

1495 874

(21) Application No. 12601/76 (22) Filed 29 March 1976 (19)

(44) Complete Specification published 21 Dec. 1977

(51) INT. CL.² C09K 7/00(52) Index at acceptance
EIF 31F(72) Inventors EARL EWALD HUEBOTTER and
MICHAEL JOHN NEVINS

(54) DRILLING FLUIDS AND METHODS OF DRILLING USING THEM

(71) We, NL INDUSTRIES INC., a Corporation organised under the laws of the State of New Jersey, of 1221, Avenue of the Americas, New York, New York 10020, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to oil well drilling fluids, and methods of drilling using such fluids. More particularly the invention relates to drilling needs of increased density and having improved retention of density.

As is well-known, in the rotary method of drilling wells for oil and gas, a drill is rotated at the bottom of the hole by a hollow drill pipe which extends to the surface, and which has a diameter substantially less than the diameter of the hole dug by the bit. A drilling fluid, commonly termed a drilling mud, completely fills the hole both inside and outside of the hollow drill pipe, and while drilling is in progress this fluid is continuously circulated down through the drill pipe to the bit, where it issues through orifices therein and thence rises in the annular space formed by the outside of the drill pipe and the walls of the hole, which to some extent may be reinforced with steel casing.

The primary function of the drilling mud is to raise cuttings to the surface as drilling progresses, so that drilling may be carried out continuously as distinguished from the highly intermittent drilling characteristic of cable tool operations. The drilling mud also serves to cool the bit and furnish lubrication for its cutting edges; and moreover it prevents ingress of formation fluids such as oil, gas and salt water into the hole while drilling proceeds. This last named function is achieved by maintaining a hydrostatic pressure differential so that the mud pressure at a given depth is greater than the pressure of formation fluids at that point. In addition, the mud should in general possess infiltrability against porous formations, since otherwise in

view of the higher hydrostatic pressure within the hole the mud would filter out leaving a filter cake on the walls of the hole which eventually would impede or even stop further drilling. A number of other characteristics and functions are present which need not be set forth in detail here since the operation is well-known and described in numerous textbooks and articles, such as for example the book by Walter F. Rogers entitled *Composition and Properties of Oil Well Drilling Fluids*, 3rd Edition, Houston, 1963; and the chapter entitled "Drilling Fluids" in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd Edition, New York 1965, Volume 7, pages 287—307. These texts are hereby included herein by reference.

Drilling fluids of the general type described may have as a base liquid either oil or water, and either liquid may have the other present therein as an emulsified phase. The drilling fluids generally have some plasticity and also thixotropy, whereby the upward transport of cuttings is facilitated and their settling when mud circulation is interrupted is prevented. These properties are generally imparted to the mud by colloidal additives, particularly of the type which swell in the liquid in question. In some cases the requisite swelling colloid may be shale drilled through in the course of drilling, or may be surface clays or bentonite or other particularly colloidal clays added for the purpose. Asebstos may also serve as a thickening or suspending agent.

Density of the mud, generally referred to as the weight of the mud, is increased where needed by loading the mud with finely divided solids of high intrinsic density. The commonest such weighting material is finely ground barite, although iron oxide, celestite, galena, and other minerals have been used at various times. As a practical matter, barite is used almost exclusively for this purpose, because of its relatively high density, insolubility, chemical inertness, and availability. One disadvantage of barite is its softness, being from 2.5 to 3.5 on the Mohs

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scale of hardness. The result is that during continued drilling the entire circulating system acts as a kind of fluid mill, so that the softer mineral particles therein are subject to attrition and become gradually reduced in particle size. A direct consequence is a gradual increase in the consistency of the mud arising from the smaller particle size and increase in the number of particles.

Weighting materials are described in the two publications already cited hereinabove, and are also described in United States Patent Numbers 1,575,945, to Stroud, 2,298,984, to Stinson et al., 2,276,075, to Wuensch; and 2,895,911, to Van Dyke.

The present invention provides a drilling fluid comprising oil, water or an emulsion thereof; a thickening agent; and ilmenite having a particle size such that at least 85% by weight passes through a 325 mesh screen in an amount sufficient to substantially increase the density of the fluid. Preferably sufficient ilmenite is added to increase the mud density from a value considered too low to one considered adequate for the drilling conditions present.

The present invention also provides a drilling fluid weighting material consisting of from 1 to 99% by weight of ilmenite and from 1 to 99% by weight of an additional heavy mineral selected from barite, hematite, celestite, galena and mixtures thereof, all of said components having a particle size such that at least 85% by weight passes through a 325 mesh screen.

Ilmenite is a commonly occurring mineral and is chemically ferrous titanite. It is described, for example, in Volume 5 of the text *Rock-Forming Minerals* by W. A. Deer et al., London, 1962, pages 28-33; and in the chapter entitled "Titanium" on pages 851-880 of the text *Industrial Minerals and Rocks*, 3rd Edition, New York 1960. Typical analyses show about 45% titanium dioxide and about 33-37% iron, although there is considerable variation and some accessory elements are often present, such as magnesium, manganese, calcium, and vanadium, generally in amounts less than 1%. Ilmenite suitable for use in our invention preferably has a density of at least 4.3. Some deposits of ilmenite are of sufficiently high grade that they may be used without beneficiation, whereas others require upgrading by the usual metallurgical procedures to achieve this preferred minimum density. In any event, for use in the invention the ilmenite is ground to a fineness of at least 85% passing a 325 mesh screen, and generally somewhat finer, such as 90% of 92% passing 325 mesh. This again is readily accomplished with standard milling procedures.

As mentioned hereinabove, drilling fluids commonly have non-Newtonian viscosity characteristics. That is, they are distinguished

from true fluids such as pure oil or pure water by possessing plasticity; that is, there exists for such a fluid a finite (though generally very small) shearing stress below which no shear occurs. This enables the drilling mud to support finely ground particles of greater density than the liquid itself without settling of the particles. This characteristic is imparted to the drilling mud by the inclusion of substances which may for convenience be termed thickening agents. For ordinary water base muds the thickening agent as already mentioned may consist of clay-bearing formations such as shale or argillaceous sands drilled through and thus incorporated into the mud. Alternatively or additionally, clays may be added to the mud, including highly colloidal clays such as montmorillonite, particularly bentonite, and attapulgite. A wide variety of other water dispersible particularly organic colloids may serve as thickening agents, including starch, cellulose derivatives, sodium polyacrylate, natural gums such as gum karaya, bacterial gums such as that elaborated by certain *Xanthomonas* species, and the like. Mixtures of such suitable thickening agents may be employed if desired. Where the base fluid of the mud is oil, the thickening agent is one producing similar effects in an oleophilic environment. Typical of this group are asphalt, particularly airblown; gilsonite, soaps of the fatty acids including tall oil fatty acids, oleophilic bentonite and oleophilic attapulgite as described in United States Patents 2,531,427 and 2,531,812, both to Hauser; humic acid derivatives of the type described in United States Patents Numbers 3,671,427 and 3,775,447, both to Andrews et al.; magnesium oxide and magnesium carbonate; natural and synthetic rubbers and polyisobutylene; asbestos; and like substances. Mixtures of such thickening agents may be employed if desired. The technology of using such thickening agents in drilling muds generally is well-developed and well-known and need not be described in further detail here. The various thickening agents have a wide diversity in weight effectiveness, that is, the number of pounds thereof which must be incorporated in a barrel of drilling mud of a given type in order to achieve proper consistency. Enough should be used so that the ilmenite is suspended, although greatly excessive amounts should be avoided because of concomitant difficulties in pumping, screening of the mud, and settling out of sand and the like at the surface.

The amount of ilmenite to be added again is completely dependent upon the density desired for the mud, which in turn is dependent upon the particular drilling conditions. The quantity of barite necessary to achieve a given increase in mud density for a mud of given initial density is well-known and tables

oil or pure water at is there exists (though generally below which no the drilling mud articles of water If without settling aracteristic is im- by the inclusion or convenience be for ordinary water agent as already clay-bearing for- argillaceous sands incorporated into or additionally, ie mud, including h as montmoril- lite, and attapul- ther water disper- colloids may serve ding starch, cellu- lyacrylate, natural a, bacterial gums y certain Xantho- like. Mixtures of gents may be em- the base fluid of ig agent is one pro- n oleophilic enviro- group are asphalt, onite, soaps of the il fatty acids, oleo- hilic attapulgit as Patents 2,531,427 100 35 auaser; humic acid escribed in United s 3,671,427 and s et al.; magnesium onate; natural and 105 40 polyisobutylene; as- s. Mixtures of such e employed if de- f using such thick- muds generally is 110 45 nown and need not ail here. The vari- ve a wide diversity at is, the number of 115 50 ist be incorporated ud of a given type roper consistency. so that the ilmenite greatly excessive led because of con- 120 55 pumping. screening out of sand and the

e to be added again : upon the density 125 60 ch in turn is depen- drilling conditions. cessary to achieve a ensity for a mud of ill-known and tables 130 65

showing this relation are widely circulated. The range of density of ilmenite as used in accordance with the invention is substantially the same as that of barite used in oil field practice, so that the same tables may be used.

From the foregoing, it will be clear that generally speaking the process involved is one which includes the following: during the course of drilling through formations subject to containing fluids under pressure, and in which a drilling fluid which may be of the class consisting of oil, water, and emulsions of oil and water and which contains a thickening agent, is circulated in the bore hole, the density of said fluid is maintained sufficient to confine said high pressure fluids to their respective formations by adding ilmenite of the particle size already specified to the circulating drilling fluid in an amount sufficient to substantially increase the density thereof to the preselected value, and carrying out said addition from time to time during the course of drilling so as to keep said density within the preselected range.

An example will now be given illustrating the operation of the invention.

Example 1

A water base drilling fluid was prepared and weighted with two different varieties of ilmenite, and also with a commercial barite weighting agent for comparison. The water base drilling mud consisted of water to which had been added 15 pounds per barrel of a commercial Wyoming bentonite, which served as thickening agent. Separate samples of this mud were weighted to a density of 16 pounds per United States gallon by adding the calculated quantity of the several weighting agents. The muds were then stirred for many hours on a laboratory high speed mixer, and at the commencement of the test and at intervals thereafter the mud properties were determined and aliquot samples of the muds were subjected to a screen analysis to determine the per cent by weight of weighting agent passing a 325 mesh screen.

The first ilmenite sample, designated B, was of Norwegian origin and had a density of 4.53 while the second, designated C, was of Canadian origin and had a density of 4.44. The commercial barite, designated A, was of domestic origin and had a density of 4.24. The screen analysis of the weighting materials showed 92.2%, 91.8% and 91.76% passing 325 mesh screen respectively, for samples B, C and A. The two muds made up with ilmenite were treated with 0.5 and 2.0 pounds per ton based on the weight of ilmenite, of sodium acid pyrophosphate respectively, for samples B and C, in order to adjust the initial mud characteristics so as to be comparable with those of the barite-weighted mud.

The quantities of weighting agent required to weight the bentonite-water mud to a density of sixteen pounds per gallon were respectively 404, 406 and 413 pounds per barrel, for B, C and A.

Some properties of these muds are illustrated in the accompanying drawings in which,

Figure 1 shows the reduction in particle size of various weighting materials during the course of mechanical working of suspensions thereof.

Figure 2 shows certain rheological properties of drilling fluids containing various weighting materials as a function of time of mechanical working.

The screen analysis as a function of the time of agitation in the high speed mixer given in Figure 1 shows that the screen analysis did not change for the muds weighted with ilmenite even after a fourteen-hour period of continuous stirring. On the other hand, the curve for the barite, labelled A in Figure 1 shows a progressive comminution of the barite. This is reflected in the mud properties, which are shown in Figure 2 for the Norwegian ilmenite, curve B and the barite, curve A. In Figure 2A the Stormer viscosity in centipoises shows a very great increase for barite after fourteen hours of stirring, whereas that for the Norwegian ilmenite shows very little increase. Figures 2B and 2C show respectively the initial gel strength in Stormer grams and the gel strength after ten minutes quiescence, respectively. Here again the barite shows a substantial increase in both values compared to very little increase in the case of the Norwegian ilmenite.

It may be noted that many ilmenite deposits contain calcium sulfate in the form of gypsum or anhydrite. If these minerals are in the finished ground ilmenite then they will have an adverse effect upon the properties of the drilling fluid to which they are added, in the case where such drilling fluid is of the ordinary aqueous type not stabilized against the flocculating action of calcium ions, which of course are furnished by the calcium sulfate.

In such cases, it is a simple matter to wash out the calcium sulfate mineral by leaching; or more conveniently it may be completely inactivated by the addition of a corresponding quantity of barium carbonate to the ilmenite. The action is that of a double precipitation, whereby the barium carbonate and calcium sulfate react to give barium sulfate and calcium carbonate, both quite insoluble. This is taught and explained more fully in U.S. Patent No. 2,393,165, British Patent, No. 605,173, and Dutch Patents No. 62,356 of 1949.

Of course, where the ilmenite is to be added to an oil-base drilling fluid, or to any

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of the types of aqueous drilling fluids which are stabilized against calcium ions and indeed generally contain substantial concentrations of the latter, it is unnecessary to remove or to counteract any calcium sulfate which might be present in the particular ilmenite or used.

WHAT WE CLAIM IS:—

1. A drilling fluid comprising oil, water or an emulsion thereof; a thickening agent; and ilmenite having a particle size such that at least 85% by weight passes through a 325 mesh screen in an amount sufficient to substantially increase the density of the fluid.
2. A fluid as claimed in claim 1 comprising water as a continuous phase and wherein the thickening agent is a clay, water dispersible organic colloids, asbestos, or a mixture thereof.
3. A fluid as claimed in claim 2 wherein the clay is bentonite or attapulgite.
4. A fluid as claimed in claim 1 comprising oil as a continuous phase and wherein the thickening agent is asphalt, air-blown asphalt, gilsonite, fatty acid soaps, oleophilic bentonite, oleophilic attapulgite, magnesium oxide, magnesium carbonate, natural and synthetic rubbers, polyisobutylene, asbestos, or a mixture thereof.
5. A fluid as claimed in any one of claims 1 to 4 wherein the ilmenite has a density of at least 4.3.
6. A fluid as claimed in any one of claims 1 to 5 including other weighting agents selected from barite, hematite, celestite, galena and mixtures thereof.

7. A fluid as claimed in any one of claims 1 to 6 and substantially as hereinbefore described in the Example or with reference to and as illustrated in any of the accompanying drawings.

8. A process for drilling a well through subterranean formations subject to containing fluids under pressure wherein a drilling fluid is circulated in the well to confine the fluids under pressure to their respective formations and wherein the drilling fluid is a drilling fluid as claimed in any one of claims 1 to 7.

9. A process as claimed in claim 8, wherein, from time to time during the course of drilling, further ilmenite is added to the drilling fluid to keep the density of the fluid within a preselected range.

10. A process as claimed in either claim 8 or claim 9 and substantially as hereinbefore described in the Example or with reference to or as illustrated in any of the accompanying drawings.

11. A drilling fluid weighting material consisting of from 1% to 99% by weight of ilmenite and from 99% to 1% by weight of an additional heavy mineral selected from barite, hermatite, celestite, galena, and mixtures thereof, all of said components having a particle size such that at least 85% by weight passes through a 325 mesh screen.

STEVENS, HEWLETT & PERKINS,
Chartered Patent Agents,
5 Quality Court, Chancery Lane,
London, W.C.2.

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4. A fluid as claimed in claim 1 comprising oil as a continuous phase and wherein the thickening agent is asphalt, air-blown asphalt, gilsonite, fatty acid soaps, oleophilic bentonite, oleophilic attapulgite, magnesium oxide, magnesium carbonate, natural and synthetic rubbers, polyisobutylene, asbestos, or a mixture thereof.
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STEVENS, HEWLETT & PERKINS,
Chartered Patent Agents,
5 Quality Court, Chancery Lane,
London, W.C.2.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1977.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.



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