components of the composition of Example 1, including their weight percentage as compared to the total weight of the composition and the CAS numbers of each component.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>% Wt Composition</th>
<th>CAS#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>60.9%</td>
<td>7732-18-5</td>
</tr>
<tr>
<td>Urea Hydrochloride</td>
<td>39.0%</td>
<td>506-89-8</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.10%</td>
<td>64-18-6</td>
</tr>
</tbody>
</table>

The resulting composition of Example 1 is a clear, odourless liquid having shelf-life of greater than 1 year. It has a freezing point temperature of approximately minus 30°C and a boiling point temperature of approximately 100°C. It has a specific gravity of 1.15±0.02. It is completely soluble in water and its pH is less than 1.

**Corrosion testing**

The composition according to the present invention of Example 1 was exposed to corrosion testing. The results of the corrosion tests are reported in Table 3.
Samples of J55 grade steel were exposed to various synthetic acid solutions for periods of time ranging up to 24 hours at 90°C temperatures. All of the tested compositions contained HCl and urea in a 1:1.05 ratio.

<table>
<thead>
<tr>
<th>Inhibitor (%)</th>
<th>Initial wt. (g)</th>
<th>Final wt. (g)</th>
<th>Loss wt. (g)</th>
<th>Surface area (cm²)</th>
<th>Density (g/cc)</th>
<th>Run time (hours)</th>
<th>Mils/yr</th>
<th>Mm/year</th>
<th>Lb/l2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl-Urea</td>
<td>37.616</td>
<td>34.524</td>
<td>3.092</td>
<td>28.922</td>
<td>7.86</td>
<td>6</td>
<td>7818.20</td>
<td>198.582</td>
<td>0.222</td>
</tr>
<tr>
<td>HCl-Urea + 0.1% formic acid</td>
<td>37.679</td>
<td>35.059</td>
<td>2.620</td>
<td>28.922</td>
<td>7.86</td>
<td>6</td>
<td>6624.738</td>
<td>168.268</td>
<td>0.186</td>
</tr>
<tr>
<td>HCl-Urea + 0.1% formic acid</td>
<td>37.679</td>
<td>32.277</td>
<td>5.402</td>
<td>28.922</td>
<td>7.86</td>
<td>24</td>
<td>3414.774</td>
<td>86.735</td>
<td>0.383</td>
</tr>
</tbody>
</table>

This type of corrosion testing helps to determine the impact of the use of such synthetic replacement acid composition according to the present invention compared to the industry standard (HCl blends or any other mineral or organic acid blends). The results obtained for the composition containing only HCl and urea were used as a baseline to compare the other compositions.

Additionally, the compositions according to the present invention will allow the end user to utilize an alternative to conventional acids that has transportation and storage advantages as well as health, safety and environmental advantages. Enhancement in short/long term corrosion control is one of the key advantages of the present invention. The reduction in skin corrosiveness, the controlled spending nature, and the high salt tolerance are some other advantages of compositions according to embodiments of the present invention.

The composition is biodegradable and is classified as a mild irritant according to the classifications for skin. The composition is non-fuming and has no volatile organic compounds nor does it have any BTEX levels above the drinking water quality levels. BTEX refers to the chemicals benzene, toluene, ethylbenzene and xylene. Toxicity testing was carried out on rats and the LD₅₀ was determined to be greater than 2000mg/kg.

With respect to the corrosion impact of the composition on typical oilfield grade steel, it was established that it was clearly well below the acceptable corrosion limits set by industry.
The compositions according to the present invention can be used directly (ready-to-use) or be diluted with water depending on their use.

The uses (or applications) of the compositions according to the present invention upon dilution thereof ranging from approximately 1 to 75% dilution, include, but are not limited to: water treatment; boiler/pipe de-scaling; soil treatment; pH control; ion regeneration; pipeline scale treatments; pH control; retail cleaner; cement etching; soil pH control and various pulp and paper industrial applications.

While the foregoing invention has been described in some detail for purposes of clarity and understanding, it will be appreciated by those skilled in the relevant arts, once they have been made familiar with this disclosure that various changes in form and detail can be made without departing from the true scope of the invention in the appended claims.
CLAIMS

1. A synthetic acid composition for use in industrial activities, said composition comprising:
   - urea and hydrogen chloride in a molar ratio of not less than 0.1:1; and
   - formic acid or a derivative thereof.

2. The synthetic acid composition according to claim 1, wherein the formic acid or a derivative thereof is selected from the group consisting of: formic acid, acetic acid, ethylformate and butyl formate.

3. The synthetic acid composition according to claim 1 or 2, wherein the formic acid or a derivative thereof is present in an amount ranging from 0.05 - 2.0%.

4. The synthetic acid composition according to claim 3, wherein the formic acid or a derivative thereof is present in an amount of approximately 0.15%.

5. The synthetic acid composition according to any one of claims 1 to 4, wherein the urea and hydrogen chloride are in a molar ratio of not less than 0.5:1.

6. The synthetic acid composition according to claim 5, wherein the urea and hydrogen chloride are in a molar ratio of not less than 0.8:1.

7. The synthetic acid composition according to claim 6, wherein the urea and hydrogen chloride are in a molar ratio of not less than 1:1.

8. The synthetic acid composition according to any one of claims 1 to 7, further comprising a phosphonic acid derivative.

9. The synthetic acid composition according to claim 8, wherein the phosphonic acid derivative is aminoalkylphosphonic salt.

10. The synthetic acid composition according to claim 9, wherein the aminoalkylphosphonic salt is amino tris methylene phosphonic acid.
11. The synthetic acid composition according to any one of claims 1 to 10, further comprising a metal iodide or iodate selected from the group consisting of: potassium iodide, sodium iodide, cuprous iodide and lithium iodide.

12. The synthetic acid composition according to claim 11, wherein the metal iodide or iodate is cuprous iodide.

13. The synthetic acid composition according to claim 11, wherein the metal iodide or iodate is potassium iodide.

14. The synthetic acid composition according to claim 11, wherein the metal iodide or iodate is sodium iodide.

15. The synthetic acid composition according to claim 11, wherein the metal iodide or iodate is lithium iodide.

16. The synthetic acid composition according to any one of claims 1 to 15, further comprising an alcohol or derivative thereof.

17. The synthetic acid composition according to claim 16, wherein the alcohol or derivative thereof is an alkynyl alcohol or derivative thereof.

18. The synthetic acid composition according to claim 17, wherein the alkynyl alcohol or derivative thereof is propargyl alcohol or a derivative thereof.

19. The synthetic acid composition according to claim 9, wherein the aminoalkylphosphonic salt is present in a concentration ranging from 0.25 to 1.0% w/w.

20. The synthetic acid composition according to claim 19, wherein the aminoalkylphosphonic salt is present in a concentration of 0.5% w/w.

21. The synthetic acid composition according to claim 17 wherein the alkynyl alcohol or derivative thereof is present in a concentration ranging from 0.01 to 0.25% w/w.
22. The synthetic acid composition according to claim 21, wherein the alkynyl alcohol or derivative thereof is present in a concentration of 0.1% w/w.

23. The synthetic acid composition according to any one of claims 11 to 15, wherein the metal iodide is present in a concentration ranging from 100 to 1000 ppm.

24. The use of a synthetic acid composition according to any one of claims 1 to 23 in the mining industry said use being selected from the group consisting of: treating scale and adjusting pH levels in fluid systems.

25. The use of a synthetic acid composition according to any one of claims 1 to 23 in the water treatment industry said use being selected from the group consisting of: adjusting pH and neutralizing alkaline effluent.

26. The use of a synthetic acid composition according to any one of claims 1 to 23 in the fertilizer/landscaping industry to adjust the pH level of a soil.

27. The use of a synthetic acid composition according to any one of claims 1 to 23 to regenerate ion exchange beds.

28. The use of a synthetic acid composition according to any one of claims 1 to 23 in the construction industry said use being selected from the group consisting of: etching concrete and cleaning concrete.

29. The use of a synthetic acid composition according to any one of claims 1 to 23 in the electrical generation industry, said use being selected from the group consisting of: descaling pipelines and related equipment and descaling facilities.

30. The use of a synthetic acid composition according to any one of claims 1 to 23 in the food and dairy industry, said use being selected from the group consisting of: manufacturing protein, manufacturing starch, demineralizing whey, manufacturing casein and regenerating ion exchange resins.
31. The use of a synthetic acid composition according to any one of claims 1 to 23 in the pool industry to lower the pH of fluids.

32. The use of a synthetic acid composition according to any one of claims 1 to 23 in the manufacturing industry to perform an operation selected from the group consisting of: pickling steel and cleaning metal.

33. The use of a synthetic acid composition according to any one of claims 1 to 23 in the retail industry as a low pH cleaning additive.
INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2015/000514

A. CLASSIFICATION OF SUBJECT MATTER
   IPC: C09K 3/00 (2006.01) , A23C 21/00 (2006.01) , A25J 7/00 (2006.01) , 425/5/50 (2006.01) , 425/2/65 (2006.01) (more IPCs on the last page)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K 3/00, A23C 21/00, A23J 1/00, A23J 3/10, A23J 3/30, A23L 2/68, B01J 49/00, B08B 3/08, C02F 1/66, C04B 41/00, C09K 8/528, CUD 3/00, C13K 1/00, C23F 15/00, C23G 1/08 (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
n/a

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

Databases used: Intellect, Questel-Orbit, Espacenet advanced search, Google patents and scholar, Scopus, ScienceDirect, American Chemical Society publication search, Royal Society of Chemistry publication search.

Keywords used: urea hydrochloride, urea and hydrochloric acid corrosion, formic acid, corrosion inhibitor and steel, urea + hydrogen chloride + acetic acid/formic acid/ethyl formate, urea hydrochloride + cleaning + removing scale, alternative to HCl, environment and cleaning solutions, formic acid + phosphoric acid, acetic acid + phosphoric acid, potassium iodide + formic acid/acid + urea hydrochloride, urea hydrochloride + propargyl alcohol.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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✔️ Further documents are listed in the continuation of Box C. ✔️ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search 18 November 2015 (18-11-2015)

Date of mailing of the international search report 18 December 2015 (18-12-2015)

Name and mailing address of the ISA/CA

Canadian Intellectual Property Office

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Form PCT/ISA/210 (patent family annex) (January 2015)
INTERNATIONAL SEARCH REPORT

PCT/CA2015/000514

BOIJ 49/00 (2006.01) , B08B 3/08 (2006.01) , C02F 1/66 (2006.01) , C04B 41/00 (2006.01) ,
C09K 8/528 (2006.01) , CUD 3/00 (2006.01) , C13K 1/00 (2006.01) , C23F 15/00 (2006.01) ,
C23G 1/08 (2006.01)