

[54] **ALUMINATE-THICKENED WELL
TREATING FLUID AND METHOD OF USE**

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Primary Examiner—Stephen J. Novosad

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175/65, 252/317

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[58] Field of Search **166/292, 308, 281, 283;**
252/315, 8.55 R, 8.5 B, 317; 175/65, 72, 64;
61/36

[56] **References Cited**

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[57]

ABSTRACT

A metal hydroxide-thickened well treating fluid comprises an aqueous liquid containing a water-soluble salt of an amphoteric metal and enough water-soluble base to form a viscosifying amount of a hydrated oxide of the metal.

12 Claims, 8 Drawing Figures

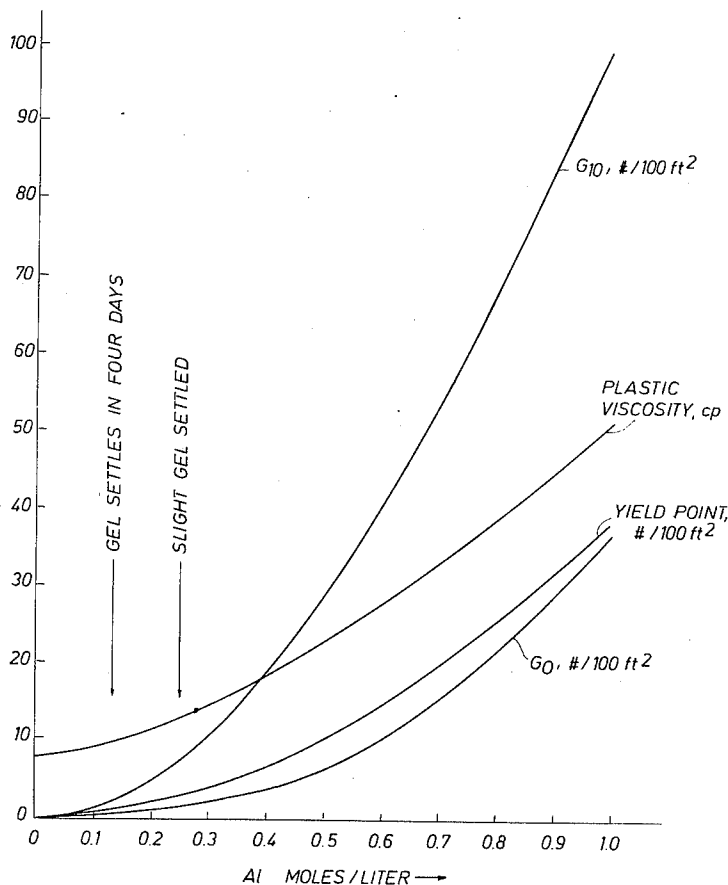


FIG. 1

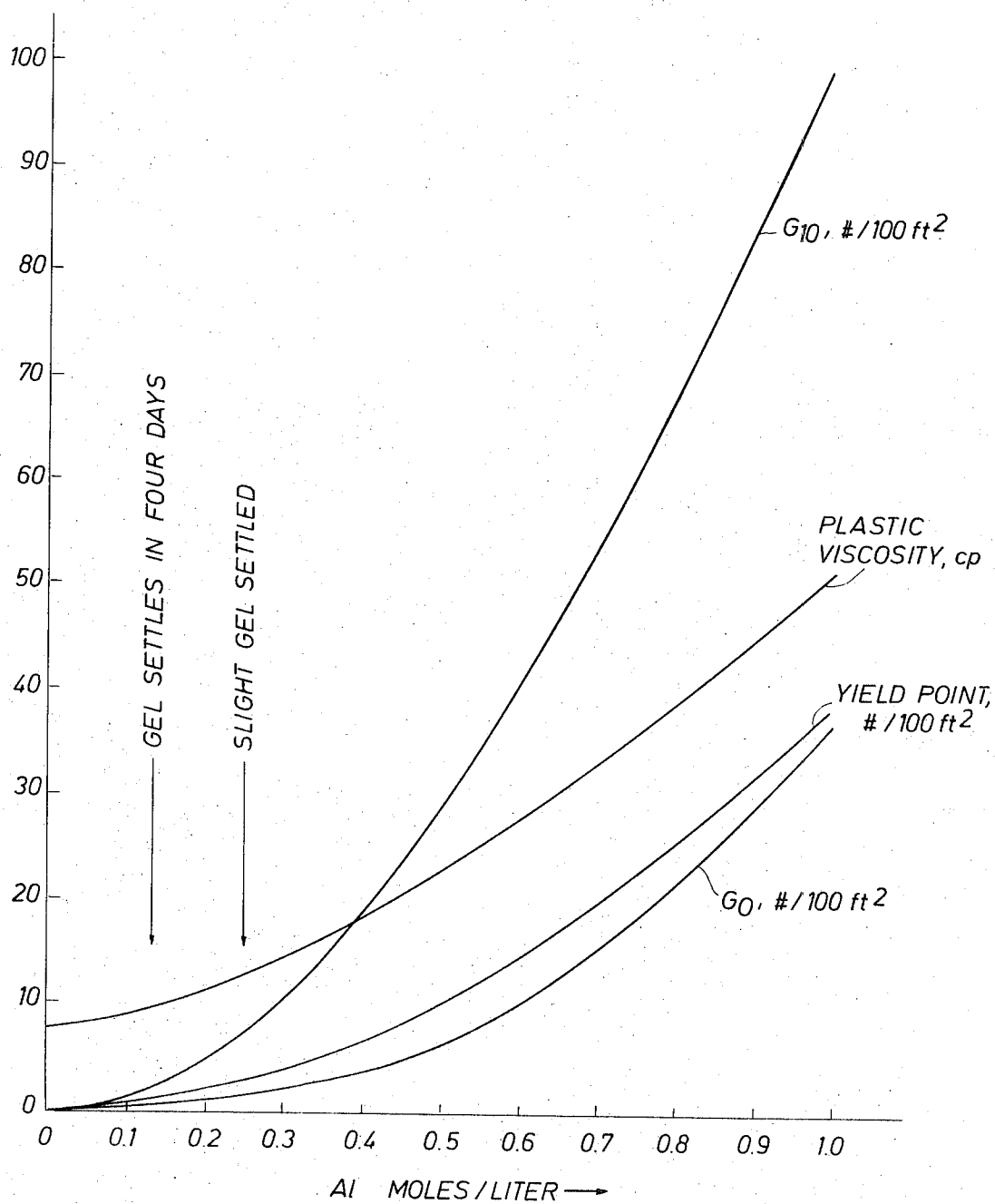
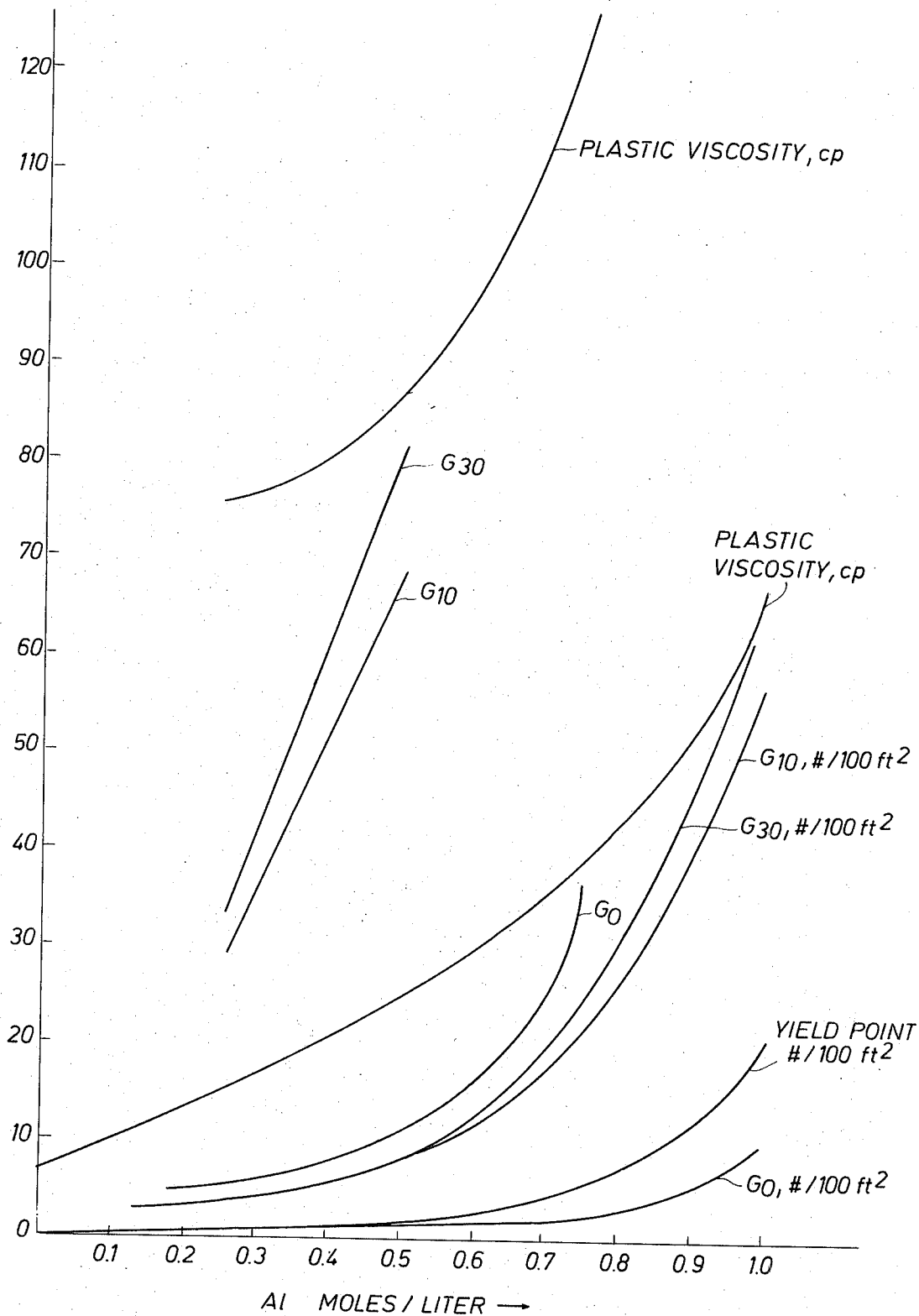


FIG. 2



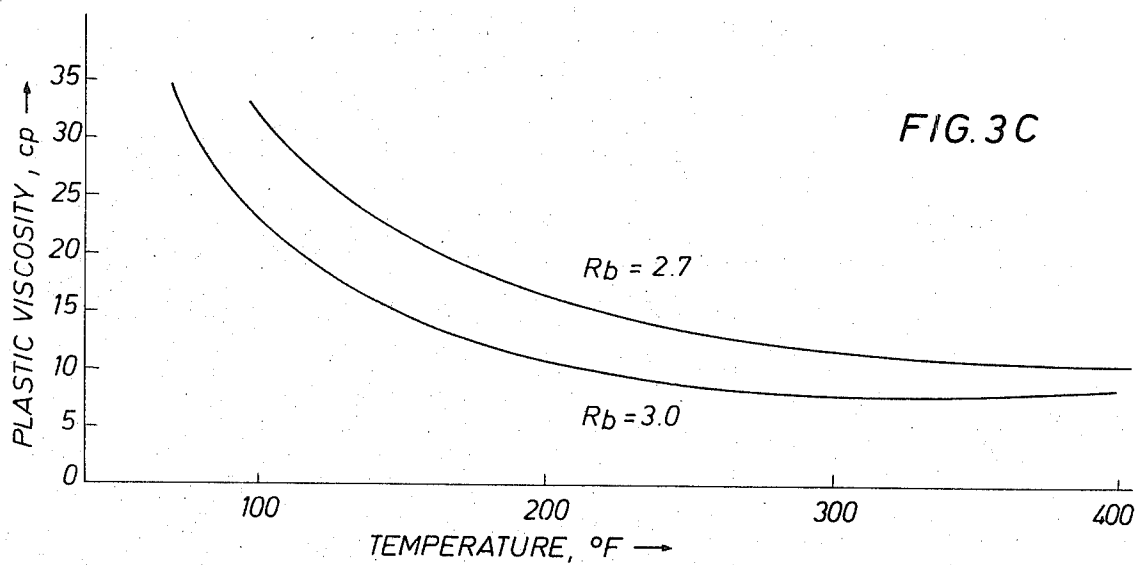
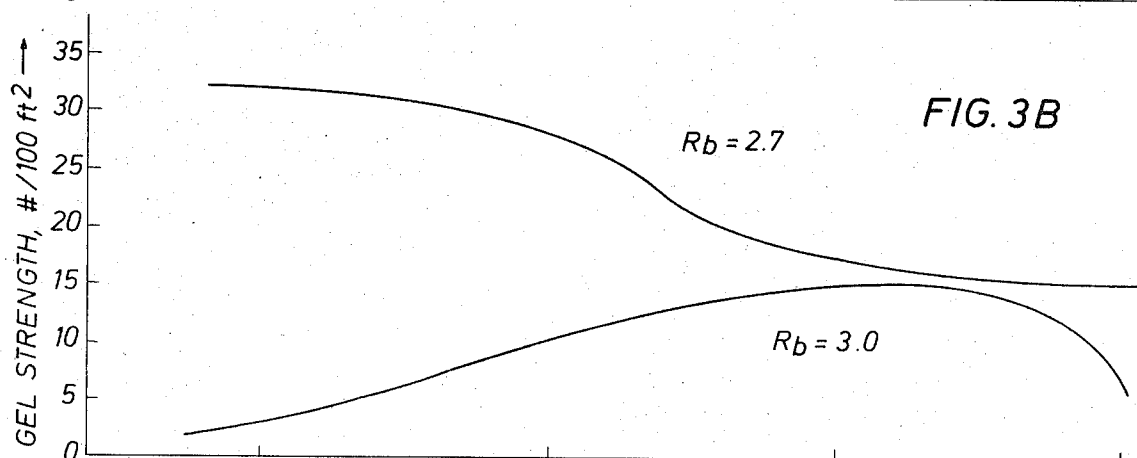
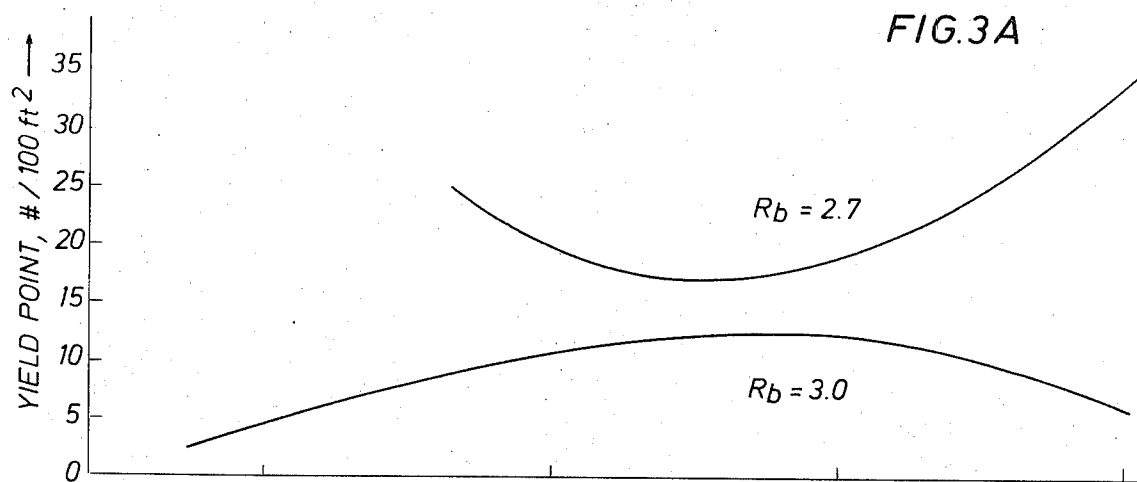


FIG. 4A

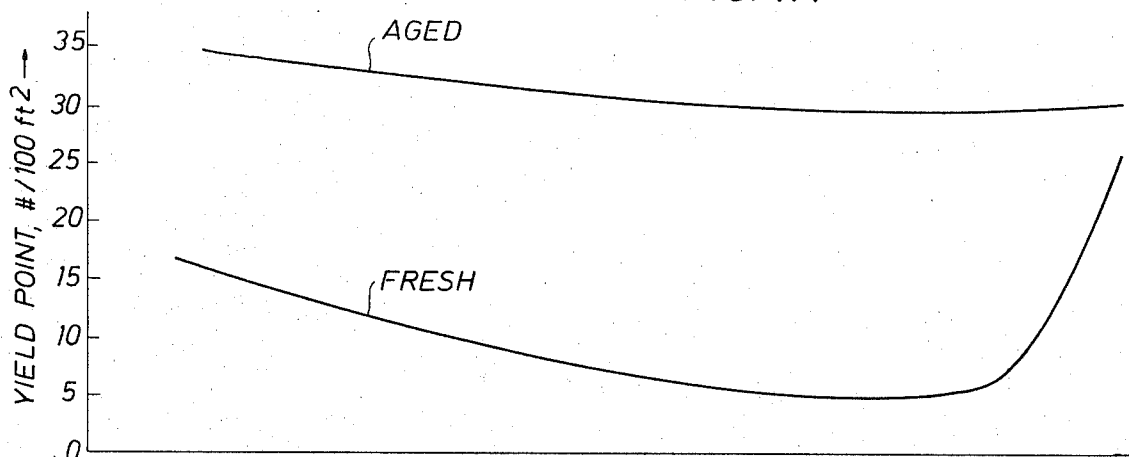


FIG. 4B

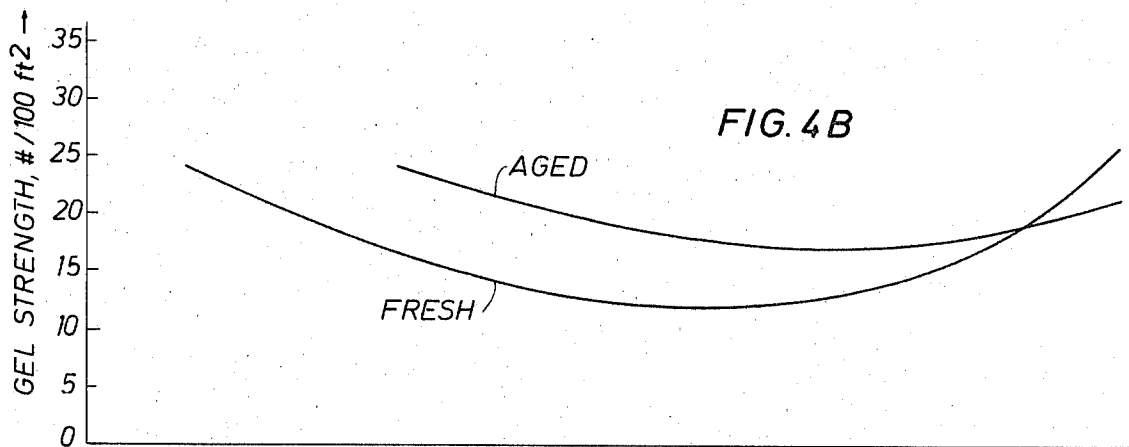
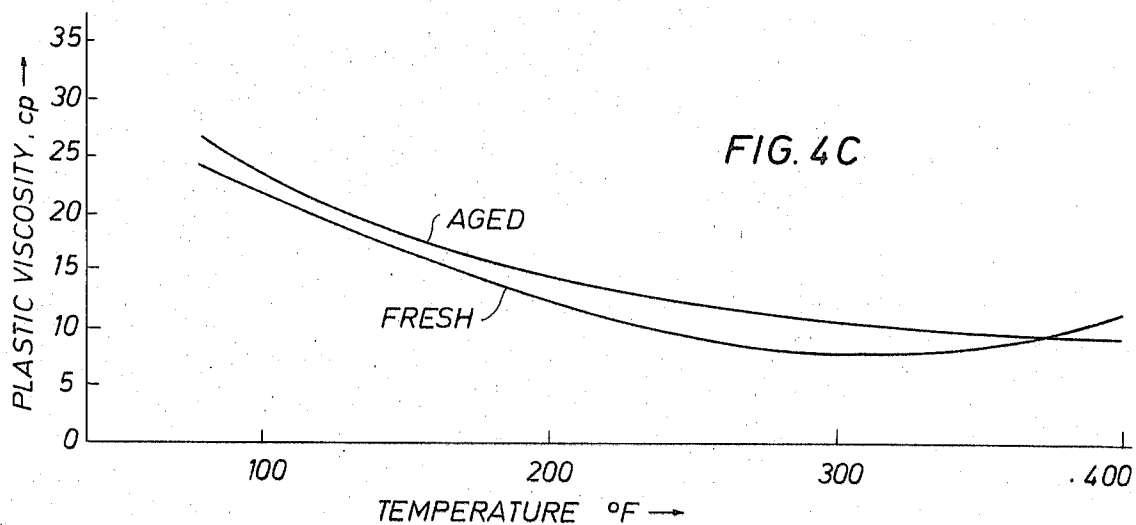


FIG. 4C



ALUMINATE-THICKENED WELL TREATING FLUID AND METHOD OF USE

BACKGROUND

This invention relates to well treatments for temporarily plugging and/or fracturing a portion of a subterranean reservoir. More particularly, it relates to a relatively viscous aqueous liquid (useful as well completion or fracturing fluid) that contains chemically removable viscosifying and/or fluid loss-preventing materials. In general, a fluid used for well completion or fracturing should provide (1) at least enough hydrostatic head to at least counterbalance the fluid pressure in the subterranean reservoir being treated, (2) liquid components that cause little or no damage to the reservoir, (3) an adequate prevention of fluid loss, (4) an adequate capability of transporting suspended solid materials, etc.

The conventional well-treating fluids that satisfy such requirements usually depend on organic materials. For example they contain natural or synthetic polymers (as viscosifiers and/or fluid-loss preventers) or comprise a relatively viscous hydrocarbon oil-base or oil-emulsion. Such organic components are undesirably susceptible to being entrained, or dissolved and stripped-out, or diluted, by gaseous hydrocarbons or light oil components of fluids apt to be encountered in oil reservoirs.

SUMMARY OF THE INVENTION

The invention relates to a metal hydroxide-thickened aqueous liquid containing a combination of enough water-soluble salt of amphoteric metal and enough water soluble base to form a viscosity-increasing proportion of gelatinous hydrated metal oxide and provide a pH that is relatively non-corrosive to ferrous metal.

The present invention also provides a well treating fluid that has a low fluid loss and contains substantially completely chemically removable viscosifying and fluid-loss-preventing components. This fluid comprises a metal hydroxide-thickened aqueous liquid suspension of particles of a solid material that is soluble in either a relatively strongly acidic or a basic aqueous liquid. Such a completion fluid preferably also contains enough of either, but not both, dissolved calcium bromide or calcium chloride to provide a fluid system having a selected specific gravity.

The present invention also provides a metal hydroxide-thickened fluid that contains relatively slow reacting pH-reducing reactant that subsequently yields at least enough acidic material to dissolve the thickening material. Such a reaction is advantageous in subsequently converting the thickened fluid (and any acid-soluble particles that are suspended in the fluid) to a liquid having a viscosity substantially as low as that of water.

The present invention also provides a metal hydroxide-thickened fluid that contains a relatively high proportion of suspended solid particles and is adapted to be used as a well drilling mud which can be converted (within the borehole) to a relatively competent cement-like solid mass by dissolving the thickening material and thus reducing the viscosity of the liquid phase so that the suspended particles are allowed to settle.

DESCRIPTION OF THE DRAWINGS

FIGS. 1, 2, 3A, 3B, 3C, 4A, 4B and 4C, each are plots of data obtained by tests of the present metal hydroxide-thickened fluids.

DESCRIPTION OF THE INVENTION

Prior utilizations of hydroxides or hydrated metal oxides of amphoteric metals in well treating fluids have involved properties distinctly different from the rheological properties needed for a well completing or fracturing fluid. For example, the E. A. Richardson U.S. Pat. 3,614,985 describes a process for plugging a subterranean reservoir by permeating its pores with a solution that contains an amphoteric metal salt and a pH-increasing reactant that subsequently causes a precipitation within the pores of the reservoir. U.S. Pat. No. 3,603,399 describes a process for treating a water-sensitive formation by permeating its pores with a "hydroxy-aluminum solution" that contains an aluminum salt and a base in proportions providing a clear and relatively non-viscous solution. And, the G. O. Suman, R. F. Scheuerman and E. A. Richardson U.S. Pat. No. 3,756,315 describes a process for plugging and/or consolidating a subterranean reservoir by permeating its pores with a strongly alkaline solution of an amphoteric metal oxide and a pH-decreasing reactant that subsequently causes a precipitation that increases the strength of and/or plugs the pores of the reservoir formation.

In each of such prior hydrated metal oxide-using processes it has been important that the solution of amphoteric metal salt have both a relatively low viscosity and a high filter loss, to ensure that the solution penetrates into the matrix (or pores) of the reservoir. In contrast, in a well completing fluid or fracturing fluid, it is important that the fluid have a viscosity and/or filter loss prevention sufficient to ensure that it does not penetrate into the matrix of the reservoir.

Applicants have discovered that, by using a combination of at least one water soluble amphoteric metal salt and base in the presently specified concentration and ratio, a substantially non-corrosive and appropriately thickened fluid can be prepared and utilized in a well completion procedure in which it is desirable to avoid the entry of fluid into the matrix of the reservoir. The composition of such a fluid can be adjusted so that the fluid (a) contains only materials which are substantially insoluble in normally gaseous or liquid hydrocarbons and/or H₂S or CO₂, etc., that are apt to be encountered in a petroleum reservoir, (b) is relatively heat-stable, e.g., can remain substantially unchanged after as much as 67 hours at 400°F., (c) is adapted to have a selected specific gravity that can range from about 8.5 to 18 ppg (pounds per gallon), (d) is adapted to provide little or no fluid loss into a reservoir of relatively high permeability although it contains only components that are substantially completely chemically removable by dissolving them in a strongly acidic or a basic aqueous liquid, and (e) is adapted to be a self-breaking viscous fluid which is adapted to revert to a thin fluid having a viscosity substantially as low as that of water.

Water-soluble salts of amphoteric metal suitable for use in the present invention comprise individual or mixed salts of substantially any amphoteric metal, such as aluminum, chromium, tin, zinc, arsenic, antimony or lead, etc., that are adapted to form an

aqueous-solution-viscosifying gelatinous hydrated metal oxide. The aluminum salts are particularly preferred.

Aqueous liquids suitable for use in the present metal hydroxide-thickened fluids include natural or treated waters and/or water solutions of substantially any salt that is relatively inert to or is compatible with the dissolving of enough amphoteric metal salt and the formation of enough gelatinous hydrated metal oxide to provide the desired viscosity. Suitable inert metal salts include the alkali metal salts of strong acids, e.g., sodium chloride, or the like; the water-soluble alkaline earth metal salts of strong acids, e.g., calcium chloride, calcium bromide, or the like; etc. However, it should be noted that although various mixtures of such salts are suitable, some such mixtures may not be suitable. For example, although an aqueous solution that is saturated with a mixture of calcium chloride and calcium bromide has an advantageously high density of 15.1 ppg, the solubility at room temperature of an aluminum chloride containing 6 molecules of water of hydration, is less than about 0.05 molar and may be too low to provide an adequate viscosity or gel strength.

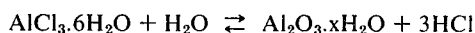
The concentrations of amphoteric metal salt and relative proportions of base that are suitable in the present metal hydroxide-thickened fluids may range from less than 0.1 to more than 1 molar (i.e., moles per liter of the amphoteric metal salt and/or the metal ion) with a ratio of moles of base to moles of amphoteric metal ion of at least about 2.8.

Where solids are suspended in the metal hydroxide-thickened fluids, the metal content of the final fluid (e.g. " f_s " or fraction by volume of solid in the suspension) will depend on the solids loading. In such situations the preferred value is determined experimentally. For example, in a moderately viscous 18 ppg (pounds per gallon) suspension having an f_s value of 0.3, an aluminum concentration of as low as 0.08 molar (in the liquid phase of that suspension) is suitable. Alternatively, in a similarly viscous solids free fluid, the aluminum concentration should be at least 1.0 molar.

The pH, viscosity, gel-strength, and the like, fluid properties, (or rheological properties) of the metal hydroxide-thickened fluids are strongly affected by such concentrations and relative proportions of the amphoteric metal salt and base. It appears that the gel structure of the gelatinous hydrated metal oxide is, to some extent, stabilized by incorporating protons within its structure. For example, with respect to such fluids in which the amphoteric metal is aluminum, tests have indicated that the magnitude of the rheological properties decrease with increasing ratios of base to amphoteric metal ion. But, for most well treating applications, molar ratios of at least about 2.8 are desirable in order to provide a thickened fluid that is relatively non-corrosive to ferrous metal.

For convenience of language, typical examples of particularly preferred concentrations and test results are described herein with reference to metal hydroxide-thickened fluids in which the amphoteric metal salt is aluminum chloride and the base is sodium hydroxide. Similar concentration ranges are applicable to such fluids containing substantially any salt of an amphoteric metal and such test results are generally representative with respect to fluids containing those salts.

In an aqueous solution, aluminum chloride hydrolyzes according to the following equation:



In such a solution the addition of a base, such as sodium hydroxide, can neutralize the hydrochloric acid, raise the pH of the solution, and precipitate enough of the hydrated aluminum oxide to form a gel structure that increases the viscosity of the solution. Further additions of such a base can re-dissolve the hydrated oxide, by forming a strongly alkaline solution of, for example, sodium aluminate. Alternatively, an addition of hydrochloric acid can dissolve the hydrated oxide by forming a relatively acidic solution of aluminum chloride. The relative proportion of base to metal ion has been defined (for the aluminum-containing systems) in terms of a R_b value in which:

$$R_b = \text{Moles of base/Moles of aluminum ion}$$

In the aluminum chloride/sodium hydroxide-containing system, a particularly suitable aluminum concentration is from about 0.4 to 0.6 molar. With such an aluminum concentration, an R_b of from about 2.5 to 2.7 has been found to provide a gel-thickened solution that has desirably high rheological properties. But such a solution has a pH of from about 2 to 3, which is potentially corrosive and thus is undesirable for uses such as those involving relatively long or high temperature contacts with metallic equipment. An R_b value of about 3 tends to provide moderate rheological properties (which can be increased by increasing the aluminum concentration) and a near-neutral pH (from 6-7) which exhibits little or no corrosivity.

Chemically removable solids for increasing the specific gravity and/or decreasing the fluid loss of metal hydroxide-thickened fluids, can comprise substantially any relatively water-insoluble carbonate salt of a metal that is adapted to form a water-soluble salt of a strong acid, or substantially any solid material (such as metallic aluminum or other metal) that is adapted to be dissolved by an aqueous base or an aqueous acid. Typical examples of preferred solids include alkaline earth metal carbonates, such as calcium or barium carbonate, ferric or ferrous carbonates or the like.

As known to those skilled in the art, particles size plays a dominant role in setting the gel strength necessary to keep suspended particles from settling within a suspension. The density, or specific gravity of the solids, although of importance, is secondary to particle size. An increase in the size of the particles causes both a reduction in the fluid viscosity and an increase in the gel strength needed to prevent the settling. On the other hand, decreasing the size of the particles causes both an increase in the fluid viscosity and a decrease in the gel strength needed to prevent settling. For example, the gel strength necessary to suspend 20-mesh calcium carbonate is almost 25 times greater than that required for 325-mesh particles.

Reactants for reducing pH that are suitable for use in self-breaking metal hydroxide-thickened fluids can be substantially any relatively slowly reacting material that yields a water soluble acidic product that decreases the pH of an aqueous liquid. Suitable reactants are exemplified by: hydrolytically reactive halogenated organic compounds such as those described in the R. E. Dilgren et al. U.S. Pat. No. 3,215,199, 3,297,090 and 3,307,630; esters of water-soluble acids, such as the methyl or ethyl esters of formic, acetic, chloracetic, or the like, carboxylic acids; such esters of phosphoric,

sulfuric, nitric, sulphonic, sulfamic, or the like acids; etc.

FIG. 1 shows a plot of the variations in the specified gel strengths, plastic viscosities, and yield points with increases in the moles per liter of aluminum ions, regarding aluminum hydroxide-thickened solids-free fluids having an R_b of 3, at room temperature. All fluid properties referred to herein were measured on a Fann, Model 50B rotational viscometer. The " G_0 lb./100 ft.²" (pounds per 100 square foot) values were measured immediately after the solution has been sheared. The

mains essentially constant over the temperature range most commonly encountered in well treating operations.

Table 1 lists data obtained from tests of the loading effects of adding calcium carbonate particles to an aluminum hydroxide-thickened fluid, having an R_b of 3.0, and enough CaBr_2 to provide a density of 14.2 ppg. The properties of solids-free solutions of various aluminum chloride concentrations are compared to those of solutions containing enough CaCO_3 to provide a solids volume fraction of 0.325 and a density of 17 ppg.

TABLE 2

no solids —, solids + [Al ⁺⁺⁺]	Solids	PV	YP	G_0	G_{10}	G_{30}
0.25 M	—	16	1.5	1	4	4
	+	76	9.5	5.5	29	33
	percent increase	375	533	550	625	725
0.50 M	—	25	2	1	8	8
	+	87	23	10	68	82
	percent increase	248	1050	900	750	925
0.75 M	—	42	5.5	2	21	25
	+	127	—	37	219	>300
	percent increase	202	—	1750	942	>1100

G_{10} and G_{30} values were measured at the ends of, respectively; 10 and 30 minute intervals during which the fluid remained motionless.

FIG. 2 shows plots of plastic viscosities, gel-strengths, and yield points, regarding a metal hydroxide-thickened fluid containing aluminum chloride and sodium hydroxide in an aqueous solution of calcium bromide having a density of 14.2 lb./gal. and, respectively, no solids and enough (f_s volume fraction of solids = 0.325) 325-mesh calcium carbonate particles to provide a density of 17 ppg.

During such testing, it was observed that, at a relatively low aluminum concentration (of about 0.125 moles per liter), the hydrated aluminum oxide settled rather extensively. Such a settling was somewhat less at 0.25 moles per liter. At relatively high concentrations (such as 0.75 to 1.0 mole aluminum ion per liter) the solutions, upon standing, set up to rigid semi-solids that were incapable of being poured. However, on mild stirring or agitation, such rigidly-set gels reverted to easily handled, but relatively viscous, fluids. Such tests suggest that for many well treating operations, a particularly desirable aluminum concentration is from about 0.4 to 0.6 moles per liter, where the hydroxide-thickened fluid is used to suspend particles having a size in the order of 325 mesh.

FIGS. 3A through 3C show plots of variations with temperature of, respectively, yield points, gel strengths, and plastic viscosities, of metal hydroxide-thickened solutions containing 0.5 moles per liter aluminum chloride, calcium bromide providing a density of 14.2 lbs/gal., and enough sodium hydroxide to provide R_b values of, respectively, 3.0 and 2.7. The plots indicate that the magnitude of the rheological properties is uniformly higher at a lower R_b value. An R_b of 2.7 provides a relatively low pH of from about 2 to 3. The pH is 6 to 7 for an R_b of 3.0 and, at such a value, the rheological properties are moderately high.

FIGS. 4A through 4C are similar except that the fluids tested are, respectively, a freshly prepared fluid, and one that has been aged for 67 hours at 400° F. The data indicate that there is little change in the plastic viscosity and gel strengths between such fresh and aged fluids. The yield point shows a marked increase, but re-

The data in Table 1 indicate that the presence of solids has a large effect on rheological properties. A statistical treatment of such data to determine the effects of aluminum concentration, solids, and the solids-aluminum interaction, indicate that at all aluminum concentrations, the solid effect predominates, and the aluminum and solids-aluminum interaction effects having a similar magnitude that is lower than the solids effect. Gel-strength values (both initial and later gel strengths) are most changed. Initial gel strengths are quite low in the absence of solids, but increase rapidly in the presence of solids. A possible physical explanation of this phenomena could be as follows: at low aluminum concentrations, there are insufficient number of gel particles to bridge and effectively gel the fluid. Small particles of a suspended solid help to span the gel particles so that they can bridge and raise the gel strength of the fluid.

What is claimed is:

1. A process for temporarily plugging a subterranean reservoir, which process comprises:

compounding a metal hydroxide-thickened aqueous fluid containing enough water-soluble salt of an amphoteric metal and enough watersoluble base to form a viscosity-increasing proportion of gelatinous hydrated metal oxide and provide a pH that is relatively non-corrosive to ferrous metal;

adjusting the specific gravity and fluid loss prevention properties of the fluid relative to the depth and fluid pressure of the reservoir to the extent required to provide a hydrostatic head that at least counter-balances the reservoir fluid pressure and a fluid loss prevention property that substantially prevents loss into the reservoir; and
flowing the so-adjusted fluid into the well to form a column of fluid extending from a near-surface location to the depth of the reservoir.

2. The process of claim 1 in which a substantially solids-free fluid is formed by adjusting the concentrations of water soluble salts and base that are dissolved in said metal hydroxide-thickened aqueous fluid to effect said adjustment of specific gravity and fluid loss prevention properties.

3. The process of claim 1 in which particles of a solid material that is soluble in a relatively strongly acidic or basic aqueous liquid are suspended in the metal hydroxide-thickened aqueous fluid.

4. The process of claim 1 in which a relatively slow reacting material that reacts to yield a water-soluble acidic product that reduces the pH of an aqueous liquid is dissolved in the metal hydroxide-thickened fluid.

5. The process of claim 1 in which the metal hydroxide-thickened aqueous fluid is compounded by dissolving at least one each of a water soluble aluminum salt, an alkali metal hydroxide and an alkaline earth metal chloride in an aqueous liquid.

6. The process of claim 1 in which the metal hydroxide-thickened aqueous fluid is compounded by dissolving at least one each of a water soluble aluminum salt, an alkali metal hydroxide and an alkaline earth metal bromide in an aqueous liquid.

7. A fluid composition that temporarily plugs a subterranean reservoir when it is positioned so that it forms a column of fluid extending between the reservoir and a near surface location, which composition comprises:

a metal hydroxide-thickened aqueous fluid that contains enough water-soluble salt of an amphoteric metal and enough water-soluble base to provide, within said aqueous fluid, both a viscosity-increasing proportion of gelatinous hydrated metal oxide and a pH that is relatively non-corrosive to ferrous metal; and

within said aqueous fluid, a combination of specific gravity and fluid loss prevention properties that are correlated relative to the depth and fluid pressure of said reservoir to provide a hydrostatic head that at least counter-balances the reservoir fluid pressure and a fluid loss prevention property that substantially prevents fluid loss into the reservoir when

the aqueous fluid is positioned so that it forms a column of fluid extending from the reservoir to a near surface location.

8. The composition of claim 7 in which there are suspended particles of a solid material that is soluble in a relatively strongly acidic or basic aqueous liquid.

9. The composition of claim 7 in which a relatively slow reacting material that reacts to yield a water-soluble acidic product that reduces the pH of an aqueous liquid is dissolved in the metal hydroxide-thickened fluid.

10. The composition of claim 7 in which said salt and base are respectively an aluminum salt and an alkali metal hydroxide.

11. The composition of claim 7 in which there is dissolved an alkaline earth metal salt of one, but not both, of such chloride and bromides.

12. A process for temporarily plugging a subterranean reservoir, which process comprises:

compounding a metal hydroxide-thickened aqueous fluid containing enough water-soluble salt of an amphoteric metal and enough water-soluble base to form a viscosity-increasing proportion of gelatinous hydrated metal oxide and provide a pH that is relatively non-corrosive to ferrous metal; adjusting the specific gravity and fluid loss prevention properties of the fluid relative to the depth and fluid pressure of the reservoir to the extent required to provide a hydrostatic head that at least counter-balances the reservoir fluid pressure and a fluid loss prevention property that substantially prevents loss into the reservoir; and flowing the so-adjusted fluid into the well to form a reservoir contacting portion of a column of fluid extending from a near surface location to the depth of the reservoir.

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