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(54) **ACIDIZING STIMULATION METHOD
USING VISCOELASTIC GELLING AGENT**

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(57) **ABSTRACT**

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Related U.S. Application Data

(60) Provisional application No. 60/530,577, filed on Dec. 18, 2003.

A method of acidizing a subterranean formation involves the use of a composition containing a solution of a viscoelastic amidoamine oxide surfactant and an HF-containing acidizing solution. The composition typically contains from about 0.1 to about 8 weight percent of surfactant solution and from about 92 to about 99.9 weight percent of HF-containing acidizing solution. The composition is pumped into the subterranean formation. As the acid reacts, the composition viscosifies and becomes a self-diverting agent created in-situ. When the acid is further spent, the fluid viscosity declines eventually returning to a low viscosity state, allowing for easy cleanup. The process allows for selective acidizing of less permeable zones of the formation and more uniform stimulation of the hydrocarbon bearing formulation.

ACIDIZING STIMULATION METHOD USING VISCOELASTIC GELLING AGENT

[0001] This application claims the benefit of U.S. patent application Ser. No. 60/530,577 filed on Dec. 18, 2003.

FIELD OF THE INVENTION

[0002] The present invention relates generally to the field of stimulating sandstone formations of oil and gas wells by use of an acidizing solution containing hydrofluoric acid and a viscoelastic gelling agent.

BACKGROUND OF THE INVENTION

[0003] Subterranean sandstone or siliceous formations in oil and gas wells have been treated in the past with acid treatments to increase their permeability, thus enhancing the flow of hydrocarbons to the wellbore, thereby increasing or improving production from the formation. As used herein the term "siliceous" refers to the characteristic of having silica and/or silicate. Most sandstone formations are composed of over 50-70% sand quartz particles, i.e. silica (SiO_2) bonded together by various amounts of cementing material including carbonate (calcite or CaCO_3) and silicates.

[0004] Acidizing can cause the dissolution of existing formation material or the removal and/or bypass of blockage, often referred to as "damage to the well" which can be caused by natural or man-made conditions. Further acidizing (or acid stimulation) opens up the channels around the wellbore, thereby improving the flow rate. Early attempts at acidizing formations focused on the injection of a simple acidic solution into a wellhead. Such attempts proved to be inefficient as the fluid would often react or spend too quickly; and therefore be incapable of penetrating deep into the formation, thereby limiting effectiveness to very near-wellbore applications. Also, many subterranean formations contain sections with varying permeability. When acid is injected into a formation, it typically acidizes the section of the formation with the highest permeability and which has the highest degree of water saturation.

[0005] By far the most common method of treating sandstone formations involves introducing corrosive, very low pH acids into the wellbore and allowing the acid to react with the surrounding formation. Such acids are often referred to as "mud acids" and are characterized by a pH of less than zero. Mixtures of hydrofluoric acid and hydrochloric acid are the generally preferred mud acids because of the reactivity of HF acid with silica and silicates. Precipitation of various aluminum and silicon complexes occur as a result of the reaction of the acid with the siliceous minerals. The precipitation products plug pore spaces and reduce the porosity and permeability of the formation, thus impairing flow potential. Because clays are normally a part of the cementitious material that holds the sand grains of sandstone formations together, the dissolution of clay also weakens and de-consolidates the sandstone matrix in the vicinity of the wellbore, thus causing damage to the formation. The damaging effects due to both the de-consolidation of the matrix and the precipitation of complexes which clog the pore spaces of the formation can eliminate or even revert the stimulation effect of the acid treatment. Means of reducing the reaction rate of HF within the area surrounding the wellbore consist of the slow hydrolysis of ammonium bifluoride to convert it to HF, either at the surface or within the

well. While such methods allow the acid to penetrate slightly further into the formation, they do not eliminate precipitates from forming and clogging the matrix.

[0006] Recently, acidizing systems have been developed that employ organic acids, in place of all, or part, of the hydrochloric or hydrofluoric acid. U.S. Pat. No. 5,529,125 which is incorporated by reference, discloses a method of treating siliceous or sandstone formations using a treatment solution containing, in addition to hydrofluoric acid, a phosphonate compound. Such compositions reduce the amount of precipitates produced and inhibit or retard the reactivity of the hydrofluoric acid with the clay or silicate elements of the formation.

[0007] Further, U.S. Pat. No. 6,443,230 discloses use of a treatment solution containing citric acid, a phosphonate and hydrofluoric acid to enhance the productivity of hydrocarbons from such siliceous formations. The pH of such acid mixtures is generally much higher than conventional mud acids, being generally in the range of pH 3.2 to about 4.8, yet these systems have the same dissolving capability with respect to siliceous minerals as mud acids. This elevated pH has obvious advantages in terms of corrosion and general reactivity, allowing deeper matrix penetration of live acid and reduced requirements for corrosion inhibitors. Other advantages of these higher pH formulations include reduced risk to surface equipment including pipelines, reduced risk to the environment and personnel, reduced chemical requirement for neutralization, reduced risk of creating sludges and emulsions and reduced risk of upset to process facilities.

[0008] Often, however, such materials have difficulty in controlling the flow of the acidizing fluid. For instance, in some applications, it has been noted that a control mechanism for diverting or forcing the acid from a higher permeability and/or water saturated sections of the formation to the lower permeability or oil bearing sections is lacking.

[0009] A need exists therefore for an acidizing system which improves the penetration of acid and is capable of being delayed to allow maximum penetration and further exhibits a viscosity to adequately divert incoming fluids. The system should further be stable at high temperature while the acid is being spent.

SUMMARY OF THE INVENTION

[0010] The present invention involves the use of a composition comprising a solution of an amidoamine oxide viscoelastic surfactant and an HF-containing acidizing solution. The viscoelastic surfactant serves as a gelling agent and does not react quickly with the formation. As a result, the system of the invention is capable of being spread deeper into the formation than the systems of the prior art.

[0011] Typically, introduction of the composition of the invention into the formation is preceded by a preflush and, optionally followed by an overflush; the preflush and overflush generally consisting of hydrochloric acid and/or ammonium chloride. Other flush systems known in the art, such as acetic or formic acid solutions, may also be used. Other suitable preflushes, such as those disclosed in U.S. Pat. No. 6,443,230, herein incorporated by reference, contain citric acid and a phosphonate compound. One reason for pumping these flushes is to dissolve carbonate minerals within a certain distance of the wellbore, prior to injecting

the composition of the invention, thereby minimizing the risk of damage that could be caused by precipitating insoluble calcium fluoride. Another reason is to maintain low pH conditions to remove protective films that can form on some formation minerals or to reduce iron hydroxide precipitation.

[0012] Use of the composition of the invention improves penetration of acid into the wellbore. Further, the composition of the invention further acts as a diverting fluid by selectively blocking certain pores temporarily and forcing the fluid into a different direction. For example, the composition of the invention is capable of selectively blocking higher permeability zones and streaks, thereby forcing the acid fluid into the lower permeability sections.

[0013] The fluid system of the invention is further void of polymers, thereby reducing any potential damage the fluid may do to the formation. For instance, the composition of the invention minimizes rock disaggregation at the interface of the acid and rock.

[0014] The gelling process of the amidoamine oxide gelling agent occurs in-situ and does not depend on the introduction of chemical triggers.

[0015] In one embodiment of the invention, the composition is used in the acidizing of hydrocarbon-bearing formations, wherein the composition serves as an in-situ generated self-diverting fluid. This process is accomplished by first creating a fluid composition which exhibits low viscosity at room temperature. This composition is created by mixing a solution of an amidoamine oxide gelling agent with a HF-containing acidizing solution. The fluid is then pumped into the formation and allowed to gel in the formation, thereby generating a diverting fluid.

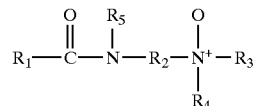
[0016] In another embodiment, the composition of the invention is pumped into a high permeability zone of the formation and generates in situ a gel as it reacts, which then diverts additional fluid as it enters the formation.

[0017] Another embodiment of the present invention relates to selectively acidizing the lower permeable zones of a subterranean formation having a plurality of zones with varying permeabilities communicating with a well. First, a composition containing (i.) HF-containing acidizing solution and (ii.) a solution of amidoamine oxide gelling agent is introduced into the well. Next, a self-diverting fluid is generated in-situ. The gelled self-diverting acid fluid diverts a portion of the acid from the more permeable zones of the formation to the less permeable zones.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The composition of the invention contains (i.) a HF-containing acidizing solution and (ii.) a solution of an amidoamine oxide gelling agent. In a preferred embodiment, the amidoamine oxide gelling agent solution is a glycol solution. Typically, the amount of HF-containing acidizing solution in the composition is between from about 92 to about 99.9 weight percent, preferably from about 94 to about 99.75 weight percent.

[0019] In a preferred mode, the amidoamine oxide is of the structural formula:



[0020] wherein R_1 is a saturated or unsaturated, straight or branched chain aliphatic group of from about 7 to about 30 carbon atoms, preferably from about 14 to about 21 carbon atoms. More preferably, R_1 is a fatty aliphatic derived from natural fats or oils having an iodine value of from about 1 to about 140, preferably from about 30 to about 90, and more preferably from 40 to about 70. R_1 may be restricted to a single chain length or may be of mixed chain length such as those groups derived from natural fats and oils or petroleum stocks. Preferred are tallow alkyl, hardened tallow alkyl, rapeseed alkyl, hardened rapeseed alkyl, tall oil alkyl, hardened tall oil alkyl, coco alkyl, oleyl, or soya alkyl. R_2 is a straight chain or branched, substituted or unsubstituted divalent alkylene group of from 2 to about 6 carbon atoms, preferably, of 2 to 4 carbon atoms and more preferably of 3 carbon atoms. R_3 and R_4 are the same or different and are independently selected from alkyl or hydroxyalkyl groups of from 1 to about 4 carbon atoms and are preferably hydroxyethyl or methyl. Alternatively, R_3 and R_4 in the amido amine oxide of formula I, together with the nitrogen atom to which these groups are bonded, form a heterocyclic ring of up to 6 members. Finally, R_5 is hydrogen or a C_1 - C_4 alkyl or hydroxyalkyl group.

[0021] Such amidoamine oxides are disclosed in U.S. patent application 2002/0147114 A1, herein incorporated by reference, and include that sold under the trade name Aromox APA-T ("APA-T") by Akzo-Nobel. The concentration of the gelling agent in the amidoamine oxide gelling agent solution is typically between from about 1 to about 70, preferably between from about 40 to about 65, most preferably about 50, percent by weight. The amount of gelling agent solution in the composition of the invention is typically between from about 0.1 to 8, preferably from about 0.25 to about 6, weight percent and is dependent on the unstimulated permeability of the rock, the rock mineralogy and the formation temperature.

[0022] Other examples of amidoamine oxides for use in the invention include but are not limited to those selected from the group consisting of tallow amidoalkylamine oxide, hardened tallow amidoalkylamine oxide, rapeseed amidoalkylamine oxide, hardened rapeseed amidoalkylamine oxide, tall oil amidoalkylamine oxide, hardened tall oil amidoalkylamine oxide, coco amidoalkylamine oxide, stearyl amidoalkylamine oxide, oleyl amidoalkylamine oxide, soya amidoalkylamine oxide, and mixtures thereof. Preferred specific examples of the amidoamine oxides of the present invention include but are not limited by the following: tallow amidopropyl dimethylamine oxide, hydrogenated tallow amidopropyl dimethylamine oxide, soya amidopropyl dimethylamine oxide, oleyl amidopropyl dimethylamine oxide, erucyl amidopropyl dimethylamine oxide, rapeseed amidopropyl dimethylamine oxide, hydrogenated rapeseed amidopropyl dimethylamine oxide, tall oil amidopropyl dimethylamine oxide, hydrogenated tall oil

amidopropyl dimethylamine oxide, C₁₄-C₂₂ saturated or unsaturated fatty acid amidopropyl dimethylamine oxides, and mixtures thereof.

[0023] The amine oxide gelling agent composition can be prepared by reacting a tertiary amine, for example, a tertiary amidoamine, with a concentrated hydrogen peroxide in a solvent. The preferred solvent is a miscible glycol. The amount of glycol to be added is determined by the concentration of the amine oxide solution to be prepared.

[0024] The glycols employed are high flash point solvents that solubilize the tertiary amine, amine oxide and water from the hydrogen peroxide reagent. If water is used as the solvent, the result is a gel/paste with a maximum amine oxide concentration of 20-30%. The use of glycols in accordance with the present invention allows for the preparation of concentrated amine oxide viscoelastic compositions having a superior thickening ability.

[0025] In the alternative, the amine oxide gelling agent composition can be prepared by reacting a tertiary amine with a concentrated hydrogen peroxide in an alcohol solvent such as isopropanol but, since alcohol solvents such as isopropanol may have a deleterious effect on the performance of the gelling agent, it is preferred that the alcohol be removed from the final product and replaced with a glycol solvent.

[0026] Although any glycol solvent can be employed in accordance with the present invention, the most preferred glycols include but are not limited to ethylene glycol, butylene glycol, diethylene glycol, polypropylene glycol, polyethylene glycol, glycerin, propylene glycol, tetramethylene glycol, tetramethylethylene glycol, trimethylene glycol, and the like. Propylene glycols (e.g., 1,2 propanediol) are the most preferred glycols.

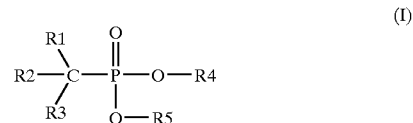
[0027] In a preferred mode, the amidoamine oxide gelling agent solution contains between from about 40 to about 65 weight percent amidoamine oxide, from about 25 to about 40 weight percent propylene glycol and from about 5 to about 10 weight percent water. The amine oxide gelling agent can also be provided in dry product form.

[0028] It is also important to minimize the amount of free fatty acid formed since free fatty acid may be harmful to the performance of the gelling agents. More specifically, the gelling agents useful in the invention give greater viscosity to an aqueous solution if the amine oxide has less than 5% free fatty acid, preferably less than 3% free fatty acid, and most preferably, less than 1% free fatty acid. In order to achieve these low levels of free fatty acid, it is important to utilize an oxidation catalyst in the aforementioned process for preparing the gelling agents of the present invention. Preferred oxidation catalysts include, but are not limited to dissolved carbon dioxide, a carbonate salt, a bicarbonate salt and the like. Catalyst systems such as this are described in U.S. Pat. No. 4,960,934 which is incorporated herein by reference.

[0029] The amount of HF in the acidizing solution is generally between from about 0.25 to about 6.0 weight percent. (HF acid is by definition, a weak acid, being only partially dissociated in water, pKa=3.19.) In a preferred mode, the acidizing solution further contains an organic acid. Sandstone acidizing solutions containing organic acids often produce a delayed reaction on clay minerals, signifi-

cantly slowing the HF acid reaction rate. Suitable as the sandstone acidizing solution are those acid systems known in the art for dissolving the silicate and clay formations of the sandstone to increase its permeability.

[0030] Especially preferred are those acidizing solutions described in U.S. Pat. No. 5,529,125, herein incorporated by reference. Such acidizing solutions contain phosphonate acids and salts as well as esters thereof. Such systems may contain phosphonate materials of the formula:



[0031] wherein R1, R2 and R3 may be hydrogen, alkyl, aryl, phosphonates, phosphates, acyl amine, hydroxyl and carboxyl groups and R4 and R5 may consist of hydrogen, sodium, potassium, ammonium or an organic radical. The concentration of the phosphonate acid in the acidizing solution is generally between from about 0.25 to about 6.0, preferably about 3, percent by volume of the total solution without regard to the HF acid concentration.

[0032] Examples of these materials include aminotri (methylene phosphonic acid) and its pentasodium salt, 1-hydroxyethylidene-1,1-diphosphonic acid and its tetrasodium salt, hexamethylenediaminetetra (methylene phosphonic acid) and its hexapotassium salt, and diethylenetriaminepenta (methylene phosphonic acid) and its hexasodium salt. Among the commercial phosphonate materials, preferred are amino phosphonic acids, such as 1-hydroxyethylidene-1,1-diphosphonic acid, otherwise known as "HV acid," available in 60% strength as "DEQUEST 2010" from Monsanto Co.

[0033] Such phosphonate materials are used in conjunction with hydrofluoric acid or hydrochloric acid or such conventional acid systems as hydrochloric/hydrofluoric acid systems and organic/hydrofluoric acid systems which include formic/hydrofluoric acid mixtures. Commercially available acid systems which are particularly preferred are fluoroboric acid solutions, hydrochloric acid and hexafluorophosphoric acid mixtures, such as "RMS ACID," commercially available from BJ Services Company. Further preferred are hydrofluoric acid systems consisting of hydrochloric acid and hydrofluoric acid, and including those using ammonium bifluoride as the source of hydrofluoric acid and an aluminum salt as a retarder.

[0034] The acidizing solution for use in the invention may further include an organic acid, such as citric acid, acetic acid, or formic acid as well as those set forth in U.S. Pat. No. 6,443,230, herein incorporated by reference.

[0035] A particularly preferred sandstone acidizing solution for use in the invention is a retarded acid system (RAS) as described in U.S. Pat. No. 5,529,125.

[0036] The composition for use in the invention may further contain additional additives that may affect the gelling process. These additives include corrosion inhibitors and intensifiers. The purpose of these additives is to reduce the corrosive effects that the acids may have on the well

tubulars. Although the introduction of corrosion inhibitors has shown to reduce the maximum attainable viscosity of the system, the inhibitors should not have an effect on the system in terms of its gelling and its behavior as a diverting agent.

[0037] Corrosion inhibitors can include alkali metal nitrites, nitrates, phosphates, silicates and benzoates. Representative suitable organic inhibitors include hydrocarbyl amine and hydroxy-substituted hydrocarbyl amine neutralized acid compound, such as neutralized phosphates and hydrocarbyl phosphate esters, neutralized fatty acids (e.g., those having 8 to about 22 carbon atoms), neutralized carboxylic acids (e.g., 4-(t-butyl)-benzoic acid and formic acid), neutralized naphthenic acids and neutralized hydrocarbyl sulfonates. Mixed salt esters of alkylated succinimides are also useful. Corrosion inhibitors can also include the alkanolamines such as ethanolamine, diethanolamine, triethanolamine and the corresponding propanolamines as well as morpholine, ethylenediamine, N,N-diethylethanolamine, alpha- and gamma-picoline, piperazine and isopropylaminoethanol.

[0038] The compositions of the invention are particularly useful as self-diverting acid fluids. The composition is initially thin when pumped into the formation. As the acid enters the formation, the viscosity increases. The composition primarily enters the high permeability zone. As such, the composition of the invention functions as an in-situ generated self-diverting acid evidenced by the diversion from high to low permeability zones of the formation in light of the change in viscosity during the course of the treatment. Sandstones which cannot be fracture stimulated may be treated in accordance with the invention. In light of such diversion, larger sections of the formation may be acidized effectively. Hydrocarbon contacting the fluid during flow-back, or complete spending of the acid, will break the gel.

[0039] The initial viscosity of the composition for use in the invention is below about 100 cP; the preferred viscosity is typically below 90 cP at a shear rate of 17 sec^{-1} . This means that when the composition is pumped into the formation, there is a reduction in effort associated with the operation. In contrast, many diverting agents are highly viscous in their initial state. While this may work well within the formation, it makes it difficult to pump the fluid initially, particularly in lower permeability regions of the formation.

[0040] Once in the formation, the low viscosity fluid gels resulting in an increase in viscosity. No additional products or chemical triggers are required to be pumped into the formation. This simplifies the treatment and eliminates the need for other products that could possibly damage the formation.

[0041] Another advantage of the method of the invention is that the gelling of the low viscosity fluid in the hydrocarbon formation is based on the single reaction of the acid with the surroundings. It is therefore much easier to control the system. It is also much easier to predict when diversion occurs from pressure changes observed at the surface.

[0042] In addition to the in situ diverting process, the composition of the invention has suitable acid strength and can be gelled on mixing and pumped as a traditional viscous diverting stage.

[0043] The following examples will illustrate the practice of the present invention in its preferred embodiments. Other

embodiments within the scope of the claims herein will be apparent to one skilled in the art from consideration of the specification and practice of the invention as disclosed herein. It is intended that the specification, together with the examples, be considered exemplary only, with the scope and spirit of the invention being indicated by the claims which follow.

[0044] The following abbreviations are used in the examples that follow:

[0045] APA-T refers to Aromox® APA-T, a gelling agent composed of tallow amidopropyldimethylamine oxide in glycol, available from Akzo Nobel Surface Chemistry LLC, Chicago, Ill., the preparation of which is taught in U.S. patent application Publication U.S. 2002/0147114 A1, herein incorporated by reference. The APA-T is believed to contain about 50 weight percent amidopropyldimethylamine oxide, about 40 weight percent glycol and about 10 weight percent water.

[0046] RAS is a retarded acid system as described in U.S. Pat. No. 5,529,125.

[0047] CI-27 refers to an organic corrosion inhibitor, a product of BJ Services Company. It provides effective protection of tubulars and downhole equipment in bottom-hole temperatures up to about 250° F.

[0048] NE-118 refers to a nonionic surfactant, a product of BJ Services Company.

[0049] Mud Acid refers to blend of HCl/HF acid, as noted.

[0050] Ferrotrol-300L refers to an iron control additive, a product of BJ Services Company.

[0051] Example Nos. 1-5. Diversion systems were tested on feldspathic quartz arenite having minor carbonate and between from 2 to 8 percent by weight of clay minerals. The diversion systems tested were RAS and "mud acid." Acid strengths or concentrations are presented as percent acid by weight. The weight percent of APA-T in each sample was varied.

[0052] Each of the tests was run several times. The data reported in Table I is the average of the several tests. Each solution was tested in a plug seated in a rubber sleeve. The apparatus was gradually heated to a formation temperature of approximately 210° F. Uniform radial and axial stress of approximately 1500 psi was applied to prevent leakage of the treatment fluid around the core plug. The flow through the core plug was from formation to wellbore and humidified nitrogen gas was employed until steady state (little or no change in permeability with increasing time) was obtained.

[0053] Into each core plug, the following was injected:

[0054] a. 3 pore volumes of preflush ammonium chloride, 2 weight percent;

[0055] b. 5 pore volumes of solution containing HCl (15 weight percent) and corrosion inhibitor, NE-118, and Ferrotrol-300L;

[0056] c. 10 pore volumes of the HF Acid Treatment, APA-T, corrosion inhibitor, NE-118 and Ferrotrol-300L;

[0057] d. 5 pore volumes of solution containing HCl (15 weight percent) and corrosion inhibitor, NE-118, and Ferrotrol-300L; and

[0058] e. 3 pore volumes of preflush ammonium chloride, 2 weight percent.

[0059] Excess water was then removed from the core by flowing humidified nitrogen gas until mobile water was no longer observed. The flow was then reestablished in the formation to wellbore direction to steady state with humidified nitrogen gas. Gas permeability was then determined and the results recorded in Table I below.

TABLE I

Ex. No.	HF Acid Treatment	Wt. % APA-T	Initial Gas Permeability (md)	Gas Permeability (md)
1	4.5% HF RAS	2	5	109
2	6% HF RAS	1	26	3010
3	9% HCl/1% HF	0.75	25	333
4	12% HCl/3% HF	0.50	8	158
5	4.5% HF RAS	0.25	1	151

[0060] The increase in permeability in the core of each of the Examples shows significant stimulation in the lower permeability formation. The use of the viscoelastic gelling agent renders acid formulations that exhibit improved penetration of live acid while minimizing rock disaggregation at the core face.

[0061] From the foregoing, it will be observed that numerous variations and modifications may be effected without departing from the true spirit and scope of the novel concepts of the invention.

What is claimed is:

1. A process for enhancing the productivity of a hydrocarbon well which comprises introducing into the well a composition comprising:

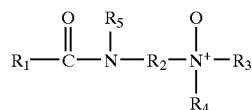
(a) an HF-containing acidizing solution; and

(b) a solution of an amidoamine oxide gelling agent.

2. The process of claim 1, wherein the solution of amidoamine oxide gelling agent further comprises at least one glycol.

3. The process of claim 2, wherein the weight percent of the glycol solution in the composition is between from about 0.1 to about 8 weight percent.

4. The process of claim 1, wherein the gelling agent comprises at least one amidoamine oxide of the formula:

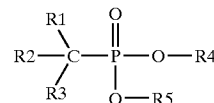


wherein R₁ is a saturated or unsaturated, straight or branched chain aliphatic group of from about 7 to about 30 carbon atoms, R₂ is a straight chain or branched, substituted or unsubstituted divalent alkylene group of from 2 to about 6 carbon atoms, R₃ and R₄ are independently selected from alkyl or hydroxyalkyl groups of from 1 to about 4 carbon atoms or R₃ and R₄ together with the nitrogen atom to which these groups are bonded form a heterocyclic ring of up to 6 members; and R₅ is hydrogen or a C₁-C₄ alkyl or hydroxyalkyl group.

5. The process of claim 2, wherein the amount of amidoamine oxide gelling agent in the glycol solution is between from about 40 to about 65 weight percent.

6. The process of claim 5, wherein the preferred amount of amidoamine oxide gelling agent in the glycol solution is about 50 weight percent.

7. The process of claim 1, wherein the acidizing solution further comprises a phosphonate of the formula:



wherein R₁, R₂ and R₃ are independently selected from hydrogen, alkyl, aryl, phosphonates, phosphates, acyl, amine, hydroxyl and carboxyl groups and R₄ and R₅ are independently selected from hydrogen, sodium, potassium, ammonium or an organic radical.

8. The process of claim 7, wherein the acidizing solution further comprises citric acid, formic acid or acetic acid.

9. The process of claim 8, wherein the acidizing solution comprises about 1 to about 50 weight percent citric acid, up to about 20 weight percent HF and from about 0.5 to about 50 weight percent phosphonate compound.

10. The process of claim 1, wherein the amidoamine oxide gelling agent is selected from the group consisting of tallow amidoalkylamine oxide, hydrogenated tallow amidoalkyl dialkylamine oxide, rapeseed amidoalkylamine oxide, hydrogenated rapeseed amidoalkylamine oxide, tall oil amidoalkylamine oxide, hydrogenated tall oil amidoalkylamine oxide, coco amidoalkylamine oxide, stearyl amidoalkylamine oxide, oleyl amidoalkylamine oxide, soya amidoalkylamine oxide, erucyl amidoalkylamine oxide, C₁₄-C₂₂ saturated or unsaturated fatty acid amidoalkyl amine oxides, and mixtures thereof.

11. The process of claim 2, wherein the at least one glycol is selected from ethylene glycol, butylene glycol, diethylene glycol, polypropylene glycol, polyethylene glycol, glycerin, propylene glycol, tetramethylene glycol, tetramethylethylene glycol and trimethylene glycol.

12. A process for acidizing a formation penetrated by a well, comprising:

(a). forming a mixture of an HF-containing acidizing solution and a glycol solution of an amidoamine oxide gelling agent;

(b). pumping the mixture of step (a). into a portion of the formation.

13. The process of claim 12, wherein the amidoamine oxide gelling agent is tallow amidopropyldimethylamine oxide.

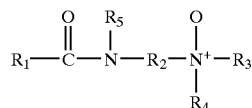
14. A method for selectively acidizing the less permeable zones of a subterranean formation penetrated by a well having a plurality of zones with varying permeabilities communicating with the well, which comprises:

(a). introducing into the formation a low viscosity fluid mixture of an HF-containing acidizing solution and a glycol solution of an amidoamine oxide gelling agent;

(b). generating in situ a self-diverting acid fluid by increasing the viscosity of the low viscosity fluid mixture; and

- (c). selectively reducing flow to the more permeable zones of the formation with the self-diverting acid fluid, thereby diverting additional fluid into less permeable zones of the formation.

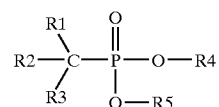
15. The method of claim 14, wherein the gelling agent comprises at least one amidoamine oxide of the formula:



wherein R_1 is a saturated or unsaturated, straight or branched chain aliphatic group of from about 7 to about 30 carbon atoms, R_2 is a straight chain or branched, substituted or unsubstituted divalent alkylene group of from 2 to about 6 carbon atoms, R_3 and R_4 are independently selected from alkyl or hydroxyalkyl groups of from 1 to about 4 carbon atoms or R_3 and R_4 together with the nitrogen atom to which these groups are bonded form a heterocyclic ring of up to 6 members; and R_5 is hydrogen or a C_1 - C_4 alkyl or hydroxyalkyl group.

16. The process of claim 14, wherein the amount of amidoamine oxide gelling agent in the glycol solution is between from about 40 to about 65 weight percent.

17. The process of claim 14, wherein the acidizing solution further comprises a phosphonate of the formula:



wherein R_1 , R_2 and R_3 are independently selected from hydrogen, alkyl, aryl, phosphonates, phosphates, acyl, amine, hydroxyl and carboxyl groups and R_4 and R_5 are independently selected from hydrogen, sodium, potassium, ammonium or an organic radical.

18. The process of claim 17, wherein the acidizing solution further comprises citric acid, formic acid or acetic acid.

19. The process of claim 14, wherein the amidoamine oxide gelling agent is selected from the group consisting of tallow amidoalkylamine oxide, hydrogenated tallow amidoalkyl dialkylamine oxide, rapeseed amidoalkylamine oxide, hydrogenated rapeseed amidoalkylamine oxide, tall oil amidoalkylamine oxide, hydrogenated tall oil amidoalkylamine oxide, coco amidoalkylamine oxide, stearyl amidoalkylamine oxide, oleyl amidoalkylamine oxide, soya amidoalkylamine oxide, erucyl amidoalkylamine oxide, C_{14} - C_{22} saturated or unsaturated fatty acid amidoalkyl amine oxides, and mixtures thereof.

20. The process of claim 14, wherein the at least one glycol is selected from ethylene glycol, butylene glycol, diethylene glycol, polypropylene glycol, polyethylene glycol, glycerin, propylene glycol, tetramethylene glycol, tetramethylethylene glycol and trimethylene glycol.

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