June 8, 1954 J. D. UPHAM 2,680,595

METHOD OF SEALING OFF POROUS FORMATIONS IN BOREHOLES

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Fig. 1.

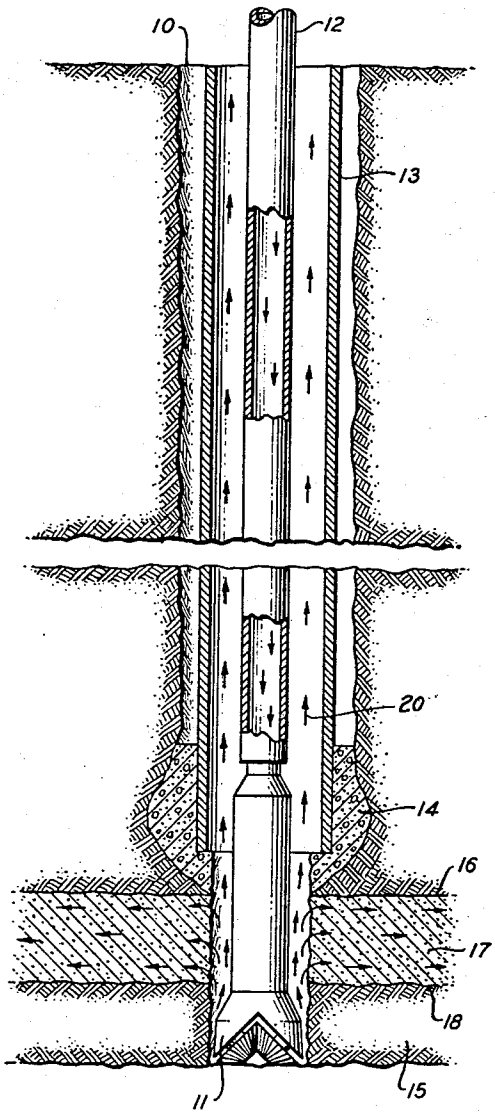
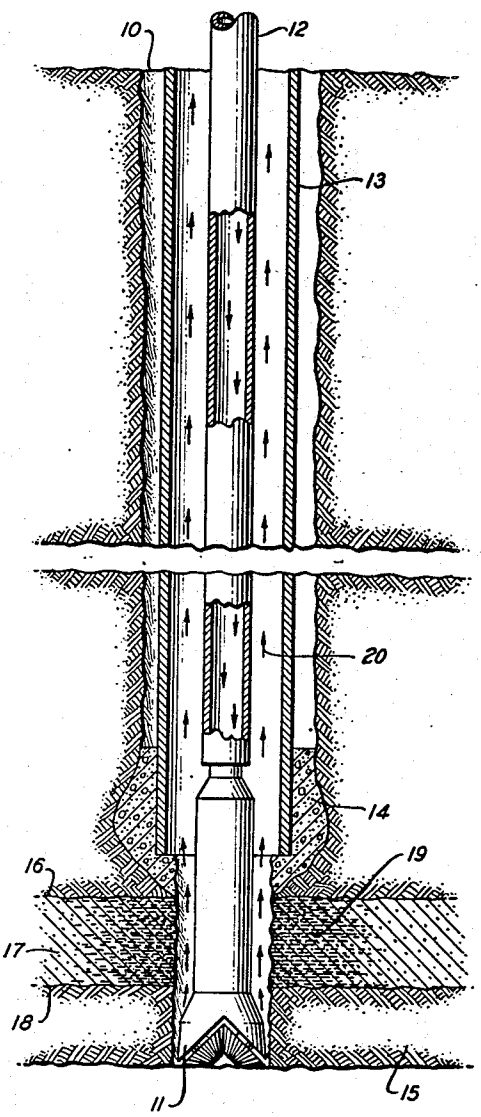


Fig. 2.



INVENTOR.
J. D. Upham
BY
Hudson & Young
ATTORNEYS

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METHOD OF SEALING OFF POROUS FORMATIONS IN BOREHOLES

John D. Upham, Dayton, Ohio, assignor to Phillips Petroleum Company, a corporation of Delaware

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8 Claims. (Cl. 255—1.8)

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This invention relates to a method of sealing wells. In one of its aspects this invention relates to a method of temporarily or permanently sealing earth formations containing or producing petroleum and which are traversed by a bore hole.

In the drilling of wells porous oil sands are often encountered at relatively shallow depths which contain oil and through and past which it is desired to drill in order to obtain a depth sufficient to reach the major oil bearing stratum. In numerous other instances, and for various reasons, it is often desired to prevent the oil, at various stages of the drilling operation from flowing into the well as the same under certain conditions materially hinders the operation.

When such oil bearing strata as those above described are encountered it has been the practice to attempt to seal off the same to prevent leakage therefrom into the well hole. To effect such a sealing, various liquids including those containing solid matter in suspension have been used. These in the majority have been unsatisfactory, and where such a sealing medium as mud and water, which is commonly used, are employed, the mud cakes or plasters up the crevices of the oil sand stratum in such a manner that when it is later desired to re-establish the oil flow from the stratum it is almost entirely impossible for the reason that the crevices are completely clogged by the mud thus preventing escape of the oil.

Furthermore when drilling through a stratum of porous oil sand with a rotary tool there is the danger that the circulation fluid of mud and water necessary to such operations will escape through the stratum and be lost.

It is an object of this invention to provide a method of sealing off porous oil sands occurring adjacent the well hole in such a manner as to positively prevent the liquids contained therein from flowing into the hole, yet whereby the flow from such sands can easily be re-established when desired.

Another object is to provide a method of sealing off porous oil sands from a well hole in such a manner as to prevent leakage thereinto and wherein the sealing medium can easily and completely be removed when the flow of oil from the stratum into the well is later desired and which does not hinder the drilling operations.

Still another object of this invention is to provide a method of sealing off oil sands encountered while drilling wells in such a manner that when desired the seal may be readily broken and the oil allowed to flow into the well.

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A still further object of this invention is to provide a method of sealing wells during drilling operations as will positively guard against the escape of such liquids as are desirable to be retained therein to facilitate drilling.

It is desirable, under certain conditions, to effectively seal off from the well hole any deposits of strata containing such substances as oil which are encountered during the drilling operations, and the sealing off of such deposits and positively preventing the liquids of the same from leaking into the well hole and the escape thereinto of liquids desired to be retained constitutes a major object of this invention.

Still other objects and advantages and a more complete appreciation of the invention will be had from a consideration of the following specification and attached drawing forming a part thereof, wherein:

Figure 1 is a vertical sectional view of a well hole illustrating a part of my invention, and which has been drilled by a rotary tool, and wherein an oil sand stratum has been encountered.

Figure 2 is a vertical sectional view of the same or similar hole as that shown in Figure 1, but wherein the hole has been sealed off from the oil sand stratum and drilling resumed.

It has recently been discovered that certain amides form solid complexes with chemicals normally found in petroleum. This discovery has been utilized to provide improved processes for the fractionation of mixtures of compounds normally obtained in the refining of petroleum derivatives. It was found that urea forms solid crystalline complexes with organic compounds of substantially straight chain structure while it appears to be inert in this respect toward branched chain compounds such as the isoparaffins, or cyclic compounds such as most aromatics and naphthenes. Thiourea on the other hand was found to form solid complexes with organic compounds having either a branched configuration such as the isoparaffins or having a cycloaliphatic structure such as the naphthenes.

As a general rule compounds of greater molecular weight (and hence longer chain length) form solid crystalline complexes which are more stable, and do so with greater ease and under more severe conditions of temperature. In the case of urea a solid complex between an n-C_{20} hydrocarbon and urea would be much more easily formed and be more stable than a similar complex with a C_6 normal paraffin.

The general methods for forming solid com-

plexes between urea or thiourea and suitable complex forming compounds are generally known in the prior art. Usually, the amide is employed in the form of a concentrated solution, preferably water, and can contain a small amount of an activator, usually a low boiling aliphatic alcohol or ketone such as methanol, ethanol, propanol, acetone and methylethyl ketone. Also, nitrogen-containing activators may be employed. The activating nitrogen-containing compound which can be employed to activate urea or thiourea in accordance with this invention should be selected from those which do not form an adduct with urea or thiourea, as the case may be, and should be further selected from those in which urea or thiourea, as the case may be, is soluble to an appreciable extent, say 5 per cent or more, or from those which are substantially soluble, say 5 per cent or more, in a mutual solvent, preferably water, in which urea or thiourea is likewise substantially soluble. It has been found that the nitrogen-containing compound can be ammonia either as liquid ammonia or a concentrated aqueous solution containing from 14 to 28 per cent or more of ammonia or it can be an ammonia derivative selected from those substituted ammonia compounds in which urea or thiourea, as the case may be, is soluble at least to the extent of 5 per cent by weight or from those which are soluble in a mutual solvent to the extent of at least 5 per cent by weight and in which mutual solvent the urea or thiourea is likewise soluble and such ammonia derivative can have the general formula of

$$R_1—N(—R_2)—R_3$$

wherein R_1, R_2 and R_3 are selected from the group consisting of hydrogen and of the organic radicals consisting of alkyl, alkylene, hydroxyalkyl, acyl and aminoalkyl radicals wherein any aliphatic carbon atom chain contains at least one but not more than five carbon atoms per radical; provided that not more than two of R_1, R_2 and R_3 can be hydrogen. Thus, R_1, R_2 and R_3 can all be the same or different organic radicals above enumerated or any one or two of R_1, R_2 and R_3 can be hydrogen with the remaining R_1, R_2 and/or R_3 being one of the above radicals. Representative of the group of compounds comprising a substituted ammonia are the alkyl amines wherein the alkyl group contains a total of from one to five carbon atoms such as mono-n-propyl, monomethyl, dimethyl, trimethyl, monoethyl, diethyl, monopropyl, di-n-propyl, monobutyl, and monopentyl amines; the alkylene amines wherein the alkylene group contains from two to five carbon atoms such as monovinyl, divinyl, monoallyl, monopropenyl, and monobutenyl amines; the alkyl-alkylene amines such as dimethylaminopropene, monoethylaminopropene and monopropylaminoethylene; the hydroxyalkyl amines such as monoethanolamine, diethanolamine, and monopropanolamine; the amino alkyl amines such as diethylenediamine, putrescine and codaverine; acyl amines or amides such as formamide and acetamide; the amines having radicals selected from two or three of the above enumerated radicals such as hydroxypropylaminoethane, propenylaminoethane and methoxyaminobutene.

In addition to ammonia and its derivatives as above illustrated, heterocyclic organic nitrogen base amines can be employed as activators. Among such compounds can be mentioned pyrrole, pyridine, piperidine, morpholine, the picolines, the collidines, quinoline, isoquinoline, indole, pyrimidine, pyrrolidine, pyrroline, pyridazine, pyrazole, pyrazoline and pyrazine. Solid phase contacting can also be employed, such as fixed beds of amide, or slurry processes. When solid amide is employed it is usually preferred that an activator as hereinbefore described be employed. Also, when solid amide is contacted with an adduct-forming compound the resulting complex has a volume greater than the original amide due to a "swelling" of the particles. This feature is particularly useful in the process of my invention since the "swelled" adduct particles fill the crevices of an oil-containing stratum and effectively seal same against leakage. The temperatures employed vary depending upon the nature of the compounds undergoing complex formation. As a practical matter with compounds of high molecular weight, such as paraffin waxes, found in crude petroleum, the upper temperature limit should not exceed 210° F. The complex reaction is an equilibrium reaction and proceeds more readily at lower temperatures. Thus, it is quite probable that an n-C_7 hydrocarbon would not form a solid complex with urea at a temperature much above 100° F. while a C_{25} paraffin wax would still form a solid complex at temperatures in excess of 200° F.

Crude petroleum is a complex mixture of hydrocarbons and it is difficult to predict the exact composition thereof. Crude oils may vary, some containing high percentage of paraffin waxes and others containing high percentage of asphalt and naphthenes. In the practice of my invention the sealing reagent employed will in many instances depend upon the nature of the crude petroleum obtained in the formation which it is desired to effectively seal against leakage into the bore hole. Thus, if a waxy crude is encountered, a concentrated aqueous solution or a fine slurry of urea can be effectively employed as the sealing agent. If a crude oil containing a high naphthene content is encountered, the sealing reagent is best comprised of a concentrated aqueous solution or fine slurry of thiourea. As a preferred method of operating, the sealing reagent employed is a finely divided aqueous slurry of a mixture of urea and thiourea containing in the aggregate equal amounts of urea and thiourea, generally in the range of 20 to 45 weight per cent each of urea and thiourea. The particles are of a size sufficiently small to penetrate the crevices of the oil-containing formation. A small amount of an activator is preferably incorporated into the reagent, usually about 10 to 40 weight per cent of methanol or methylethyl ketone. An activator is necessary when the crude petroleum contains inhibitors for the adduct-forming reaction such as certain heteropolycyclic sulfur compounds found in small concentrations in some West Texas virgin gas oils and Mid-Continent gas oils. In this embodiment of my invention solid complexes are formed between urea and the normal paraffin constituents of the crude and between thiourea and the isoparaffin and naphthenic constituents of the crude thereby providing a double possibility of effectively sealing the porous oil containing formation against leakage into the bore hole.

Referring now in detail to Figure 1 of the drawings there is illustrated a well hole 10 which has been drilled by rotary tool 11 and drill pipe 12 and which contains a pipe casing 13 held in

place by cement 14. The drill hole has been sunk to a level 15 and at level 16 a stratum of porous oil sand 17 has been encountered which extends downwardly to level 18. Oil or gas from the stratum 17 has a tendency to seep into the well hole and materially hinder the drilling operations. If oil enters the well bore hole from the stratum its presence at certain stages will materially hinder the drilling operations, particularly if it is desired to advance the hole to a greater depth. Again, the escape of gas from the stratum into the bore hole may set up serious conditions resulting in a blow out due to the gas pressure. So for various reasons it is highly desirable to seal the bore hole against leakage thereinto of the fluids from stratum 17.

To overcome the evils above described I have found that the crevices of such a porous oil sand stratum as that shown at 17 and which faces upon the wall of the bore hole may be completely sealed against further leakage. An efficient and positive sealing reagent for such sands has been found to be a reagent comprising a finely divided aqueous slurry of a mixture of urea and thiourea containing in the aggregate about 20–45 weight per cent each of urea and thiourea and containing about 10 to 30 weight per cent methanol.

When such an oil sand stratum as that described is encountered a sealing reagent as hereinbefore described may be introduced into the well at the top thereof through the drill pipe 12 and pressure applied to force it downwardly into the well to the porous stratum shown in the drawing; or the sealing reagent may be pumped under pressure directly into the well directly through the drill pipe.

In practice it has been found convenient to add the sealing reagent as a slug in the circulation of the drilling mud. The direction of flow is represented by the arrows 20. The pressure applied to the circulating drilling mud carries the sealing reagent down to the porous stratum. The sealing reagent is forced into the porous stratum and the pressure maintained there for a period of time sufficient for a solid complex to form between the reagent and the reacting constituents in the oil and thus effectively seal the formation against leakage into the bore hole. The induction period or time which it takes for the complex to be formed will vary depending upon the conditions existing in said stratum and the composition of the crude oil contained therein. A reasonable induction period is within the range of 1 minute to 1 hour.

After the seal has been effected the drilling progresses, and Figure 2 represents the condition of the bore hole after the sealing reagent has ultimately been forced into the stratum 17 and the solid complex formed in the crevices thereof effecting a positive seal at 19 against the migration or leakage in either direction of liquids or fluids in the bore hole or the stratum 17.

The circulation fluid or drilling mud is now almost entirely free of the sealing reagent as the same has been forced back into the stratum 17.

When it is desired to unseal the formation this is readily done by pumping down a suitable solvent such as hot water or methanol, or by otherwise raising the temperature to provide conditions sufficient to decompose the solid complex formed between the sealing reagent and the complex forming compounds. The resulting solution of urea and thiourea can be pumped out of the bore hole into the mud pit, or otherwise mixed with the drilling mud, in which it will aid in controlling the viscosity of the drilling mud as described in U. S. Patent 2,280,996 (1942).

While I have described my invention in terms of its preferred embodiments those skilled in the art will readily appreciate that modifications can be made without departing from the spirit and scope of my invention as disclosed therein.

The term "crevice" as used herein includes any interstice of an oil-bearing formation, including pore and/or fissure. While oil-bearing sand has been mentioned particularly herein, the invention is also applicable to all other oil-bearing earth formations, for example limestone. When the sealing reagent is introduced into the well as a slug in the drilling fluid, circulation is ordinarily stopped for the period during which the slug is held under pressure opposite the formation for the purpose of penetrating and forming the sealing complex therein.

I claim:

1. In drilling bore holes through an oil containing earth formation wherein the temperature therein does not exceed 210° F., the method of preventing oil from leaking into the bore hole which comprises introducing into the bore hole a sealing reagent comprising an aqueous mixture concentrated with respect to at least one from the group consisting of urea and thiourea, applying pressure within said hole to force the sealing reagent downwardly into said hole and against the side wall thereof and into the crevices of the oil containing formation facing on said bore hole walls, and maintaining said pressure for a period sufficient to form a solid complex between the sealing reagent and constituents in the oil in said crevices whereby said formation is sealed against leakage into the bore hole.

2. The method according to claim 1 wherein the sealing reagent employed contains an activator for the solid complex forming reaction.

3. The method according to claim 2 wherein methylethyl ketone is employed as activator.

4. The method according to claim 1 wherein a saturated aqueous solution of urea containing a small amount of methanol is employed as the sealing reagent.

5. A method according to claim 1 wherein a saturated aqueous solution of thiourea containing a small amount of methanol is employed as the sealing reagent.

6. In drilling bore holes through oil containing earth formations wherein the temperature therein does not exceed 210° F., the method of preventing oil from leaking into the bore hole which comprises introducing into the bore hole a sealing reagent consisting of a finely divided aqueous slurry of urea and thiourea containing in the aggregate from 20 to 45 weight per cent each of urea and thiourea and containing about 10 to 30 weight per cent of methylethyl ketone, applying pressure within said hole to force the sealing reagent downwardly into said hole and against the side wall thereof and into the crevices of the oil containing formation facing on said bore hole walls, and maintaining said pressure for a period of time to form a complex between said sealing reagent and constituents in the oil in said crevices whereby said formation is sealed against leakage into the bore hole.

7. In drilling bore holes through oil containing earth formations wherein the temperature does not exceed 210° F., the method of preventing oil from leaking into the bore hole which comprises introducing into the bore hole as a slug in the

drilling mud a sealing reagent comprising an aqueous mixture concentrated with respect to at least one of the group consisting of urea and thiourea, applying pressure within said hole to force the sealing reagent downwardly into said hole to the location of the oil containing formation facing on said bore hole walls, forcing said sealing reagent into the crevices of said oil containing formation, and maintaining pressure for a period sufficient to form a solid complex between the sealing reagent and the constituents in the oil in said crevices whereby said formation is sealed against leakage into the bore hole, continuing drilling of said hole to a greater depth and circulation of the drilling mud for a period of time, and unsealing said oil containing earth formation by passing a quantity of water into said hole and down to said oil containing formation and into the

crevices thereof to decompose the solid complex formed between the sealing reagent and constituents in the oil.

8. A method of unsealing an oil-containing earth formation facing on a bore hole and sealed by forming in the crevices of said formation a solid complex between constituents of the oil and at least one from the group consisting of urea and thiourea, which comprises subjecting the solid complex in said crevices to the decomposing action of water.

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