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CA 2509649 A1 2006/12/09

(21) **2 509 649**

(12) **DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION**

(13) **A1**

(22) Date de dépôt/Filing Date: 2005/06/09

(41) Mise à la disp. pub./Open to Public Insp.: 2006/12/09

(51) Cl.Int./Int.Cl. *E21B 43/22* (2006.01)

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(54) Titre : METHODE DE TRAITEMENT D'ACIDIFICATION A FLUIDE UNIQUE

(54) Title: SINGLE FLUID ACIDIZING TREATMENT

(57) **Abrégé/Abstract:**

An acidizing formulation for use in the stimulation of hydrocarbon production is stable when packaged and stored as a single fluid for periods exceeding one year. The formulation contains a miscibility solvent which substantially prevents any phase separation between the constituents and lack of dispersion of the additives in the fluid.



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ABSTRACT

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An acidizing formulation for use in the stimulation of hydrocarbon production is stable when packaged and stored as a single fluid for periods exceeding one year. The formulation contains a miscibility solvent which substantially prevents any phase separation between the constituents and lack of dispersion of the additives in the fluid.

1 **“SINGLE FLUID ACIDIZING TREATMENT”**
2

3 FIELD OF THE INVENTION

4 Embodiments of the invention relate to fluids used for acidizing
5 wellbores and formations and more particularly to acidizing formulations
6 containing additives to prevent corrosion of wellbore equipment and additives to
7 prevent sludge formation, precipitation and the like.

8
9 BACKGROUND OF THE INVENTION

10 Matrix acidizing treatments are conventionally performed to
11 increase permeability of oil and gas formations, dissolve mineral deposits and to
12 remove various types of damage therein. Mineral acids, such as hydrochloric
13 acid (HCl), hydrofluoric acid (HF) and mixtures thereof called Mud Acid, and
14 organic acids, such as acetic acid, have been used. The major function of an
15 acidizing formulation is to remove damage by dissolving scale and formation
16 fines and to stimulate the formation.

17 Due to the highly corrosive nature of the acids used in the acidizing
18 treatment, anti-corrosive additives are typically added to the fluid to protect metal
19 surfaces of wellbore tubulars and other equipment from corrosive attack.

20 Further, other additives may be added to the acidizing formulation
21 to improve injectivity and return of the stimulation fluids. Other additives may
22 include wetting agents, foaming agents, silt-suspending agents, anti-sludging
23 agents, iron-control additives such as reducing or chelating agents, non-
24 emulsifiers or emulsifiers depending upon the formulation and small amounts of
25 mutual solvents.

1 Additives may be more or less soluble or dispersible in the
2 aqueous acid solutions used for acidizing and thus may precipitate out or phase
3 separate into an oil phase in the formation. Further, the products of the acidizing
4 treatment may precipitate out or form sludges in the formation creating additional
5 formation damage. Little specific literature is found regarding the stability of the
6 formulations once mixed together prior to injection into the formation. Applicant
7 however is aware that it is a standard industry practice to mix the formulation
8 ingredients together immediately prior to injection or within 24-48 hours prior to
9 injection due to the industry recognized instability of conventional acidizing
10 formulations. So unstable are the formulations considered to be that in some
11 cases Applicant is aware that formulations prepared only hours in advance of an
12 expected use and which have been shipped only a few miles by truck to wellsites
13 are discarded if the intended use does not occur as scheduled. Most often
14 separate ingredients are shipped to the wellsite and the ingredients mixed
15 together only as required and at the time required.

16 Significant literature is found directed toward the use of mutual
17 solvents in formation stimulation. Solvents such as ethylene glycol monobutyl
18 ether (EGMBE) or commercial preparations of mixtures of alcohols such as A-
19 Sol and Super A-Sol (available from Baker-Petrolite, Calgary, Alberta, Canada)
20 have been used to assist in the removal or stripping of oil or hydrocarbon which
21 coats scale or other deposits to be dissolved which prevent the acid from acting
22 thereon or to retard the functionality of the acid so that it can be displaced further
23 into the formation before the acid becomes spent. Typically, mutual solvents are
24 used as a pre-flush or an after-flush alone or in combination with brine, acid or
25 the like. While the mutual solvent may be combined with the acid or other fluids,

1 preparation is typically on site immediately prior to injection and concentrations
2 are reported to be typically about 3-10% (Dayvault et al., "Solvent and Acid
3 Stimulation Increase Production in Los Angeles Basin Waterflood", SPE 18816
4 April 1989).

5 Aromatic solvents, typically used to strip hydrocarbons, are highly
6 immiscible in aqueous solutions and therefore attempts to add aromatic solvents
7 to aqueous acid solutions for this purpose would result in highly phase separated
8 fluids, additives and the like partitioning between the phases and reducing the
9 effectiveness of the acid treatment fluid.

10 Historically, mutual solvents, particularly EGMBE, have been used
11 alone or in combination with a mud acid to increase permeability and leave the
12 formation water-wet. It has also been reported that fines are thus prevented from
13 moving back to the wellbore. Further, mutual solvents have been credited with
14 deterring the formation of sludges and emulsions.

15 As reported by Dabbousi et al. in "Influence of Oilfield Chemicals
16 on the Surface Tension of Stimulating Fluids", SPE 50732, February 1999,
17 mutual solvents such as EGMBE at concentrations of 10% by weight or lower act
18 to reduce the surface tension of organic acids, however concentrations above 10
19 wt% appeared to have no effect. G.E. King reported in "Evaluation of Mutual
20 Solvents used in Acidizing" May 2, 1983 in Amoco report F83-P-26 that mutual
21 solvents such as A-Sol may be used at 5% by volume in 15% HCl and at 10% by
22 volume in 28% HCl. EGMBE and A-Sol were tested at 10% and 35%
23 respectively in 15% HCL and 80% Super A-Sol in 15% HCl were also tested. In
24 some cases the increased amounts of mutual solvent resulted in longer emulsion
25 break times.

1 Additives are typically added to acidizing formulations to prevent
2 unwanted damage to the formation or to the equipment used for the acidizing
3 process, such as tubulars. As previously stated, corrosion inhibitors are added to
4 acidizing formulations to assist in mitigation of corrosion of carbon steel tubing
5 and casing found in wellbores . Typically, the industry standard for corrosion of
6 carbon steel in contact with mineral acids such as HCl is below 0.05 pounds per
7 square foot. The inhibitors chosen to prevent corrosion must dissolve and remain
8 compatible with the acid and other additives to provide the standard level of
9 protection at various temperatures, typically from ambient temperature to
10 elevated downhole temperatures, to at least 150°C. A diverse number of
11 chemicals have been used historically to prevent corrosion. Acetylenic alcohols,
12 such as propargyl alcohol are the most widely reported. Other corrosion
13 inhibitors used and reported are organic amines, dimer/trimer acids derived from
14 tall oil or other bases, quaternary amines derived from coconut, canola, tallow,
15 tall oil or other bases, fatty alcohols, derivatized quinolines, alkyl pyridines and
16 oxyalkylated resin amines.

17 The presence of iron, particularly in the ferric form rather than the
18 ferrous form, may increase the likelihood of an asphaltene sludge forming when
19 the acid comes into contact with native oil. Should iron sludge form, the
20 permeability of the formation may be severely impaired. Typically, as the acid
21 spends, the pH begins to rise. Ferric sludge begins to form at pH above about
22 1.9, while ferrous sludge does not begin until a pH well above 5. Historically,
23 acidizing treatments typically result in pH no higher than about 3.5 in the fluid
24 returns after treatment and thus, it is of greater interest to prevent the formation
25 of ferric sludge. Many types of iron control additives are known, particularly

1 reducing additives and chelating additives. Historically additives have included
2 erythorbic acid, citric acid, nitriloacetic acid (NTA), ethylenediamine tetraacetic
3 acid (EDTA), glycolic acid, thioglycolic acid, 2-mercaptoethanol, thioglycerol,
4 hypophosphorous acid, inorganics such as copper, antimony, bismuth, iodide
5 and the like in combination with organics such as quaternary ammonium
6 compounds and reducing agents, such as 2-mercaptoethanol and stannous
7 chloride.

8 Sludge generally refers to any solids which are generated when the
9 acid comes into contact with virgin oil in the subterranean formation. The sludge
10 is typically formed by precipitation of wax/paraffins or asphaltenes due to
11 destabilization or emulsions that occur, often as a result of intimate contact
12 between aqueous and non-aqueous fluids. Many chemistries have been
13 employed in acidizing formulations to prevent sludge formation. A primary
14 characteristic of anti-sludge agents is that they act as dispersants. One such
15 dispersant noted in the literature is dodecyl benzene sulphonic acid (DDBSA),
16 which is dispersible in mineral acids rather than being soluble. DDBSA readily
17 separates from acidizing formulations upon standing unless blended immediately
18 prior to use on site. Instability of formulations containing DDBSA is particularly
19 problematic at elevated temperatures such as are found in many formations.

20 Optionally, demulsifiers are added to acidizing formulations to
21 prevent formation of emulsions when the aqueous acid comes into contact with
22 hydrocarbons in the formation. The formation of emulsions is typically very
23 detrimental to acidizing treatments. Even more problematic, emulsions may be
24 stabilized by solids such as paraffins, asphaltenes, corrosion by-products and
25 undissolved minerals from the formation. Conventional demulsifiers may include

1 amine oxyalkalates, alkyl polyols, resin oxyalkalates, glycol esters, poly glycol
2 derivatives and diepoxides. An API industry standard (API RP 42) requires that
3 acidizing formulations exhibit a maximum emulsion break time of 15 minutes in
4 the acid returns.

5 The addition of additives to an acidizing formulation must be
6 carefully designed so to as to prevent precipitation of the additives in the fluid
7 which may be detrimental and cause damage to the formation. Further, phase
8 separation may result in additives partitioning between an aqueous and an oily
9 phase and therefore being incapable of acting efficiently, if at all, for the
10 purposes for which they are added.

11 Clearly what is desired is an acidizing and stripping formulation
12 which can be premixed as a single fluid to reduce costs and hazards resulting
13 from on-site preparation and which is stable for relatively long periods of time to
14 reduce waste and costs related to disposal of unused, unstable formulations.
15 Ideally, fluids used are miscible and the additives either soluble or stably
16 dispersed therein.

17

A single fluid acidizing formulation comprising a relative high level of organic acid, a miscibility solvent and at least an anti-corrosion additive, when pre-mixed, is surprisingly stable for extended periods and for periods exceeding 1 year and possibly longer at both ambient and elevated temperatures (when under wellbore pressure), the miscibility solvent comprising an effective amount of aromatics to strip oils and greases from surfaces to be acidized and an effective amount of a blend of surfactants to ensure miscibility of the aromatics and the additives in the aqueous phase. Preferably, the density of the formulation is maintained below 1.0 g/cm³ to permit positioning of the formulation at areas of interest without precipitation of the acid in water or brine situated in the wellbore or the

7

1 added to the formulation to assist in maintaining a stable dispersion of the
2 additives therein.

3

4 DESCRIPTION OF EMBODIMENTS OF THE INVENTION

5 An acidizing formulation, primarily for the treatment of dolomitic
6 formations and for removal of acid soluble wellbore and formation damage such
7 as calcium carbonate buildup (scale) or precipitation of iron compounds, such as
8 carbonates, oxides and sulphides, from both dolomitic and sandstone-type
9 formations is mixed as a single fluid treatment package which can be stored
10 indefinitely at ambient temperatures and which is stable at elevated borehole
11 temperatures, often as high as 150°C.

12 Applicant has stored the single fluid acidizing formulation in excess
13 of 72 hours, being the industry recognized limitation for conventional acidizing
14 formulations, surprisingly without adverse effects to the stability of the
15 formulation and further, has stored samples of the single fluid acidizing
16 formulation for about one year without observable precipitation therein or
17 significant phase separation and partitioning of additives therein.

18 The formulation comprises at least an organic or mineral acid, an
19 anti-corrosive additive and a miscibility solvent. Preferably, a mineral acid such
20 as hydrochloric acid HCL at either 15% concentration or 28% concentration is
21 used. Common other acids include mineral acid HF and organic acids including
22 formic, acetic and citric acids. The miscibility solvent, comprising aromatic
23 solvents and alcohols, is selected to have a relatively high amount of aromatic
24 solvent therein to effectively strip oils and hydrocarbons which coat scale and
25 deposits of interest exposing said scale or deposits to the acid. Preferably, the

1 aromatic solvent comprises about 10 - 20% of the miscibility solvent and more
2 preferably about 14 – 18%. Preferably, the ratio of the miscibility solvent to
3 corrosion inhibited acid is about 50/50 vol% which provides significant acid
4 functionality. The alcohols are a blend of long and short chain alcohols selected
5 from the group comprising aliphatic alcohols, glycols, polyglycols and glycol
6 esters as well as mixtures thereof, preferably in a range of about 50 - 70% of the
7 miscibility solvent. The alcohols that can be used include methanol, ethanol,
8 propanol, isopropanol, 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, 3-pentanol,
9 1-hexanol, 2-ethylhexanol, 1-heptanol, 2-heptanol, 3-heptanol, 1-n-octanol, 2-n-
10 octanol, nonyl alcohol, and 1-decanol, to maintain the miscibility between the
11 aqueous acid and the aromatic solvent.

12 Further, a surfactant selected from the group consisting of fatty
13 alcohol alkoxylates, fatty alcohol ethoxylates, nonylphenol ethoxylates,
14 nonylphenol alkoxylates, block copolymers, reverse block copolymers, tetrols
15 and reverse tetrols, and the like, is added to enhance the stability of the
16 dispersion of the additives in the formulation. The surfactant can be added in a
17 range from 10 – 40 wt% of the miscibility solvent and is preferably added in a
18 range from 19 – 24 wt %.

19 Applicant believes that the miscibility solvent, particularly in
20 amounts at about or greater than 50 vol%, acts to bridge between the additives
21 in the formulation some of which are more acid dispersible rather than soluble in
22 the aqueous acid itself and to hold these dispersible additives in solution rather
23 than allowing them to precipitate or oil-out and degrade the functionality of the
24 formulation.

1 In addition to the added stability of the formulation, as a result of
2 the addition of the mutual solvent, additional benefits result from the preferred
3 formulation which has a density of less than 1.0, preferably about 0.95g/mL, and
4 a density greater than most oils encountered in the formations. Thus, produced
5 brine may be displaced into the formation without any significant dilution of the
6 acid which is being injected.

7 Historically, conventional 15% hydrochloric acid formulations,
8 having a higher density than water or brine, and when injected into wellbores
9 containing significant amounts of water, either produced or injected, fell through
10 the column of water where the acid mixed and diluted in the water to a uniform
11 concentration. The final concentration of the acid/water mixtures was dependant
12 upon the amount of water in the wellbore at the time of the injection of the acid,
13 however any amount of dilution resulted in a decrease in effectiveness of the
14 acid to dissolve scale and the like. Further, if the acid formulation was to be used
15 to treat scale in wellbore tubulars, the full strength acid, being heavier than the
16 water in the tubular, would fall past the scale and into the sump of the well.
17 When the volume was sufficient to reach the spot in the tubular to be treated, the
18 concentration of the acid would be dependant upon the amount of dilution that
19 had occurred.

20 In embodiments of the present invention, the preferred
21 embodiment has a density of about 0.95 g/mL, being lower than fresh water,
22 typically having a density of 1.0 g/mL and produced water, typically having a
23 density of about 1.01g/mL or greater. The single fluid acidizing formulation
24 having a lower density will not fall through columns of water and can therefore be
25 loaded or spotted at full strength above produced water on scale deposits within

1 the tubulars regardless of the location. Further, the formulation can be used to
2 displace water into the formation without dilution of the acid, thus presenting the
3 formation to be treated with full strength acid and achieving greater dissolution of
4 solids per cubic meter of acid used.

5 Advantageously, the acid formulation is stabilized by the miscibility
6 solvent and surfactant contained therein at ambient temperatures for longterm
7 storage. Further, the formulation is also stabilized at wellbore temperatures,
8 often up to at least 150° C. Additives, such as DDBSA, which are conventionally
9 used and which are often susceptible to precipitation out of solution or dispersion
10 in oil in conventional acidizing formulations, even when small amounts of a
11 mutual solvent are added, are prevented from loss in embodiments of the
12 present invention as a result of the addition of the miscibility solvent and the
13 surfactant.

14 In a preferred embodiment of a single fluid acidizing formulation for
15 use with 15% HCl, the formulation comprises:

- 16 • Miscibility solvent, preferably about 59% by weight; (30 – 60% by wt.) and
17 having aromatic solvents contained therein in an amount of about 15% by
18 wt., alcohols about 63% (about 35 – 65%) and surfactant about 23%
19 (about 10 – 30%) in the miscibility solvent;
- 20 • Hydrochloric Acid (23 Be HCl), preferably about 13.8% by weight of the
21 single fluid;
- 22 • Corrosion inhibitor, preferably about 1 - 5% by weight of the single fluid;
- 23 • Demulsifier, preferably about 0.04% by weight of the single fluid
- 24 • Anti-sludge additive, preferably about 0.4% by weight of the single fluid;
- 25 • Iron control additive, preferably about 1.5% by weight of the single fluid ;
26 and
- 27 • Water making up the balance.

28 The preferred miscibility solvent comprises a mixture of organic,
29 aromatic solvents and alcohols. Most preferably, the alcohols comprise about 5 -
30 15% long chain alcohols and 40 - 60% short chain alcohols.
31

1 If 28% HCl is used, such as is typically used in gas wells, the
2 preferred amounts of the additives must be altered to ensure appropriate
3 corrosion inhibition and the like. The preferred formulation for 28% HCl is as
4 follows:

- 5 • Mutual solvent, preferably about 63.2% by weight; range 40 – 65%
- 6 • Hydrochloric Acid (23 Be HCl), preferably about 24.5% by weight; range
7 20 – 30%
- 8 • Corrosion inhibitor, preferably about 1.1% by weight; range 0.5 – 5%
- 9 • anti-sludge additive, preferably about 0.4% by weight; range 0 – 3.0%
- 10 • Demulsifier, preferably about 0.03% by weight; range 0 – 1%
- 11 • Iron control additive, preferably about 1.3% by weight; range 0 – 5% and
- 12 • Water making up the balance.

13
14 The preferred corrosion inhibitor comprises 35 wt% isopropyl
15 alcohol, 5wt% water, 20 wt% C12-alkyl pyridine, 20 wt% oxyalkylated resin
16 amines and 20 wt% propargyl alcohol.

17 The preferred anti-sludge additive is dodecyl benzene sulphonic
18 acid (DDBSA) and the preferred demulsifier is a combination of 70 wt%
19 methanol, 20 wt% polymerized polyol (relative solubility # ~7.0) and 5 wt% nonyl
20 phenol resin adducts (relative solubility # ~17.0)

21 The preferred iron control additive is stannous chloride which acts
22 to reduce ferric ions to ferrous ions to prevent iron sludge from forming at the pH
23 of the spent acid returned from the formation.

24 Depending upon formation characteristics, some or all of the
25 aforementioned additives may be removed from the formulation.

26 Preferred embodiments of the invention have the following
27 advantages:

- 1 • the dispersion of the acid dispersible components is
2 stabilized indefinitely and at temperatures which vary from ambient to
3 150°C;
- 4 • reaction products resulting from the action of the acid on the
5 deposits to be dissolved are stabilized in the fluids to permit flowing of the
6 fluid and reaction products from the well after acidizing;
- 7 • elevated percentages of acid are possible in a miscible
8 single fluid without phase separation, partitioning of additives therein or
9 precipitation in the formation;
- 10 • the single fluid is capable of stripping hydrocarbon coating
11 from surfaces of interest increasing the efficiency and effectiveness of the
12 acid by allowing direct contact of the acid on the surface;
- 13 • the density of the fluid, being lower than that of fresh water
14 and produced water/brine permits spotting of the acidizing formulation at
15 zones of interest without significant dilution of the acid in formation and
16 wellbore water and brine; and
- 17 • the formation is left water wet following treatment so as to
18 enhance the production of non-aqueous fluids due to the lowering of flow
19 resistance forces, such as hydrocarbon fluids, that would otherwise be
20 present .
21

1 IN USE

2 A single fluid acidizing formulation is prepared according to an
3 embodiment of the invention, including an aqueous acid solution, a miscibility
4 solvent comprising an effective amount of aromatic solvents, preferably from
5 about 10 – 20% of the miscibility solvent, a blend of long and short chain
6 alcohols and a surfactant and at least a corrosion inhibitor. The fluid is
7 packaged for addition to the wellbore, such as in drums which can be stored
8 substantially for periods exceeding 1 year and possibly longer and readily
9 shipped to a wellsite for pumping into a wellbore and formation without further
10 preparation.

11 Preferably, additional additives including, but not limited to those
12 disclosed above, are added in an amount effective in a majority of formations
13 containing a wide variety of crude oils and thus, the single fluid is substantially
14 universal in applicability at temperatures ranging from ambient to at least 150°C.
15 Formulations containing 15% acid may be prepared and sold separately from
16 those prepared containing 28% acid which permit treatments at both conventions
17 concentrations currently known in the industry. Thus, the single fluid treatments
18 avoid problems related to onsite preparation and to disposal if unused and do
19 not need to be adjusted for alterations in the formation characteristics.

1 **THE EMBODIMENTS OF THE INVENTION IN WHICH AN**
2 **EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS**
3 **FOLLOWS:**
4

5 1. An acidizing formulation for the stimulation of hydrocarbon
6 production comprising:

7 an aqueous acid solution, being from about 35 volume% to about
8 60 volume% of the formulation;

9 an effective amount of at least a corrosion inhibitor; and

10 a miscibility solvent being from about 40 volume% to about 65
11 volume% of the formulation for forming a substantially stable single fluid, the
12 miscibility solvent further comprising:

13 an effective amount of an aromatic solvent;

14 a blend of an effective amount of short chain alcohols and an
15 effective amount of long chain alcohols, the blend of alcohols
16 acting to substantially prevent phase separation between the
17 aromatic solvent and the aqueous acid solution; and

18 an effective amount of a surfactant.

19

20 2. The acidizing formulation of claim 1 wherein the density is
21 less than about 1 g/mL.

22

23 3. The acidizing formulation of claim 1 or 2 wherein the
24 aromatic solvent comprises from about 10 wt% to about 20 wt% of the miscibility
25 solvent.

26

1 4. The acidizing formulation of claim 1 or 2 wherein the
2 aromatic solvent comprises from about 14 wt% to about 18 wt% of the miscibility
3 solvent.

4
5 5. The acidizing formulation of any one of claims 1 – 4 wherein
6 the ratio of miscibility solvent to aqueous acid solution and at least a corrosion
7 inhibitor is about 50/50 volume%.

8
9 6. The acidizing formulation of any one of claims 1 – 5 wherein
10 the blend of long and short chain alcohols comprise from about 50 wt% to about
11 70 wt% of the miscibility solvent.

12
13 7. The acidizing formulation of any one of claims 1 – 6
14 wherein the blend of long and short chain alcohols comprises about 5 % to about
15 15 % long chain alcohols and about 40 % to about 60 % short chain alcohols.

16
17 8. The acidizing formulation of claim 7 wherein the short chain
18 alcohols are C₁ to C₇ alcohols.

19
20 9. The acidizing formulation of claim 7 or 8 wherein the long
21 chain alcohols are C₈ to about C₁₀ alcohols.

22
23 10. The acidizing formulation of claim 8 wherein the short chain
24 alcohols are selected from the group consisting of methanol, ethanol, propanol,

1 isopropanol, 1-butanol, 2-butanol, 3-heptanol, 3-pentanol, 1-hexanol, 1-heptanol,
2 2-heptanol and 3-heptanol.

3

4 11. The acidizing formulation of claim 9 wherein the long chain
5 alcohols are selected from the group consisting of 2-ethylhexanol, 1-n-octanol, 2-
6 n-octanol, nonyl alcohol and 1-decanol.

7

8 12. The acidizing formulation of any one of claims 1 - 12
9 wherein the surfactant comprises from about 10 wt% to about 40 wt% of the
10 miscibility solvent.

11

12 13. The acidizing formulation of any one of claims 1 - 12
13 wherein the surfactant is selected from the group consisting of fatty alcohol
14 alkoxylates, fatty alcohol ethoxylates, nonylphenol ethoxylates, nonylphenol
15 alkoxylates, block copolymers, reverse block copolymers, tetrols and reverse
16 tetrols.

17

18 14. The acidizing formulation of any one of claims 1 -13 further
19 comprising an anti-sludge additive.

20

21 15. The acidizing formulation of any one of claims 1 -14 further
22 comprising a demulsifier.

23

24 16. The acidizing formulation of any one of claims 1 - 15 further
25 comprising an iron control additive.

1

2 17. The acidizing formulation of any one of claims 1 - 16
3 wherein the acid is an organic acid.

4

5 18. The acidizing formulation of any one of claims 1 - 17
6 wherein the acid is a mineral acid.

7

8 19. The acidizing formulation of any one of claims 1 - 16
9 wherein the acid is hydrochloric acid.

10

11 20. The acidizing formulation of any one of claims 1 - 16
12 wherein the acid is hydrofluoric acid.

13

14 21. The acidizing formulation of claim 19 wherein the
15 hydrochloric acid is 15% hydrochloric acid.

16

17 22. The acidizing formulation of claim 19 wherein the
18 hydrochloric acid is 28% hydrochloric acid.

19

20 23. The acidizing formulation of claim 21 wherein:

21 the 15% hydrochloric acid is about 13.8% by weight of the
22 formulation,

23 the miscibility solvent is about 59% by volume of the formulation

24 and comprises:

25 about 15 wt% aromatic solvent:

1 about 63 wt% of the blend of alcohols, the blend of alcohols being
2 about 5 % to about 15 % long chain alcohols and about 40 % to
3 about 60 % short chain alcohols; and
4 about 19 wt% to about 24 wt% of the surfactant,
5 the at least a corrosion inhibitor is about 1.5 wt% of the formulation;
6 the formulation further comprising:
7 a demulsifier being about 0.04 wt% of the formulation
8 an anti-sludge additive being about 0.4 wt% of the formulation;
9 an iron control additive being about 1.5 wt% of the formulation; and
10 the balance being water.

11

12 24. The acidizing formulation of claim 23 wherein the corrosion
13 inhibitor comprises:

14 35 wt% isopropyl alcohol;
15 5 wt% water;
16 20 wt% C₁₂-alkyl pyridine;
17 20 wt% oxyalkylated resin amines; and
18 20 wt% propargyl alcohol.

19

20 25. The acidizing formulation of claim 23 or 24 wherein the anti-
21 sludge additive is dodecyl benzene sulphonic acid.

22

1 26. The acidizing formulation of claim 23, 24 or 25 wherein the
2 demulsifier comprises:

3 70 wt% methanol;

4 20 wt% polymerized polyol having a relative solubility number of
5 about 7.0; and

6 5 wt% nonyl phenol resin adducts having a relative solubility
7 number of about 17.

8

9 27. The acidizing formulation of any one of claims 23 - 26 claim
10 23 wherein the iron control additive is stannous chloride.

11

12 28. The acidizing formulation of claim 22 wherein:

13 the 28% hydrochloric acid is about 24.5% by weight of the
14 formulation,

15 the miscibility solvent is about 63.2% by volume of the formulation
16 and comprises:

17 about 15 wt% aromatic solvent:

18 about 63 wt% of the blend of alcohols, the blend of alcohols being
19 about 5 % to about 15 % long chain alcohols and about 40 % to
20 about 60 % short chain alcohols; and

21 about 19 wt% to about 24 wt% surfactant

22 the at least a corrosion inhibitor is about 1.1 wt% of the formulation;

23 the formulation further comprising:

24 a demulsifier being about 0.03 wt% of the formulation

25 an anti-sludge additive being about 0.4 wt% of the formulation;

1 an iron control additive being about 1.3 wt% of the formulation; and
2 the balance being water.

3

4 29. The acidizing formulation of claim 28 wherein the corrosion
5 inhibitor comprises:

6 35 wt% isopropyl alcohol;

7 5 wt% water;

8 20 wt% C₁₂-alkyl pyridine;

9 20 wt% oxyalkylated resin amines; and

10 20 wt% propargyl alcohol.

11

12 30. The acidizing formulation of claim 28 or 29 wherein the anti-
13 sludge additive is dodecyl benzene sulphonic acid.

14

15 31. The acidizing formulation of claim 28, 29 or 30 wherein the
16 demulsifier comprises:

17 70 wt% methanol;

18 20 wt% polymerized polyol having a relative solubility number of
19 about 7.0; and

20 5 wt% nonyl phenol resin adducts having a relative solubility
21 number of about 17.

22

23 32. The acidizing formulation of any one of claims 28 – 31
24 wherein the iron control additive is stannous chloride.