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PROCESS FOR AERATED DRILLING

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This invention relates to a process for aerated drilling is subsurface boreholes, and more particularly to improvement of the aerated drilling process by incorporation of chemical additives into the aerated drilling fluid, to produce improved foam for removal of cuttings from the well and for lubrication of the drilling tools.

It is well known in the petroleum industry that gases are very efficient drilling fluids. Whenever conditions are favorable, gases are used because they give higher penetration rates and longer bit lives. In the aerated drilling process, compressed gas is injected into the drilling pipe. The gas passes downward through the drill pipe to the bottom of the borehole and then upward through the annular space between the borehole and the drill pipe to the surface. During its passage through the annular space to the surface, the gas removes cuttings from around the bit and from the borehole. Unfortunately, the usefulness of gases as drilling fluids is limited. When formations penetrated by the borehole contain liquids such as water or hydrocarbons, these liquids seep into the borehole to wet the borehole cuttings. The wetted cuttings tend to gum and ball on the bit as well as form mud rings around the drill pipe itself. These balls of mud and mud rings on the drilling tools blocks the flow of gas in the annular space so that the gas circulating pressure becomes erratic and does not satisfactorily remove cuttings from the borehole.

It was found that these difficulties in removal of cuttings could be overcome by introduction of a solution of foaming agent into the gas being used as the drilling fluid. When this solution is mixed with the formation liquids seeping into the borehole, a foam or froth is produced. This foam or froth acted as a collecting or flotation agent to improve adhesion between the bubbles in the foam and the cuttings to be removed from the borehole so that removal of cuttings from the borehole was facilitated. Use of these foams as drilling fluids was found to have several advantages and to overcome some of the difficulties which were experienced when gases were used as drilling fluid. For example, use of these foams increased drilling rates, reduced bit wear and decreased drilling cost. These foams had lower densities than conventional drilling fluids such as water base oil or base muds. The lower density of the foams made rupture of weak formations in the borehole less likely and reduced the danger of lost circulation. Foams had the further advantage that they did not dissolve salt formations as readily as water base drilling fluids so boreholes closer to gauge size could be drilled.

However, foams were found to have certain disadvantages as drilling fluids. Many of the foaming agents used were unsatisfactory because they did not make efficient use of the gas being injected into the well and produced foams which were weak and quick breaking. When inefficient foaming agents were used, fluid displacement in the borehole was unsatisfactory and the efficiency of cutting removal was reduced. Other difficulties arose. The foaming action of certain agents was found to be adversely affected or dampened by salts encountered in the borehole. These salts were introduced into the foam either by formation fluids seeping in the borehole or by drilling through strata containing large quantities of inorganic salts such as sodium chloride, calcium sulfate or

other saline materials. Oil seepage from hydrocarbon bearing formations was also found to adversely affect foams. Often, these hydrocarbons made the foaming agent ineffective. Seepage of oil into the borehole also presented another problem. It created a fire hazard.

Most of the foaming agents used in aerated drilling were found to have a further disadvantage. They were very efficient metal cleaning agents and in aqueous systems readily removed the oil from the metal surfaces of the drilling tools. Removal of this oil from the metal surfaces created a lubrication problem. Lubrication when gases were used as drilling fluids was not a problem. The oil originally present in the bearings of the drilling bit lubricated these bearings and the drill pipe was lubricated by oil seepage into the borehole from the hydrocarbon producing formations. In foam drilling, lubrication became a serious problem. The detergent action of the foaming agent removed the two principal sources of lubrication that were present in air drilling and excessive wear of the drilling tools occurred.

It was also found that once these two sources of lubrication were removed that they could not be readily replaced by injecting lubricants into the aerated drilling fluid. Most of the common extreme pressure lubricants such as sulphurized lard oil, isobutyl paraffins, asphalt, fatty acids, tall oil acids or the like were water insoluble and could not be mixed with aqueous systems such as foams or froths. These lubricants were also effective defoaming agents and would break foams of the type used in aerated drilling operations. In addition to the removal of these sources of lubrication, these foaming agents also had another undesirable property. They were quite corrosive to various metals in aqueous media and produced excessive metal corrosion which greatly reduced the expected life of the drilling tools.

It is an object of the present invention to provide aerated drilling fluids which will improve the efficiency of fluid displacement from the borehole. Another object of this invention is to provide for improved lubrication of the drilling tools during the drilling process. Still another object of this invention is to improve the cutting carrying capacity of aerated drilling fluids. It is also an object of this invention to provide surfactants which will produce improved foams for use in aerated drilling. Another object of this invention is to reduce the wear of drilling tools. A further object of this invention is to reduce the corrosion of ferrous metal drilling tools. Other objects and advantages of this invention will become apparent as this description proceeds.

The attainment of the above objects of this invention is made possible by the discovery that in a process of drilling a well wherein there is circulated through the well during said drilling, a drilling fluid into which gases are injected to produce foam for carrying cuttings from the well; the improvement which comprises incorporating in said drilling fluid as a foaming agent, antiwear agent, and corrosion inhibition agent, a minor amount of a phosphate selected from the group consisting of

(1) mono- and
(2) di-esters and
(3) tri-esters and
(4) mixtures thereof of phosphoric acid with a nonionic surfactant derived by condensation of
(5) an organic compound containing at least 6 carbon atoms and containing a reactive hydrogen atom and
(6) at least 3 moles of ethylene oxide,

to improve fluid displacement during drilling, to reduce friction on the drilling tools and to decrease corrosion of the drilling tools to thereby improve the efficiency of the drilling process and extend the life of said drilling tools.

In carrying out the aerated drilling process in accordance with this invention, the required amount of phosphate ester is mixed with water in a tank equipped with a pump for delivery of the ester mixture into the efflux from the manifold of the air compressors used in the drilling operation. This mixture of foaming agent in water is injected into the air line at a fixed rate such as 10 bbl./hr. (barrels per hours). Normally, a fixed rate of injection is selected which will produce a foam that will carry up to 100 bbl./hr. of fresh influx water, that is, waters entering from the formations penetrated by the borehole. Typical ester and water mixtures are usually about 5 to 70 pounds of foaming agent in 10 barrels of injection water or 0.5 to 7 lb./bbl. However, the concentration of foaming agent in the mixture may be as low as 0.1 lb./bbl. and as high as 14 lb./bbl.

It will be understood by those skilled in the art that the amount of foaming agent required may vary during the drilling process. The concentration and amount of foaming agent required is determined by the penetration rate and the amount of water influx into the borehole. It may be advisable to use high injection rates and high foaming agent concentrations for short periods of time initially to prevent balling of the bit with mud and pressure surges. Once the air pressure becomes stable and pressure surges cease, the injection rate and concentration of foaming agent may be reduced to the minimum levels which will give the lowest practical circulating pressures and still keep the borehole clean and free of cuttings.

Sometimes it may be desirable to change from one foaming agent to another during aerated drilling operations. This is particularly true when water seeping into the borehole from the formations during the initial phase of drilling is either fresh water or water containing relatively low concentrations of salts. A foaming agent which produces satisfactory foams in low salt content waters may be used during this phase. However, if the concentration of salts in the formation waters increases or salt water flows are encountered in later phases, it may be desirable or necessary to use a salt-resistant foaming agent, i.e. one which is more resistant to high salt concentrations and whose foaming properties are not adversely affected at these concentrations. It may also be necessary to use salt-resistant foaming agents in certain other applications such as where salt water is the only water available for making foaming agent solutions. Salt-resistant foaming agents should also be used when long sections of rock salt are being drilled. If fresh water solutions of foaming agents are used in drilling salt sections, salt will dissolve in the foaming agent solution and will dampen the foaming action if a salt-resistant foaming agent is not used. Often when long sections of rock salt are being drilled, it may be advantageous to use saturated salt solutions of foaming agents to reduce solution of the rock salt being drilled so that the borehole diameter is maintained closer to gauge size.

Waters seeping into the borehole from the formations are often acidic, particularly if they contain carbon dioxide or hydrogen sulfide. Acidic formation waters may create serious corrosion problems in aerated drilling operations. Sometimes this type of corrosion may be reduced by adjusting the pH of the foaming agent solution being injected into the well to a pH of 10 or higher by the addition of lime or soda ash. When the pH of the solution is adjusted with lime or soda ash, it is necessary to use foaming agents whose properties will not be affected by these materials.

It is also desirable to use foaming agents whose properties will not be adversely affected by oil or other hydrocarbons particularly when hydrocarbon producing formations are being drilled. Otherwise, hydrocarbons seeping into the borehole may act as defoaming agents and break or destroy the foam being used in the drilling process. It is a further advantage if the foaming agents used are also effective hydrocarbon emulsifiers. If they are effective hydrocarbon emulsifiers, hydrocarbons seeping into the borehole will be emulsified and dispersed in the foam so the hydrocarbons do not create fire hazards.

We have discovered that the phosphate esters derived from nonionic surfactants (surface active agents) are useful and effective foaming agents in the aerated drilling processes used for drilling subsurface boreholes. These phosphate esters have a number of advantages in this type of drilling operation. They are effective foaming agents in both fresh water and salt water. They are also effective foaming agents in these waters when hydrocarbons are present. In addition to their foaming properties, they are efficient lubricants and antiwear agents. Their lubrication and antiwear properties are particularly advantageous because the foaming agents previously used did not have these desirable properties and actually removed oil and other materials from the drilling tools which might have served as lubricants. These phosphate esters also have the further advantage that they do not cause ferrous metal corrosion whereas the surfactants previously used in aerated drilling often caused severe ferrous metal corrosion.

Foaming agents for use in this invention were evaluated by two laboratory test methods, the Shake Foam Test and the Air Diffusion Test. Four liquid systems were used in these tests. These systems were chosen because they simulate the principal types of fluids that are frequently encountered during aerated drilling operations. The compositions of these four liquid systems are as follows:

System A: 1% foaming agent+99% of 20% salt solution

System B: 1% foaming agent+99% saturated lime solution

System C: 1% foaming agent+10% Diesel Oil No. 2+89% of 20% salt solution

System D: 1% foaming agent+10% Diesel Oil No. 2+89% of 20% salt solution

The Shake Foam Test involves placing 50 ml. of a solution of foaming agent prepared in one of the liquid systems described above in a 100 ml. graduate. After the graduate is stoppered, it is shaken vigorously 20 times by hand. Foam height is read immediately after the shaking by hand is stopped and is recorded as foam height at 0 min. (minutes). The foam height is read against 2 min. and 5 min. after shaking is stopped. The Shake Foam Test provides a convenient means for determining the foaming properties of surfactants as well as their foam stabilities.

The Air Diffusion Test, ASTM–D892–58T revised 1958, "Tentative Method of Test for Foaming Characteristics of Lubricating Oils," is the other laboratory test method used. In this method a 1000 ml. graduate is equipped with a diffusing stone placed near the bottom of the inside of the graduate and 200 ml. of a solution of foaming agent prepared in one of the liquid systems described above is placed in the graduate. Air is diffused through the stone and into the solution at a constant flow rate. The time necessary to produce 800 ml. of foam or the foam height after 5 min., whichever occurs first is recorded. The flow rate of air, amount of foam produced, time required to produce the foam and type of foam (Foam Nature) are recorded. The Air Diffusion Test provides a dynamic method for evaluation of foam production and foaming properties.

We have discovered that the Shell Four Ball Test Method, J. Inst. Petr. Tech. 1946, 201–229, and the Falex Load Test Method, Refiner Nat. Gasoline Mfg. 18,329–324 (1934), which are used for the evaluation of lubricants, are useful in the evaluation of lubricating properties of conventional drilling fluids for use in subsurface boreholes. Since lubrication in the aerated drilling proc-

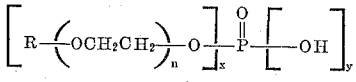
ess is supplied by coatings of the foaming agent solution on the metal surfaces of the drilling tools and on the walls of the borehole, the lubrication properties of foaming agent solutions used in aerated drilling operations may be evaluated by using a solution of the foaming agent itself in these two test methods.

Briefly, the Four Ball Test Method involves rotating a hard steel ball against three stationary steel balls by using various applied loads to produce wear on the stationary balls. The test is carried out in the presence of the desired test fluid under fixed conditions of time, temperature, rotational speed and applied load. Wear is measured in terms of the average diameter of the three scars worn on the stationary balls. Friction is measured by determining the amount of force required to counteract frictional torque. Generally, this test is conducted at loads sufficient to give measurable amounts of wear but below those producing seizure.

The Four Ball Test is usually carried out in the following manner. The three steel balls are locked into their positions and the foaming agent solution is placed in the test cup containing the balls. The apparatus is then heated to the desired temperature and the movable steel ball is rotated at the desired speed (r.p.m.). Load is then applied slowly to avoid shock loading. Once the desired load is reached, the test is carried out under this load at the desired temperature, rotational speed and time. When the test is complete, the three stationary balls are removed from the machine and cleaned with solvent. Scar diameters on these three balls are measured under a microscope and the average diameter of the three scars is reported in millimeters.

The Falex Load Test Method employs a Faville Le Vally lubricant tester equipped with an automatic loading device, load gauge, torque indicating gauge, brass shear pins, steel journals and steel V bearing blocks. The foaming agent solution is placed in the machine and torque readings are taken at 250 lb. increments until failure occurs or the maximum load 4500 lbs. is reached. Failure is indicated by either (1) sudden shearing of the brass locking pins or (2) wear occurring at such a rate that the loading ratchet is not able to maintain the load and the load actually decreases.

Phosphate esters useful in attaining the objects of this invention are phosphate esters selected from the group corresponding to the general formula



wherein R represents a member selected from the group consisting of alkyl, alkenyl and aryl radicals containing at least six carbon atoms, n represents an integer from 3 to 150, x represents an integer of from 1 to 3, y represents an integer including 0 of from 0 to 2, and the sum of the integers of x and y is 3.

Phosphate esters of nonionic surfactants useful in attaining the objects of this invention which are herein contemplated are obtained from precursor nonionic surfactants selected from the group consisting of polyoxyethylene ethers of organic compounds containing at least 6 carbon atoms and having a reactive hydrogen and condensed with at 3 moles of ethylene oxide. The number of ethylene oxide groups reacted with the reactive hydrogen compound may vary from 3 to 150 moles.

Nonionic surfactants which may be employed in the manufacture of phosphate esters for use in this invention include the polyoxyethylated derivatives of alkylphenols and monohydric alcohols. Many of these derivatives have been used extensively as nonionic surfactants and are well known in the art. Numerous methods for their preparation and descriptions of their properties may be found in patents and other publications. As such compounds containing a reactive hydrogen atom there may be mentioned alcohols, phenols, thiols, primary and secondary amines, carboxylic and sulfonic acids and their amides. The

amount of ethylene oxide which is condensed with the reactive hydrogen containing compound will depend primarily on the hydrophobic nature of the particular organic compound with which it is condensed. As a convenient rule of thumb an amount of ethylene oxide should be employed which will produce a condensation product containing about 10 to 99.9% by weight of ethylene oxide. However, the amount of ethylene oxide required to obtain the desired hydrophobic-hydrophilic balance in a compound for a particular aerated drilling operation may be determined by preliminary tests or experiments.

A preferred group of nonionic surfactants which may be employed in preparation of phosphate esters for use in this invention is the group derived from phenol and alkylphenol compounds. Members of this group, i.e., polyoxyethylene oxide derivatives of phenolic compounds containing one or more alkyl substituents are described in U.S. Patents 2,213,477 and 2,593,112. Among those prefererd are the polyoxyethylene derivatives of alkylphenols in which the total number of alkyl carbon atoms in the phenolic compound is from 1 to 36 carbon atoms. As examples of such alkylphenols there may be mentioned cresols, ethylphenols, propylphenols, butylphenols, amylphenols, hexylphenols, heptylphenols, octylphenols, nonylphenols, decylphenols, dodecylphenols, tetradecylphenols, octadecylphenols, their mixtures or their isomers. The polyoxyethylene derivatives of secondary alkylphenols obtained by alkylating phenols or cresols with α-olefins of the type obtained by condensation of ethylene in the presence of Ziegler type catalysts or by wax cracking techniques are of particular value. α-Olefins useful in preparation of these alkylphenols may contain odd or even number carbon atoms which may be an advantage in many applications. Mixtures of α-olefins having various ranges of carbon atoms such as C_6–C_7, C_7–C_9, C_9–C_{11}, C_{11}–C_{15}, C_{15}–C_{20} and higher may be used in the preparation of these alkylphenols. Olefins containing even number carbon atoms such as those derived from fats are also useful. Alkylphenols such as m-pentadecylphenol may also be used. In the preparation of these various phenols, olefins obtained by polymerization of low molecular weight olefins such as propylene, butylene, amylene, their isomers or their mixtures may be used. Likewise, the di and trialkyl substituted derivatives of the aforementioned alkylphenols may be used. Among the substituted phenols that may be employed to produce nonionic surfactants for conversion to phosphate esters to accomplish the objects of this invention, there may be mentioned cresol, butylphenol, hexylphenol, diisobutylphenol, nonylphenol, nonylcresol, dodecylphenol, diamylphenol, didodecylphenol, dinonylcresol, tri-t-butylphenol, trinonylphenol, octadecylphenol, dioctadecylphenol and o-phenylphenol.

Another preferred group of nonionic surfactants which may be employed in preparing phosphate esters for use in the process embodied in this invention are the polyoxyethylene derivatives of alcohols containing from 6 to 27 carbon atoms. These include polyoxyethylene derivatives of hexyl alcohol, octyl alcohol, decyl alcohol, dodecyl alcohol, tetradecyl alcohol, hexadecyl alcohol, octadecyl alcohol, docosyl alcohol, heptacosyl alcohol, their isomers or their mixtures. The alcohols used in these surfactants may be produced by a variety of methods.

One of the common methods for synthesis of alcohols for use in synthesis of these nonionic surfactants is by hydrogenation of fatty acids or glycerides obtained from animal or vegetable oils and waxes such as coconut oil, castor oil, tall oil, peanut oil, menhaden oil, sperm oil, tallow or the like. Alcohols derived from these materials include lauryl alcohol, oleyl alcohol, stearyl alcohol, tallow alcohols or the like.

Another method for preparation of alcohols that are useful in synthesis of nonionic surfactants is the Oxo process. This process involves catalytic reaction of α-olefins with carbon monoxide and hydrogen under pressure

to give primary aliphatic alcohols which have branched chains. α-Olefins of the type described above as well as olefin polymers such as dimers, trimers, tetramers, and pentamers obtained by polymerization of low molecular weight olefins may be used in the Oxo process. Polyolefins which may be employed in the Oxo process include tripropylene, tetrapropylene, pentapropylene, propylene-isobutylene, triisobutylene and tetraisobutylene. Alcohols from the Oxo process are obtained as mixtures and may be used as mixtures. Such Oxo alcohol mixtures include those of isooctyl alcohols, decyl alcohols, tridecyl alcohols, pentadecyl alcohols or heptadecyl alcohols.

A third method for producing alcohols which are useful in the synthesis of nonionic surfactants is by polymerization of ethylene with Ziegler type catalysts and subsequent reaction of the metal alkyls formed by this polymerization to obtain mixtures of straight chain alcohols of the type known as the Alfols (Continental Oil Company). Alcohols prepared by this method may be used as mixtures or specific alcohols may be separated and used individually. Examples of alcohols produced by this method include hexyl alcohol, octyl alcohol, decyl alcohol, higher alcohols or mixtures of these alcohols.

In addition to the above described nonionic surfactants, poyoxyethylene derivatives of organic mercapto compounds such as the products described in U.S. Patent 2,205,021, i.e., the polyoxyethylene derivatives of mercapto compounds such as dodecyl mercaptan, oleyl mercaptan, cetyl mercaptan, benzomercaptan, thiophenols or thionaphthols may be used. Other useful polyoxyethylene derivatives include the carboxylic acid amide derivatives described in U.S. Patent 2,085,706 and the sulfonamide derivatives described in U.S. Patent 2,002,613. Polyoxyethylene derivatives of aliphatic organic compounds such as those obtained from higher fatty acids and hydroxy fatty acids may also be used.

The following nonionic surfactants may be employed as reactants in the preparation of phosphate esters useful in the process disclosed in this invention. In the illustrations of these nonionic surfactants, E.O. means ethylene oxide; the number immediately preceding each formula refers to the number of moles of oxide thereof reacted with one mole of the given reactive hydrogen containing compound. Such nonionic surfactants include phenol+3 E.O., dioctadecylphenol+10 E.O., phenol+10 E.O., o-cresol+20 E.O., diisobutylphenol+30 E.O., nonylphenol+6 E.O., diamylphenol+8 E.O., dodecylphenol+20 E.O., diamylphenol+150 E.O., hexylphenol+15 E.O., octadecylphenol+20 E.O., nonylphenol+50 E.O., trinonylphenol+100 E.O., dioctadecylphenol+150 E.O., tall oil+18 E.O., castor oil+60 E.O., lauryl alcohol+40 E.O., isooctyl alcohol (Oxo alcohols)+5 E.O., decyl alcohol (Oxo alcohols)+15 E.O., tridecyl alcohol (Oxo alcohols)+9 E.O., tallow alcohol+30 E.O., stearyl alcohol+20 E.O., t-butylphenol+18 E.O., phenol+12 E.O., n-hexyl alcohol+11 E.O., isooctyl alcohol+50 E.O., stearyl alcohol+140 E.O., or octadecyl alcohol (Alfol alcohols)+150 E.O.

Phosphate esters derived from the above nonionic surfactants may be prepared by a variety of methods. Numerous methods for the preparation of phosphate esters may be found in patents and other publications. Generally, we prefer to use one of the three following methods.

The first method involves reaction of 1 mole of P_2O_5 with 2 to 4.5 moles of nonionic surfactant as described and claimed in U.S. Patent 3,004,056 by Nunn and Hesse and in U.S. Patent 3,004,057 by Nunn. As disclosed in these patents, reaction between P_2O_5 and nonionic surfactant is conducted under substantially anhydrous conditions at temperatures below 110° C. This method gives mixtures of mono- and di-substituted phosphate esters.

The second method for preparing phosphase esters useful in the present invention is that disclosed in the copending application of Papalos, Serial Number 243,721 filed December 11, 1962. In this method, from 1 to 3 moles of P_2O_5 are reacted with 1 mole of nonionic surfactant in the presence of a small amount of water or a mineral acid at temperatures from 120° to 200° C. This method favors the formation of mono-substituted phosphate esters.

The third preferred method for producing phosphates is that disclosed in the copending application of Nehmsmann, Nunn and Schenck Serial Number 275,222 filed April 24, 1963. This method involves oxidation of mono-, di- or tri-substituted phosphites to the corresponding phosphates. In this method the phosphite is oxidized to a phosphate by use of elemental oxygen in the presence of a small amount of peroxide as a catalyst at temperatures between 25° and 200° C. This method may be used to produce mono-, di-, or tri-substituted phosphate esters in high states of purity as well as mixtures of these esters in which the concentration of each of these three types of esters may be maintained within close limits. The three methods for preparation of phosphate esters described in these patents and copending applications as well as the complete disclosures and teachings therein are herein incorporated by reference.

The above described mono- and di-substituted phosphate esters may be used in this invention in their free unneutralized form or in the form of partially or completely neutralized salts containing as cations, alkali metals, alkaline earth metals, other metals, ammonium or organic amines. Frequently it may not be necessary to neutralize the phosphate ester because the drilling fluid itself may be alkaline. However, sometimes it may be preferable or necessary to neutralize the phosphate ester before use. It is to be understood that such salts are to be regarded as equivalents of the phosphate esters in their free form. As examples of suitable cations for neutralizing the mono- and di-substituted phosphate esters, there may be mentioned sodium, potassium, lithium, calcium, strontium, barium, magnesium, iron, tin, cadmium, aluminum, antimony, chromium, manganese, mercury, nickel, ammonia or organic amines such as mono, di, and trimethylamines, ethylamines, propylamines, butylamines, hexylamines, octylamines, decylamines, laurylamines, stearylamines, ethanolamines, propanolamines, butanolamines, hexanolamines, cyclohexylamines, phenylamines, pyridine, morpholine or the like.

In some aerated drilling applications it may be an advantage to use phosphate esters of polyoxyethylene ethers derived from hydrophobic materials such as crude alkylation mixtures containing mixed phenols and unreacted olefins, alkylation mixtures which have been stripped to remove unreacted olefins, residues from distillation of alkylation mixtures in which high boiling polyalkylphenols are present, crude alcohol mixtures prepared by the alcohol syntheses described above or alcohol mixtures containing dissimilar alcohols. The advantages of such compositions are well known to those skilled in surfactant chemistry. Frequently hydrophobic materials containing isomers of dissimilar compounds when alkoxylated and phosphated have unusual surfactant properties. Examples of such compositions include the polyoxyethylene ethers of alkylation mixtures of nonylphenol, still bottoms from dodecylphenol alkylations, alcohol mixtures obtained from cataytic hydrogenation of natural products such as vegetable and animal oils, or alcohol mixtures obtained from the alcohol processes described above.

Combinations of phosphate esters having different ethylene oxide contents also have certain advantages. Esters containing from 3 to 15 moles of ethylene oxide are very effective lubricants while those containing from 15 to 150 moles of ethylene oxide are very effective foaming agents. It is possible to obtain combinations of these two types of phosphate esters which have improved lubrication and foaming properties by combining those having outstanding lubricating properties with those having outstanding foaming properties.

Phosphate esters prepared by the processes disclosed in the above patents and copending applications may also contain unreacted nonionic surfactants. The presence of nonionic surfactant in phosphate esters may be an advantage in some applications. The nonionic surfactant may function as an auxiliary surfactant to improve emulsification or other properties of the foam used in aerated drilling. It is possible in some applications that benefits may be realized by adding a dissimilar nonionic surfactant to the phosphate ester. It will be understood that these modifications are to be included in the scope of the present invention.

The following examples are illustrative of this invention and are not to be regarded as limitative. It will be understood that all parts and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

EXAMPLE 1

The Shake Foam and the Air Diffusion Tests were used to evaluate the foaming properties of a group of phosphate ester surfactants in the four systems described above (i.e., Systems A, B, C and D respectively). Tables I–IV (inclusive) give results of these tests. Phosphate esters used in these tests were prepared by the method disclosed in U.S. Patent 3,004,057.

In these tables the composition of each phosphate ester is shown under the caption Phosphate Ester in terms of the formula of the particular nonionic surfactant used in its synthesis such as dodecylphenol+2 E.O. in which E.O. represents ethylene oxide and 2 the number of moles of E.O. reacted with the particular reactive hydrogen containing organic compound, dodecylphenol used to produce the nonionic surfactant. Unless otherwise indicated, the molar ratio used in these ester syntheses was 2.7 moles of nonionic surfactant per mole of P_2O_5 and the esters were evaluated in their unneutralized forms.

Several factors were considered in analysis of the foam data in Tables I–IV. The Shake Foam Test measured initial foaming properties as well as foam stability. Esters which produced large volumes of foam initially and showed little if any change in foam volume after 15 minutes standing were considered to be very effective foaming agents. Foam Nature in the table describes the general appearance of the foam and its bubble size. One of the preferred types of foam is heavy foam having small bubble size which is designated as HF in the tables. The Air Diffusion Test is a dynamic test which measures the time required to produce the indicated volume of foam. If a foaming agent produced 800 ml. of foam within five minutes or less, it was considered to be a very efficient foaming agent.

Analysis of the data in the four tables showed that phosphate esters prepared from nonionic surfactants containing large numbers of moles of E.O. produced 800 ml. of foam in shorter periods of time than those containing small numbers of moles of E.O. Although esters containing smaller numbers of moles of E.O. were not as efficient as foaming agents, they were very effective lubricants. It was possible to prepare combinations of esters containing smaller numbers of E.O. with those esters containing larger numbers of moles of E.O. to produce mixtures which had the desirable properties of both types of esters. These esters containing smaller numbers of moles of E.O. also had the added advantage that they functioned as foam stabilizers.

TABLE I.—FOAMING PROPERTIES

Foaming Agent, Phosphate Ester	System A: 1% Foaming Agent+99% of 20% Salt Solution—Air Diffusion Test			
	Fog Nature [1]	Foam, ml.	Air, cc./min.	Time, min.
Dodecylphenol+2 E.O	LL	25	2,600	5.00
Dinonylphenol+7 E.O	LL	550	1,400	5.00
Dinonylphenol+15 E.O	MM	800	270	3.67
Nonylphenol+15 E.O	HS	800	270	2.93
Nonylphenol+30 E.O	HS	800	270	2.89
Nonylphenol+50 E.O	HS	800	270	2.00
Nonylphenol+100 E.O	HS	800	270	2.71
Tridecyl alcohol+6 E.O	HS	800	270	2.68
Tridecyl alcohol+15 E.O	HS	800	270	2.65
Dodecylphenol+18 E.O	HS	800	270	2.53
Nonylphenol+4 E.O [2]	HS	800	270	2.73

[1] Where the symbols used have the following meanings: LL—light foam, large bubble; LM—light foam, medium bubbles; LS—light foam, small bubbles; ML—medium foam; large bubbles; MM—medium foam, medium bubbles; MS—medium foam, small bubbles; HL—heavy foam, large bubbles; HM—heavy foam, medium bubbles; HS—heavy foam, small bubbles.

[2] Sodium salt of molar ratio: 4 nonionic/P_2O_5.

TABLE II.—FOAMING PROPERTIES

Foaming Agent, Phosphate Ester	System B: 1% Foaming Agent+99% of 20% Saturated Lime Solution—Air Diffusion Foam Test			
	Foam Nature [1]	Foam, ml.	Air, cc./min.	Time, min.
Dodecylphenol+2 E.O	LL	----------	2,600	5.00
Dinonylphneol+7 E.O	LL	800	270	2.60
Dinonylphenol+15 E.O	MM	800	270	2.44
Nonylphenol+15 E.O	HS	800	270	2.62
Nonylphenol+20 E.O	HS	800	270	2.80
Nonylphneol+30 E.O	HS	800	270	2.38
Nonylphenol+50 E.O	HS	800	270	2.56
Nonylphenol+100 E.O	HS	800	270	2.79
Tridecyl alcohol+6 E.O	HS	800	270	2.50
Tridecyl alcohol+15 E.O	HS	800	270	2.69
Dodecylphenol+18 E.O	HS	800	270	2.42
Nonylphenol+4 E.O [2]	HS	800	270	2.80

[1] Where the symbols used have the following meanings: LL—light foam, large bubbles, LM—light foam, medium bubbles; LS—light foam, small bubbles; ML—medium foam; large bubbles; MM—medium foam, medium bubbles; MS—medium foam, small bubbles, HL—heavy foam, large bubbles; HM—heavy foam, medium bubbles; HS—heavy foam; small bubbles.

[2] Sodium salt of molar ratio: 4 nonionic/P_2O_5.

TABLE III.—FOAMING PROPERTIES

Foaming Agent, Phosphate Ester	System C: 1% Foaming Agent+10% Diesel No. 2+89% of 20% Salt Solution						
	Shake Foam Test, ml.			Air Diffusion Test			
	0 min.	2 min.	5 min.	Foam [1] Nature	Foam, ml.	Air, cc./min.	Time, min.
Dodecylphenol+2 E.O	10	0	0	LL	600	2,600	5.00
Dinonylphenol+7 E.O	8	1	0	LL	----------	2,600	5.00
Dinonylphenol+15 E.O	22	6	3	MM	620	2,600	5.00
Nonylphenol+15 E.O	23	14	14	LL	700	3,600	5.00
Nonylphenol+20 E.O	24	10	5	LL	800	2,600	0.81
Nonylphenol+30 E.O	40	25	23	HS	800	2,600	0.86
Nonylphenol+50 E.O	28	15	13	HS	800	270	3.26
Nonylphenol+100 E.O	18	16	14	HS	800	270	2.92
Tridecyl alcohol+6 E.O	3	1	0	LL	60	2,600	5.00
Tridecyl alcohol+15 E.O	30	15	9	MM	800	2,600	0.99
Dodecylphenol+18 E.O	30	4	2	MM	800	2,600	0.48
Nonylphenol+4 E.O.[2]	5	1	0	HS	----------	2,600	5.00

[1] Where the symbols used have the following meanings: LL—light foam, large bubble; LM—light foam, medium bubble; LS—light foam, small bubble; ML—medium foam, large bubble; MM—medium foam, medium bubble; HL—heavy foam, large bubble; HM—heavy foam, medium bubble; HS—heavy foam, small bubble.
[2] Sodium salt of molar ratio: 4 nonionic/P_2O_5.

TABLE IV.—FOAMING PROPERTIES

Foaming Agent, Phosphate Ester	System D: 1% Foaming Agent+10% Diesel No. 2+89% Saturated Lime Solution						
	Shake Foam Test, ml.			Air Diffusion Test			
	0 min.	2 min.	5 min.	Foam [1] Nature	Foam, ml.	Air, cc./min.	Time, min.
Dodecylphenol+2 E.O	17	15	14	LL	70	2,600	5.00
Dinonylphenol+7 E.O	3	0	0	LL	50	2,600	5.00
Dinonylphenol+15 E.O	15	0	0	MM	----------	2,600	5.00
Nonylphenol+15 E.O	12	1	0	LL	400	2,600	5.00
Nonylphenol+20 E.O	25	20	10	MM	800	2,600	0.38
Nonylphenol+30 E.O	35	30	25	HS	800	2,600	0.56
Nonylphenol+50 E.O	22	2	0	LS	800	2,600	2.49
Nonylphenol+100 E.O	45	35	34	MS	800	2,600	0.94
Tridecyl alcohol+6 E.O	5	2	2	LL	50	2,600	5.00
Tridecyl alcohol+15 E.O	20	1	0	MM	800	2,600	0.56
Dodecylphenol+18 E.O	30	6	4	MM	800	2,600	0.33
Nonylphenol+4 E.O.[2]	1	0	0	LL	200	2,600	5.00

[1] Where the symbols used have the following meanings: LL—light foam, large bubble; LM—light foam, medium bubble; LS—light foam, small bubble; ML—medium foam, large bubble; MM—medium foam, medium bubble; MS—medium foam, small bubble; HL—heavy foam, large bubble; HM—heavy foam, medium bubble; HS—heavy foam, small bubble.
[2] Sodium salt of molar ratio: 4 nonionic/P_2O_5.

EXAMPLE 2

A phosphate ester derived from the nonionic surfactant, nonylphenol+100 E.O. was prepared by the method described in Example 1 using a molar ratio of a 2.5 mole of nonionic surfactant per mole of P_2O_5. This phosphate ester was evaluated in System D against its precursor nonionic surfactant, nonylphenol+100 E.O. Both Shake Foam and Air Diffusion Tests were made. Results of these tests are tabulated below. The phosphate ester used in these tests is designated in this tabulation as phosphate ester and the nonionic surfactant as nonionic. Results of these tests demonstrated the superiority of the phosphate ester over the nonionic surfactant.

	Shake Foam Test, ml.			Air Diffusion Test		
	0 min.	2 min.	5 min.	Foam, ml.	Air, cc./min.	Time, min.
Phosphate ester	45	35	34	800	2,600	0.94
Nonionic	33	26	13	800	2,600	2.16

EXAMPLE 3

A phosphate ester obtained by reacting 4 moles of the nonionis surfactant, nonylphenol+20 E.O. with 1 mole of P_2O_5 by the method described in Example 1 was evaluated in System C by the Shake Foam and Air Duffusion Tests. Comparable tests were made with a nonionic surfactant, crude dinonylphenol+17 E.O. which has been used in field aerated drilling operations. Results of these tests are tabulated below. The phosphate ester is designated as phosphate ester and the nonionic surfactant as nonionic. These tests demonstrated the advantages of the phosphate ester over the nonionic surfactant.

	Shake Foam Test, ml.			Air Diffusion Test		
	0 min.	2 min.	5 min.	Foam, ml.	Air, cc./min.	Time, min.
Phosphate ester	24	10	5	800	2,600	0.81
Nonionic	10	3	0	400	2,600	5.00

EXAMPLE 4

A phosphate ester of the nonionic surfactant, nonylphenol+50 E.O. was prepared by reacting 2 moles of surfactant with 1 mole of P_2O_5 by the method described in Example 1. This phosphate ester was evaluated in System D against the nonionic surfactant used in its synthesis. Results of Air Diffusion Tests tabulated below show the superiority of the phosphate ester over its precursor, the nonionic surfactant. In this tabulation the phosphate ester is designated as phosphate ester and the nonionic surfactant as nonionic.

	Air Diffusion Test		
	Foam, ml.	Air, cc./min.	Time, min.
Phosphate ester	800	2,600	2.49
Nonionic	750	2,600	5.00

EXAMPLE 5

A phosphate ester of the nonionic surfactant, nonylphenol+30 E.O. was prepared by reacting 2.5 moles of nonionic surfactant with 1 mole of P_2O_5 by the method described in Example 1. Shake Foam and Air Diffusion Test data were made in System C with this ester and a nonionic surfactant, crude dinonylphenol+17 E.O. Data from these tests are tabulated below. These data show the advantages of the phosphate ester over the nonionic surfactant. In this tabulation, phosphate ester is used to designate the phosphate ester and nonionic the nonionic surfactant.

	Shake Foam Test, ml.			Air Diffusion Test		
	0 min.	2 min.	5 min.	Foam, ml.	Air, cc./min.	Time, min.
Phosphate ester	40	25	23	800	2,600	0.86
Nonionic	10	3	0	400	2,600	5.00

EXAMPLE 6

A phosphate ester of the nonionic surfactant, nonylphenol+100 E.O. was prepared by the method disclosed in the copending application of Papalos, Serial Number 243,721 filed December 11, 1962. This ester was prepared by reaction of 1 mole of the nonionic surfactant, nonylphenol+50 E.O. with 3 moles of P_2O_5. It was then adjusted to a pH of 11.6 with soda ash and evaluated in System C. Data from Air Diffusion Tests with this ester at various air diffusion rates at 80° C. are given below.

These data show the ester to be a very effective foaming agent.

Air diffusion tests.—Foam production at 80° C.

Air diffusion rate, cc./min.:	Time required to produce 800 cc. foam, min.
850	0.93
1040	0.76
1480	0.56
2070	0.42
2385	0.31

EXAMPLE 7

A 1% (by weight) mixture of the tri (nonylphenol+30 E.O.) phosphate ester in 10% brine (by weight) was prepared. This phosphate ester was synthesized by the method disclosed in the copending application of Nehmsmann, Nunn and Schenck, Serial No. 275,222, filed April 24, 1963. Foam producing properties of this mixture were evaluated in the following manner. A 500 ml. graduate was equipped with an air line attached to a diffusing stone placed near the bottom of the inside of the graduate so that air could be diffused through the stone at the rate of 500 ml./min. A polyethylene collar was placed around the graduate so that the foam which overflowed the graduate could be collected and broken in the collar with a defoaming agent. This collar was also equipped with a drain tube so that any liquid collecting in the collar would drain into a second graduate where the liquid could be measured.

A 500 ml. of aliquot of the mixture was placed in the graduate equipped with the diffusing stone. Air was diffused through the mixture. The foam which was produced and overflowed into the collar was broken with a defoaming agent. The liquid, which was obtained from breaking the foam, was allowed to drain into the second graduate and measured at 5 minute intervals. Results of this test are tabulated below and show the foam producing properties of trisubstituted phosphate esters.

Time (min.)	5	10	15	20
Ml. liquid removed as foam	395	435	450	455

EXAMPLE 8

The lubrication properties of the phosphate ester of the nonionic surfactant, dinonylphenol+7 moles of ethylene oxide described in Example 1 were evaluated by the Four Ball Test Method. These tests were made with a base oil which gave an S.D. (scar diameter) of 0.63 with a 40 kg. load at 600 r.p.m. for 60 minutes at room temperature. Addition of 7 lbs./bbl. of the phosphate ester to the base oil gave an S.D. of 0.37 under the same conditions. Similar tests with the nonionic surfactant, di-

nonylphenol+7 moles of ethylene oxide in the base oil gave an S.D. of 0.51. These tests demonstrated the superior lubricating properties of the phosphate ester.

Comparable results were obtained with the trisubstituted phosphate ester prepared by the method disclosed in the copending application of Nehmsmann, Nunn and Schenck Serial No. 275,222, filed April 24, 1963.

EXAMPLE 9

Lubrication tests similar to those described in Example 8 were made with the same phosphate ester at 20 and 40 kg. loads by using the Four Ball Test Method. These tests were made in a commercial 100 SUS neutral solvent refined base oil at 600 r.p.m. for 60 minutes at room temperature. Results of these studies are given in Table V and show the lubricating properties of the phosphate ester at these two loads.

TABLE V.—FOUR BALL WEAR TESTS ON PHOSPHATE ESTERS OF THE INDICATED NONIONIC SURFACTANTS

Phosphate Ester	Molar Ratio Nonionic/ P_2O_5	lb./bbl.	Load, kg.	S.D. [1]
Oil		0.0	20	0.51
		0.0	40	0.63
Dinonylphenol+7 E.O	2.7:1	7.0	20	0.20
	2.7:1	7.0	40	0.37

[1] Scar diameter (mm.).

EXAMPLE 10

Similar lubrication tests were made using the Four Ball Test Method. Four Ball Wear data obtained with aqueous solutions of phosphate esters prepared by the procedure given in Example 1 are shown in Table VI. These data were obtained from tests made with the indicated loads at 600 r.p.m. for 60 minutes at room temperature. These data show the improvements in lubrication which were obtained when phosphate esters were added to water. When the tests were made in water without phosphate esters, all of the water boiled out of the test cup and the balls welded together. When a test was made with a solution of the nonionic surfactant, dinonylphenol+15 E.O. at 14.0 lbs./bbl., the ball squealed after 40 minutes and the test was stopped. At this point, the balls had an average S.D. of 1.3 mm. This test further demonstrated the advantage of phosphate esters over nonionic surfactants as lubricants.

TABLE VI.—FOUR BALL WEAR TESTS ON PHOSPHATE ESTERS OF THE INDICATED NONIONIC SURFACTANT

Phosphate Ester	Molar Ratio Nonionic/ P_2O_5	lb./bbl.	Load, kg.	S.D. [1]
Water	0.0	0.0	20	[2] Welding.
	0.0	0.0	40	[2] Welding.
Dinonylphenol+15 E.O[3]	2.7:1	14.0	20	0.90
	2.7:1	14.0	40	0.90
Nonylphenol+6 E.O[4]	4.0:1	7.0	20	0.87

[1] Scar diameter (mm.).
[2] All of the water boiled out of the test cup and balls welded together.
[3] As the sodium salt at 50% activity.
[4] As the sodium salt at 90% activity.

EXAMPLE 11

Similar Four Ball lubrication tests were made with an aqueous solution of a phosphate ester prepared by the method disclosed in the copending application of Papalos, Serial No. 243,721 filed December 11, 1962, in the Four Ball Test Method. These tests were made with a 40 kg. load at 600 r.p.m. and 150° F. for 30 minutes. The nonionic surfactant used in the preparation of the phosphate ester for these tests was obtained by condensing nonylphenol with 50 moles of ethylene oxide. The phosphate ester was obtained by reacting 1 mole of this nonionic surfactant with three moles of P_2O_5 at 130° by the method described above. The phosphate ester was essentially a monoester. A Four Ball Wear Test on a solution containing 1.75 lb./bbl. of this ester gave an S.D. of 1.2 mm. and a C.O.F. (coefficient of friction) of 0.336. Similar tests on a solution containing 35 lb./bbl. solution gave an S.D. of 0.8 mm. and a C.O.F. of 0.226.

EXAMPLE 12

Water solutions of triethanolamine salts of phosphate esters of nonionic surfactants were evaluated by the Falex Load Test Method. These tests were made to determine the properties of these esters as extreme pressure lubricants. Results of these tests are shown in Table VII. The tests were made in the following manner. An initial load of 250 lb. was applied to the test solution and the solution held under this load for one minute. The load was then increased by 250 lb. increments and the solution tested at each successive increment for one minute. The point at which decrease in applied load was noted in any one minute test was the point at which initial wear begins and is shown in the table as Wear-Begins. The test was continued until either a failure load or the maximum load of 4500 lb. was reached. The failure load was the point at which either the brass pin sheared or the Falex pin sheared. These tests were at 100° F.

TABLE VII.—FALEX LOAD TESTS ON TRIETHANOLAMINE SALTS OF PHOSPHATE ESTERS OF THE INDICATED NONIONIC SURFACTANTS

Phosphate Ester	Molar Ratio Nonionic/ P_2O_5	lb./bbl.	Wear-Begins Load, lb.	Failure Load, lb.
Dinonylphenol+7 E.O	2.7:1	1.8	3,000	4,500+
	2.7:1	0.9	4,000	4,500+
Nonylphenol+4 E.O	2.7:1	1.8	2,500	4,500+
	2.7:1	0.9	3,000	4,500+
	2.7:1	0.3	3,250	3,500
Tridecyl alcohol+3 E.O	2.7:1	1.8	3,500	4,500+
	2.7:1	0.9	3,250	4,500+
	2.7:1	0.3	2,750	3,500

EXAMPLE 13

The Modified ASTM Method D665–60 procedure was used to measure the corrosion protection obtained with phosphate esters in a mixture of depolarized isooctane and brine (synthetic sea water). The conditions used in this synamic test were 20 hours at 80° F. Neither the ammonium nor t-butylamine salt of a phosphate ester obtained by reacting 2.7 moles of the nonionic surfactant, nonylphenol+4 E.O. with 1 mole of P_2O_5 by the method described in Example 1 showed any visible evidence of corrosion at 100 p.p.m. Comparable results were obtained with a phosphate ester derived from the nonionic surfactant, tridecyl alcohol+3 E.O. under the same conditions. A similar test was made as a control without additive. In this control test, 90 to 100% of the area of the steel spindle used as the test specimen was found to be covered with heavy rust.

The foregoing examples demonstrate that foam production during drilling may be improved, friction on drilling tools may be reduced and corrosion of drilling tools may be decreased by use of phosphate esters as foaming agents in aerated drilling fluids employed in aerated drilling processes for subsurface boreholes.

This invention has been disclosed with respect to certain preferred embodiments. Other modifications and variations thereof will become obvious to persons skilled in the art. It is to be understood that such modifications and variations are to be included within the spirit and scope of the present invention.

What is claimed is:

1. In a process of drilling a well wherein there is circulated through the well during said drilling a drilling fluid into which gases are injected to produce foam for carrying cuttings from the well; the improvement which comprises incorporating in said drilling fluid as a foaming agent, antiwear agent and corrosion inhibition agent, a minor amount of a phosphate selected from the group consisting of

(1) mono- and
(2) di-esters and
(3) tri-esters and
(4) mixtures thereof of phosphoric acid with a nonionic surfactant derived by condensation of
(5) an organic compound containing at least 6 carbon atoms and containing a reactive hydrogenatom and
(6) at least three moles of ethylene oxide,

to improve fluid displacement during drilling, to reduce friction on the drilling tools and to decrease corroson of the drilling tools to thereby improve the efficiency of the drilling process and extend the life of said drilling tools.

2. A process as defined in claim 1 wherein from 0.5 to 7 pounds of phosphate ester per barrel of injection water is used.

3. A process as defined in claim 1 wherein said organic compound of at least 6 carbon atoms is selected from the group consisting of phenols and aliphatic alcohols.

4. A process as defined in claim 1 wherein said organic compound is a phenol containing at least 6 carbon atoms.

5. A process as defined in claim 1 wherein said organic compound is an alcohol containing at least 6 carbon atoms.

6. A process as defined in claim 1 wherein said organic compound of at least 6 carbon atoms is condensed with at least 3 moles of ethylene oxide.

7. A process as defined in claim 1 wherein said organic compound is an alcohol containing at least 6 carbon atoms and is condensed with at least 3 moles of ethylene oxide.

8. A process as defined in claim 1 wherein said organic compound is nonylphenol and is condensed with at least 3 moles of ethylene oxide.

9. A process as defined in claim 1 wherein said organic compound is dinonylphenol and is condensed with at least 3 moles of ethylene oxide.

10. A process as defined in claim 1 wherein said organic compound is dodecylphenol and is condensed with at least 3 moles of ethylene oxide.

11. A process as defined in claim 1 wherein said organic compound is tridecyl alcohol and is condensed with at least 3 moles of ethylene oxide.

12. A process as defined in claim 1 wherein said organic compound is stearyl alcohol and is condensed with at least 3 moles of ethylene oxide.

13. A process as defined in claim 1 wherein said organic compound is a monoester of phosphoric acid.

14. A process as defined in claim 1 wherein said organic compound is a diester of phosphoric acid.

15. A process as defined in claim 1 wherein said organic compound is a triester of phosphoric acid.

16. In a process of drilling a well wherein there is circulated through the well during said drilling a drilling fluid into which gases are injected to produce foam for carrying cuttings from the well; the improvement which comprises incorporating in said drilling fluid as a foaming agent, antiwear agent, and corrosion inhibiton agent, a minor amount of a phosphate selected from the group consisting of

(1) mono- and
(2) di-esters and
(3) tri-esters and
(4) mixtures thereof of phosphoric acid with a nonionic surfactant derived by condensation of
(5) an organic compound containing from 6 to 36 carbon atoms and containing a reactive hydrogen atom and
(6) from 3 to 150 moles of ethylene oxide,

to improve fluid displacement during drilling, to reduce friction on the drilling tools and to decrease corrosion of the drilling tools to thereby improve efficiency of the drilling process and extend the life of said drilling tools.

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