



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C09K 7/02, 7/00	A1	(11) International Publication Number: WO 00/47691 (43) International Publication Date: 17 August 2000 (17.08.00)
(21) International Application Number: PCT/US99/31049 (22) International Filing Date: 27 December 1999 (27.12.99) (30) Priority Data: 09/246,932 9 February 1999 (09.02.99) US (71) Applicant (for all designated States except US): ACTISYS- TEMS, INC. [US/US]; 1409 Pine Oak Place, Edmond, OK 73034 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): BROOKEY, Tommy, F. [US/US]; 1409 Pine Oak Place, Edmond, OK 73034 (US). (74) Agent: HOUSE, Roy, F.; 5726 Ettrick Street, Houston, TX 77035 (US).		(81) Designated States: AU, BR, CA, CN, ID, MX, NO, US, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: APHRON-CONTAINING AQUEOUS WELL DRILLING AND SERVICING FLUIDS		
(57) Abstract <p>The invention provides a method and fluid for drilling or servicing a well in a subterranean formation containing lost circulation zones or depleted, low pressure reservoirs. The fluid comprises an aqueous liquid having dispersed therein a viscosifier which increases the low shear rate viscosity of the fluid to at least 10,000 centipoise, an aphron-generating surfactant, and aphrons, wherein the fluid contains less than about 20 % by volume of aphrons preferably generated by the turbulence and pressure drop as the fluid exits the drill bit in the vicinity of the formation. The method of drilling a wellbore in a subterranean formation comprises continuously re-circulating, while drilling, such a drilling fluid.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

APHRON-CONTAINING AQUEOUS WELL DRILLING AND
SERVICING FLUIDS

The patent application is a continuation-in-part application of U.S. patent application Serial No. 08/800,727 filed 02/13/97, and of P.C.T. International
5 Application No. PCT/US98/02566 filed 02/10/98, to each of which priority is claimed herein.

Background of the Invention

Formation damage due to invasion by drilling fluids is a well-known problem. Many zones contain formation clays which hydrate when in contact with water
10 such as the filtrate from drilling fluids. These hydrated clays tend to block the producing zones, primarily sands, so that oil and gas cannot move to the borehole and be produced.

These zones are also damaged by solids which are carried into the openings with the fluid. The movement of drilling fluids and filtrate through these openings
15 also causes the dislodging and migration of solids in place in the formation. These solids can lodge and block movement of produced hydrocarbons.

Invasion is caused by the differential pressure of the hydrostatic column which is generally greater than the formation pressure, especially in low pressure or depleted zones. Invasion is also due to the openings in the rock and the ability of
20 fluids to move through the rock, the porosity and permeability of the zone.

Because of this differential pressure, drillers have long used filtrate control mechanisms to control the movement of drilling fluids and filtrate into and through

the formation openings. This mechanism involves adding particles to the drilling fluid which are then deposited onto the borehole wall while circulating and drilling. These particles are generally some combination of bentonite, starch, lignins, polymers, barite, and drilled solids. They are used to plug and seal the borehole due to the particle size and shape, and some control is also due to the viscosity of the filtrate when water-soluble polymers are used. Although this wallcake forms a semipermeable barrier, some filtrate moves through and into the zone both before and after the wallcake is formed.

Wallcake control, then is not complete and some filtrate water is allowed to contact the producing zone. Another disadvantage of wallcake mud is that when filtrate moves through, the solids are screened out and left in the cake. This causes the cake to become thicker and can lead to differential sticking of the drill string.

More recent technology has seen the development of Low Shear Rate Viscosity (LSRV) fluids. LSRV may be created by the addition of specialized polymers to water or brines to form a drilling fluid. These polymers have a unique ability to create extremely high viscosity at very low shear rates. These LSRV fluids have been widely used because of their carrying capacity and solids suspension ability. They have been accepted as a way to minimize cuttings bed formation in high angle and horizontal wells, and as a way to reduce barite sag in high weight muds.

Recent studies and field experience indicate that this LSRV is helpful in controlling the invasion of drilling fluids and filtrate by creating a high resistance

to movement into the formation openings. Since the fluid moves at a very slow rate, viscosity becomes very high, and the drilling fluid is contained within the borehole with a very slight penetration. This has been beneficial in protecting the zones from damage as well as reducing differential sticking in these fluids. See for
5 example the article entitled "Drill-In Fluids Improve High Angle Well Production", Supplement to the Petroleum Engineer International, March, 1995.

Lost circulation is also a severe problem in rotary drilling. Lost circulation occurs when the differential pressure of the hydrostatic column is much greater than formation pressure. The openings in the rock are able to accept and store
10 drilling fluid so that none is returned to surface for recirculation. The fluid is lost downhole and can become an expensive and dangerous problem. Lost circulation can lead to hole instability, stuck drill pipe, and loss of well control. At the least, it halts drilling operations and requires expensive replacement volume to be used.

In addition to the fluid volume being lost, expensive lost circulation materials
15 (LCM) are required. These are usually fibrous, granular, or flake materials such as can fibers, wood fibers, cottonseed hulls, nut hulls, mica, cellophane, and many other materials. These LCM materials are added to the fluid system so that they may be carried into the loss zone and lodge to form a bridge on which other materials may begin to build and seal. These LCM materials themselves are
20 damaging to the zones, and because they must be carried many times in the drilling fluid to maintain circulation, solids removal is halted and high solids mud results.

Methods of correcting lost circulation of drilling fluids by aerating the drilling fluids are set forth in U.S. Patents 2,818,230 (Davis) and 4,155,410 (Jackson).

The use of underbalanced drilling has increased as the development of low pressure formations has acquired more importance. Horizontal drilling, in particular, has increased the need to drill across zones that are not only low pressure, but highly fractured or permeable. The exposure of numerous fractures or openings having low formation pressures has increased the problem of lost circulation and formation invasion. The necessity of down hole tools many times preclude the use of bridging materials to stop these losses. This has led to the use of underbalanced drilling techniques to control the losses and invasion of these zones. Some of these techniques include the use of air, mist, and foam drilling fluids. Problems with these fluids include hole cleaning, control of formation fluids, corrosion, and requirements for expensive, often hard to get equipment such as compressors and boosters. Such fluids are not re-circulatable and must be constantly generated as the drilling proceeds.

Summary of the Invention

A new fluid technique combines the use of low shear rate viscosity generating viscosifiers with surfactants to form colloidal gas aphrons at a concentration less than about 20% by volume at atmospheric pressure in a re-circulatable aqueous well drilling and servicing fluid. The aphrons use encapsulated air available in most circulating fluids. The aphrons reduce the density of the fluid and provide a means of bridging and sealing of the formations contacted by the fluid as the

bubbles expand and aggregate to fill the openings exposed while drilling. The viscosifiers strengthen the microbubble and also provide a resistance to movement within the formation so that losses of fluid are substantially reduced as the formation is being drilled. In this way, lost circulation is prevented. Any fluid
5 which enters the formation is clean and essentially solids-free such that damage of the formation is significantly less than with solids-containing fluids.

It is an object of this invention to provide recirculatable well drilling and servicing fluids which have an enhanced low shear rate viscosity (hereinafter abbreviated to "ELSRV") containing aphrons.

10 It is another object of this invention to provide a method of bridging and sealing subterranean formations during well drilling and servicing operations.

These and other objects of the invention will be obvious to one skilled in the art upon reading this specification and claims.

The process can comprise, consist essentially of, or consist of the stated steps
15 with the stated materials. The compositions can comprise, consist essentially of, or consist of the stated materials.

Preferred Embodiments of the Invention

In its broadest aspects, the present invention is directed to the incorporation of aphrons into aqueous well drilling and servicing fluids (hereinafter sometimes
20 referred to as "AWDASF"), or it may be a freshly prepared AWDASF having the characteristics desired. Stable aphron-containing AWDASF are obtained by increasing the low shear rate viscosity (LSRV) of the AWDASF to at least 10,000

centipoise, preferably at least 20,000 centipoise, and most preferably to at least 40,000 centipoise. Since the stability of the aphrons is enhanced as the LSRV increases, a LSRV of several hundred thousand may be desired.

The aphrons are obtained by incorporating (1) an aphron-generating surfactant
5 into the AWDASF and thereafter generating the aphrons in the AWDASF or (2) generating the aphrons in a liquid compatible with the ADWASF and mixing the aphron-containing fluid with the AWDASF.

The book by Felix Sebba entitled "Foams and Biliquid Foams – Aphrons", John Wiley & Sons, 1987, incorporated herein by reference, is an excellent source
10 on the preparation and properties of aphrons, i.e., microbubbles. An aphron is made up of a core which is often spherical of an internal phase, usually gas, encapsulated in a thin shell. This shell contains surfactant molecules so positioned that they produce an effective barrier against coalescence with adjacent aphrons.

The aphrons when first generated contain a wide size distribution ranging up
15 to about 200 μm in diameter. At atmospheric pressure, the aphrons of very small diameter diminish very rapidly leaving aphrons in the 25 μm to about 200 μm size range. This is due to the excess pressure within the aphrons which increases as the diameter of the aphrons decreases. Thus the smaller aphrons will tend to diminish in size by transferring their gas to the larger ones which would have a lower excess
20 pressure.

In the case of the aphron-containing well drilling and servicing fluids of the present invention, the aphrons are preferably generated downhole as the fluid exits

the drilling bit. The fluid is under considerable pressure composed of hydrostatic as well as pressure loss created by the circulating system. It is believed that this fluid pressure compensates for the excess pressure within the aphrons such that the aphrons smaller than about 25 μm are stabilized for a period of time until they are
5 circulated up the borehole. The aphrons thus are able to penetrate within the pore spaces of the exposed formation where they can expand and aggregate, because of the lower pore pressure within the formation, and seal the pore spaces from the entry of any fluid. Microfractures and the like will be filled with aphrons which likewise expand and aggregate within the formation to seal the microfractures.

10 Increases in vapor pressure due to pressure drops, temperature increases, and cavitation are common in downhole conditions. Certain solvents which may be present in the fluid may also effect vapor pressure to provide gasses needed to form aphrons.

Aphrons large enough to be seen without magnification can be visually
15 observed in the fluid as it flows from the borehole into the surface holding tanks ("pits") before being recirculated. Generally the fluid flows across a screen to remove the drill cuttings. Screens as fine as 200 mesh (74 μm screen openings) can be used with the fluids of the present invention. Aphrons greater than the screen size will be removed from the fluid. If desired, the particle size of the
20 aphrons in the fluid can be determined with various particle size analyzers which are commercially available. See for example the following articles: (1) "Microbubbles: Generation and Interaction with Colloid Particles", James B.

Melville and Egon Matijevic, Chapter 14 in "Foams", R.J. Akers, editor, Academic Press, 1976; (2) "Separation of Organic Dyes from Wastewater by Using Colloidal Gas Aphrons", D. Roy, K.T. Valsaraj, and S.A. Kottai, Separation Science and Technology, 27(5), pp. 573-588 (1992). These articles are incorporated herein by
5 reference.

Upon being recirculated down the drill string and through the bit additional aphrons are generated provided the concentration of the surfactant is sufficient. It is desirable to add additional surfactant to the fluid either continuously or intermittently until the desired quantity of aphrons is produced.

10 The aphrons can be generated by means known in the art. In addition to the methods disclosed by Felix Sebba in his book referenced previously, methods are disclosed in Michelsen et al. U.S. Patent No. 5,314,644, incorporated herein by reference, Yoon et al. U.S. Patent No. 5,397,001, incorporated herein by reference, Kolaini U.S. Patent No. 5,783,118, incorporated hereby by reference, Wheatley et
15 al. U.S. Patent No. 5,352,436, incorporated herein by reference, and U. S. Patents No. 4,162,970; 4,112,025; 4,717,515; 4,304,740; and 3,671,022, each incorporated herein by reference. The AWDASF can then be continuously circulated in the hole. It should be noted that common drilling fluids having lower LSRV containing entrained air can cause severe pump problems. Properly formulated
20 into aphrons and an elevated LSRV, as in the present invention, these fluids can be pumped readily.

If necessary, air or other gas can be incorporated into the fluid to entrain more

gas for forming afoams. The gas used may be any gas which is not appreciably soluble in the liquid phase of the fluid. Thus the gas may be air, nitrogen, carbon dioxide, organic gases, and the like, including air encapsulated in the fluid during mixing.

5 The quantity of afoams in the fluid depends on the density required. Generally, the fluid will contain less than about 20% by volume afoams, preferably less than about 15% by volume of afoams. Thus the density of the circulating fluid can be monitored on the surface and additional surfactant added as necessary to maintain the desired density, if the density is too high, and weight
10 material may be added if the density is too low. The quantity of afoams in the fluid can be determined by destroying or lowering the LSRV of the fluid thus destabilizing the surfactant-containing shells surrounding the afoams. Measurement of the change in volume of the fluid will indicate the volume % of afoams in the fluid. Preferably the quantity of afoams in the fluid is determined
15 by comparing the density of the fluid at atmospheric pressure with the density of the fluid under elevated pressures, such as measured with a pressurized mud balance.

The AWDASF comprises an aqueous liquid having incorporated therein a viscosifier such that the AWDASF has a LSRV of at least 10,000 centipoise,
20 preferably at least 20,000 centipoise, and most preferably at least about 40,000 centipoise, an afoam generating surfactant, and afoams, and optionally, a release agent. Any viscosifier which enhances the viscosity of the liquid phase

surrounding the aphrons will enhance their stability; however, we have found that those viscosifiers which provide the elevated LSRV required of the present invention have the unique property of delaying coalescence of the aphrons for extremely long period of time.

5 None of the known prior art disclose the use of aphrons (or microbubbles) in systems under elevated pressures as in the present use. It is well known that the hydrostatic pressure of the fluid in a borehole increases as the depth increases. Thus although the size of the microbubbles is compressed, the elevated LSRV is believed to keep the aphrons from coalescing. In this regard, the aphrons can have
10 a larger size at the surface of the well, as long as they are individual bubbles, since they will decrease in size to the aphron size range of less than about 100 micrometers as they are pumped down the borehole.

The base aqueous liquid may be fresh water, sea water, or a brine containing soluble salts such as sodium chloride, potassium chloride, calcium chloride,
15 magnesium chloride, sodium bromide, potassium bromide, calcium bromide, zinc bromide, sodium formate, potassium formate, cesium formate, and mixtures thereof. The brine may contain one or more soluble salts at any desired concentration up to saturation. Indeed, super saturated brines can be utilized where a solids free fluid is not desired or required.

20 Means are known in the art to enhance the low shear rate viscosity of liquids. Thus aqueous systems can be viscosified with certain polymers which produce a fluid exhibiting a high yield stress, shear thinning behavior. Particularly useful are

biopolymers produced by the action of bacteria, fungi, or other microorganisms on a suitable substrate. Exemplary biopolymers are the polysaccharides produced by the action of *Xanthomonas compestris* bacteria which are known as xanthan gums.

These are available commercially from several sources including: Kelco Oil Field
5 Group, Inc., under the trademarks "Xanvis" and "Kelzan"; Rhone-Poulenc Chimie
Fine, under the trademark "Rhodopol 23-p"; Pfizer Inc., under the trademark
"Flocon 4800C"; Shell International Chemical Company of London, U.K., under
the trademark "Shellflo ZA"; and Drilling Specialties Company, under the
trademark "Flowzan." See for example U.S. Patent No. 4,299,825 and U.S. Patent
10 No. 4,758,356, each incorporated herein by reference. Other biopolymers useful in
the fluids of this invention are the so-called welan gums produced by fermentation
with a microorganism of the genus *Alcaligenes*. See for example U.S. Patent No.
4,342,866, incorporated herein by reference. Gellan gums are disclosed in U.S.
Patent No. 4,503,084, incorporated herein by reference. Schleroglucan
15 polysaccharides produced by fungi of the genus *sclerotium* are disclosed in U.S.
Patent No. 3,301,848, incorporated herein by reference. Commercially available
schleroglucan is sold under the trademarks "Polytran" from the Pillsbury Company
and "Actigum CS-11" from CECA S.A. Succinoglycan polysaccharides are
produced by cultivating a slime-forming species of *Pseudomonas*, *Rhizobium*,
20 *Alcaligenes* or *Agrobacterium*, e.g., *Pseudomonas* sp. NCIB 11264, *Pseudomonas*
sp. NCIB 11592 or *Agrobacterium radiobacter* NCIB 11883, or mutants thereof, as
described in European Patent No. A40445 or A138255. Commercially available

succinoglycan biopolymer is sold by Shell International Chemical Company of London, U.K., under the trademark "Shellflo-S".

Other water soluble polymers which impart shear thinning rheology to aqueous fluids include alginic acid derivatives, such as hydroxypropyl alginate, sodium alginate, sodium calcium alginate, ammonium calcium alginate, and the like. In-situ crosslinking of sodium alginate solutions with a divalent cation, such as with a calcium salt, produces elevated low shear rate viscosities.

Miller et al. U.S. Patent No. 4,707,281, incorporated herein by reference, discloses that an additive comprising high pyruvic xanthan containing about 5 to 9 percent by weight pyruvic acid and locust bean gum, wherein the weight ratio of the high pyruvate xanthan to locust bean gum is from about 40:60 to 80:20, increases the LSRV of aqueous drilling and completion fluids.

Daigle U.S. Patent No. 3,953,336 discloses that shear thinning drilling fluids having enhanced LSRV are prepared from an aqueous liquid, a polysaccharide such as xanthan gum, and a cellulose derivative, such as hydroxyethylcellulose (HEC), carboxymethylcellulose (CMC), or hydroxypropylcellulose (HPC), wherein the weight ratio of xanthan gum to cellulose derivative, preferably HEC, is from 80:20 to 20:80.

The minimum concentration of the polymer required to increase the low shear rate viscosity of the fluid can be determined by routine testing. Thus the minimum concentration will be an amount sufficient to impart to the fluid the desired low shear rate viscosity. Generally the fluids will contain a concentration from about

1.4 kg/m³ (0.5 ppb) to about 28.5 kg/m³ (10 ppb), preferably from about 2.85 kg/m³ (1.0 ppb) to about 14.3 kg/m³ (5.0 ppb).

Patel et al. U.S. Patent No. 5,134,118, incorporated herein by reference, discloses a polymer for increasing the LSRV of aqueous drilling fluids comprising
5 a mixture of (1) a water soluble polymer being the reaction product of (i) 25-75% by weight of 2-acrylamido-2-methyl-propane sulfonic acid, (ii) 0.5 – 50% by weight N,N-dimethylacrylamide; (iii) up to 60% by weight acrylamide; (iv) up to 25% by weight styrene sulfonic acid; and (2) a gelling agent selected from the group consisting of partially hydrolyzed polyacrylamide, biopolymers, bentonite,
10 attapulgite, and combinations thereof.

Neff et al. U.S. Patent No. 4,861,499, incorporated herein by reference, discloses increasing the low shear viscosity of an aqueous liquid by dispersing therein a water-soluble composition consisting essentially of (1) a water soluble terpolymer of (a) acrylamide; (b) 2-acrylamido-2-methylpropane sulfonic acid salt,
15 acrylic acid, or dimethylaminoethyl acrylate metal chloride salt; and (c) a C₈-C₂₀ alkyl ester of acrylic acid; and (2) a water soluble inorganic salt.

Certain aqueous liquids can be viscosified with a combination of a dispersed smectite clay, such as sodium bentonite, and a mixed metal hydroxide as set forth in U.S. Patents No. 4,664,843 and 5,094,778, both incorporated herein by
20 reference. Indeed aqueous fluids can be obtained having an elevated LSRV by appropriately flocculating aqueous bentonitic clay dispersions or by incorporating 25 ppb or more non-beneficiated sodium bentonite therein.

Glass, Jr. U.S. Patent No. 4,561,985, incorporated herein by reference, discloses bentonite-containing drilling fluids containing an additive to beneficiate the bentonite, the additive comprising (1) a nonionic, water-soluble polysaccharide selected from the group consisting of (i) a non-ionic, water-soluble cellulosic derivative, (ii) a non-ionic water-soluble guar derivative; or (2) an anionic water-soluble polysaccharide selected from the group consisting of (1) a carboxymethyl cellulose or (ii) *Xanthomonas campestris* polysaccharide; or (3) a combination thereof; and (4) an intermediate molecular weight polyglycol, selected from the group consisting of polyethylene glycol, polypropylene glycol, and poly-(alkanediol), having an average molecular weight of from about 600 to about 30,000, said polyglycol being used in an amount effective to provide compatibility in the drilling fluid between the clay and the polysaccharide. The bentonite/additive combination provides aqueous base drilling fluids having elevated low shear rate viscosities which are shear thinning.

The aphron-generating surfactant for use in the spotting fluids of this invention must be compatible with the base liquid and the viscosifier therein such that the LSRV of the fluid can be maintained. The surfactant may also have one or more stabilizers incorporated therein, such as alkyl alcohols, fatty alkanolamides, and alkyl betaines. Generally the alkyl chain will contain from about 10 to about 18 carbon atoms. The aphron-generating surfactant may be anionic, non-ionic, or cationic depending on compatibility with the viscosifier. The annual publication "McCutcheon's Emulsifiers & Detergents", MC Publishing Co., McCutcheon

Division, lists many surfactants and their manufacturers. Preferred anionic foaming surfactants are alkyl sulfates, alpha olefin sulfonates, alkyl (alcohol) ether sulfates, refined petroleum sulfonates, and mixtures thereof. Typically these surfactants will contain an alkyl chain having 8 to about 18 carbon atoms, preferably about 12 to about 16 carbon atoms. Preferred non-ionic surfactants are ethoxylated alcohols and amine oxides having an alkyl chain length of about 10 to about 18 carbon atoms, preferably from about 12 to about 16 carbon atoms. Fluorocarbon based surfactants are preferred for systems in which the oleaginous liquid is the continuous phase.

10 Representative commercially available surfactants are: (1) alkyl sulfates - DUPONOL™ Brand, Witco Corp; RHODAPON™ Brand, Rhone-Poulenc; STEOL™ Brand, Stepan Co.; (2) alpha olefin sulfonates - WITCONATE™ AOS and 3203, Witco Corp.; STEPANTAN™ AS-40, Stepan Co.; RHODACAL™ A-246/6, Rhone-Poulenc; (3) alkyl ether sulfates - WITCOLATE™ Brand, Witco
15 Corp.; RHODAPLEX™ Brand, Rhone-Poulenc; SULFOCHEM™ Brand, Chemron Corp; (4) petroleum sulfonates - BASE™ Brand, Keil Chemical; MONALUBE™ 605, Mona Industries Inc.; WITCONATE™ NAS-8, Witco Corp.; (5) ethoxylated alcohols - ALFONIC™ Brand, Vista Chemical Co.; SURFONIC™ Brand, Huntsman Corp.; NEODOL™ Brand, Shell Chemical Co.; (6) amine oxides
20 - AMMONYX™ Brand, Stepan Co.; RHODAMOX™ Brand, Rhone-Poulenc; CHEMOXIDE™ Brand, Chemron Corp; (7) betaines - CHEMBETAIN™ Brand, Chemron Corp.; REWOTERIC™ Brand, Witco Corp.; MIRATAINE™ Brand,

Rhone-Poulenc; (8) fluorocarbon-based surfactants - FLUORAD™ Brand, 3M Co.; ZONYL™ Brand, E.I. Dupont De Nemours & Co.; (9) fatty alkanolamides - ALKAMIDE™ Brand, Rhone-Poulenc; AMIDEX™ Brand, Chemron Corp; WITCAMIDE™ Brand, Witco Corp.

5 There is disclosed in Schutt et al. U.S. Patent No. 5,639,443, incorporated herein by reference, that suitable surfactants for forming microbubbles include block copolymers of polyoxypropylene polyoxyethylene, sugar esters, fatty alcohols, aliphatic amine oxides, hyaluronic acid aliphatic esters, hyaluronic acid aliphatic ester salts, dodecyl poly(ethyleneoxy)ethanol, nonylphenoxy
10 poly(ethyleneoxy) ethanol, hydroxy ethyl starch, hydroxyethyl starch fatty acid esters, dextrans, dextran fatty acid esters, sorbitol, sorbitol fatty acid esters, gelatin, serum albumins, phospholipids, polyoxyethylene fatty acid esters such as polyoxyethylene stearates, polyoxyethylene fatty alcohol ethers, polyoxyethylated sorbitan fatty acid esters, glycerol polyethylene glycol oxystearate, glycerol
15 polyethylene glycol ricinolate, ethoxylated soybean sterols, ethoxylated castor oils and the hydrogenated derivatives thereof, cholesterol, fatty acids having 12 to 24 carbon atoms or salt thereof, and surfactants that form ordered structures in solution and produce non-Newtonian viscoelastic surface tensions such as sugar based surfactants and protein or glycoprotein surfactants. One preferred type of
20 such surfactant has a sugar or other carbohydrate head group, and a hydrocarbon or fluorocarbon tail group. A large number of sugars are known that can function as head groups, including glucose, sucrose, mannose, lactose, fructose, dextrose,

aldose, and the like. The tail group preferably has from 2 to 24 carbon atoms, preferably a fatty acid group (branched or unbranched, saturated or unsaturated) covalently bound to the sugar moiety through an ester bond. A preferred surfactant mixture includes a nonionic surfactant or other surfactant in combination with one
5 or more of the non-Newtonian viscoelastic surfactants.

There is disclosed in Wheatley et al. U.S. Patent No. 5,352,436, incorporated herein by reference, that suitable surfactants for forming stabilized gas microbubbles comprise a first soluble surfactant and a second dispersible surfactant. Suitable first surfactants include polyoxyethylene fatty acid esters such
10 as polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan tristearate, polyoxyethylene sorbitan monooleate, and mixtures thereof. Suitable second surfactants, which are different from the first surfactant, include sorbitan monostearate, sorbitan monooleate, and mixtures thereof.

15 D'Arrigo U.S. Patent No. 4,684,479, incorporated herein by reference, discloses surfactant mixtures comprising (a) a member selected from the group consisting of glycerol monoesters of saturated carboxylic acids containing from about 10 to about 18 carbon atoms and aliphatic alcohols containing from about 10 to about 18 carbon atoms; (b) a sterol-aromatic acid ester; (c) a member selected
20 from the group consisting of sterols, terpenes, bile acids and alkali metal salts of bile acids; (d) a member selected from the group consisting of sterol esters of aliphatic acids containing from 1 to about 18 carbon atoms; sterol esters of sugar

acids; esters of sugar acids and aliphatic alcohols containing from about 10 to about 18 carbon atoms; esters of sugars and aliphatic acids containing from about 10 to about 18 carbon atoms; sugar acids; saponins; and sapogenins; and (e) a member selected from the group consisting of glycerol, glycerol di- or triesters of
5 aliphatic acids containing from about 10 to about 18 carbon atoms and aliphatic alcohols containing from about 10 to about 18 carbon atoms; said components being present in said mixture in a weight ratio a:b:c:d:e of 2-4:0.5-1.5:0.5-1.5:0-1.5:0-1.5.

The fluorosurfactants include, but are not limited to, (i) fluorinated telomers,
10 (ii) amphoteric fluorosurfactants, (iii) polyfluorinated amine oxide, (iv) fluoroalkyl ethylthio polyacrylamides, (v) perfluoroalkyl ethylthiopolyacrylamides, (vi) derivatives of 1-propanaminium, 2-Hydroxy-N,N,N-trimethyl-3-gamma-omega-perfluoro-(C₆-C₂₀-alkyl) thio, chloride, (vii) fluoroalkyl sodium sulfonate, and (viii) sodium salts of 1-propanesulfonic acid, 2-methyl-, 2-{{1-oxo-3[gamma,-omega, -
15 perfluoro-C₁₆-C₂₆-alkyl)thio} propyl} amino} derivative.

The concentration of aphron-generating surfactant required is generally less than the critical micelle concentration (CMC) of the surfactant or surfactant mixture. An indication of the volume of aphrons generated can be obtained by determining the density reduction which occurs upon generating the aphrons in the
20 fluid. Foaming of the fluid, which is undesirable, can occur if the concentration of aphron-generating surfactant is excessive. We have determined that the concentration of surfactant can be increased, without any adverse effect on the

fluid, as the LSRV increases. Thus the concentration of aphron-generating surfactant, which can be determined by routine testing, is the amount required to generate sufficient aphrons to give the density reduction desired but which is, preferably, insufficient to create a long-lasting foam on the surface of the fluid.

5 Generally, a concentration of the surfactant from about 0.15% by volume to about 2% by volume is required, preferably from about 0.3% to about 1.0% by volume, assuming the surfactant contains about 80% by weight solids.

The density of the fluids can be adjusted, as required, by the addition of weight materials or the addition of soluble salts to the fluids as is well known in
10 the art. Preferably the weight material is added to the fluid before generation or incorporation of aphrons therein, thus adjusting the final density of the aphron-containing spotting fluid to the desired density by the concentration of aphrons therein.

As indicated, the concentration of aphrons in the fluid should be less than
15 about 20% by volume at atmospheric pressure. However, on circulation of the fluid in a borehole, the volume of the aphrons is believed to decrease as the hydrostatic pressure of the fluid increases. Indeed the aphrons may compress in size to almost no volume depending on the depth of the borehole. The measured density under pressure should be very close to the density of the fluid without any aphrons. The
20 aphrons do not disappear, however. They are still present, and additional aphrons will be generated at the face of the bit due to the pressure drop and cavitation. The aphrons are extremely small, have very high surface area, and are highly energized.

As soon as the fluid exits the bit and starts back up the annulus, some pressure drop begins to occur and the aphrons will begin to expand. As the fluid moves up the borehole and it encounters a loss to the formation, the aphrons are filtered into the pore throats, microfractures, or other types of loss zone. These loss zones are areas where pressure drops occur. The aphrons in these loss zones then expand and aggregate and hence seal the loss zones. The “% aphrons by volume” in these micro environments is highly variable and will depend on the specific pressure and pressure drop within the loss zones. Thus it is believed that the micro environment density is completely different than the density of the fluid in the borehole.

10 The density reduction at atmospheric pressure which occurs on entraining up to 20% by volume of a gas in the fluids of the invention is sufficient to provide the quantity of aphrons needed in the borehole while allowing the fluid to be recirculatable without causing pump problems.

The water base borehole fluids of this invention generally may contain materials well known in the art to provide various characteristics or properties to the fluid. Thus the fluids may contain one or more viscosifiers or suspending agents in addition to the viscosifiers which enhance the LSRV, weighting agents, corrosion inhibitors, soluble salts, biocides, fungicides, seepage loss control additives, bridging agents, lubricity additives, shale control additives, and other additives as desired.

The borehole fluids may contain one or more materials which function as encapsulating or fluid loss control additives to further restrict the entry of liquid

from the fluid to the contacted shale. Representative materials known in the art include partially solubilized starch, gelatinized starch, starch derivatives, cellulose derivatives, gums, synthetic water soluble polymers, and mixtures thereof.

The fluids of this invention should have a basic pH. The pH can be obtained
5 as is well known in the art by the addition of bases to the fluid, such as potassium hydroxide, potassium carbonate, sodium hydroxide, sodium carbonate, magnesium hydroxide, magnesium oxide, calcium oxide, calcium hydroxide, zinc oxide, and mixtures thereof.

Without being limited hereby, it is believed that the aphrons present in the
10 fluid effectively seal the formation during drilling or well servicing operations thus preventing the excessive loss of fluid to the formations being drilled or serviced.

The fluids of this invention can be used in conventional drilling and well servicing operations as conducted in the art. Thus in drilling an oil and/or gas well the fluid is circulated from the surface down the drill pipe, coiled tubing, or the like
15 through the bit and up the annulus between the drill pipe and the sides of the borehole back to the surface. The aphrons in the fluid seal the borehole surface preventing the loss of excessive amounts of fluid to the formations being drilled.

It is preferred that the aphron-containing fluid of the present invention be utilized in a drilling process wherein the drill bit is a cavitating liquid jet assisted
20 drill bit. Exemplary cavitating liquid jet assisted drill bits are set forth in Johnson, Jr. et al. U.S. Patent No. 4,262,757, incorporated herein by reference, and Johnson, Jr. et al. U.S. Patent No. 4,391,339, incorporated herein by reference. Preferably

the cavitating jet nozzle in the cavitating liquid jet assisted drill bit includes a pin received at a central position which lowers the pressure of the pressurized drilling fluid such that cavitation bubbles form in the fluid. See for example Henshaw U.S. U.S. Patent No. 5,217,163, incorporated herein by reference.

5 Similarly, the fluids of the invention can be in well servicing operations such as completion operations, workover operations, sand control operations, frac pack operations, and the like. The fluids can be used as spotting fluids to release pipes and tools stuck in the filter cake on the sides of a borehole by differential sticking.

Moreover, the aqueous base aphron-containing well drilling and servicing
10 fluids set forth in co-pending U.S. patent applications Serial No. 08/800,727 filed 02/13/97 and Serial No. 09/121,713 filed 07/24/98, as well as co-pending PCT patent application PCT/US98/02566 filed 02/10/98, can also be used in well servicing operations such as completion operations, workover operations, sand control operations, frac pack operations, and the like, including use of the fluids as
15 spotting fluids to release pipes and tools stuck in the filter cake on the sides of a borehole by differential sticking.

The following examples are presented to demonstrate the invention but should not be construed as limiting the scope of the invention. The aphron-generating surfactants evaluated are as follows: STEOL™ CS-460, sodium laureth sulfate
20 which is 60% active; and FLUORAD™ FC-740, a mixture of fluorinated aliphatic polymeric esters. Abbreviations used in the table or this specification are as follows: cp = centipoise; g = grams; bbl = 42 gallon barrel; ppg = pounds per

gallon; ppb = pounds per barrel; psi = pounds per square inch; rpm – revolutions per minute; STI = shear thinning index which is the ratio of the 0.5 rpm Brookfield viscosity and the 100 rpm Brookfield viscosity, a measure of the degree of shear thinning of a fluid; vol. = volume; LSRV = low shear rate viscosity measured on a
5 Brookfield Viscometer at 0.5 rpm.

Example 1

A fluid as set forth in Glass, Jr. U.S. Patent No. 4,561,985 was prepared containing 1.0 ppb HEC-10™ hydroxyethylcellulose, 1.0 ppb XCD™ xanthan gum, 0.2 ppb caustic soda, 1.0 ppb POLYGLYCOL™ E8000 polyethyleneglycol,
10 MW of 8000, and 15 ppb Wyoming bentonite. 1.0 ppb of BLUE STREAK aphron-generating surfactant was added while mixing in a Waring-type blender set at the lowest speed. The fluid's density and Brookfield viscosities were determined. The data obtained are set forth in Table A. The concentration of aphrons in the fluid was estimated from the density reduction using the equation:

$$15 \quad \% \text{ aphrons} = \frac{[(\text{Calculated Density}) - (\text{Measured Density})](100)}{(\text{Calculated Density})}$$

Example 2

A fluid as set forth in Daigle U.S. Patent No. 3,953,336 was prepared containing 2 ppb HEC-10™ hydroxyethylcellulose, 2.0 ppb XCD™ xanthan gum,
20 and 0.2 ppb caustic soda. 0.5 ppb BLUE-STREAK aphron-generating surfactant was added and the fluid processed and evaluated as in Example 1. The data obtained are set forth in Table A.

Table A

<u>Example</u>	<u>Brookfield Viscosity, cp</u>			<u>Density</u>	<u>Aphrons</u>
	<u>0.5 rpm</u>	<u>100 rpm</u>	<u>STI</u>	<u>ppg</u>	<u>Vol. %</u>
1	98,000	1120	87	7.01	16.0
5 2	61,000	1460	42	6.68	19.8
3	256,000	4800	53	7.4	11.2
4	168,000	4440	38	6.9	17.2

Example 3

In 350 ml of fresh water were hydrated 3.0 g (3.0 ppb) of sodium alginate.
 10 Thereafter 1.0 g of a 30% by weight solution of calcium chloride was added to crosslink the polymer, followed by 0.5 g (0.5 ppb) of BLUE STREAK™ aphron-generating surfactant. The fluid was evaluated as in Example 1. The data are set forth in Table A.

Example 4

15 An additional 0.5 g (0.5 ppb) of BLUE STREAK™ aphron-generating surfactant was added to the fluid of Example 3 and similarly evaluated. The data obtained are set forth in Table A.

What is claimed is:

1. A well drilling and servicing fluid which can be continuously recirculated in a borehole comprising an aqueous liquid having incorporated therein one or more viscosifiers such that the fluid has a low shear rate viscosity as measured with
5 a Brookfield Viscometer at 0.5 rpm of at least 10,000 centipoise, an aphron-generating surfactant, and aphrons wherein the concentration of aphrons is less than 20% by volume of the fluid at atmospheric pressure.
2. The fluid of Claim 1 wherein the density of the liquid and the concentration of aphrons are such that the fluid has the desired density.
- 10 3. The fluid of Claim 1 wherein the low shear rate viscosity is at least about 40,000 centipoise.
4. The fluid of Claim 2 wherein the low shear rate viscosity is at least about 40,000 centipoise.
5. The fluid of Claim 3 wherein the viscosifier is (1) an alginate polymer
15 selected from the group consisting of sodium alginate, sodium calcium alginate, ammonium calcium alginate, ammonium alginate, potassium alginate, propyleneglycol alginate, and mixtures thereof; or (2) mixtures of xanthan gum and a cellulose derivative wherein the weight ratio of xanthan gum to cellulose derivative is in the range from about 80:20 to about 20:80, and wherein the
20 cellulose derivative is selected from the group consisting of hydroxyethylcellulose, hydroxypropylcellulose, carboxymethylcellulose, and mixtures thereof; or (3) mixtures of a smectite clay and mixed metal hydroxides; or (4) mixtures of a

bentonitic clay and an additive comprising (a) a nonionic, water-soluble polysaccharide selected from the group consisting of (i) a non-ionic, water-soluble cellulosic derivative, (ii) a non-ionic water-soluble guar derivative; or (b) an anionic water-soluble polysaccharide selected from the group consisting of (i) a
5 carboxymethyl cellulose or (ii) Xanthomonas campestris polysaccharide; or (c) a combination thereof; and (d) an intermediate molecular weight polyglycol, selected from the group consisting of polyethylene glycol, polypropylene glycol, and poly-(alkanediol), having an average molecular weight of from about 600 to about 30,000, said polyglycol being used in an amount effective to provide compatibility
10 in the drilling fluid between the clay and the polysaccharide; or (5) compatible mixtures thereof; wherein the components of the mixtures may be added individually to the fluid to effect enhancement of the low shear rate viscosity thereof.

6. The fluid of Claim 1, 2, 3, 4, or 5 wherein the fluid has a low shear rate
15 viscosity of at least about 40,000 centipoise.

7. The process of drilling a wellbore into a subterranean formation wherein a drilling fluid is continuously recirculated in the wellbore while drilling proceeds which comprises utilizing as the drilling fluid the fluid of Claim 1, 2, 3, 4, or 5.

8. The process of Claim 7 wherein the fluid has a low shear rate viscosity of
20 at least about 40,000 centipoise.

9. The process of conducting well servicing operations within a wellbore wherein the well servicing fluid is the fluid of Claim 1, 2, 3, 4, or 5.

10. The process of Claim 8 wherein the fluid has a low shear rate viscosity of at least about 40,000 centipoise.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/31049

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C09K 7/02, 7/00

US CL : 507/102, 202 ; 175/72; 166/309

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 507/102, 202 ; 175/72; 166/309

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

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

EAST, APILIT, APIPAT

search terms: aphrons, drilling fluid

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	US 5,881,826 A (BROOKEY) 16 March 1999, see claims 7 and 8.	1-10
X, P ----- Y, P	US 5,977,030 A (HOUSE) 02 NOVEMBER 1999, see column 6, lines 1-17.	1-4, 6-10 ----- 5
Y	ROY ET AL., APILIT ABSTRACT 94: 5466, Abstract of Treatability of Water-Based Drilling Fluids using Colloidal Gas Aphrons, Fluid/Part. Sep. V5 N.1, 1992, pages 31-36.	1-6

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

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

15 MARCH 2000

Date of mailing of the international search report

04 APR 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

PHILIP C. TUCKER

Telephone No. (703) 308-0651