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# FREEING STUCK PIPE

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This invention relates to improvements in well operations wherein a rotary drill stem penetrates a permeable formation, a well fluid is circulated through the well, a cake of solids from the well fluid builds up on a wall of the well in the permeable formation and a pressure differential between hydrostatic pressure of the well fluid and pressure in the permeable formation forces the drill stem strongly against the cake of solids and causes the stem to stick when its rotation is stopped for any reason. In one aspect this invention relates to an improvement in processes for freeing such stuck drill stems; in another aspect it relates to improvements in fluids for freeing stuck drill stems and in still another aspect it relates to novel additives for petroleum oil effective to enhance greatly the ability of the petroleum oil to free a pipe stuck by such differential pressure.

Drill stem sticking is a very serious problem in the deep well drilling industry. For example, an article in the Oil and Gas Journal for September 19, 1960, volume 58, Number 38, pages 105 and following, reporting experience with drilling 1,161 oil and gas wells below 10,000 feet in southwest Louisiana, shows that 275 cases of drill stem sticking were encountered. In only 37 percent of these cases was it possible to recover drill strings completely. In an additional 32 percent of the cases, it was possible to complete the well by sidetracking the stuck drill string or partially recovering the drill string and sidetracking. An additional 26 wells, or about 10 percent, were completed by drilling through the stuck drill string or were plugged back and completed higher up; but 21 percent of the wells had to be abandoned as economically not feasible to continue drilling. While these figures are given for southwest Louisiana, California and other sections have reported somewhat similar difficulties due to drill stem sticking. For example, a single company in California has reported increased drilling costs of about $440,000.00 annually due to stuck drill stems.

Jars have been used for releasing such stuck pipes and these are sometimes effective. Another method for freeing the pipe that has been used widely in the past is passing a washover pipe around the drill stem in an attempt to cut the cake away, thus freeing the drill stem. Sometimes this method is effective, but it frequently happens that the wash pipe also becomes stuck, increasing the problem.

An article in the Oil and Gas Journal, Volume 55, Number 24, June 17, 1957, pages 132–136, has suggested that drill pipe be coated with a silicone resin, or that a wetting agent be added to a petroleum oil such as kerosene, diesel oil, crude oil, etc. and that the well bore outside drill stem be filled with such oil to free the stem. The principle of operation is the formation of a monomolecular film of oil on the drill stem thus providing an oil coating between the drill stem and the cake of water-wet well fluid solids. Since the cake of water-wet solids is impermeable to oil, filtration from the well bore into the cake is stopped; but filtration of water from the cake into the permeable formation continues. Decrease in water content of the cake causes the cake to shrink, and as it decreases in volume, petroleum oil from the well bore enters along the monomolecular layer of oil on the drill stem and relieves differential pressure. This process has been used, and it is also sometimes effective but frequently has failed to release stuck drill stems or similar piping or tools. A new approach to the problem and a more effective principle of operation is needed.

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It is an object of this invention to provide an improved process for freeing a drill stem stuck by differential pressure against a cake of water-wet well fluid solids on a wall of a well in a permeable formation in which the cake is cracked and penetrated by a petroleum oil base fluid and differential pressure on the stem is reduced.

Another object is to provide a process for freeing such stuck drill stems in which adhesion of that part of a cake of water-wet well fluid solids in contact with a drill stem to a wall of the well in the permeable formation is reduced, and at least a large portion of the cake is broken away from the wall of the well.

Another object is to provide a process for freeing such stuck drill stems in which shrinking and cracking of a cake of water-wet well solids on a wall of a well in a permeable formation are utilized in combination with capillary action to carry a petroleum oil deep into the cake to reduce differential pressure across the drill stem.

Another object is to provide such process in which hydrostatic pressure gradient from the well bore, through the cake of water-wet solids and into the permeable formation, is established, thus decreasing the differential pressure across the drill stem.

Another object is to provide an improved oil base fluid for filling a well bore outside a drill stem in a permeable formation where the stem is stuck by differential pressure which is effective in penetrating a cake of water-wet well fluid solids.

Another object is to provide an improved fluid of this class which is effective in dehydrating and cracking a cake of water-wet well fluid solids.

Still another object is to provide an improved additive for a petroleum oil for converting oil into a fluid for freeing stuck drill stems which is effective in dehydrating and cracking the cake.

Another object is to provide an additive for a petroleum oil for converting the oil into a fluid for freeing stuck drill stems which is highly effective in converting the petroleum oil into a fluid for freeing stuck drill stems, having low interfacial tension at an interface between the fluid and water, having dehydrating and cracking effect upon a cake of water-wet well fluid solids and having the property of forming water-in-oil emulsions.

Still another object is to provide such additive which is cheap, effective in small amounts and which is easily soluble in a petroleum oil.

Still another object is to provide an improved fluid for freeing stuck drill stems which contains substantially no suspended solids and is heavier than oil.

Other objects and advantages will become apparent to those skilled in the art from the following specification.

We have found that a drill stem pipe or well tool stuck against a cake of water-wet well fluid solids on a wall of a well bore in a permeable formation by differential hydrostatic pressure across the drill stem, pipe or tool may be released by substantially filling the well bore outside the drill stem in the permeable formation with a petroleum oil fluid having an interfacial tension at an interface between the fluid and water of less than 5 dynes per centimeter, preferably of less than 3 dynes per centimeter, and still better, of less than 2 dynes per centimeter.

The petroleum oil fluid is held in the well bore in contact with the cake for a period of time sufficient for the fluid to dehydrate, crack and penetrate the cake of water-wet well fluid solids, at least partially relieving differential pressure across said drill stem piping or tool by flow of fluid from the well bore into the cake through resulting cracks.

The petroleum oil fluid may be held in contact with the cake for an additional time during which it further dehydrates, cracks and penetrates the cake until the oil base fluid penetrates entirely through the cake and wets the surface of the permeable formation. Wetting the surface of the permeable formation with oil lowers the force of adhesion between the cake of water-wet solids and the face of the permeable formation so that the cake in contact with the drill stem has a strong tendency to break away from the surface of the formation while it continues to adhere to the drill stem.

Further holding of the petroleum base fluid in contact with the cake of water-wet solids results in penetration of the fluid into the permeable formation and establishes a differential pressure gradient from the bore of the well outside the drill stem through the cake and into the formation thus decreasing the differential pressure which forces the drill stem against the cake. Dehydration and cracking of the cake, accompanied by penetration of oil base fluid into it, also results in a change in friction between the cake and drill stem. As a result of some or all of these forces, the drill stem is loosened from its position against the wall of the bore.

Further holding of the petroleum base fluid in contact with the cake of water-wet solids results in penetration of the cake and free flow of the spotting fluid deep into the permeable formation. This flow into the formation, once the cake has been penetrated, is fairly rapid, in that the spotting fluid contains no solids to obstruct free flow and there is no tendency to water block the spotting oil, since interfacial tension between it and the formation water is essentially zero. Because of this positive flow of fluid deep into the formation, the pressure gradient is extended over a much longer range. Whereas the complete pressure differential between the well bore and formation pressure, which prior to spotting was extended over the relatively thin mud cake, is now extended from the bore hole to some point deep into the formation; and, in effect, the pressure of the formation immediately adjacent to the hole interface approaches that of the well bore. Because of this tendency toward equalization of pressure, differential pressure forcing the pipe against the formation is released.

In establishing the pressure gradient from the well bore through the cake into the formation, it should be noted that in the present invention penetration of the petroleum base fluid through the cracked cake is not limited to penetration through that portion of the cake against which the drill stem is stuck. Fluid penetrating through the cake at each side of this portion may penetrate freely into the formation and diffuse therein to a location behind the drill stem, setting up a pressure gradient from the bore of the well, through the cake and into the formation. While this pressure gradient probably is not a rectilinear one, it nevertheless is effective in substantially reducing the force with which the drill stem is held against the cake by hydrostatic pressure in the well bore.

After the petroleum oil base fluid has been held in the well bore in the permeable formation for a length of time sufficient for the fluid to dehydrate, crack and penetrate the cake, we prefer to work the pipe by conventional mechanical methods such as jarring in order to break the pipe away from the wall of the well bore.

The time required for the petroleum oil base fluid to dehydrate, crack and penetrate the cake cannot be estimated accurately but frequently may be from 30 minutes to several hours. It will depend upon the conditions present in the particular well such as the composition of the cake of water-wet well fluid solids, its permeability and other factors. Working the pipe as by jarring or by vibration may be begun at any time after the petroleum oil base fluid is spotted in the permeable formation.

Any suitable method for placing the petroleum oil base fluid in the well bore in the permeable formation may be used. One preferred method for filling the well bore in the permeable formation with the improved fluid of the present invention is to introduce a slug of such fluid into a well fluid circulating system and pump the slug of fluid followed by the mud used in filling the well down the drill stem and up through the well bore outside the drill stem to the desired location and stopping circulation when the fluid is in place. This manner of spotting fluids at particular locations in a well bore is well known to the art and is believed to need no further description in this specification.

The petroleum oil fluid used in this process contains an ionic oil soluble surface active agent capable of reducing interfacial tension at an interface between the oil and water to not more than 5 dynes per centimeter, preferably to not more than 3 dynes per centimeter, and still better, to not more than 2 dynes per centimeter. This material also must be present in quantity to reduce interfacial tension at such interface to values given above. The term "surface active agent" is used herein to include mixtures of surface active agents as well as single compounds.

The materials used are ionic; that is, either anionic or cationic and are oil soluble. The DuNouy tensiometer is widely used in determining the strength of interfacial tension and may be used for selecting any desired interfacial tension lowering agent from the many ionic oil soluble surface active agents known, in addition to the preferred materials specifically set forth below.

The preferred surface active agents of this invention are the group consisting of 2-heptadecenyl 4-4 dimethoxy 2 oxazoline, 2-heptadecenyl 4 methoxy 4 methyl 2 oxazoline, the sodium salt of dioctyl sulfosuccinate, and a mixture of a product made by acid cracking wool grease, and containing high molecular weight free fatty acids, esters and alcohols, with about one fourth its weight of the sodium salt of sulfated oleyl alcohol.

The oxazolines of the preferred group may be prepared according to processes described in U.S. Patents 2,905,644, 2,402,791, 2,372,409 and 2,372,410. These patents describe the preparation of a great many oxazolines which are ionic, oil soluble and have varying degrees of surface active power. Many of the oxazolines will be found to have sufficient surface active power to reduce interfacial tension at an interface between the petroleum oil and water to far less than 5 dynes per centimeter.

Another large class of well known surface active agents are the imidazolines. Many other broad, general classes of surface active agents are also known; and in our process, we contemplate the use of any ionic, oil soluble surface active agent which has the ability to so reduce interfacial tension at an interface between the petroleum oil and water to the required degree. These may be selected at will by making a simple measurement according to methods widely known and used in the art.

The acid cracked wool grease containing high molecular weight free fatty acids, esters and alcohols is at present a standard article of commerce under the trade name "degras" having the following specifications:

| | |
|---|---|
| Specific gravity 20° C./20° C. | 0.940–0.960. |
| Free fatty acid (as oleic acid) | 11.0–14.0%. |
| Moisture | 0.5–1.2%. |
| Ash | 0.1% maximum. |
| Melting point | 36.0°–44.0° C. |
| Flash point | 540° F. approximate. |
| Fire point | 570° F. approximate. |
| Saybolt viscosity at 210° F. | 155 seconds approximate. |
| Iodine value (Hanus) | 20.0–35.0. |
| Saponification number | 100.0–116.0. |
| Penetration at 77° F. unworked | 150–180 mm./10. |
| Penetration at 77° F. worked | 340–370 mm./10. |
| Solor ASTM (max.): | |
| 10% | 4.5. |
| 30% | Greater than No. 8. |

This material when used alone is not very effective in reducing the interfacial tension at an interface between petroleum oil and water and does not greatly decrease the force required to loosen a drill bit stuck by differential pressure against a water-wet cake of well solids; but when mixed with about one-fourth its weight of the sodium salt of sulfated oleyl alcohol, the mixture is oil soluble, highly effective in reducing interfacial tension at an interface between petroleum oil and water and greatly reduces the pull load necessary to free a stuck drill stem. The reason for the synergistic effect of the two surface active agents present in this mixture is not known, but we have found that the mixture is much more effective than either of the ingredients alone.

The 2-heptadecenyl 4-4 dimethoxy 2 oxazoline is a standard article of commerce sold under the trade name "Alkaterge T." The 2-heptadecenyl 4 methoxy 4 methyl 2 oxazoline is also a standard article of commerce and is sold under the trade name "Alkaterge C." Dioctyl sodium sulfosuccinate is sold under the trade name "Triton GR–7," and the sodium salt of sulfated oleyl alcohol appears on the market under the trade name "Duponol LS paste." These trade names will be used in tables given below to save space. It is to be understood, however, that the compounds set forth above are usable in this process, and the process is not limited to the product of any particular manufacturer.

The petroleum oil fluid preferably also contains a small amount of a coupling agent such as an alcohol, toluene or perchloroethylene. The alcohols having less than 15 carbon atoms are the materials of choice, and we have used materials selected from the group consisting of methyl, isopropyl, secondary butyl, furfuryl, capryl, tridecyl and tertiary amyl alcohols with equally good results. Our preferred coupling agent is isopropyl alcohol because of the cheapness and ready availability of this material.

The alcohols function as coupling agents in the petroleum oil base fluid to couple between the oil and water and are quite effective in removing water from the water-wet cake of well fluid solids. While presumably any alcohol will have this effect to a greater or less degree, all of those recited in the group above have been used with equally good results.

The petroleum oil may be a crude oil or any of the light refined oils such as kerosene, diesel oil, distillate, etc. Heavier oils such as motor oil having Saybolt viscosities above 10 seconds at 210° F. are not as good as the lighter oils since they penetrate the cake much more slowly.

The petroleum oil containing the surface active agent in solution should be substantially free of suspended weighting materials such as barite. A minor disadvantage sometimes results from this requirement in that the fluid which in use is normally spotted between two columns of heavy mud is lighter than the mud and has some tendency to rise in the well bore when circulation is stopped. Ordinarily the initial gel strength of the mud above the fluid is sufficient to keep it in place; but when certain heavy fluids having rather low initial gel strength are used in drilling the well, it may be necessary to weight the petroleum oil by including therein a concentrated solution of calcium chloride emulsified in the oil.

We have found that substantially saturated calcium chloride solution may be emulsified in the oil to form a water-in-oil type emulsion having a weight of about 9.8 pounds per gallon and that the resulting emulsion is quite effective in dehydrating, cracking and penetrating the cake of water-wet well solids. Brines, generally, may be used for increasing the specific gravity of the solution so long as the brines do not contain suspended solids. For example a zinc chloride brine of 70° Bé. concentration may be used to increase the weight of the emulsion to more than 11 pounds per gallon, although it is necessary to add caustic to $ZnCl_2$ brines to increase the pH to a point where emulsification will occur. Addition of caustic has not proven detrimental to water-in-oil emulsion fluid. So long as the oil phase is the continuous phase in an emulsion of this type, dehydration and cracking of the cake occur as when the petroleum base fluid is used without including emulsified calcium chloride solution.

Other coupling agents such as toluene or perchloroethylene also have been used, but these are not quite so efficient as the alcohols.

This invention also contemplates the preparation of a concentrated additive for mixing with a suitable petroleum oil to produce the petroleum oil base fluid to be spotted around a stuck drill stem in a permeable formation. This additive will contain a suitable interfacial tension reducing agent, a coupling agent for coupling the water into the oil and will usually contain a hydrocarbon solvent in quantity to dissolve the surface active agent and coupling agent to produce a pourable fluid which is easily miscible with the petroleum oil.

One preferred additive of this type may contain the components and percentages thereof indicated in the following table:

| Component: | Percent variation |
|---|---|
| Hydrocarbon solvent | 1 to 85 |
| Alkaterge T | 3 to 85 |
| Degras | 1 to 31 |
| Duponol LS paste | ¼ to 8 |
| Isopropyl alcohol | 2 to 20 |

It will be noted that the variations in the percentages given above are quite wide, and such wide variations are usable because the active materials need contain only sufficient hydrocarbon solvent to render them fluid and easily miscible with petroleum oil under the conditions and temperatures ordinarily prevailing at well heads. Among the materials listed in this table, Alkaterge T is solid at common outdoor temperatures; but when mixed with a relatively large proportion of degras and Duponol LS paste, it requires only a very little hydrocarbon solvent in addition to the alcohol to render the material fluid and easily miscible with oil.

While the above table is given as an example of one usable concentrated additive, our additives are not limited to the materials shown above. Any one surface active agent may be present in solution in hydrocarbon solvent and a suitable alcohol, or various combinations of surface active agents may be included as will be shown in the examples below.

Alcohol in amounts less than 1 percent can be used with fair results but should be present in the range from 1 to 20 percent and preferably in the range from 2 to 10 percent with about 2 percent being the most preferred concentration. With amounts less than 1 percent, the desired coupling effect will not be realized to the most advantageous degree. Amounts above the preferred range can readily be used without any appreciable disadvantage except for increase in cost without producing equivalent increase in efficiency of the fluid. The preferred concentration of about 2 percent has been arrived at by balancing cost against efficiency determined in laboratory experiments, and fluids containing 2 percent of alcohol have been determined to be highly efficient in loosening stuck pipe under adverse conditions actually encountered in the wells.

In commercial use, it will be preferred that the additive be relatively dilute in hydrocarbon solvent to make its accurate measurement easy and to prevent waste of the more expensive surfactant. For example, we have used one particular additive containing the following components and percentages in freeing stuck drill stems under operating conditions in many wells:

FORMULA XP–15

| Component: | Percentage |
|---|---|
| Hydrocarbon solvent | 85 |
| Alkaterge T | 8 |
| Degras | 4 |
| Duponol LS paste | 1 |
| Isopropyl alcohol | 2 |

With a solution of additives having such dilute concentration, it is very easy to measure a sufficient amount of the additive to furnish an 0.1 percent solution of the surface active materials in petroleum oil. We have found this quantity of particular additives listed in these tables to be highly effective in reducing interfacial tension at an interface between the oil and water to less than 2 dynes per centimeter. Miscibility with the petroleum oil is very high and a petroleum oil solution is very easily prepared. Excess hydrocarbon solvent present in the dilute additive merely extends the petroleum oil and supplements it. The proportions of surface active materials in this table are chosen so that one gallon of the solution (hereinafter referred to as XP–15) per barrel of petroleum oil will furnish about 0.3 percent of surface active agent.

The preparation of the petroleum oil solution is most easily accomplished by the use of a concentrate of this kind which is merely poured into a desired quantity of petroleum oil and is mixed therewith. However, we do not wish to exclude other methods of preparing the petroleum oil base solution since the surface active agent or agents and alcohol may be added directly to the oil and dissolved therein if preferred. However, the degree of mixing required is greatly reduced by use of solutions such as those given in the formulae above.

*Example I*

Several hundred determinations of the effect of petroleum oil base fluid containing various surface active agents in freeing stuck pipe were made on special laboratory differential pressure sticking apparatus.

The apparatus used in this series of studies comprises a 4½ inch outer steel cylinder with a smaller cylinder of porous "Aloxite" mounted inside with a space between the two. This space was connected to a small vacuum pump through a clear, plastic cylinder used to collect filtrate for measurement.

A small pump was used to circulate mud through the bore of the Aloxite cylinder and back into a mud container. A side connection from the filtrate line to the laboratory water supply was made so that the Aloxite cylinder could be flushed and cleaned between tests.

A 1.656 inch diameter mild steel pipe filled with mercury was used to simulate a drill pipe or collar, and the entire cylinder arrangement was set at an angle of 25° from the vertical so that the complete length of the pipe would be forced against the filter cake by differential pressure between the inside and the outside of the Aloxite cylinder as filtration proceeded.

The end of the pipe was connected over a roller to a spring balance which was in turn connected to a 50-pound weight resting on a hand jack that could be lowered gradually assuring smooth, gradual increased pull on the pipe.

A gauge at the top of the filtrate collecting cylinder registered the differential pressure across the filter cake in inches of mercury which approached total vacuum, or 29.9 inches, at substantially all times.

A laboratory prepared mud system was used in comparative tests. The mud used had the following composition:

16.5 lbs./bbl. of a medium quality clay sold under the trade name of "Xact Clay"
14.0 lbs./bbl. attapulgite



8.0 lbs./bbl. Wyoming bentonite
0.75 lb./bbl. quebracho
0.75 lb./bbl. sodium hydroxide
0.10 lb./bbl. Magcophos (sodium phosphate)
Sufficient barite to raise the weight of the mud to 11.1 lbs./gal.

The properties of this mud varied within the following ranges:

| | |
|---|---|
| Apparent viscosity ____cps__ | 20–24 |
| Plastic viscosity ____cps__ | 15–20 |
| Yield point | 4–12 |
| Initial gel strength | 2 |
| 10 min. gel strength | 10–33 |
| pH | 0.3–10.2 |
| Fluid loss (30 lbs.) | 12.2–14.4 |

The operating procedure followed in the test was as follows:

(1) Run complete physical and chemical properties of the mud.

(2) Circulate fluid mud through the system for approximately two minutes and stop mud circulation with the porous Aloxite cylinder filled with mud.

(3) Place the pipe simulating a drill stem in the bore of the Aloxite cylinder and determine the number of pounds necessary to move the pipe with no differential pressure applied thereto, and remove the pipe from the cylinder.

(4) Start circulation of the mud again; evacuate the system with a vacuum pump for eight minutes. It was found that the time for the vacuum to reach its maximum was approximately five minutes, and this time was used to allow an additional three minutes for cake to build up on the wall of the porous Aloxite cylinder.

(5) Insert the pipe simulating a drill stem in the bore of the Aloxite cylinder, jiggle it slightly to insure full length contact with the cake of water-wet solids on the wall of the Aloxite cylinder, and stop circulation of the mud with the vacuum still on.

(6) Hold vacuum for 14 minutes with the pipe in place against the cake to insure substantially uniform differential pressure across the pipe in duplicate tests.

(7) Apply an axial pull upon the pipe stuck against the cake of water wet solids by applying weight at a rate of one pound/5 seconds. At the instant of release note the number of pounds shown by the gauge and record as force pounds to release the laboratory pipe.

(8) Thoroughly clean the unit between tests, backwashing with water and using a brush, water and detergent.

(9) After cleaning, the process was repeated down to and including step 6, above, allowing 14 minutes for differential pressure to develop across the stuck pipe and drain mud from around the pipe. Replace the drained off mud with a petroleum oil spotting fluid.

(10) With vacuum on, allow 30 minutes for the spotting fluid to penetrate the cake of water wet mud solids, recording the time of first oil penetration and keeping the pipe covered at all times with the spotting fluid.

(11) At the end of 30 minutes, pull the pipe free as in step 7, above, recording the force necessary to free the pipe and the total amount of filtrate and spotting fluid penetrating through the cake.

It was found to be difficult to duplicate results exactly. Consequently in the following table the figures given are averages of from 3 to 9 separate determinations for each surface active agent used. The petroleum oil used as the base of the spotting fluid was diesel fuel in each case.

All the surface active agents tested which resulted in cake cracking and release of stuck pipe were effective to lower interfacial tension at an interface between the oil spotting fluid and water to a very low value. Since it was difficult to see the effect the various spotting fluids had upon the cake on the wall inside the Aloxite cylinder, an alternate method for determining the extent of cake cracking by various surfactants was designed. A half-inch threaded hole was drilled into the top of a standard Fann filter cell and a plug screwed into it. A fifteen-minute fluid loss at 100 lbs./sq. in pressure was run on the base mud. The pressure was then released, the plug was unscrewed without disturbing the cake and excess mud was poured out of the drill hole and replaced with 50 ml. of the various spotting fluids. The plug was replaced, pressure put back on the cell and filtration was resumed until all the water was squeezed out of the cake and approximately 25 ml. of spotting fluid was emitted or for a total of 30 minutes further filtration, whichever resulted first.

It was observed that spotting fluid containing several surfactants had the ability to drastically crack the cake into extremely fine cracks and convert the cake into an almost friable state. Diesel oil containing no surfactant did not crack the cake but did squeeze out substantially all the water from the cake. In all cases in which the surfactants were highly effective in cracking the cake, a rapid rate of spotting fluid flow occurred after the cake was finally cracked; and, in general, the first appearance of spotting fluid coming through the cake was observed after 10 to 15 minutes. For other less effective surfactants, no penetration of cake or appearance of spotting fluid resulted in the total 30-minute period. The following table illustrates the force required to free the pipe when various fluids were used as spotting fluid.

| | Force to free pipe (pounds) |
|---|---|
| No spotting fluid | 35 |
| Water spotting fluid | 39 |
| Diesel oil spotting fluid | 34 |
| Motor oil, 30 weight, without surfactant | 37 |
| 2 lbs./bbl. Alkaterge C | 23 |
| 3 lbs./bbl. Triton GR-7 | 21 |
| 2 lbs./bbl. degras | 26 |
| ¼ lb./bbl. Alkaterge T | 26 |
| 1 lb./bbl. Alkaterge T+1 lb./bbl. degras | 17 |
| ½ lb./bbl. Alkaterge T+20% isopropanol | 15 |

A large part of the cake in contact with the drill stem, usually in excess of 30 percent, broke away from the wall of the Aloxite cylinder and adhered to the simulated drill stem when an oil soluble ionic surface active agent was used in the oil. This contrasted with the cases where plain diesel oil or oil containing other types of surface active agents were used, and in which practically all separation occurred at the area of contact between the stem and cake.

*Example II*

The laboratory scale work as described in Example I was repeated using ionic oil soluble surface active agents capable of reducing interfacial tension at an interface between petroleum oil and water to less than 5 dynes per centimeter as well as surface active agents which were not oil soluble or were non-ionic in nature. The following table is illustrative of typical results obtained.

COMPARISON OF CHEMICAL TYPE, FORMULA, SURFACTIVE CHARACTERISTICS, AND PERFORMANCE OF VARIOUS INDIVIDUAL MATERIALS

| Trade name | Chemical type | Chemical formula | Interfacial tension against water 0.1% solution in mineral oil (dynes/cn.) Oil only 28.0 | Relative pull-load rating, lbs. at indicated concentration in diesel oil or oil phase fluid — Lab mud pull-load, 42 lbs. Diesel oil spot, 34 lbs. — Pull load, lbs. | Diesel oil, lbs./bbl. | Relative cracking effect on laboratory mud filter cake |
|---|---|---|---|---|---|---|
| Alkaterge C | Cationic oxazoline | (1) | 2.0 | 18 | 2 | Extreme fine cracking throughout. |
| | | | | 25 | 0.6 | Very little cracking. |
| Alkaterge T | Cationic oxazoline | (1) | <1 (3) | 18 | 2 | Extreme fine cracking throughout. |
| | | | | 25 | 0.6 | Extreme fine cracking throughout. |
| Triton GR-7 | Anionic dioctyl sodium sulfosuccinate. | (2) 64% active in light petroleum distillate as solvent. | 1.5 | 21 | (4) 3 | Extreme fine cracking throughout. |
| | | | | 27 | (5) 0.9 | Extreme fine cracking throughout. |
| NI-O | Nonionic | Alkyl phenol ethylene oxide condensate. | 1.5 | 30 | 8 | No cracking. |
| | | | | 34 | 2 | Very little cracking. |
| | | | | 34 | 0.6 | Very little cracking. |
| Degras | Complex natural product produced by acid cracking of crude wool grease. Contains high molecular weight free fatty acids, esters, and alcohols. | | 5.4 | 33 | 2 | No cracking. |
| | | | | 34 | 0.6 | Medium cracking. |
| Duponol LS paste | Anionic | Sodium salt of sulfated oleyl alcohol. | Oil-insoluble | 33 | 2 | Extreme fine cracking throughout. |
| | | | | | 0.4 | Extreme fine cracking throughout. |
| Degras + Duponol LS paste. | See above | See above | 0.9 | 29 | 1.6+0.4 | Extreme fine cracking throughout. |
| Sipon ES | Sodium ethoxylated lauryl sulfate. | Oil-insoluble | 8.7 | 30 | 8 | Medium cracking. |

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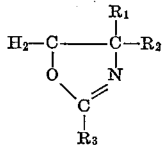

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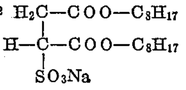

3 Too low to measure. 4 2 lbs./bbl. active. 5 0.6 lb./bbl. active.

In the above table it is to be noted that Alkaterge T, Alkaterge C and Triton GR–7, which are ionic and oil soluble and reduce the interfacial tension to values below 2, had very strong cracking effect upon the cake whereas a non-ionic surface active agent, alkylphenol ethylene oxide condensate, although it had the ability to reduce the interfacial tension to values below 2, had substantially no effect in cracking the cake and did not decrease the pull load required to free the pipe appreciably. The sodium ethoxylated lauryl sulfate which has been used as an additive for petroleum oil to free stuck drill stems in the past is not oil soluble and does not reduce interfacial tension of oil against water sufficiently and does not cause much cracking of the cake although it is effective in lowering the force necessary to pull the pipe from the cake. It apparently operates by an entirely different mechanism. It is also to be noted that Duponol LS paste when used alone is an oil insoluble material; and while it does cause cracking of the cake, a petroleum oil fluid containing this material does not penetrate the cake well, and there is substantially no reduction in pull load necessary to free a stuck pipe. However, when this material is used in combination with degras, the resulting mixture is oil soluble, reduces interfacial tension between oil and water to a low value and causes extremely fine cracking of the cake and is effective in reducing the pull load necessary to free a stuck pipe.

*Example III*

Mixtures of various surface active agents were made and the resulting mixtures were used in additional experimental work conducted as described under Example I, above. Similar experiments were conducted using a calcium petroleum sulfonate to compare the effect of a surface active agent which does not reduce interfacial tension at an interface between oil and water to a value below 5 dynes per centimeter. The following results were obtained:

| Trade Name | Type | Chemical Formulation (Remarks) | Concentration lbs./bbl. D.O. | Interfacial Tension vs. Water (dynes/cn.) | Pull Load Rating | Relative Cracking of Lab. Mud Cake |
|---|---|---|---|---|---|---|
| Alkaterge T<br>Alkaterge C | Cationic | 50:50 Mixture | 0.32 | 1 | 29 | Considerable. |
| Alkaterge T<br>Triton GR–7 | Cationic<br>Anionic | do | 0.32 | 5.0 | 30 | Do. |
| Formula III* | Mixture | 8:2, Alk:Degras | 8.0 | 1 | 23–28 | Extreme. |
| Formula IV* | do | 8:4, Alk:Degras | 8.0 | 1 | 29 | Do. |
| Formula V* | do | 8:8, Alk:Degras | 8.0 | 1 | 29 | Do. |
| Formula VI* | do | 8:16, Alk:Degras | 8.0 | 1 | 29 | Medium. |
| CaSulfonate 30A | | 30% Active Calcium Petroleum Sulfonate. | 4.7 | 17.0 | 34 | None. |
| Diesel Oil | None | | None | | 35 | |

*See the following table:

| | Formula III | Formula IV | Formula V | Formula VI |
|---|---|---|---|---|
| | *Percent* | *Percent* | *Percent* | *Percent* |
| Alkaterge T | 9.9 | 8 | 5.8 | 3.7 |
| Degras | 2.5 | 4 | 5.8 | 7.5 |
| Duponol LS Paste | 0.6 | 1 | 1.4 | 1.8 |
| Isopropanol, 75X Extract | 2.0<br>85 | 2<br>85 | 2.0<br>85 | 10.0<br>85 |
| | 100.0 | 100 | 100.0 | 100.0 |

*Example IV*

A study was made to determine the efficiency of various alcohols as coupling agents for coupling water into the petroleum oil base fluid using the technique for studying cracking in cakes described in Example I. For the purposes of this study, an alcohol-surface active agent solution was made up as follows:

| | Percent |
|---|---|
| Alkaterge T | 8 |
| Alcohol | 10 |
| Hydrocarbon solvent | 82 |



Sixteen pounds per barrel of oil were added to the mud described in Example I, and the cracking effect on the cake was noted. Seven different alcohols were used in various tests. No difference in the effect of the various alcohols in cracking the cake could be noticed. The following results were obtained:

| | |
|---|---|
| Methyl alcohol | Extreme fine cracks. |
| Isopropyl alcohol | Do. |
| Sec. butyl alcohol | Do. |
| Furfuryl alcohol | Do. |
| Capryl alcohol | Do. |
| Tridecyl alcohol | Do. |
| Tert. amyl alcohol | Do. |

No distinction could be made in cake cracking effect.

*Example V*

A well near Chacahoula, Lafourche Parish, Louisiana, was drilled to 11,338 feet in depth. Drilling was shut down to take a picture; and when drilling was resumed, it was found that a drill line was twisted. After untwisting the drill line, it was found that the pipe had stuck by differential pressure. This pipe was worked for three hours without effect and was backed off at 10,820 feet.

Jars were picked up, but the drilling crew was unable to screw into the fish until 34 hours later. This well was being drilled with a caustic quebracho mud of low pH weighing 10.8 pounds per gallon and having an apparent viscosity of 48.

The location of sticking was found to be at the string of drill collars just above the bottom of the well. A pipe releasing fluid was prepared by adding 55 gallons of Formula XP–15, above, to 47 barrels of diesel oil. Thirty barrels of this mixture, calculated as sufficient to fill the well bore outside the drill collars for a distance of 500 feet, were pumped into the bottom of the well.

The collars were then jarred for 30 minutes but remained stuck. An additional half barrel of releasing fluid was added and jarring was continued for one hour without effect. One half barrel releasing fluid was added again and jarring was resumed. The pipe came loose immediately.

*Example VI*

In another well, near Esther, Vermilion Parish, Louisiana, the pipe was also freed by using a spotting fluid containing the XP–15 formula given above.

The pipe in this well stuck while drilling at 12,204 feet, and the drilling crew began to wash over after backing off at 12,043 feet. The washover pipe stuck at 12,149 feet. In attempting to spot diesel oil containing a mixture of degras and Duponol LS paste, the driller lost returns and some time was spent in getting return circulation. After return circulation was established, 15 barrels of diesel oil containing two gallons per barrel of Formula XP–15 above were spotted in the well bore outside the drill stem at the point of sticking. Three hours later the wash pipe came loose after having been stuck for over 126 hours.

Before the pipe stuck, 7-inch casing had been set at 11,911 feet. After the wash pipe was freed, the mud that had been used in drilling the well, a low pH mud containing a chromium magnesium lignosulfonate complex was converted to a gyp mud and a mixture of degras and Duponol LS paste was added to the mud. The drill pipe was washed over, using the converted mud and the well was completed at a depth of 12,900 feet.

*Example VII*

In drilling another well, near South Jennings, Jefferson Davis Parish, Louisiana, to 10,102 feet after a 9⅝-inch casing was cemented, reaming below the casing was begun. Ten feet off bottom of the well, the drill pipe was stuck. The free-point indicator showed the pipe being free down to the top of the drill collars which had a total length of 364 feet. Forty-five barrels of diesel oil containing one 55-drum of Formula XP–15 above was introduced to fill the bore outside the drill stem at the location of sticking and the pipe was worked for three hours. There was doubt as to the displacement of the XP–15 oil mixture, so two more barrels were added through the drill pipe and the pipe was worked for 20 minutes when the pipe came free.

*Example VIII*

In another well, near Chacahoula, Lafourche Parish, Louisiana, completed to a new depth of 15,085 feet, the pipe stuck while 22 feet off bottom while going in the hole after a short trip. The drill crew then backed off at approximately 14,500 feet, leaving a fish having a total length of approximately 563 feet in the hole.

After backing off the fish, 34 barrels of diesel oil were mixed with one gallon of Formula XP–15 above per barrel of oil. The drill stem was lowered into the hole, screwed into the fish, and 11 barrels of the XP–15 mixture were spotted around the drill collar. One barrel of this mixture was pumped every 30 minutes and the pipe was worked for five hours without result. The drill pipe was then backed off, pulled out of the hole and the following day was introduced into the hole with nine drill collars and jars. The jars were operated for four hours while waiting for diesel oil without result. Eighty gallons of Formula XP–15 were mixed with 34 barrels of diesel oil, and 11 barrels of this mixture were spotted around the fish. The jars were operated for five minutes and the pipe came free. This well was being drilled with a low lime mud having a weight of 16 pounds per gallon, viscosity of 49, fluid loss of 2.3 cc's. and an oil content of 8 percent. These cases of actual well operation are illustrative of the results attained using the petroleum oil spotting fluids of this invention.

From the foregoing, it will be seen that this invention is one well adapted to attain all of the ends and objects hereinabove set forth, together with other advantages which are obvious and which are inherent to the process and method.

It will be understood that certain features and subcombinations are of utility and may be employed without reference to other features and subcombinations. This is contemplated by and is within the scope of the claims.

The invention having been described, what is claimed is:

**1.** In a well operation wherein a well fluid is circulated through a drill stem in a well, a cake of water-wet well fluid solids accumulates on the face of a permeable formation penetrated by the well bore, and the drill stem becomes stuck against the cake of water-wet solids by a differential in hydrostatic pressure between fluid in the well and in the permeable formation applied across the drill stem, that improvement which comprises substantially filling the well bore outside the drill stem in the permeable formation with a petroleum oil containing an ionic oil-soluble surfactant capable of reducing interfacial tension at an interface between the petroleum oil and water to not more than 2 dynes per centimenter in amount sufficient to accomplish such reduction and a coupling agent effective to couple between oil and water and thereby substantially increase solubility of water in said petroleum oil; dissolving water from the cake of water-wet solids in the petroleum oil in quantity to crack the cake by dehydration; passing petroleum oil from the well bore through the resulting cracked cake to the permeable formation, whereby the differential pressure across the drill stem is decreased; and releasing the drill stem.

**2.** In a well operation wherein a well fluid is circulated through a drill stem in a well, a cake of water-wet well fluid solids accumulates on the face of a permeable formation penetrated by the well bore, and the drill stem becomes stuck against the cake of water-wet solids by a differential in hydrostatic pressure between fluid in the well and in the permeable formation applied across the drill stem, that improvement which comprises substantially filling the well bore outside the drill stem in the permeable formation with a petroleum oil containing a material selected from the group consisting of 2-heptadecenyl-4-4-dimethyoxy - 2 - oxazoline, 2 - heptadecenyl - 4 - methoxy-4-methyl-2-oxazoline, the sodium salt of dioctyl sulfosuccinate, a mixture of a product containing high molecular weight free fatty acids, esters and alcohols made by acid cracking wool grease with about one-fourth its weight of the sodium salt of sulfated oleyl alcohol, and mixtures thereof, in quantity sufficient to reduce interfacial tension at an interface between the petroleum oil and water to not more than 2 dynes per cenimeter; dissolving water from the cake of water-wet solids in the petroleum oil in quantity to crack the cake by dehydration; passing petroleum oil from the well bore through the resulting cracked cake to the permeable formation, whereby the differential pressure across the drill stem is decreased; and releasing the drill stem.

**3.** In a well operation wherein a well fluid is circulated through a drill stem in a well, a cake of water-wet well fluid solids accumulates on the face of a permeable formation penetrated by the well bore, and the drill stem becomes stuck against the cake of water-wet solids by a differential in hydrostatic pressure between fluid in the well and in the permeable formation applied across the drill stem, that improvement which comprises substantially filling the well bore outside the drill stem in the permeable formation with a petroleum oil containing a material selected from the group consisting of 2-heptadecenyl - 4 - 4 - dimethoxy - 2 - oxazoline, 2-heptadecenyl-4-methoxy-4-methyl-2-oxazoline, the sodium salt of dioctyl sulfosuccinate, a mixture of a product containing high molecular weight free fatty acids, esters and alcohols made by acid cracking wool grease with about one-fourth its weight of the sodium salt of sulfated oleyl alcohol, and mixtures thereof, in quantity sufficient to reduce interfacial tension at an interface between the petroleum oil and water to not more than 2 dynes per centimeter, and a coupling agent effective to increase solubility of water in said petroleum oil; dissolving water from the cake of water-wet solids in the petroleum oil in quantity to crack the cake by dehydration; passing petroleum oil from the well bore through the resulting cracked cake to the permeable formation, whereby the differential pressure across the drill stem is decreased; and releasing the drill stem.

**4.** The process of claim **3** wherein the coupling agent is a material selected from the group consisting of methyl alcohol, isopropyl alcohol, secondary butyl alcohol, furfuryl alcohol, capryl alcohol, tridecyl alcohol, and tertiary amyl alcohol.

**5.** The process of claim 4 wherein the coupling agent is isopropyl alcohol.

**6.** In a well operation wherein a well fluid is circulated through a drill stem in a well, a cake of water-wet well fluid solids accumulates on the face of a permeable formation penetrated by the well bore, and the drill stem becomes stuck against the cake of water-wet solids by a differential in hydrostatic pressure between fluid in the well and in the permeable formation applied across the drill stem, that improvement which comprises substantially filling the well bore outside the drill stem in the permeable formation with a petroleum oil containing an ionic oil-soluble surface active agent capable of reducing interfacial tension at an interface between the petroleum oil and water to not more than 2 dynes per centimeter in amount sufficient to accomplish such reduction, a coupling agent effective to couple between oil and water and thereby increase solubility of water in the petroleum oil and a concentrated brine solution dispersed in said petroleum oil in quantity to increase the specific gravity of the oil substantially; dissolving water from the cake of water-wet solids in the petroleum oil in quantity to crack the cake by dehydration; passing petroleum oil from the well bore through the resulting cracked cake to the permeable formation, whereby the differential pressure across the drill stem is decreased; and releasing the drill stem.

**7.** The process of claim **6** wherein the concentrated brine solution is a solution of zinc chloride.

**8.** In a well operation wherein a well fluid is circulated through a drill stem in a well, a cake of water-wet well fluid solids accumulates on the face of a permeable formation penetrated by the well bore, and the drill stem becomes stuck against the cake of water-wet solids by a differential in hydrostatic pressure between fluid in the well and in the formation applied across the drill stem, that improvement which comprises substantially filling the well bore outside the drill stem in the permeable formation with a petroleum oil containing at least 0.1 percent of a material selected from the group consisting of 2-heptadecenyl-4-4-dimethoxy-2-oxazoline, 2-heptadecenyl-4-methoxy-4-methyl-2-oxazoline, the sodium salt of dioctyl sulfosuccinate, a mixture of a product containing high molecular weight free fatty acids, esters and alcohols made by acid cracking wool grease with about one-fourth its weight of the sodium salt of sulfated oleyl alcohol, and mixtures thereof, and from 1 to 20 percent of a material selected from the group consisting of methyl alcohol, isopropyl alcohol, secondary butyl alcohol, furfuryl alcohol, capryl alcohol, tridecyl alcohol and tertiary amyl alcohol; dissolving water from the cake of water-wet solids in the petroleum oil in quantity to crack the cake by dehydration; passing petroleum oil from the well bore through the resulting cracked cake to the permeable formation, whereby differential pressure across the drill stem is decreased; and releasing the drill stem.

**9.** In a well operation wherein a well fluid is circulated through a drill stem in a well, a cake of water-wet well fluid solids accumulates on the face of a permeable formation penetrated by the well bore, and the drill stem becomes stuck against the cake of water-wet solids by a differential in hydrostatic pressure between fluid in the well and in the permeable formation applied across the drill stem, that improvement which comprises intimately mixing with a petroleum oil a solution containing about 13 percent of a material selected from the group consisting of 2-heptadecenyl-4-4-dimethoxy-2-oxazoline, 2-heptadecenyl-4-methoxy-4 - methyl-2 - oxazoline, the sodium salt of dioctyl sulfosuccinate, a mixture of a product containing high molecular weight free fatty acids, esters and alcohols made by acid cracking wool grease with about one-fourth its weight of the sodium salt of sulfated oleyl alcohol, and mixtures thereof, from 1 to 20 percent of a material selected from the group consisting of methyl alcohol, isopropyl alcohol, secondary butyl alcohol, furfuryl alcohol, capryl alcohol, tridecyl alcohol and tertiary amyl alcohol, and a hydrocarbon solvent in quantity to make 100 percent, said solution being mixed with said petroleum oil in quantity to reduce interfacial tension at an interface between the petroleum oil and water to not more than 2 dynes per centimeter; substantially filling the well bore outside the drill stem and in the permeable formation with the mixture of solution and petroleum oil; dissolving water from the cake of water-wet solids in the petroleum oil in quantity to crack the cake by dehydration; pressing petroleum oil from the well bore through the resulting cracked cake to the permeable formation, whereby differential pressure across the drill stem is decreased; and releasing the drill stem.

**10.** The process of claim **9** wherein the solution contains from 3 to 85 percent of 2-heptadecenyl-4-4-dimethoxy-2-oxazoline, from 1 to 51 percent of a product containing high molecular weight free fatty acids, esters and alcohols made by acid cracking wool grease, from ¼ to 8 percent of a sodium salt of sulfated oleyl alcohol, and from 1 to 85 percent of a hydrocarbon solvent.

**11.** The process of claim **9** wherein the solution contains about 8 percent of 2-heptadecenyl-4-4-dimethoxy-2-oxazoline, about 4 percent of a product containing high molecular weight free fatty acids, esters and alcohols made by acid cracking wool grease, about 1 percent of the sodium salt of sulfated oleyl alcohol, about 2 percent of isopropyl alcohol and about 85 percent of a hydrocarbon solvent.

**12.** An additive for converting a petroleum oil into a fluid effective to dehydrate, crack and penetrate a cake of water wet well fluid solids on a wall of a well bore in a permeable formation which comprises from 3 to 85% of 2-heptadecenyl-4-4-dimethoxy - 2 - oxazoline; from 1 to 31% of a product containing high molecular weight free fatty acids, esters and alcohols made by acid cracking wool grease; from ¼ to 8% of the sodium salt of dioctyl sulfosuccinate; and from 1 to 85% of a hydrocarbon solvent.

**13.** An additive for converting a petroleum oil into a fluid effective to dehydrate, crack and penetrate a cake of water wet well fluid solids on a wall of a well bore in a permeable formation which comprises about 8% of 2-heptadecenyl-4-4-dimethoxy-2-oxazoline; about 4% of a product containing high molecular weight free fatty acids, esters and alcohols made by acid cracking wool grease; about 1% of the sodium salt of dioctyl sulfosuccinate; about 2% of isopropyl alcohol; and about 85% of a hydrocarbon solvent.

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