

UNITED STATES PATENT OFFICE

2,073,413

DRILLING FLUIDS

Roy Cross and Matthew Forbes Cross, Kansas
City, Mo.

No Drawing. Application November 25, 1933,
Serial No. 112,701

7 Claims. (Cl. 235-1)

This invention relates to the art of earth boring, more particularly oil well drilling and new and improved oil well drilling fluids. The whole application is a continuation in part of our co-pending application Serial No. 85,334, filed June 15, 1936, which in turn is a continuation of our applications Serial No. 67,530, filed March 6, 1936, and Serial No. 70,554, filed March 17, 1936, the latter having matured into United States Patent No. 2,044,758, granted June 16, 1936.

As is well known in the art, a fluid mud is pumped downwardly through the drilling stem of a rotary drilling rig and passes through holes in the bit, washes over the cutting faces of the bit, and rises to the surface through the annular space surrounding the drill pipe, this annular space approximating the amount by which the diameter of the bit exceeds the diameter of the drill stem. There are two essential characteristics of oil well drilling muds required to accomplish two more or less distinct functions. One characteristic required is that the mud contain a material which will effectively seal the walls of the open hole made and homogeneously support the cuttings which pass from the bit upwardly through the annular spaces surrounding the drill stem at times when the pumps are not circulating the mud. There are a number of other effects obtained from a good wall building mud which have previously been discussed. The second requirement for an oil well mud very often is that the mud have a weight per unit volume considerably in excess of the weight of water in order to produce a head resistant to unusual gas or water pressures encountered during boring, and to assist in forcing wall building mud into formations for better sealing characteristics.

The accomplishment of these two requirements for an oil well drilling mud is in many instances co-mingled; for example, in the present art, if a mud is to be weighted to 12 pounds per gallon, material under the first classification must be available in the mud to homogeneously support the weighting material as well as the cuttings. The greatest part of the weighting material used at the present time in the art consists of either finely ground barytes or iron oxide, both of which have strong settling tendencies. For purposes of clarity in this specification we will term mud requirements of the first classification gel-type, and requirements of the second classification weighting-type.

An object of this invention is to provide a new and improved weighting type of drilling mud and in combination with this a new and improved gel-type mud. Other objects will appear hereinafter.

The ideal weighted drilling mud is one in which the maximum weight per gallon can be attained with a minimum rise in viscosity. Gas pressures

greatly in excess of hydrostatic head pressures have been encountered in many formations. The following table demonstrates the rapid increase in pressure per square inch for comparatively small additions to the weight of one gallon of mud.

TABLE I

Hydrostatic head in a typical well 10,000 feet deep

Sp. gr.	Wt. per gal. lbs.	Actual pressure, lbs. per sq. in.	Increase in pressure, lbs. per sq. in.
1.00	8.34	4,335	0
1.078	9.09	4,678	343
1.159	10.00	5,198	863
1.319	12.00	5,718	1,383
1.439	12.00	6,237	1,902
1.559	13.00	6,757	2,422
1.679	14.00	7,277	2,942
1.798	15.00	7,797	3,462
1.918	16.00	8,316	3,981
2.038	17.00	8,836	4,501
2.158	18.00	9,356	5,021

The weighting materials used in the present art, i. e., iron oxide and barytes, when allowed to settle after being mixed with water will reach a critical density of between 18 and 19 pounds per gallon. For example, if a mixture of either of these weighting materials and water, weighing 12 pounds per gallon, is allowed to stand for approximately 48 hours, the settled portion of the weighting material left after decanting the supernatant water will have a density of between 18 and 19 pounds. The addition of gel-type material to such a mixture will decrease the density of the settled material, but to accomplish the complete suspension of the material it is necessary to make such a viscous mass that its use would not be practical in an oil well. For example, a brine gel was made containing 5% of brine gel material treated with 5% of its dry weight of lime, and there was added finely ground weighting material. The mixture was thoroughly agitated. The resultant viscosity was 86 centipoises and the weight per gallon was 13.1 pounds. The maximum desirable viscosity for practical use approximates 40 centipoises. After settling for 24 hours the weight of the settled material was 14.6 pounds per gallon. Similar tests showed that the weight of an 11-pound mud increased to a 12.5-pound settled mud. It is characteristic of these materials that the most dense settling takes place at the bottom of the column, which in an oil well tends to stick the bit. Thus, it is evident that in drilling practice with heavy muds the rate of circulation must be considerably depended upon to prevent settling in the hole. In many instances drills have been stuck when the circulation, for one reason or another, has been shut down for a period of time. Furthermore, when the mud has been pumped from the hole into settling pits it is

found that the weighting material settles out to a considerable extent, falling to the bottom of the pit along with the heavier cuttings that are being discarded. The refuse is customarily jetted out of a settling pit into a discard pit and it is obvious that a considerable amount of weighting material goes into discard in this way. In actual practice it is often necessary to use two or three times the amount of weighting material which would be necessary to make the mud to fill the hole and the pits provided none of the weighting material were discarded. In addition to this, it is often true that where a mud weighing more than 11 or 12 pounds per gallon is so viscous and contains so much solid matter that it is impossible to drop the cuttings brought up from the bottom of the hole, it is causing increased wear on the equipment and defeating the purpose of the settling pits.

Our present invention eliminates all of these difficulties besides providing new advantages for the mud. We have found that by adding to oil well drilling fluids a water-soluble heavy metal salt or a combination of salts which are soluble in water, it is possible to increase the weight of the drilling fluid without the necessity of adding a suspended type of solid weighting material such as is now used in the art. We have found that where single soluble heavy metal salts are added for weighting purposes, a salt, which when dissolved in water at ordinary temperatures will form a solution of minimum specific gravity of 1.4, is desirable, it being thus possible to increase the weight of drilling fluid much more than that of normal fluid and into the range of what may be called heavy drilling fluids, for instance, more than 11.5 pounds per gallon weight.

We have found that there is considerable economic advantage in making heavy drilling fluids by the use of more than one salt in the solution. There is also a great technical advantage in this procedure. We have found, for instance, that to a saturated solution of sodium chloride, zinc chloride may be continuously added at ordinary temperatures to an extent 55% by weight of the total solution without precipitating either salt. Also, zinc chloride can be added to a saturated solution of calcium chloride to a very considerable extent without precipitating either salt.

The following table illustrates the proportions of water, sodium chloride, and zinc chloride, as well as the proportions of water, calcium chloride, and zinc chloride with the respective specific gravities, and weights per gallon of these solutions, required to produce a certain total weight per gallon.

TABLE II

Composition of solution (by wt.)								Sp. grav.	Total wt. per gal.	
60	Water		NaCl		CaCl ₂		ZnCl ₂			
	%	Lbs./ gal.	%	Lbs./ gal.	%	Lbs./ gal.	%			Lbs./ gal.
65	75.0	7.46	25.0	2.50	-----	-----	0	0	1.20	9.90
	67.7	7.14	22.3	2.35	-----	-----	10	1.05	1.27	10.54
	60.0	6.63	20.0	2.21	-----	-----	20	2.21	1.33	11.04
	52.5	6.27	17.5	2.09	-----	-----	30	3.32	1.44	11.95
	45.0	5.79	15.0	1.93	-----	-----	40	5.15	1.55	12.87
	37.5	5.28	12.5	1.77	-----	-----	50	7.06	1.70	14.11
	30.0	4.92	-----	-----	50.0	4.62	0	0	1.59	15.54
	51.0	6.33	-----	-----	55.0	4.42	10	1.23	1.48	12.23
70	48.0	6.25	-----	-----	52.0	4.17	20	2.61	1.57	13.03
	42.0	5.79	-----	-----	58.0	3.85	30	4.13	1.65	13.78
	35.0	5.20	-----	-----	64.0	3.46	40	5.78	1.74	14.44
	33.0	4.93	-----	-----	62.0	3.27	45	6.60	1.79	14.86

It will be apparent that the maximum weight 75 per gallon shown in the table is not the maximum

weight attainable since an 80% solution of zinc chloride alone will produce a solution of specific gravity 2.25 with a weight of 18.23 pounds per gallon of solution. Other combinations of salts are equally advantageous. For example, there may be added to 70 parts of a saturated solution of sodium chloride, 25 parts of ferrous sulfate to obtain a specific gravity of 1.312. Another example is the addition of 40 parts of ferric sulfate to 60 parts of a saturated solution of sodium chloride to give a specific gravity of 1.49. It is of advantage to use ferrous or ferric sulfate in saturated solution as a base and to add a heavy metal salt such as zinc chloride thereto. An example of this is the addition of 40 parts of zinc chloride to 60 parts of 50% ferric sulfate solution to give a specific gravity of 1.66. Solutions containing a combination of sodium chloride, ferric sulfate and zinc chloride are very efficient in imparting weight to a drilling fluid at the lowest cost. The combinations of salt above shown are not intended as limitations on combinations or on single salts, but are intended as concise examples of the practice of this invention.

It will be obvious that heavy solutions disclosed herewith overcome all the difficulties contingent upon the use of insoluble weighting material, now making it possible to use a heavy drilling fluid of low viscosity which will quickly drop the cuttings brought up from the bottom of the hole. There will be a minimum loss of weighting material since it will be unnecessary to jet any appreciable amount of it out of the bottom of the settling pit into the refuse pit. Furthermore, it should be noted that this heavy drilling fluid can be filtered and yet retain its characteristics, thus allowing it to be cleaned of refuse, whereas that is impossible in the present art. Recovery of any fluid placed in the refuse pit may also be accomplished by filtering. In many cases it is of advantage to separate the cuttings from the drilling fluid by means of centrifuging. For example, the specific gravity of the unadulterated drilling fluid may be at a value of 2 whereas the cuttings have a specific gravity of 2.5. This type of separation is easily accomplished and may be continuously done by the use of any one of the continuous centrifugal separators now on the market.

In the practice of this invention it is very often the case that a solution of a salt or a combination of salts may be used per se as a drilling fluid. In these cases there is usually a considerable amount of fine material embodied in the fluid by the process of drilling certain formations, and the bulk of this fine material may serve to prevent settling of the cuttings where the progress of the drilling is fairly steady and the periods during which circulation is stopped are short. In many other cases, however, it is necessary to produce a gel-type weighted drilling fluid in order to accomplish the wall sealing, supporting and weighting requirements of the mud. To accomplish this we add to the solution a gel-type clay capable of forming brine gels. A base exchange zeolitic clay as described in our United States Patent No. 2,044,753 is adaptable for this use. Optionally, a gel can be made with this clay and the soluble salts added afterward. An agent to increase the viscosity and gelling characteristics of the clay may be used. There is no question but what the use of gel-type clay will give superior wall building characteristics to this type of drilling fluid. We preferably use 1% to 10% of a base exchange zeolitic clay.

2,078,418

3

By variations in the concentrations of zinc chloride and zeolitic clay a viscous fluid varying in viscosity from 1 to 80 centipoises and weighing more than 18 pounds per gallon may be obtained without the addition of solid materials such as barytes, iron oxide, etc.

In many heavy producing oil districts there occurs what is termed "heaving shale". For example, the Jackson shale found in the south of Texas is generally termed a heaving shale. There are gradations in the heaving shale. One of these is the bentonitic type which when hydrated by the drilling mud balls on the bit and forms rings or doughnuts around the drill pipe. This causes the hole to be swabbed when the bit is raised through it, thus destroying the wall. It is many times difficult to raise the bit into the surface casing due to the fact that the ball and doughnut effect sticks at the bottom of the casing. This shale will heave into the hole, very often stopping circulation of mud, sticking the bit and causing abandonment of the hole. Another type of heaving shale is one which cracks or decrepitates into small pieces when hydrated by the drilling mud and appears at the surface in tremendous quantities. This is commonly called buckshot shale and heaves into the hole with the same effect as described above. We have found that drilling fluids comprised of a single soluble heavy metal salt or a combination of salts including a soluble heavy metal salt partially or completely prevent the hydration of decomposition of heaving shales. A variation of shales subjected to a solution of a given salt will show a variation of results. Also, the variation of salts contacted with a given shale will give varying results. For example, a saturated solution of sodium chloride inactivated or prevented the decomposing of an Ariola, Texas shale, whereas it did not completely inactivate Matagorda county, Texas shale. However, a combination of zinc chloride and sodium chloride in solution did completely inactivate the latter shale. The addition of various soluble salts to a drilling mud is very important in preventing a shale from heaving.

It is well known in the art of drilling that many formations contain sufficient colloidal matter in the cuttings to seriously thicken the drilling fluid and it is often necessary to dilute the fluid. Further, when a fluid contains a reasonable amount of this type of material it is often the case that a viscosity stimulating agent in the formation will suddenly thicken the drilling mud. In such instances drilling must be stopped until the mud can be thinned out and got into proper shape. Our invention eliminates this difficulty due to the fact that muds found in formations will not make a gel or show an increase in viscosity. For example, bentonite will not gel when placed in our heavy salt solutions. Thus, our addition of soluble heavy metal salts to the drilling fluid stabilizes the mud. Still another advantage of our addition of soluble salts is that the accompanying increase of specific gravity of the solution lends power to support cuttings. Thus, the homogeneous suspension of the particles in the mud of a well is accomplished with lower viscosity than is now possible. Furthermore, the fact that the heavy solution may be cleaned of refuse by filtration or centrifuging allows a mud of greater viscosity to be used than has been possible heretofore.

Another advantage of our drilling fluid weighted by means of soluble heavy metal salts or a

combination of metal salts is that insoluble weighting materials may be added thereto for a further increase in weight per unit volume without the undesirable viscosity increase. By adding insoluble weighting material to a fluid partly or wholly saturated with soluble salts, a far heavier mud may now be made than was formerly possible. In fact, it is now possible to make fluids of approximately double the present weight.

It will be apparent that many combinations of soluble salt weighting materials and insoluble suspendable weighting materials may be made. For example, a dry base weighting material may be prepared by mixing together 2.2 pounds of sodium chloride, 2.2 pounds of zinc chloride and 2.2 pounds of finely ground barytes. This material may be marketed as such and when added to 6.15 pounds of water, will give a mud weighing 12.75 pounds per gallon. Thus, fairly heavy muds may be obtained without undue increase in viscosity and at a low cost.

Examples of other heavy salts that may be used according to the teachings herein are ferric sulfate; ferric chloride, which in 60% solution has a specific gravity of 1.63; cadmium chloride, which in 60% solution has a specific gravity of 1.80; zinc sulphate, which in 60% solution has a specific gravity of 1.45; and tin chloride, which in 64% solution has a specific gravity of 1.64. It is not intended, however, to limit the soluble salts for use according to these specifications to the specific ones disclosed. The number of soluble salts well adapted to use alone or in combination as disclosed herein is so great that they cannot be conveniently listed. It is intended that the scope of this invention cover the use of soluble heavy metal salts singly; and the use of a combination of two or more soluble salts without regard to their classification as to being heavy metal salts.

The salts or combination of salts which we employ in oil well drilling in accordance with this invention often form acid solutions in water. For instance, commercial sodium chloride is slightly acid, calcium chloride more so, and zinc chloride quite acid. The pH may be varied by various combinations of salts.

We prefer to maintain the pH of the brine solutions as high as is possible without causing precipitation of compounds formed from the salt in the brine. By maintaining a drilling fluid on the alkaline side, corrosion may be greatly prevented. A pH of 8 or more is desirable. It is also desirable, in cases where a tendency to precipitate compounds from the salt exists, to add an inhibitor to this action. A buffer salt may be added to prevent substantial variation of the hydrogen ion concentration. It is often necessary to add an acid inhibitor to the brine to prevent corrosion of the equipment with which the fluid is used. Examples of such inhibitors are arsenious oxide and quinoline ethiodide. The use of about .001 to 1 part of either inhibitor per 100 parts of solution is usually sufficient.

In the drilling of oil wells it is often desirable to wall the hole more permanently than is done by the use of a gel-type mud. The use of our drilling fluids composed of soluble salts with certain phosphates, sulfides, silicates, carbonates, and oxalates will allow the formation of a solid precipitate in the interstices of the wall. For example, a zinc chloride brine may be treated with mono-sodium phosphate, di-sodium phosphate or tri-sodium phosphate to form a precipitate. Hydrogen sulphide plus methane and so-

dium sulphide may be used to form precipitates from the zinc chloride or iron sulfate brine. Sodium silicate, sodium carbonate and sodium oxalate are other examples of materials that may be used for this purpose. A solution of zinc nitrate and sodium phosphate may be used to form a very hard precipitate.

So much of the present application as relates to oil well drilling fluids prepared from waters or brines and fuller's earth of the Florida-Georgia type is described and claimed in our co-pending application Serial No. 35,384, filed June 5, 1936.

The term "heavy metal" as employed herein covers metals having a specific gravity greater than four, in accordance with the generally accepted definition given by Hackh, "Chemical Dictionary", page 348, (1929).

Having thus described the invention, what we claim as new and desire to secure by Letters Patent of the United States is:

1. An oil well drilling fluid containing as a weighting agent a substantial quantity of zinc chloride.
2. An oil well drilling fluid weighted with a substantial quantity of zinc chloride dissolved in a saturated sodium chloride solution.
3. An oil well drilling fluid weighted with a

substantial quantity of zinc chloride dissolved in a saturated solution of calcium chloride.

4. An oil well drilling fluid containing as a weighting agent a plurality of water-soluble salts including substantial amounts of zinc chloride, at least one of said salts being present as a substantially saturated solution in water.

5. An oil well drilling fluid containing a plurality of water-soluble salts, one of which is of the heavy metal group and at least one of which is present in the form of a substantially saturated solution.

6. In the art of earth boring, the step which comprises conducting the drilling operation in the presence of an aqueous salt solution having a specific gravity of from 1.4 to 2.25, said solution including a substantial quantity of a water soluble salt of a metal whose specific gravity is greater than four.

7. In the art of earth boring, the step which comprises conducting the drilling operation in the presence of an aqueous solution having dissolved therein a substantial quantity of a water soluble salt whose specific gravity is greater than four.

ROY CROSS.

MATTHEW FORBES CROSS.

2,5571
CERTIFICATE OF CORRECTION.

Patent No. 2,073,413.

March 9, 1937.

ROY CROSS, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 26, for "suspended" read suspensoid; and line 44, after "extent" insert the word of; and page 3, first column, line 32, for "of" read or; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of June, A. D. 1937..

Henry Van Arsdale

Acting Commissioner of Patents.

(Seal)

255-1
CERTIFICATE OF CORRECTION.

Patent No. 2,073,413.

March 9, 1937.

ROY CROSS, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 26, for "suspended" read suspensoid; and line 44, after "extent" insert the word of; and page 3, first column, line 32, for "of" read or; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of June, A. D. 1937..

Henry Van Arsdale

(Seal)

Acting Commissioner of Patents.