

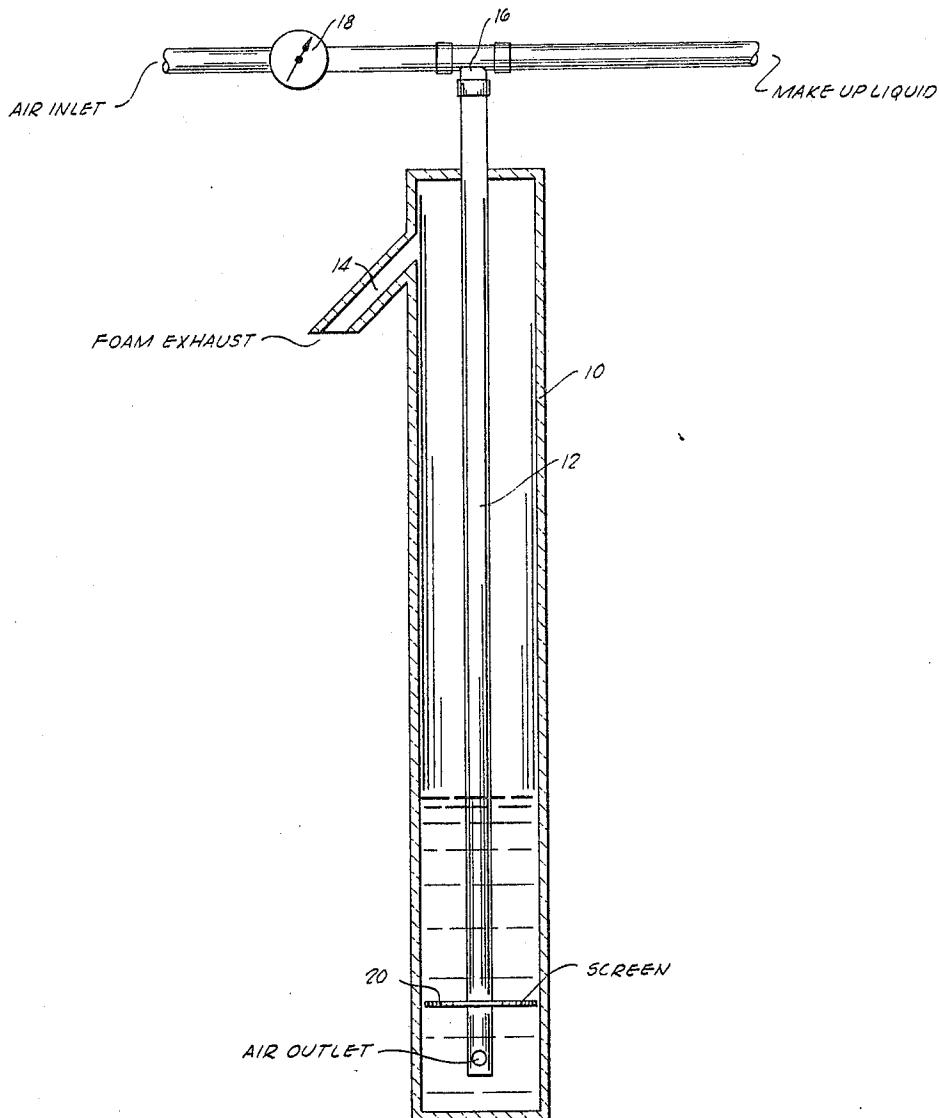
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FOAMING AGENTS FOR USE IN AIR DRILLING OF WELLS

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FOAMING AGENTS FOR USE IN AIR DRILLING
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This invention relates to the use of foaming agents for removing subterranean liquids from well bores, underground hydrocarbon storage facilities and the like. More particularly, but not by way of limitation, the present invention relates to the provision of improved foaming agents for use in removing encroaching formation fluids from the well bore of an oil or gas well which is being drilled utilizing a compressed gas as the drilling fluid.

The drilling of oil and gas wells using compressed gas as the circulation medium rather than mud has increased rapidly during recent years. The major problem which is encountered in air drilling is that of water intrusion into the well bore from the water-bearing zones which are penetrated in the process of drilling. The water wets the bit cuttings, increasing the load on the bit, and causing the cuttings to become sticky and ball up on the bit, drill collar, and drill pipe, resulting in a loss of return, and possibly, in stuck drill pipe, if corrective action is not taken. Also, if water-sensitive shales or clays are traversed by the bore, swelling of these formation materials by contact with the water can intensify the sticking problem. Not only is the accumulation of water in well bores a problem in well drilling, particularly in natural gas production, but it also poses a problem in the underground storage of natural gas or other gaseous products.

Attempts to overcome the problems posed by the influx of formation fluids have heretofore been directed along several lines. Syphons and accompanying equipment, such as gas lift valves and time devices, probably are the most logical choices to relieve this problem where water production is profuse. However, such systems are expensive and often are not justified for marginal wells or those which produce only a little water. Although bailing and swabbing usually will remove the liquids from wells, these practices are relatively expensive and time consuming.

In the case of low rates of water influx, or so-called "weeping wells," periodic injection of water into the air stream can prevent balling and sticking of the cuttings, but it must be done at the right intervals to prevent too much buildup on the sides of the bore hole. An early variation of this "weeping well" technique was to use slugs of water and drilling mud to disperse the wet cuttings and prevent balling. However, this slugging technique required high pressure air and almost continuous slugging. Moreover, it has now been recognized that the penetration rate during drilling is adversely affected by increased fluid column pressure, and the use of slugs of water, or water and mud, by increasing the liquid head, increases the pressure in the bore hole and therefore substantially reduces the drilling rate.

The most recent technique which has been employed for removing formation fluids from air drilled well bores and underground storage facilities is that of foam generation. The use of foam or mist in air drilling has already proven highly effective in maintaining high drilling rates in the presence of inflowing formation water ranging, for example, from 2 to 60 barrels per hour. Foam drilling remains economical in drilling competent formations at a depth as great as 4,000 feet, and a water influx rate as high as 500 barrels per hour. As drilling proceeds below this depth, the amount of water that can be economically handled decreases. In addition to the forego-

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ing advantages, foam drilling permits wet cuttings to be removed from the well bore at low pressures, and there is less sloughing of the well bore since bore hole pressure is more stabilized.

In foam drilling, the chemicals used to produce foams are injected into the air stream prior to the air entering the drill stem. After passing the bit, the air-aqueous chemical mixture flows up the annulus, contacting and lifting the formation water. A dense, light, metastable foam is formed which rises to the surface in the annulus of the well. At the surface, the foam and entrained cuttings are diverted by a drilling head assembly into a blow line leading away from the well.

The quantity of foaming agent which is injected is, of course, variable, depending upon the quantity of water in the hole, and its salt, cuttings and hydrocarbon content. In general, foaming agent and water additions should be the smallest quantities which will produce constant circulation at a low, even circulation pressure in order to achieve the maximum penetration rate while maintaining chemical costs at a minimum.

With the rapidly increasing interest in the use of foam for removing subterranean liquids, efforts are constantly being extended to the development and testing of new and improved foaming agents. The technology of surfactants and foams is not, in general, of as recent vintage as that of foam drilling of wells. Nevertheless, relatively little is known about the factors which influence foam formation, and the conditions which impart certain properties to different types of foams. Dynamic foams, in particular, are highly complicated physicochemical systems, the properties of which cannot be explained or predicted from simple observations. Moreover, because of the unusual characteristics of subterranean formation fluids and the conditions which exist in subterranean cavities and in well bores, many of the guide lines heretofore set up for the selection of a particular foaming agent for other uses are inapplicable to the selection of an agent for use in foam drilling. Many of the best surfactants and detergents supplied commercially for household and other uses have been found to perform poorly in removing formation liquids from well bores. For example, it may be stated that generally the agents listed in the literature as the best foamers are anionic surfactants and do, indeed, perform excellently as foam producers in shampoo and in dish-washing formulations. However, the effectiveness of such anionics has usually been destroyed completely when used in attempting to remove subterranean waters. Although several commercial anionic agents are effective for foaming fresh water or light brines, many exhibit decreased effectiveness in nearly saturated brines or those containing large amounts of divalent metals such as calcium or barium. As a result of these shortcomings, anionic surfactants have come to be viewed by workers in the field as generally inferior to other types of surfactants, particularly the nonionics.

Cationic surface active agents have been generally considered to be more tolerant of brines than anionic agents. However, they are very strongly adsorbed on bit cuttings and can become completely inactive in the presence of pulverized solids.

Because of their relative insensitivity to such formation water contaminants as sodium chloride and calcium sulfate, it has been supposed that nonionic foaming agents were best suited for use in foam drilling operations. Effective agents have been developed for use in both fresh water and brines, though generally, some reduction in foaming efficiency is encountered in heavy brines. Also, many of the agents are deleteriously affected in foaming efficiency by the presence of substantial quantities of clay cuttings. In view of the fact that cuttings are nearly al-

ways present in the bore hole of wells being drilled, this constitutes a particularly detrimental characteristic.

Another problem of the majority of nonionic foaming agents now in use is their inability to afford any protection against the swelling of certain up-hole formations, such as bentonitic clays, which are water-sensitive and may swell upon contact with the water being removed from the well bore to the extent that the drill pipe becomes stuck.

Yet another problem which has not been solved satisfactorily is that of corrosion. Although not necessarily corrosive per se, most of the effective foaming agents are also effective detergents. They therefore clean the metal surfaces of the drill string of oily films, exposing these surfaces to the saline formation waters and expediting their corrosion. In an effort to counteract the corrosion problem, it has become the usual practice to add a substantial amount of a suitable corrosion inhibitor such as lime to formation fluids. However, the presence of large concentrations of calcium ions in the fluids in turn renders ineffective many types of otherwise suitable foaming agents.

It is an object of the present invention to provide new types of foaming agents adapted for use in air or foam drilling of oil and gas wells, and also suitable for use in removing connate waters from underground storage reservoirs. The foaming agents of the invention are broadly certain specific types of anionic surfactants, and we have found them effective in both fresh water and brines. High lime concentration does not affect the efficiency of the foaming agents, which, in each of the mentioned instances, produces a dense, slow-draining foam. The agents are operable over a wide range of concentrations and air flow rates. These properties are especially unexpected in view of the anionic character of the surfactants which are employed.

An additional object of the present invention is to provide less expensive foaming agents for use in the foaming of connate subterranean liquids for the purpose of removing these liquids to the surface of the ground.

A further object of the invention is to provide foaming agents which demonstrate substantially improved efficiency in producing foams in waters containing large amounts of clay cuttings.

Another object of the invention is to provide new foaming agents which may be effectively utilized in the foam drilling of oil and gas wells and which afford protection from the swelling of up-hole formations which are water-sensitive.

Another object of the invention is to provide effective foaming agents for use in air drilling, which agents are much less costly than the agents heretofore utilized.

Other objects and advantages of the invention will become apparent from the following detailed description of the invention.

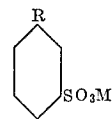
The sole drawing accompanying the specification is a schematic illustration of the apparatus used for evaluating the effectiveness of materials as foaming agents.

Broadly, the present invention comprises a method for foaming subterranean fluids of the type which present the hereinbefore described problems which are encountered in the air drilling of wells. The foaming of such fluids is accomplished by adding certain novel foaming agents to the fluids and agitating the mixture of foaming agent and fluid to mix air or other gas therewith. The invention also contemplates the provision of certain novel foaming agent compositions of matter for use in practicing such method.

To elaborate to some extent upon the broad or summary statement of the invention set forth in the preceding paragraph, the term fluid is employed in its generic sense and is intended to include both liquids and gases, since the materials which interfere with air drilling by their ingress into the bore hole of the well may include both, even though it is, of course, the liquid which

is primarily responsible for such interference. Also, although, in the process of air drilling, the foaming agents of the invention are usually brought into association with such fluids by injecting the agents, or aqueous solutions or dispersions of the agents, into the circulating air, the agents are also highly useful when introduced to such fluids in other ways when it is desired to move the foamed fluids from one location to another, as in removing water from subterranean gas storage reservoirs, etc. Agitation of the mixture of fluid and foaming agent may be accomplished in a number of ways, including, of course, the circulation, during air drilling, of the gaseous circulation medium therethrough. Where the agents are used to unload water from producing gas wells, the produced gas may itself provide the necessary agitation.

The anionic surfactants contemplated by the present invention may be generally described as water soluble alkyl benzene sulfonates which can be used individually or in admixture and have the generic structural formula



where R is an alkyl radical branched or unbranched containing an average of 6 to 10 carbon atoms and the individual alkyls can contain from 4 to 12 carbon atoms, and M is selected from a group consisting of an ammonium radical, an amino radical and a metal ion including the metals of the alkali and alkaline earth groups of the periodic table, as for example, sodium, lithium, potassium, magnesium, calcium, strontium, and barium. Examples of such compounds are sodium n-hexyl benzene sulfonate, calcium iso-heptyl benzene sulfonate, ammonium n-octyl benzene sulfonate, magnesium iso-nonyl benzene sulfonate, sodium n-decyl benzene sulfonate, calcium iso-octyl benzene sulfonate, calcium iso-undecyl benzene sulfonate, sodium n-dodecyl benzene sulfonate, magnesium iso-undecyl benzene sulfonate, iso-decyl benzene sulfonate isopropyl amine, lithium isooctyl benzene sulfonate, potassium n-hexyl benzene sulfonate, strontium iso-nonyl benzene sulfonate and ammonium n-dodecyl benzene sulfonate.

In addition to the use of individual compounds having the specified structural formula as foaming agents for use in the various applications hereinbefore described, the invention also contemplates the use of a mixture of homologous compounds each having such structural formula wherein the alkyl radical of the compounds in the mixture averages about 8 carbon atoms in chain length. Since such mixtures of the alkyl benzene sulfonate compounds may be more economically produced than the specific individual compounds containing between 4 and 12 carbon atoms in the alkyl chain, the mixture of the homologues constitutes the preferred embodiment of the invention. Such mixture has been found to be equally or even more effective than the use of any one specific alkyl benzene sulfonate.

We have surprisingly noted that the length of the alkyl chain in the preferred compounds of the present invention is less than that of the normal chain length of the most molecularly similar commercial detergents, or stated differently, the compounds of this invention are more hydrophilic than the detergents which are normally used, and which are effective foamers in other applications, such as in ordinary household uses. Ordinarily, the lower limit of alkyl chain length in such commercial detergents is about 12 carbon atoms. Yet the preferred materials of the present invention are alkyl benzene sulfonates containing about 8 carbon atoms in the alkyl chain, or mixtures of these sulfonates having an average of 8 carbon atoms in the alkyl chains of the several compounds in the mixture. The theoretical explanation of why the more hydrophilic nature of these materials seems to enhance their effectiveness as foaming agents in the applications with which the

present invention is concerned is not completely and thoroughly understood and will not be discussed herein.

The alkyl benzene sulfonates of the invention may be produced by alkylating benzene utilizing a Friedel-Crafts type of reaction in which aluminum chloride is utilized as the catalyst. The alkyl benzenes are then sulfonated and neutralized to produce the sulfonate salt. The most suitable and preferred compounds of the invention are prepared by alkylating the benzene ring utilizing a propylene tetramer. Processes of this type are currently in commercial usage to prepare dodecyl benzene, which, when sulfonated and neutralized, in itself constitutes one of the less preferred foaming agents of the present invention. In the process of alkylating benzene with the propylene tetramer to produce dodecyl benzene, a substantial quantity of side product comprising a mixture of alkyl benzenes ranging from about 120 to about 188 in molecular weight and having an average of about 8 carbon atoms in each of the alkyl substituents is produced. Since the mixture of alkyl benzenes so produced, when sulfonated and neutralized, constitutes a preferred foaming agent of the present invention, its composition and properties will be described in detail.

In the described mixture of alkyl benzenes, analysis of the mixture indicates that about 17.1 percent of the homologues present have alkyl chains of 3 or 4 carbon atoms in length. Approximately 18.6 percent of the compounds in the mixture have alkyl chains having 5 carbons therein. The compounds containing 6 carbon atoms in the alkyl radical constitute about 9.9 percent of the mixture. About 18.1 percent of the total weight of the mixture is constituted by compounds having 7 carbon atoms in the alkyl chain, and the balance of the compounds having between 8 and about 15 carbon atoms in the alkyl chain constitutes the remaining 36.5 percent of the total weight of the mixture.

Typical physical properties of a mixture of alkyl benzene compounds produced by the described alkylation process and suitable for conversion to sulfonate salts for use in the present invention are as follows:

Distillation range (° F.), ASTM D-86:

I.B.P. -----	344
1% -----	346
5% -----	351
10% -----	354
50% -----	371
90% -----	410
95% -----	425
97% -----	436
F.B.P. -----	444
Specific gravity -----	0.8275
Molecular weight -----	160
Aniline point (° F.) -----	95
Bromine No. -----	0.27
Saybolt color -----	29
Refractive index at 25° C. -----	1.4550
Percent aromatics -----	63
Appearance—clear and water white.	
Flash point (closed cup) ° F. -----	129.5
Viscosity, centipoises at—	
68° F. -----	5
32° F. -----	6

Whether specific alkyl benzene sulfonate salts or mixtures thereof are utilized as foaming agents in accordance with the present invention, it is preferred to use the sodium, calcium, ammonium and amino salts.

An apparatus employed for testing various materials for their effectiveness as foaming agents in various types of aqueous solutions is depicted in the sole figure of the drawings. The apparatus is designed to simulate the situation appertaining in the bore hole of the well. A cylindrical glass column 10 about 118 inches in height and about 2½ inches in outside diameter is used to simulate the well bore. The hollow drill string used to convey

water to the bottom of the hole is represented by a tube 12 positioned concentrically in the glass cylinder and extending from the top to the bottom thereof. A downwardly inclined side arm 14 is provided near the top of the cylinder 10 to facilitate the discharge of foam from the cylinder. A T-connection 16 is located at the top of the tube to permit air and make-up liquid to be introduced through the tube to the bottom of the cylinder 10. A suitable pressure gauge 18 is provided in the air inlet to the tube 12 to facilitate the measurement of the air pressures applied in foam generation. A screen shelf 20 is mounted just above the lower end of the tube 12 to hold clay, sand or bit cuttings.

In conducting the tests, one liter of the particular test solution of interest (lime water containing 5 percent sodium chloride, etc.) is initially placed in the column 10. If desired, clay, sand or other solid materials may then be placed on the screen shelf 20 to give a more realistic test of foam performance under field conditions. Air flow through tube 12 is commenced with the air escaping through radial holes formed in the bottom of the tube.

Comparative tests utilizing the apparatus illustrated in the drawing were conducted to determine the relative effectiveness of the materials of the present invention as compared to several of the most commonly used and effective commercially available foaming agents.

In the tests, air flow was maintained at two cubic feet per minute. The temperature of the system was maintained at 75° F. Make-up liquid was pumped down the tube 12 with the air at the approximate rate at which liquid is carried over by the foam passing out of the column 10 via the side arm 14. Foam discharged through the side arm 14 was collected and deflated with alcohol spray.

In Table 1 are reported the results of comparative tests which were conducted using several of the most effective commercially available agents and agents of the present invention. Agent 1X in the table is a mixture of homologues of calcium alkyl benzene sulfonate and agent 2X is a mixture of homologues of sodium alkyl benzene sulfonate. In the dynamic foam tests, the materials were used to produce foam in two types of liquid compositions which are frequently encountered in well bores.

TABLE 1

Foaming Agents	Wt. Percent of Agent Required to Carry Over 800 m. of Liquid in 10 Minutes	
	Saturated Lime Water+5% NaCl	Saturated Lime Water+5% NaCl+Clay Cuttings
COMMERCIAL TYPES		
Nonionic:		
1C-----	.037	.160
2C-----	.031	.049
3C-----	.056	.210
4C-----	.036	.140
5C-----	.033	.135
Anionic: 6C-----	.032	.059
Cationic: 7C-----	.023	.105
Agents of the Present Invention:		
1X-----	.050	.046
2X-----	.048	.045

By reference to Table 1, it will be noted that in lime water containing 5 percent sodium chloride, the agents of the invention are not quite so effective as the commercial foaming agents tested, and yet are sufficiently effective to justify their use, particularly in view of their much lower cost, in this solution. The most striking advantage of the agents of the present invention with respect to the commercial agents tested is the effectiveness of the agents in the brine solution in which were mixed clay cuttings. The clay cuttings did not deleteriously affect the foaming efficiency of the agents of the present invention, but lowered the efficiency of the commercial agents in a market manner. Since cuttings

are almost universally present at the bottom of the bore hole of wells being drilled with either gas or mud, it is believed that this is a highly significant characteristic of the present invention and is such as to recommend its use in lieu of many of the presently used commercially available agents, not only because of the great economic advantage which obtains, but because of the higher effectiveness of the agents in the presence of clay cuttings.

We have found that the preferred foaming agents of the present invention produce an adequate foaming action in concentrations of from 0.2 to 1 percent by weight based upon the total amount of water to which they are added. Moreover, these materials, unlike nonionic surfactants, afford protection from the swelling of water-sensitive materials, such as bentonitic clays, which may be present in up-hole formations.

An indication of the effect of the foaming agents of the invention on the swelling tendency of bentonite and low yield clay may be derived from the results obtained when varying quantities of a mixture of calcium alkyl benzene sulfonates conforming to the specifications of the invention were added to both drilling mud and water containing such clays. In every instance, a substantial decrease in the viscosity of the material to which the agent was added was observed, indicating an actual reduction in the extent of swelling of the clay resulting from such addition. The results of these tests are set forth in Table 2.

TABLE 2

Inhibiting effects of calcium alkyl benzene sulfonates

	Pounds Per Barrel Additive			
	0	0.5	1	2
Viscosity Readings ¹ for—				
System I ²	33	24	16	14
System II ³	215	115		

¹ All systems were stirred on a multimixer for 15 to 20 minutes. Viscosity was determined on a Fann VG meter and is in Fann readings at 600 r.p.m.

² System I was a drilling mud composed of: 14 lb./bbl. bentonite; 28 lb./bbl. low yield clay; 6 lb./bbl. gyp; 5 lb./bbl. thinner; 1 lb./bbl. caustic soda; 10 percent diesel oil, to which 20 pounds of bentonite were added per barrel of the drilling mud.

³ System II was plain water plus 40 pounds of bentonite per barrel of water.

Within the range of effective concentrations specified above, the specific concentration utilized, and the manner of adding the foaming agent to the formation fluids is subject to considerable variation. Foaming agent concentrations and water-foam injection rates will depend on lithology, well depth, formation water influx rate and penetration rate. Generally, if the formation water flow is sufficient to disperse the cuttings, the foaming agent may be advantageously continuously injected with only enough water added to carry the foam to the bit. Conversely, if there is not enough formation water to disperse the cuttings, more water is added at the surface along with the foam. Normally, 3 to 5 gallons of foaming agent in 10 barrels of water will produce a good foam. Concentrations considerably lower than this may be expected with the agents of the present invention by virtue of their improved efficiency in the presence of clay cuttings. The injection rate will vary from 1 to 2 barrels of the mixture per hour to 1 barrel per minute on special occasions.

It should also be noted that, under certain well conditions occasionally encountered, it may be desirable to add a small amount of foam stabilizing compound to the foaming agent to improve the stability of the foam which is generated, and to reduce the rate of drainage of water from the foam film. Examples of such foam stabilizing compounds are alkanol amides of fatty acids, such as lauric isopropanol amide, lauric diethanol amide, etc.; tertiary amine oxides, dimethyl amine oxide; proteins and hydrolyzed proteins; dispersed fine solids or liquids,

for example, carbon, lauryl alcohol, lauric acid etc.; and hydrophilic colloids, such as starch, methyl cellulose, hydroxy ethyl cellulose, sodium carboxy methyl cellulose, sodium alginate and polyvinyl alcohol.

As a general rule, foaming agent and water additions should be the smallest quantities which will produce constant circulation and low, even circulation pressure in order to achieve maximum penetration rate while maintaining chemical costs at a minimum. Large quantities of fluid are sometimes more economically handled by intermittently slugging the input air or gas with a few barrels of the water containing a higher concentration of foaming agent. This causes a pressure surge in the well which flows out a large quantity of water and may permit a lower average pressure to be maintained. When producing a foam during air drilling, the exact amount of water or fluid to be removed is, as pointed out above, usually not known accurately. The efficiency of mixing also is unknown. Because of these two unknown quantities, it normally would be better to err in the direction of too high a concentration, as this usually causes only a slight or no decrease in foaming effectiveness in most instances. Moreover, a slight excess of the foaming agent over that which is required to produce the necessary amount of foam initially is generally desirable since the concentration of the foaming agent is constantly decreasing as the foam is lifted from the bore of the well. These considerations relating to concentration are specially true in the case of the foaming agents of the present invention by virtue of their very low costs relative to the heretofore employed agents.

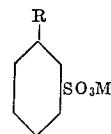
In addition to the use of the foaming agents of the present invention for removing inflowing formation liquids from the bore hole of a well being drilled, the foaming agents are also useful in such other applications as drilling lost circulation zones, drilling seismic shot holes and percussion drilling. The agents are also useful in unloading water from producing gas wells, and in removing water after fracturing, acidizing and other completion operations. Where hydraulic fracturing with water is contemplated, the foaming agents may be introduced to the fracturing liquid following completion of the fracture. Use of the foaming agents has the further advantage of washing away paraffin deposits, sludge and mud cake. In some instances, the foaming agents may therefore actually increase the hole diameter through the productive zone. Additionally, foaming agents may be utilized in coring low pressure pay zones.

From a consideration of the above described methods of air drilling and the foaming agents herein proposed for the first time, it will be appreciated that many changes may be made in the described process conditions, foaming agent concentrations, and molecular make-up of foaming agents without departing from the broad principles of the invention which are herein enumerated. Insofar as such modifications and innovations do not depart from the principles underlying the invention, such modifications and innovations are deemed to fall within the spirit and scope of the invention as defined by the following claims.

We claim:

1. In the method of removing cuttings and formation fluids from the bore of a well being drilled utilizing a gaseous circulation medium wherein said formation fluids are utilized to form a foam within the well bore, which foam is swept from the well bore with said gaseous circulating medium so as to carry with it said cuttings, the improvement which comprises adding to said fluids

(a) a foaming agent having the structural formula



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where R is an alkyl radical containing from 4 to 12 carbon atoms, and M is selected from the group consisting of an ammonium radical, amino radicals, and metals selected from the group consisting of alkali and alkaline earth metals, and

(b) a foam stabilizer selected from the group consisting of alkanol amides of fatty acids and tertiary amine oxides.

2. The method of claim 1 wherein said foaming agent comprises a mixture of homologous compounds, the alkyl benzene precursor of each of said homologous compounds having a molecular weight between about 120 and 188 and the alkyl substituent averaging from 6 to 10 carbon atoms.

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