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**(54) USING SYNTHETIC ACID COMPOSITIONS AS ALTERNATIVES TO CONVENTIONAL ACIDS TN
THE OIL AND GAS INDUSTRY**

VERWENDUNG SYNTETISCHER SÄUREZUSAMMENSETZUNGEN ALS ALTERNATIVEN ZU
HERKÖMMLICHEN SÄUREN IN DER ÖL- UND GASINDUSTRIE

UTILISATION DE COMPOSITIONS D'ACIDE SYNTHÉTIQUE EN ALTERNATIVE À DES ACIDES
TRADITIONNELS DANS L'INDUSTRIE PÉTROLIÈRE ET GAZIÈRE

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WO-A1-2006/136262 **US-A- 5 672 279**
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Description**FIELD OF THE INVENTION**

5 **[0001]** This invention relates to compositions for use in performing various applications in the oil & gas industry, more specifically to synthetic acid compositions as alternatives to conventional acids.

BACKGROUND OF THE INVENTION

10 **[0002]** In the oil & gas industry, stimulation with an acid is performed on a well to increase or restore production. In some instances, a well initially exhibits low permeability, and stimulation is employed to commence production from the reservoir. In other instances, stimulation is used to further encourage permeability and flow from an already existing well that has become under-productive.

15 **[0003]** Acidizing is a type of stimulation treatment which can be performed above or below the reservoir fracture pressure in an effort to restore or increase the natural permeability of the reservoir rock. Acidizing is achieved by pumping acid into the well to dissolve typically limestone, dolomite and calcite cement between the sediment grains of the reservoir rocks.

20 **[0004]** There are three major types of acid applications: matrix acidizing, fracture acidizing, and breakdown acidizing (pumped prior to a fracturing pad or cement operation in order to assist with formation breakdown (reduce fracture pressures, increased feed rates), as well as clean up left over cement in the well bore or perforations. A matrix acid treatment is performed when acid is pumped into the well and into the pores of the reservoir formation below the fracture pressure. In this form of acidization, the acids dissolve the sediments and mud solids that are inhibiting the permeability of the rock, enlarging the natural pores of the reservoir (wormholing) and stimulating flow of hydrocarbons. While matrix acidizing is done at a low enough pressure to keep from fracturing the reservoir rock, fracture acidizing involves pumping highly pressurized acid into the well, physically fracturing the reservoir rock and etching the permeability inhibitive sediments. This type of acid treatment forms channels or fractures through which the hydrocarbons can flow, in addition to forming a series of wormholes.

25 **[0005]** There are many different mineral and organic acids used to perform an acid treatment on wells. The most common type of acid employed on wells to stimulate production is hydrochloric acid (HCl), which is useful in stimulating carbonate reservoirs.

30 **[0006]** Some of the major challenges faced in the oil & gas industry from using hydrochloric acid include the following: extremely high levels of corrosion (which is countered by the addition of 'filming' type corrosion inhibitors that are typically themselves toxic and harmful to humans, the environment and equipment) reactions between acids and various types of metals can vary greatly but softer metals, such as aluminum and magnesium, are very susceptible to major effects causing immediate damage. Hydrochloric acid produces Hydrogen chloride gas which is toxic (potentially fatal) and corrosive to skin, eyes and metals. At levels above 50 ppm (parts per million) it can be Immediately Dangerous to Life and Health (IDLH). At levels from 1300-2000 ppm death can occur in 2-3 minutes.

35 **[0007]** The inherent environmental effects (organic sterility, poisoning of wildlife etc.) of acids in the event of an unintended or accidental release on surface or downhole into water aquifers or other sources of water are devastating which 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 or livestock and wildlife exposed to/or drinking the water. An unintended release at surface can also cause a hydrogen chloride gas cloud to be released, potentially endangering human and animal health. This is a common event at large storage sites when tanks split or leak. 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.

40 **[0008]** The inability for acids and blends of such to biodegrade naturally results in expensive cleanup-reclamation costs for the operator should an unintended release occur. Moreover, the toxic fumes or vapours produced by mineral & organic acids are harmful to humans/animals and are highly corrosive and/or potentially explosive. Transportation and storage requirements for acids are restrictive and taxing in such that you must haul the products in acid approved tankers or intermediate bulk containers (IBC) that are rated to handle such corrosive products. As well, the dangers surrounding exposure by personnel handling the blending of such corrosive/dangerous products limits their use/implementation.

45 **[0009]** Another concern is the potential for exposure incidents on locations due to high corrosion levels of acids causing storage container failures and/or deployment equipment failures i.e. coiled tubing or treatment iron failures caused by high corrosion rates (pitting, cracks, pinholes and major failures). Other concerns include; downhole equipment failures from corrosion causing the operator to have to execute a work-over and replace down hole pumps, tubing, cables, packers etc.; inconsistent strength or quality level of mineral & organic acids; potential supply issues based on industrial output levels; high levels of corrosion on surface pumping equipment resulting in expensive repair and maintenance

levels for operators and service companies; the requirement of specialized equipment that is purpose built to pump acids greatly increasing the capital expenditures of operators and service companies; and the inability to source a finished product locally or very near its end use; transportation and onsite storage difficulties.

5 [0010] Typically, acids are produced in industrial areas of countries located far from oil & gas applications, up to 10 additives can be required to control various aspects of the acids properties adding to complications in the handling and shipping logistics. Having an alternative that requires minimal additives is very advantageous.

10 [0011] Extremely high corrosion and reaction rates with temperature increases can cause conventional acids to "spend/react or become neutral" prior to achieving its desired effect such as penetrating an oil or gas formation to increase the wormhole "pathway" effectively to allow the petroleum product to flow freely to the surface. As an example, hydrochloric acid or a "mud acid" can be utilized in an attempt to free stuck drill pipe in some situations. Prior to getting to the required depth to dissolve the formation that has caused the pipe/tubing to become stuck many acids spend or neutralize due to increased bottom hole temperatures and increased reaction rate, so it is advantageous to have an alternative that spends or reacts more methodically allowing the slough to be treated with a solution that is still active, allowing the pipe/tubing to be pulled free.

15 [0012] When used to treat scaling issues on surface due to water contamination, conventional acids are exposed to human and mechanical devices as well as expensive pumping 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 high amount of thermal energy (exothermic reaction) causing potential safety concerns and equipment damage, acids typically need to be blended with fresh water (due to their intolerance of highly saline water, causing potential precipitation of minerals) to the desired concentration requiring companies to pre-blend off-site as opposed to blending on-site with field-produced water thereby increasing costs associated with transportation.

20 [0013] Conventional mineral acids used in a pH control situation can cause rapid degradation of certain polymers/additives requiring increased loadings or chemicals to be added to counter these negative effects. Many offshore areas of operations have very strict regulatory rules regarding the transportation/handling and deployment of acids causing increased liability and costs for the operator. When using an acid to pickle tubing or pipe, very careful attention must be paid to the process due to high levels of corrosion, as temperatures increase, the typical additives used to control corrosion levels in acid systems begin to degrade very quickly (due to the inhibitors "plating out" on the steel) causing the acids to become very corrosive and resulting in damage to downhole equipment/tubulars. Conventional acids are also very destructive to most elastomers found in the oil & gas industry such as those found in blow out preventers (BOP's) /downhole tools/packers/submersible pumps/seals etc. Having to deal with spent acid during the back flush process is also very expensive as these acids typically are still at a low pH and remain toxic. It is advantageous to have an acid blend that can be exported to production facilities through pipelines that once spent or applied, is commonly close to a neutral pH greatly reducing disposal costs/fees.

25 [0014] Acids perform many actions in the oil & gas industry and are considered necessary to achieve the desired production of various petroleum wells, maintain their respective systems and aid in certain functions (i.e. freeing stuck pipe). The associated dangers that come with using acids are expansive and tasking to mitigate through controls whether they are chemically or mechanically engineered

30 [0015] Eliminating or even simply reducing the negative effects of acids while maintaining their usefulness is a struggle for the industry. 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 conventional acids.

35 [0016] 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 corrosiveness to carbon steels.

40 [0017] 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.

45 [0018] 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 nonylphenyl (0.022% by wt); methyl vinyl ketone (0.022% by wt); acetone (0.0022% by wt); and acetophenone (0.0022% by wt) for use in specific oil industry applications, namely oil drilling and hydraulic fracturing.

50 [0019] 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.

55 [0020] US Patent no. 4,466,893 teaches gelled acid compositions comprising a gelling agent selected from the group

consisting of galactomannans such as guar gum, gum karaya, gum tragacanth, gum ghatti, gum acacia, gum konjak, shariz, locus, psyllium, tamarind, gum tara, carrageenan, gum kauri, modified guars such as hydroxypropyl guar, hydroxyethyl guar, carboxymethyl hydroxyethyl guar, carboxymethyl hydroxypropyl guar and alkoxylated amines. This patent teaches that presence of urea has a marked impact on the viscosity of the gelled acid and the gelled acid compositions are used in fracking activities. WO2006/136262 discloses compositions and methods for inhibiting corrosion in pipes, pumps and other metallic materials that can be in contact with highly acidic solutions used in the stimulation of oil wells. Composition examples comprise urea and HCl, together with butylglycol, potassium jodide, cinnamaldehyde and water.

[0021] Several operations in the oil industry expose fluids to very high temperatures (some upward of 200°C), the compositions used in these various operations need to withstand these high temperatures without losing their overall effectiveness. These compositions must be capable of being used in operations over a wide range of temperatures while not affecting the equipment with which it comes in contact.

[0022] Synthetic acid compositions are mostly applicable in the cleaning industry. However, such compositions require the addition 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 temperatures (above 65°C) and therefore makes them useful in the oil and gas industry. The composition according to the present invention can ideally be used in various oilfield operations, such as: spearhead breakdown acid, acid fracturing operations, injection-disposal well treatments, scale removal treatments (surface and subsurface-, equipment, pipelines, facilities), formation filter cake removal, tubing pickling, matrix acid squeezes and soaks, cement squeeze breakdowns, fluid pH control, stuck pipe operations, and coiled tubing acid washes, soaks, squeezes.

[0023] The present invention provides a simpler/safer synthetic acid compositions for use in high temperature/volume applications such as various downhole operations in the oilfield.

[0024] Consequently, there is still a need for compositions for use in the oil industry which can be used over this range of applications which can decrease a number of the associated dangers/issues typically associated with conventional acid applications to the extent that these acid compositions are considered much safer for handling on worksites.

30 SUMMARY OF THE INVENTION

[0025] Compositions according to the present invention have been developed for the oil & gas industry and its associated applications, by targeting the problems of metal corrosion, logistics/handling, human/environmental exposure and formation/fluid compatibilities.

[0026] It is an object of the present invention to provide a synthetic acid composition as set out in the claims.

[0027] According to one aspect there is provided a synthetic acid composition which, upon proper use, results in a very low corrosion rate of oil and gas industry tubulars/equipment.

[0028] According to another aspect there is provided a synthetic acid composition for use in the oil industry which is biodegradable.

[0029] According to another aspect there is provided a synthetic acid composition for use in the oil industry which has a controlled spending (reacting) nature that is near linear as temperature increases, non-fuming, non-toxic, and has a highly controlled manufacturing process ensuring consistent end product strength.

[0030] According to another aspect there is provided a synthetic acid composition for use in the oil industry which has a pH below 1.

[0031] According to another aspect there is provided a synthetic acid composition for use in the oil industry which has minimal exothermic reactivity upon dilution or reaction. Typically adding a strong acid to a fluid (water, base etc.) will cause an aggressive rise in fluid temperature. Certain preferred embodiments of the present invention do not exhibit this effect to the same degree such that the exothermic reaction is minimal when combined with typical industrial fluids, such saline water, fresh water or even a high pH fluid.

[0032] According to another aspect there is provided a synthetic acid composition for use in the oil industry which is compatible with existing industry additives.

[0033] According to another aspect there is provided a synthetic acid composition for use in the oil industry which has high salinity tolerance. A tolerance for high salinity fluids, or brines, is desirable for onshore and offshore acid applications. Conventional acids are normally blended with fresh water and additives, typically far offsite, and then transported to the area of treatment as a finished blend. It is advantageous to have an alternative that can be transported as a concentrate safely to the treatment area, then blended with a saline produced water or sea water greatly reducing the logistics requirement. A conventional acid system may precipitate salts/minerals heavily if blended with fluids of an excessive saline level resulting in formation plugging or ancillary damage inhibiting production and substantially increasing costs.

Brines are also typically present in formations, thus having an acid system that has a high tolerance for brines greatly reduces the potential for formation damage or emulsions forming down-hole during or after product placement/spending occurs.

[0034] According to another aspect there is provided a synthetic acid composition for use in the oil industry which is immediately reactive upon contact/application. Many acids that are considered safe have a slower reaction rate, a reduced capacity to solubilize, or a delayed reaction rate, making them ineffective or uneconomical in some applications. Strong mineral acids have very high hazards associated to them, but are immediately reactive. Preferred embodiments of the present invention are immediately active, even at lower concentrations. This immediate activity allows for a standard operating procedure to be followed, minimizing operational changes. Many operations that utilize a mineral acid, such as HCl, will not need to alter their standard operating procedure to utilize preferred compositions of the present invention.

[0035] According to another aspect there is provided a synthetic acid composition for use in the oil industry which results in less unintended near wellbore erosion due to the controlled reaction rate. This, in turn, results in deeper formation penetration, increased permeability, and reduces the potential for zonal communication during a typical 'open hole' mechanical isolation application treatment. As a highly reactive acid, such as hydrochloric acid, is deployed into a well that has open hole packers for isolation (without casing) there is a potential to cause a loss of near-wellbore compressive strength resulting in communication between zones or sections of interest as well as potential sand production, and fines migration. It is advantageous to have an alternative that will react with a much more controlled rate or speed, thus greatly reducing the potential for zonal communication and the above potential negative side effects of traditional acid systems.

[0036] According to another aspect there is provided a synthetic acid composition for use in the oil industry said composition having a low evaporation rate. Acids normally utilized in industrial operations typically have a high tendency to evaporate or fume, especially at higher concentrations. Preferred embodiments of the present invention do not exhibit this tendency and have very low fuming effect, even in at high concentration. Hydrochloric acid will produce hazardous fumes, such as chlorine gas, which can be fatal in higher concentrations. Preferred embodiments of the present invention do not produce hazardous fumes, in any concentration.

[0037] According to another aspect there is provided a synthetic acid composition for use in the oil industry which provides a controlled and comprehensive reaction throughout a broad range of temperatures. Preferred embodiments of the present invention have reaction rates that can be controlled or greatly "slowed or increased" for specific applications where a reduced (or increased) reaction rate is an advantage simply by adjusting the amount of water blended with the product. Preferred compositions of the present invention can be diluted substantially <10%, yet still remain effective in many applications, such as scale control, as well as further increasing the HSE benefits. As preferred compositions of the present invention are diluted the reaction rate, or solubilizing ability, of the product will remain linear.

[0038] Accordingly, the product would overcome many of the drawbacks found in the use of compositions of the prior art related to the oil & gas industry.

[0039] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to stimulate formations.

[0040] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to assist in reducing breakdown pressures during downhole pumping operations.

[0041] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to treat wellbore filter cake post drilling operations.

[0042] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to assist in freeing stuck pipe.

[0043] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to descale pipelines and/or production wells.

[0044] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to increase the injectivity rate of injection wells.

[0045] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to lower the pH of fluids.

[0046] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to remove undesirable scale in surface equipment, wells and related equipment and/or facilities.

[0047] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to fracture wells.

[0048] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to perform matrix stimulations.

[0049] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to conduct annular and bullhead squeezes & soaks.

[0050] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to pickle tubing, pipe and/or coiled tubing.

[0051] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to increase effective permeability of formations.

[0052] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to reduce or remove wellbore damage.

5 [0053] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to clean perforations.

[0054] According to an aspect of the present invention, there is provided a use of a synthetic acid composition in the oil industry to solubilize limestone, dolomite, calcite and combinations thereof.

10 [0055] According to an aspect of the invention, there is provided a synthetic acid composition comprising:

- urea & hydrogen chloride in a molar ratio ranging from 0.1:1 to 1.05:1.0 inclusively;
- a metal iodide or iodates, preferably cupric iodide, potassium iodide, lithium iodide or sodium iodide; in an amount ranging from 0.01 - 0.5 %, preferably in an amount of approximately 0.022%; potassium iodide is the preferred compound;
- an alcohol or derivative thereof, preferably alkynyl alcohol, more preferably a derivative of propargyl alcohol; in an amount ranging from 0.1 - 2.0 %, preferably in an amount of approximately 0.25%; 2-Propyn-1-ol, complexed with methyloxirane is the preferred component;
- optionally, formic acid or a derivative thereof selected from the group consisting of: acetic acid, ethylformate and butyl formate are present in an amount ranging from 0.05 - 2.0 %, preferably in an amount of approximately 0.1%; formic acid is the preferred compound;
- optionally, cinnamaldehyde or a derivative amine thereof; present in an amount ranging from 0.01 - 1.0 %, preferably in an amount of approximately 0.03%; cinnamaldehyde is the preferred compound;
- optionally a propylene glycol or a derivative thereof present in an amount ranging from 0.05 - 1.0 %, preferably in an amount of approximately 0.05%; propylene glycol is the preferred compound; and water and
- optionally, a phosphonic acid or derivatives, preferably alkylphosphonic acid or derivatives thereof and more preferably amino tris methylene phosphonic acid and derivatives thereof.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

30 [0056] The description that follows, and the embodiments described therein, is 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.

[0057] Urea-HCl 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 & Hydrogen chloride in a molar ratio from 0.1:1 to 1.05:1.0; preferably in a molar ratio from 0.5:1, and more preferably in a molar ratio from 1.0:1.

[0058] It is preferable to add the urea at a molar ratio greater than 1 to the moles of HCl acid (or any acid). This is done in order to bind any available Cl⁻ ions, thereby creating a safer, more inhibited product. Preferably, the composition according to the present invention comprises 1.05 moles of urea per 1.0 moles of HCl. 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 on its own.

[0059] The use of formic acid as a 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.

[0060] In the present invention, formic acid or a derivative thereof such as formic acid, acetic acid, ethylformate and butyl formate can be added in an amount ranging from 0.05 - 2.0%, preferably in an amount of approximately 0.1%. Formic acid is the preferred compound, and is included on the PLONOR (Pose Little Or NO Risk to the environment) list for offshore oilfield use.

[0061] 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 however a very toxic/flammable chemical to handle as a concentrate, so care must be taken when exposed to the concentrate. In the composition according to the present invention, it is preferred to use 2-Propyn-1-ol, complexed with methyloxirane, as this is a much safer derivative to handle. This is also a product that is approved for use offshore in the North Sea oilfield areas.

[0062] Metal iodides or iodates such as potassium iodide, sodium iodide, cuprous iodide and lithium 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, and is included on the PLONOR (Pose Little Or NO Risk to the environment) list for offshore oilfield use.

[0063] 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 or protection. It has a good environmental profile, is readily available and reasonably priced.

[0064] Amino tris (methylenephosphonic 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.

[0065] 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.

[0066] Amino tris (methylenephosphonic 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 (methylenephosphonic 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.

[0067] In preferred embodiments of the present invention, 2-Propyn-1-ol, complexed with methyloxirane can be present in a range of 0.1 - 2.0 %, preferably it is present in an amount of approximately 0.25%. Potassium Iodide can be present in a range of 0.01 - 0.5 %, preferably it is present in an amount of approximately 0.022%. Formic Acid can be present in a range of 0.05 - 2.0 %, preferably it is present in an amount of approximately 0.1%.

[0068] As a substitute for traditional propargyl alcohol, a preferred embodiment of the present invention uses 2-Propyn-1-ol, complexed with methyloxirane. As a substitute for potassium iodide one could use sodium iodide, copper iodide and lithium iodide. However, potassium iodide is the most preferred. As a substitute for formic acid one could use acetic acid. However, formic acid is most preferred. As a substitute for propylene glycol one could use ethylene glycol, glycerol or a mixture thereof. Propylene glycol being the most preferred. As a substitute for cinnamaldehyde one could use cinnamaldehyde derivatives and aromatic aldehydes selected from the group consisting of: dicinnamaldehyde p-hydroxy cinnamaldehyde; p-methylcinnamaldehyde; p-ethylcinnamaldehyde; p-methoxycinnamaldehyde; p-dimethylaminocinnamaldehyde; p-diethylaminocinnamaldehyde; p-nitrocinnamaldehyde; o-nitrocinnamaldehyde; 4-(3-propenal)cinnamaldehyde; p-sodium sulfocinnamaldehyde p-trimethylammoniumcinnamaldehyde sulfate; p-trimethylammoniumcinnamaldehyde o-methylsulfate; p-thiocyanocinnamaldehyde; p-(S-acetyl)thiocinnamaldehyde; p-(S,N,N-dimethylcarbamoylthio)cinnamaldehyde; p-chlorocinnamaldehyde; α -methylcinnamaldehyde; β -methylcinnamaldehyde; α -chlorocinnamaldehyde α -bromocinnamaldehyde; α -butylcinnamaldehyde; α -amylcinnamaldehyde; α -hexylcinnamaldehyde; α -bromo-p-cyanocinnamaldehyde; α -ethyl-p-methylcinnamaldehyde and p-methyl- α -pentylcinnamaldehyde. The most preferred is cinnamaldehyde.

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

[0069] 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 ATMP is then added followed by propargyl alcohol (or derivative), and potassium iodide. Circulation is maintained until all products have been solubilized. Additional products are added now as required (iron control, demulsifier, etc.).

[0070] Table 1 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 1 - Composition of a certain embodiment of the present invention

Chemical	% Wt Composition	CAS#
Water	60.315	7732-18-5
Urea Hydrochloride	39.0%	506-89-8
Amino tris methylene phosphonic acid	0.576%	6419-19-8
Propargyl Alcohol	0.087%	107-19-7
Potassium Iodide	0.022%	7681-11-0

[0071] 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.

[0072] The composition is biodegradable and is classified as a non-irritant according to the classifications for skin tests. 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 calculated using surrogate information and the LD₅₀ was determined to be greater than 2000mg/kg.

[0073] 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 for certain applications, such as spearhead applications or lower temperature scaling.

Example 2

[0074] Table 2 lists the components of the composition of Example 2 including their weight percentage as compared to the total weight of the composition and the CAS numbers of each component.

Table 2 - Composition according to an embodiment of the present invention

Chemical	% Wt Composition	CAS#
Water	58.92%	7732-18-5
Urea Hydrochloride	40.6%	506-89-8
2-Propyn-1-ol, complexed with methyloxirane	0.2%	38172-91-7
Potassium Iodide	0.05%	7681-11-0
Formic Acid	0.15%	64-18-6
Propylene Glycol	0.05%	57-55-6
Cinnamaldehyde	0.03%	14371-10-9

CORROSION TESTING

[0075] The composition of Example 2 according to the present invention was exposed to corrosion testing. The results of the corrosion tests are reported in Table 3.

[0076] 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 t:1.05 ratio.

Table 3 Corrosion testing comparison between HCl-Urea and the composition of Example 2 at a 100% concentration

Inhibitor (%)	Initial wt. (g)	Final wt. (g)	Loss wt. (g)	Surface area (cm ²)	Density (g/cc)	Run time (hours)	Mils/yr	mm/year	lb/ft ²
HCl-Urea	37.616	34.524	3.092	28.922	7.86	6	7818.20	198.582	0.222
HCl-Urea	37.616	31.066	6.550	28.922	7.86	24	4140.46	105.168	0.470
Example #2	37.524	37.313	0.211	28.922	7.86	6	533.519	13.551	0.015
Example #2	37.524	35.540	1.984	28.922	7.86	24	1254.149	31.855	0.142

[0077] 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.

[0078] 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 elimination of corrosive fumes, the controlled spending nature, and the high salt tolerance are some other advantages of compositions according to the present invention.

AQUATIC TOXICITY TESTING

[0079] The biological test method that was employed was the Reference Method for Determining acute lethality using rainbow trout (1990 - Environment Canada, EPS 1/RM/9 - with the May 1996 and May 2007 amendments).

[0080] The Trout 96 hour Acute Test (WTR-ME-041) was performed at 5 different concentrations of compositions (62.5, 125, 250, 500 and 1000 ppm) one replicate per treatment, ten fish per replicate.

[0081] The test results indicate that at concentrations of the composition of Example 2 of up to and including 500 ppm there was a 100% survival rate in the fish sample studied. This is an indicator that the composition of Example 2 demonstrates an acceptable environmental safety profile.

DERMAL TESTING

[0082] The objective of this study was to evaluate the dermal irritancy and corrosiveness of the composition of Example 2, following a single application to the skin of New Zealand White rabbits. The undiluted test substance was placed on the shaved back of each of the three rabbits used in the study. The treated site was then covered by a gauze patch and secured with porous tape. The entire midsection of each rabbit was wrapped in lint-free cloth secured by an elastic adhesive bandage. The untreated skin site of each rabbit served as a control for comparison purposes. All wrapping materials were removed from each rabbit 4 hours following application of the test substance. The application site was then rinsed with water and wiped with gauze to remove any residual test substance. The skin of each rabbit was examined at 30-60 minutes and 24, 48 and 72 hours following removal of the wrappings. Descriptions of skin reactions were recorded for each animal. Dermal irritation scores were calculated for each time point, and a Primary Dermal Irritation Score was calculated according to the Draize descriptive ratings for skin irritancy.

[0083] Tables 4 and 5 report the results of the dermal testing. The scores for edema and erythema/eschar formation were "0" at all scoring intervals for all three rabbits. According to the Draize descriptive ratings for skin irritancy, the Primary Dermal Irritation Score (based on the 24- and 72-hour scoring intervals) for the test substance under the conditions employed in this study was 0.00. Thus, the composition of Example 2 was determined to be a non-irritant to the skin of New Zealand White rabbits. However, this conclusion was drawn without characterization of the test substance.

Table 4 Description of Individual Skin Reactions upon exposure to composition of Example 2

5 Number (sex)		Scoring Interval (Time Following Removal of Wrappings)			
		30-60 Minutes	24 Hours	48 Hours	72 Hours
		Skin Reactions Scores			

20 819 (F)	Edema^b	0	0	0	0
	Erythema/eschar^c	0	0	0	0
25 820 (F)	Edema	0	0	0	0
	Erythema/eschar	0	0	0	0
821 (F)	Edema	0	0	0	0
	Erythema/eschar	0	0	0	0

^a see protocol Table 1 (Appendix A) for a detailed description of the Draize scoring scale (Draize, J.H., Appraisal of the Safety of Chemicals in Foods, Drugs, and Cosmetics, Assoc. Food & Drug Officials of the U.S., Austin, TX, 1959)

^b edema: 0 = none, 1 = very slight, 2 = slight, 3 = moderate, 4 (maximum possible) = severe

^c erythema/eschar: 0 = none, 1 = very slight, 2 = well-defined, 3 = moderate to severe, 4 (maximum possible) = severe erythema to slight eschar formation

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Table 5 Primary Dermal Irritation Score of Individual Skin Reactions upon exposure to composition of Example 2

		Scoring Interval (Time Following Removal of Wrappings)				
		30-60 Minutes	30-60 Minutes	30-60 Minutes	30-60 Minutes	
Edema Score		Skin Reactions Scores Summary ^b				
0		3/3	3/3	3/3	3/3	
1		0/3	0/3	0/3	0/3	
2		0/3	0/3	0/3	0/3	
3		0/3	0/3	0/3	0/3	
4		0/3	0/3	0/3	0/3	
Positive Score Mean		0.00	0.00	0.00	0.00	
Erythema and/or Eschar Formation Score		Skin Reactions Scores Summary ^b				
0		3/3	3/3	3/3	3/3	
1		0/3	0/3	0/3	0/3	
2		0/3	0/3	0/3	0/3	
3		0/3	0/3	0/3	0/3	
4		0/3	0/3	0/3	0/3	
Positive Score Mean		0.00	0.00	0.00	0.00	
Irritation Score Subtotal^c		0.00	0.00	0.00	0.00	
PRIMARY DERMAL IRRITATION SCORE (DRAIZE):		$0.00 \text{ (24-hour subtotal)} + 0.00 \text{ (72-hour subtotal)} = 0.00 \text{ (total score)}$ $0.00 \text{ (total score)} / 2 = 0.00 \text{ (Primary Dermal Irritation Score)}$				

^a see protocol Table 1 (Appendix A) for a detailed description of the Draize scoring scale (Draize, J.H., Appraisal of the Safety of Chemicals in Foods, Drugs, and Cosmetics, Assoc. Food & Drug Officials of the U.S., Austin, TX, 1959)

^b Number of animals with score/number of animals dosed

^c Irritation score subtotal = mean erythema score + mean edema score

CORROSION TESTING

[0084] Corrosion testing using the composition of Example 2 was carried out under various conditions of temperature and on different steels to show the breadth of the applications for which compositions according to the present invention can be used. Table 6 sets out the test results of corrosion test that were carried out on N-80 steel (density of 7.86 g/cc) using the composition of Example 2 at a 50% concentration. Table 7 reports the test results of corrosion tests that were carried out on J-55 steel (density of 7.86 g/cc) using the composition of Example 2 at a 50% concentration. Table 8 reports the test results of corrosion tests that were carried out on various metal samples using the composition of Example 2 at a 100% concentration. These test results show that the composition of Example 2 meets the regulatory standards for the transportation industry on mild steel, and provides a strong level of protection with respect to aluminum.

Table 6 Corrosion tests carried out on N-80 steel (density of 7.86 g/cc) using the composition of Example 2 at a 50% concentration

Temp	Initial Wt.	Final wt.	Loss wt.	Surface Area	Run Time	Mils/yr	mm/year	lb/ft2
°C	(g)	(g)	(g)	(cm ²)	(hours)			
70°C	40.898	40.863	0.035	27.11	6	94.41353	2.398	0.003

70°C	40.898	40.816	0.082	27.11	24	55.29936	1.405	0.006
90°C	40.896	40.838	0.058	27.11	6	156.4567	3.974	0.004
90°C	40.896	40.740	0.156	27.11	24	105.2037	2.672	0.011

Table 7 Corrosion tests carried out on J-55 steel (density of 7.86 g/cc) using the composition of Example 2 at a 50% concentration

Temp	Initial Wt.	Final wt.	Loss wt.	Surface Area	Run Time	Mils/yr	mm/year	lb/ft2
°C	(g)	(g)	(g)	(cm ²)	(hours)			
30°C	37.705	37.700	0.005	28.922	6	12.64263	0.321	0.000
30°C	37.705	37.692	0.013	28.922	24	8.217709	0.209	0.001
30°C	37.705	37.676	0.029	28.922	72	6.110604	0.155	0.002
50°C	37.513	37.502	0.011	28.922	6	27.81378	0.706	0.001
50°C	37.513	37.485	0.028	28.922	24	17.69968	0.450	0.002
70°C	37.435	37.396	0.039	28.922	6	98.61251	2.505	0.003
70°C	37.435	37.350	0.085	28.922	24	53.73117	1.365	0.006
90°C	37.514	37.430	0.084	28.922	6	212.3962	5.395	0.006
90°C	37.514	37.255	0.259	28.922	24	163.7221	4.159	0.018

Table 8 Corrosion tests carried out on various metal samples using the composition of Example 2 at a 100% concentration

	Temp	Initial Wt.	Final wt.	Loss wt.	Surface Area	Density	Run Time	Mils/yr	mm/year	lb/ft ²
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Coupon	°C	(g)	(g)	(g)	(cm ²)	g/cc	(hours)			
1018 steel	55 °C	13.994	13.955	0.039	28.503	7.82	72	8.381163	0.213	0.003
7075 aluminum	25 °C	6.196	6.185	0.011	29.471	2.81	6	76.35013	1.939	0.001
7075 aluminum	25 °C	6.196	6.080	0.116	29.471	2.81	24	201.2867	5.113	0.008
7075 aluminum	25 °C	6.196	1.344	4.852	29.471	2.81	48	4209.668	106.926	0.344

Example 3

[0085] Table 9 lists the components of the composition of Example 3 including their weight percentage as compared to the total weight of the composition and the CAS numbers of each component.

Table 9 – Composition of a preferred embodiment of the present invention

Chemical	% Wt Composition	CAS#
Water	59.028%	7732-18-5
Urea Hydrochloride	40.6%	506-89-8
2-Propyn-1-ol, complexed with methyloxirane	0.25%	38172-91-7
Potassium Iodide	0.022%	7681-11-0
Formic Acid	0.1%	64-18-6

CORROSION TESTING

[0086] The compositions of Example 2 and 3 according to the present invention were exposed to corrosion testing. The results of the corrosion tests are reported in Table 10.

[0087] 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 10 Corrosion testing comparison between HCl-Urea and the compositions of Example 2 and 3 at a 100% concentration

Inhibitor (%)	Initial wt. (g)	Final wt. (g)	Loss wt. (g)	Surface area (cm ²)	Density (g/cc)	Run time (hours)	Mils/yr	mm/year	lb/ft ²
HCl-Urea	37.616	34.524	3.092	28.922	7.86	6	7818.20	198.582	0.222
HCl-Urea	37.616	31.066	6.550	28.922	7.86	24	4140.46	105.168	0.470
Example #2	37.524	37.313	0.211	28.922	7.86	6	533.519	13.551	0.015
Example #2	37.524	35.540	1.984	28.922	7.86	24	1254.149	31.855	0.142
Example #3	37.714	37.520	0.194	28.922	7.86	6	490.534	12.460	0.014
Example #3	37.714	37.329	0.385	28.922	7.86	24	243.371	6.182	0.027

[0088] 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 the down-hole performance advantages, transportation and storage advantages as well as the 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 elimination of corrosive fumes, the controlled spending nature, and the high salt tolerance are some other advantages of compositions according to the present invention.

AQUATIC TOXICITY TESTING

[0089] The biological test method that was employed was the Reference Method for Determining acute lethality using rainbow trout (1990 - Environment Canada, EPS 1/RM/9 - with the May 1996 and May 2007 amendments).

[0090] The Trout 96 hour Acute Test (WTR-ME-041) was performed at: 5 different concentrations of compositions (62.5, 125, 250, 500 and 1000 ppm) one replicate per treatment, ten fish per replicate.

[0091] The test results indicate that at concentrations of the composition of Example 3 of up to and including 500 ppm there was a 100% survival rate in the fish sample studied. This is an indicator that the composition of Example 3 demonstrates a highly acceptable environmental safety profile.

[0092] Additional testing was carried out to assess the inhibition of marine algal growth, acute toxicity and biodegradability establish the safety for the environment.

ELASTOMER TESTING

[0093] When common sealing elements used in the oil and gas industry come in contact with acid compositions they tend to degrade or at least show sign of damage. A number of sealing elements common to the industry were exposed to a composition according to a preferred embodiment of the present invention to evaluate the impact of the latter on their integrity. More specifically, the hardening and drying and the loss of mechanical integrity of sealing elements can have substantial consequences to the operations of wells and result in undesirable shut downs to replace defective sealing elements. Testing was carried out to assess the impact of the exposure of composition of Example 3 to various elastomers. Long term (72 hour exposure) elastomer testing on the concentrated product of Example 3 at 70°C and 28,000 kPa showed little to no degradation of various elastomers, including Nitrile 70, Viton 75, Aflas 80, and EPDM 70 style sealing elements.

CORROSION TESTING

[0094] Corrosion testing using the composition of Example 3 was carried out under various conditions of temperature and on different steels to show the breadth of the applications for which compositions according to the present invention can be used. Table 11 sets out the test results of corrosion test that were carried out on N-80 steel (density of 7.86 g/cc) using the composition of Example 3 at a 50% concentration. Table 12 reports the test results of corrosion tests that were carried out on J-55 steel (density of 7.86 g/cc) using the composition of Example 3 at a 50% concentration. Table 13 reports the test results of corrosion tests that were carried out on various metal samples using the composition of Example 3 at a 100% concentration. These test results show that the composition of Example 3 meets the regulatory standards for the transportation industry on mild steel, and provide a strong level of protection with respect to aluminum. Table 14

lists a number of applications for which compositions according to the present invention can be used as well as proposed dilution ranges.

5 **Table 11** Corrosion tests carried out on N-80 steel (density of 7.86 g/cc) using the composition of
Example 3 at a 50% concentration

Temp	Initial Wt.	Final wt.	Loss wt.	Surface Area	Density	Run Time	Mils/yr	mm/yea r	lb/ft2
°C	(g)	(g)	(g)	(cm2)	g/cc	(hours)			
70°C	40.757	40.708	0.049	27.11	7.86	6	132.1789	3.357	0.003

70°C	40.757	40.609	0.148	27.11	7.86	24	99.80859	2.535	0.010
90°C	40.712	40.617	0.095	27.11	7.86	6	256.2653	6.509	0.007
90°C	40.712	40.475	0.237	27.11	7.86	24	159.8286	4.060	0.017

20 **Table 12** Corrosion tests carried out on J-55 steel (density of 7.86 g/cc) using the composition of
Example 3 at a 50% concentration

Temp	Initial Wt.	Final wt.	Loss wt.	Surface Area	Density	Run Time	Mils/yr	mm/yea r	lb/ft2
°C	(g)	(g)	(g)	(cm2)	g/cc	(hours)			
50°C	38.366	38.342	0.024	28.922	7.86	6	60.68462	1.541	0.002
50°C	38.366	38.323	0.043	28.922	7.86	24	27.18165	0.690	0.003
70°C	38.728	38.596	0.132	28.922	7.86	6	333.7654	8.478	0.009
70°C	38.728	38.448	0.280	28.922	7.86	24	176.9968	4.496	0.020
90°C	37.543	37.463	0.080	28.922	7.86	6	202.2821	5.138	0.006
90°C	37.543	37.106	0.437	28.922	7.86	24	276.2415	7.017	0.031

Table 13 Corrosion tests carried out on various metal samples using the composition of Example 3 at a 100% concentration

	Temp	Initial Wt.	Final wt.	Loss wt.	Surface Area	Density	Run Time	Mils/yr	mm/year	lb/ft2
Coupon	°C	(g)	(g)	(g)	(cm ²)	g/cc	(hours)			
1018 steel	55 °C	13.994	13.955	0.039	28.503	7.82	72	8.381163	0.213	0.003
7075 aluminum	25 °C	6.196	6.080	0.116	29.471	2.81	24	201.2867	5.113	0.008
7075 aluminum	25 °C	6.196	1.344	4.852	29.471	2.81	48	4209.668	106.926	0.344

[0095] 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: injection/disposal treatments; matrix acid squeezes, soaks or bullheads; acid fracturing, acid washes; fracturing spearheads (breakdowns); pipeline scale treatments, cement breakdowns or perforation cleaning; pH control; and descaling applications.

Table 14 Applications for which compositions according to the present invention can be used as well as proposed dilution ranges

Application:	Suggested Dilution:	Benefits:
Injection/Disposal Wells	50%	Compatible with mutual solvents and solvent blends, very cost effective.
Squeezes & Soaks - Bullhead - Annular	33% - 50%	Ease of storage & handling, cost effective compared to conventional acid stimulations. Ability to leave pump equipment in wellbore.
Acid Fracs	50% - 75%	Decreased shipping and storage compared to conventional acid, no blend separation issues, comprehensive spend rate encourages deeper formation penetration.

5	Frac Spearheads (Break-downs)	33% - 66%	Able to adjust concentrations on the fly. Decreased shipping and storage on location.
10	Cement Break-downs	50%	Higher concentrations recommended due to lower temperatures, and reduced solubility of aged cement.
15	pH Control	0.1% - 1.0%	Used in a variety of applications to adjust pH level of water based systems.
	Liner De-Scaling, Heavy Oil	1% - 5%	Continuous injection/de-scaling of slotted liners, typically at very high temperatures.

Use of a composition according to the present invention in spearhead on multi-well pad

[0096] An operator in Western Canada was performing horizontal multi-stage fracturing completions on a multiple well pad, using plug and perforate technology. Traditional methods of formation breakdown required the use of 6-10 m³ of 15% HCl acid to be pumped down the casing prior to each fracturing stage.

[0097] Prior to testing, multiple samples of the high salinity fracturing water (recycled fracturing fluid) were tested for compatibility, as this was proposed to be used as the diluents for the concentrated synthetic acid. By storing the concentrated synthetic acid composition in a tank and diluting it with the fracturing water on site, only two storage tanks were required for the treatments (± 360 m³ of spearhead acid). These are intended on being refilled periodically.

[0098] For each treatment, the tank of concentrated synthetic acid composition was blended on site through the fracturing blender with the fracturing water down to reach a concentration of $\pm 33\%$ of the initial composition. 6-10 m³ of the synthetic acid composition was pumped for each spearhead stage, all other operational components and procedures remained the same as traditional methods using HCl acid (15% HCl acid was on location for a comparison well).

[0099] A total of 18 stages per well were treated on more than 8 wells, with 100% breakdown success on every stage. Breakdown pressure differentials in the range of 10-15 MPa were observed, and were found to be very comparable to HCl acid.

[0100] The main advantages of the use of the synthetic acid composition included: the reduction of the total loads of acid, and the required number of tanks by delivering concentrated product to location and diluting with fluids available on location (high salinity production water). Other advantages of the composition according to the present invention include: operational efficiencies which led to the elimination of having to periodically circulate tanks of HCl acid due to chemical separation; reduced potential corrosion to downhole tubulars; and reduced HCl acid exposure to personnel by having a non-hazardous, non-fuming acid on location.

40 Claims

1. A synthetic acid composition for use in downhole oil industry activities, said composition comprising:

45 - urea and hydrogen chloride in a molar ratio ranging from 0.1:1.0 to 1.05:1.0 inclusively;
 - a metal iodide or iodate;
 - an alcohol or derivative thereof; and water and
 - optionally, a phosphonic acid derivative.

50 2. The synthetic acid composition according to claim 1, wherein the urea and hydrogen chloride are in a molar ratio ranging from 0.5:1.0 to 1.05:1.0 inclusively.

3. The synthetic acid composition according to any one of claims 1 to 2, wherein the phosphonic acid derivative is amino tris methylene phosphonic acid.

55 4. The synthetic acid composition according to any one of claims 1 to 3, wherein the metal iodide or iodate is selected from the group consisting of: cuprous iodide; potassium iodide; sodium iodide; and lithium iodide.

5. The synthetic acid composition according to any one of claims 1 to 4, wherein the metal iodide or iodate is potassium iodide.
6. The synthetic acid composition according to any one of claims 1 to 5, wherein the alcohol or derivative thereof is an alkynyl alcohol or derivative thereof selected from the group consisting of: propargyl alcohol or a derivative thereof.
7. The synthetic acid composition according to any one of claims 3 to 6, wherein the amino tris methylene phosphonic acid is present in a concentration ranging from 0.25 to 1.0% w/w.
10. The synthetic acid composition according to claim 7, wherein the alkynyl alcohol or derivative thereof is present in a concentration ranging from 0.1 to 2.0% w/w.
15. The synthetic acid composition according to claim 8, wherein the alkynyl alcohol or derivative thereof is present in a concentration of 0.25% w/w.
10. The synthetic acid composition according to any one of claims 1 to 9, wherein the metal iodide is present in a concentration ranging from 100 to 500 ppm.
20. The synthetic acid composition according to any one of claims 1 to 10, further comprising a formic acid or a derivative thereof is selected from the group consisting of: formic acid, acetic acid, ethylformate and butyl formate in an amount ranging from 0.05 - 2.0% by weight of the composition.
25. The synthetic acid composition according to any one of claims 1 to 11, further comprising a compound selected from the group consisting of: propylene glycol or derivative thereof, ethylene glycol, glycerol or a mixture thereof, in a concentration ranging from 0.05 - 1.0 % by weight of the composition.
13. The synthetic acid composition according to any one of claims 1 to 12, further comprising cinnamaldehyde or a derivative thereof in a concentration ranging from 0.01 - 1.0 % by weight of the composition.
30. 14. The use of a synthetic acid composition according to any one of claims 1 to 13 in the oil industry to perform an activity selected from the group consisting of: stimulating formations; assisting in reducing breakdown pressures during downhole pumping operations; treating wellbore filter cake post drilling operations; assisting in freeing stuck pipe; descaling pipelines and/or production wells; increasing injectivity of injection wells; lowering the pH of a fluid; fracturing wells; performing matrix stimulations; conducting annular and bullhead squeezes & soaks; pickling tubing, pipe and/or coiled tubing; increasing effective permeability of formations; reducing or removing wellbore damage; cleaning perforations; solubilizing limestone, dolomite, and calcite; and removing undesirable scale on a surface selected from the group consisting of: equipment, wells and related equipment and facilities.
- 35.

40 Patentansprüche

1. Synthetische Säurezusammensetzung für die Verwendung bei Bohrlocharbeiten in der Ölindustrie, wobei die Zusammensetzung umfasst:
 - 45 - Harnstoff und Chlorwasserstoff in einem Molverhältnis in dem Bereich von einschließlich 0,1:1,0 bis 1,05:1,0;
 - ein Metalliodid oder -iodat;
 - einen Alkohol oder ein Derivat davon; und Wasser und
 - gegebenenfalls ein Phosphonsäurederivat.
50. 2. Synthetische Säurezusammensetzung gemäß Anspruch 1, wobei der Harnstoff und der Chlorwasserstoff in einem Molverhältnis in dem Bereich von einschließlich 0,5:1,0 bis 1,05:1,0 vorliegen.
3. Synthetische Säurezusammensetzung gemäß einem der Ansprüche 1 bis 2, wobei das Phosphonsäurederivat Aminotrimethylenphosphonsäure ist.
55. 4. Synthetische Säurezusammensetzung gemäß einem der Ansprüche 1 bis 3, wobei das Metalliodid oder -iodat ausgewählt ist aus der Gruppe bestehend aus: Kupferiodid; Kaliumiodid; Natriumiodid; und Lithiumiodid.

5. Synthetische Säurezusammensetzung gemäß einem der Ansprüche 1 bis 4, wobei das Metalliodid oder -iodat Kaliumiodid ist.

5 6. Synthetische Säurezusammensetzung gemäß einem der Ansprüche 1 bis 5, wobei der Alkohol oder das Derivat davon ein Alkinylalkohol oder ein Derivat davon ausgewählt aus der Gruppe bestehend aus: Propargylalkohol oder ein Derivat davon ist.

10 7. Synthetische Säurezusammensetzung gemäß einem der Ansprüche 3 bis 6, wobei die Aminotrimethylenphosphonsäure in einer Konzentration in dem Bereich von 0,25 bis 1,0 % w/w vorhanden ist.

15 8. Synthetische Säurezusammensetzung gemäß Anspruch 7, wobei der Alkinylalkohol oder das Derivat davon in einer Konzentration in dem Bereich von 0,1 bis 2,0 % w/w vorhanden ist.

15 9. Synthetische Säurezusammensetzung gemäß Anspruch 8, wobei der Alkinylalkohol oder das Derivat davon in einer Konzentration von 0,25 % w/w vorhanden ist.

20 10. Synthetische Säurezusammensetzung gemäß einem der Ansprüche 1 bis 9, wobei das Metalliodid in einer Konzentration in dem Bereich von 100 bis 500 ppm vorhanden ist.

20 11. Synthetische Säurezusammensetzung gemäß einem der Ansprüche 1 bis 10, ferner umfassend eine Ameisensäure oder ein Derivat davon, ausgewählt aus der Gruppe bestehend aus: Ameisensäure, Essigsäure, Ethylformiat und Butylformiat in einer Menge in dem Bereich von 0,05-2,0 Gew.-% der Zusammensetzung.

25 12. Synthetische Säurezusammensetzung gemäß einem der Ansprüche 1 bis 11, ferner umfassend eine Verbindung ausgewählt aus der Gruppe bestehend aus: Propyenglycol oder ein Derivat davon, Ethylenglycol, Glycerol oder ein Gemisch davon in einer Konzentration in dem Bereich von 0,05-1,0 Gew.-% der Zusammensetzung.

30 13. Synthetische Säurezusammensetzung gemäß einem der Ansprüche 1 bis 12, ferner umfassend Zimtaldehyd oder ein Derivat davon in einer Konzentration in dem Bereich von 0,01-1,0 Gew.-% der Zusammensetzung.

30 14. Verwendung einer synthetischen Säurezusammensetzung gemäß einem der Ansprüche 1 bis 13 in der Ölindustrie für die Durchführung einer Arbeit ausgewählt aus der Gruppe bestehend aus: Anregen von Formationen; Unterstützung zum Verringern von Ausfalldrücken bei Bohrlochpumpvorgängen; Behandeln von Bohrlochfilterkuchen nach Bohrvorgängen; Unterstützung zum Freimachen festsitzender Rohre; Ablagerungsentfernung in Pipelines und/oder Produktionsbohrlöchern; Erhöhen der Injektivität von Injektionsbohrlöchern; Senken des pH-Werts eines Fluids; Frakturieren von Bohrlöchern; Durchführen von Matrixanregungen; Durchführen von ringförmigem und Bull-head-Druck und -Tränkung; Beizen von Rohren, Leitungen und/oder Rohrschlangen; Erhöhen der effektiven Durchlässigkeit von Formationen; Verringern oder Beseitigen von Bohrlochschäden; Reinigen von Perforationen; Solutibilisieren von Kalkstein, Dolomit und Calcit; und Entfernen unerwünschter Ablagerungen auf einer Oberfläche ausgewählt aus der Gruppe bestehend aus: Ausrüstung, Bohrlöcher und zugehörige Ausrüstung und Anlagen.

Revendications

45 1. Composition acide synthétique pour utilisation dans des activités de fond dans l'industrie pétrolière, ladite composition comprenant :

50 - de l'urée et du chlorure d'hydrogène dans un rapport molaire dans la plage de 0,1:1,0 à 1,05:1,0 inclus ;
 - un iodure ou iodate métallique ;
 - un alcool ou un dérivé de celui-ci ;
 et de l'eau et
 - facultativement, un dérivé d'acide phosphonique.

55 2. Composition acide synthétique selon la revendication 1, dans laquelle l'urée et le chlorure d'hydrogène sont dans un rapport molaire dans la plage de 0,5:1,0 à 1,05:1,0 inclus.

3. Composition acide synthétique selon l'une quelconque des revendications 1 et 2, dans laquelle le dérivé d'acide phosphonique est l'acide amino-tris-méthylène phosphonique.

4. Composition acide synthétique selon l'une quelconque des revendications 1 à 3, dans laquelle l'iodure ou iodate métallique est choisi dans le groupe constitué de : l'iodure cuivreux ; l'iodure de potassium ; l'iodure de sodium ; et l'iodure de lithium.

5. Composition acide synthétique selon l'une quelconque des revendications 1 à 4, dans laquelle l'iodure ou iodate métallique est l'iodure de potassium.

10. 6. Composition acide synthétique selon l'une quelconque des revendications 1 à 5, dans laquelle l'alcool ou un dérivé de celui-ci est un alcool d'alcynyle ou un dérivé de celui-ci choisi dans le groupe constitué de : l'alcool propargylique ou un dérivé de celui-ci.

15. 7. Composition acide synthétique selon l'une quelconque des revendications 3 à 6, dans laquelle l'acide amino-tris-méthylènephosphonique est présent à une concentration dans la plage de 0,25 à 1,0 % m/m.

20. 8. Composition acide synthétique selon la revendication 7, dans laquelle l'alcool d'alcynyle ou un dérivé de celui-ci est présent à une concentration dans la plage de 0,1 à 2,0 % m/m.

25. 9. Composition acide synthétique selon la revendication 8, dans laquelle l'alcool d'alcynyle ou dérivé de celui-ci est présent à une concentration de 0,25 % m/m.

20. 10. Composition acide synthétique selon l'une quelconque des revendications 1 à 9, dans laquelle l'iodure métallique est présent à une concentration dans la plage de 100 à 500 ppm.

25. 11. Composition acide synthétique selon l'une quelconque des revendications 1 à 10, comprenant en outre un acide formique ou un dérivé de celui-ci qui est choisi dans le groupe constitué des : acide formique, acide acétique, formiate d'éthyle et formiate de butyle en une quantité dans la plage de 0,05 à 2,0 % en poids de la composition.

30. 12. Composition acide synthétique selon l'une quelconque des revendications 1 à 11, comprenant en outre un composé choisi dans le groupe constitué des : propylène glycol ou un dérivé de celui-ci, éthylène glycol, glycérol ou un mélange de ceux-ci, à une concentration dans la plage de 0,05 à 1,0 % en poids de la composition.

35. 13. Composition acide synthétique selon l'une quelconque des revendications 1 à 12, comprenant en outre du cinnamaldéhyde ou un dérivé de celui-ci à une concentration dans la plage de 0,01 à 1,0 % en poids de la composition.

40. 14. Utilisation d'une composition acide synthétique selon l'une quelconque des revendications 1 à 13 dans l'industrie pétrolière pour conduire une activité choisie dans le groupe constitué de : la stimulation de formations ; l'aide à la réduction des pressions de rupture pendant des opérations de pompage de fond ; le traitement de gâteau de filtration de puits de forage après des opérations de forage ; l'aide au déblocage d'un tube bloqué ; le détartrage de canalisations et/ou de puits de production ; l'augmentation de l'injectivité de puits d'injection ; la diminution du pH d'un fluide ; la fracturation de puits ; la conduite de stimulations de matrice ; la conduite d'esquiches et d'injections annulaires et forcées ; le décapage de tube, de tuyau et/ou de tube spiralé ; l'augmentation de la perméabilité effective de formations ; la réduction ou l'élimination de dommages de puits de forage ; le nettoyage de perforations ; la solubilisation de calcaire, dolomite, et calcite ; et l'élimination de tartre indésirable sur une surface choisie dans le groupe constitué de : un équipement, des puits et un équipement et des installations associées.

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REFERENCES CITED IN THE DESCRIPTION

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