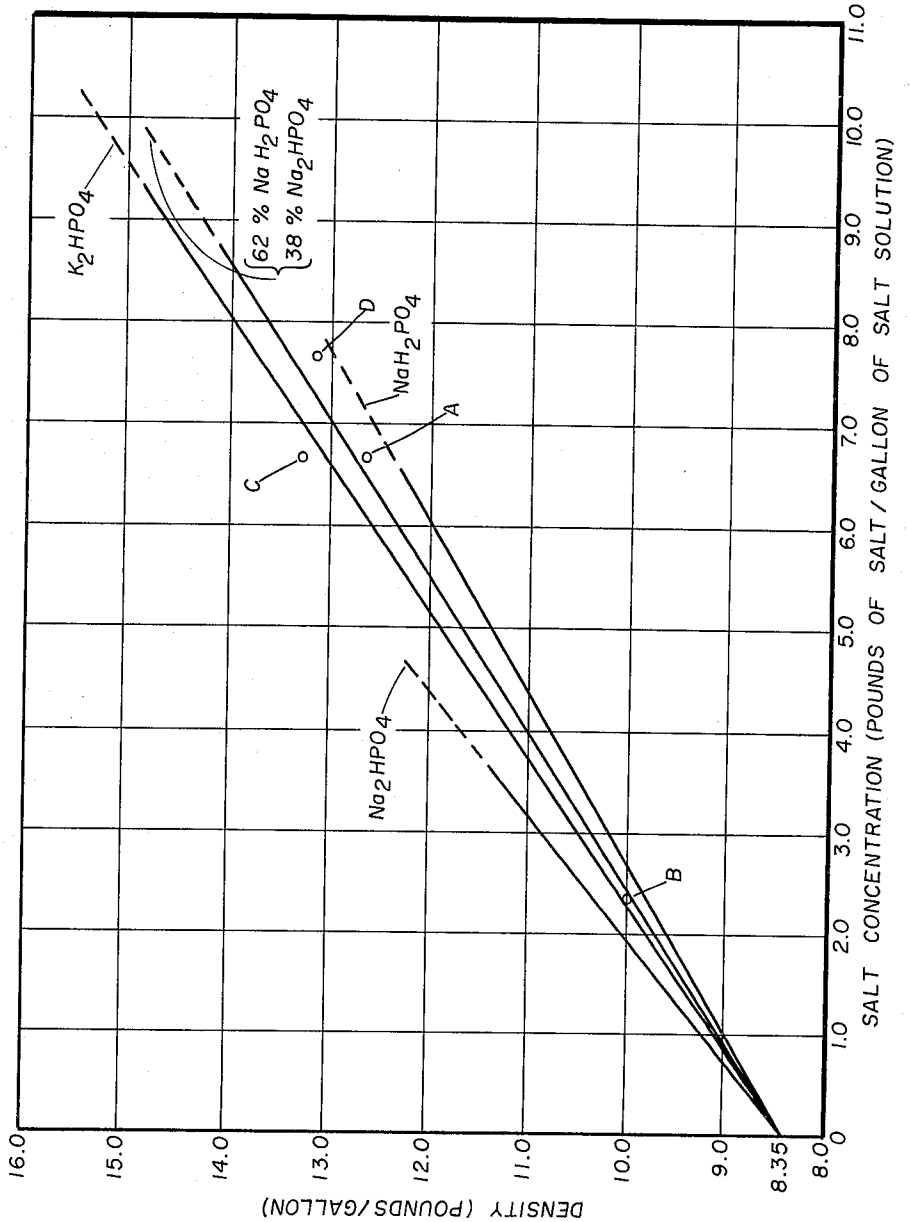
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METHOD EMPLOYING WEIGHTED WELL FLUID

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METHOD EMPLOYING WEIGHTED WELL FLUID

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This invention relates to wells drilled into the earth and relates more particularly to a process used in connection with such wells to prevent the unintentional expulsion thereinto of formation fluids, particularly petroleum hydrocarbons, from subterranean formations penetrated by such wells.

Wells are drilled into the earth for various reasons. For example, wells are drilled into the earth to penetrate subterranean formations which may contain petroleum hydrocarbons. These petroleum hydrocarbons, whether crude oil, natural gas, or a mixture of both, are often contained within the formations under high pressures.

Upon the penetration of such petroleum hydrocarbon-containing formations by a well, or borehole, the petroleum hydrocarbons can escape into the well and thence to the earth's surface. This situation can exist during the drilling and the completion of the well. It may also exist from a formation during production of petroleum hydrocarbons from another formation.

In the past, liquids such as natural or weighted muds and certain salt solutions have been used to fill the well at least partially. The liquids employed impose a hydrostatic pressure upon the petroleum hydrocarbon-containing formation adjacent to the well. This pressure, most desirably, is in excess of the pressure of the petroleum hydrocarbons in the formation. The hydrostatic pressure imposed upon the formation is determined by the density of the liquid and the height of the column of the liquid in the well.

Previously, the natural muds employed had sufficient density to hold the moderate fluid pressures encountered in formations at shallow depths. As deeper wells were drilled into petroleum hydrocarbon-containing formation, however, where greater fluid pressures existed, high density solids had to be added to the muds to provide the hydrostatic pressure necessary to prevent unintentional expulsion of petroleum from the formations. Thus, weighted muds were developed to provide high density liquids.

The temperature increases, for each 60 feet in depth of a well, approximately 1° F. above the ambient temperature at the earth's surface. The temperature in a well 10,000 feet deep, for example, can thus be about 250° F. Such high temperatures have required special weighted muds which are more expensive than the other more commonly used muds.

The use of the natural and weighted muds as high density liquids is costly. Further, such muds suffer from many deficiencies caused by the deleterious effects of high pressures and temperatures, salt contamination, and the like. Additionally, the preparation of certain weighted muds requires complex or critical steps. In most instances, different types of muds have to be used as drilling fluids, as completion fluids, and as packer fluids.

As a substitute for muds, salt solutions, such as sodium chloride solutions, or brines have been used. However, the density of such brines is limited to about 10 pounds per gallon of solution. Other salts, such as sodium nitrate and calcium and zinc chlorides, have been mixed into brines to obtain greater densities. However, these mixed salt solutions have not been found to be entirely satisfactory for reasons which include severe

corrosion to steel casing, tubing, and the like. On the other hand, the use of aqueous liquids containing salts to produce high density fluids capable of containing formation fluids under high pressures within formations penetrated by a well is most desirable because of the relatively low cost of these liquids and the relatively simple procedures required for their preparation.

It is an object of this invention to provide a novel process for providing an aqueous liquid containing salts at a position adjacent a subterranean formation containing formation fluids, particularly petroleum hydrocarbons, under pressure to prevent unintentional expulsion of such fluids into a well formed into the earth and penetrating such formation.

Another object of this invention is to provide a process in accordance with the preceding object wherein said aqueous liquid will have imparted to it a sufficiently high density to prevent unintentional expulsion of the petroleum hydrocarbons from a formation and the use of expensive natural or weighted muds with their inherent deficiencies and the use of highly corrosive salts are avoided.

A further object of this invention is to provide a process utilizing an aqueous liquid that is stable at high temperatures and pressures, is nontoxic, and is not harmful to the formation and does not require complex or critical steps for its preparation or use.

Still another object of this invention is to provide a process utilizing an aqueous liquid of sufficiently high density to contain great pressures within a well in the earth and which is especially suited for use in gas wells.

The foregoing objects, together with other objects and advantages of the present invention, will more fully appear from consideration of the following specification together with the drawing in which there is graphically shown one preferred illustrative embodiment of the present invention. The drawing shows by several curves the relationship of an aqueous liquid having various salt concentrations (in pounds of salt per gallon of salt solution) to the density of the resultant aqueous liquid (in pounds per gallon). Each curve is comprised of a solid line portion indicating the concentrations of dissolved salt obtainable at approximately 77° F. and a chain-line portion indicating the concentrations of dissolved salt obtainable at higher temperatures.

In accordance with the present invention, there is provided a process using certain salts, to be hereinafter disclosed, of orthophosphoric acid in high density aqueous liquid solutions for imposing sufficiently high hydrostatic pressures within a well to prevent the escape thereinto of hydrocarbon fluids under high fluid pressures. More particularly, mixtures of these certain salts are utilized to obtain salt solutions of greater density than can be obtained with the individual salts in the same total salt concentration. In this connection, as will be disclosed in greater detail hereinafter, the amount of such mixtures of salts which can be placed in solution greatly exceeds that of any amount of the individual salts which can be placed in solution at the same temperature.

The individual certain salts of orthophosphoric acid, as well as the mixtures thereof, found usable in the process of the present invention will be described prior to the description of the process itself.

Referring to the drawing, a detailed description of the use of monosodium and disodium salts of orthophosphoric acid, and mixtures of these salts, will be given.

In each of the following tables which are utilized to set forth illustrative examples of the present invention shown graphically in the drawing, the concentrations of the various individual and mixed salts of orthophosphoric acid are given in "pounds of salt per gallon of salt solution" and the density of the resultant solution is given as

"pounds per gallon." The solvent in each solution is water.

It has been found that either monosodium phosphate, (NaH_2PO_4), or disodium phosphate, (Na_2HPO_4), has a relatively low solubility in water at normal ambient temperatures at the earth's surface. Some solubilities of these salts, and the densities of the resulting solutions, are set forth in the drawing and below in Tables I and II.

TABLE I

[NaH_2PO_4 at 77° F.]

Salt concentration	6.12	[1] 6.44
Density	12.0	12.3

[1] Saturated solution.

TABLE II

[Na_2HPO_4 at 90° F.]

Salt concentration	1.74	2.92	[1] 3.69
Density	9.85	10.8	11.3

[1] Saturated solution.

Disodium phosphate at the indicated elevated temperatures can produce the following solutions:

Salt concentration	4.39	4.88	5.18	5.52
Density	11.7	12.0	12.2	12.4
Temperature,° F	106	117	124	129

The density of a saturated solution of disodium phosphate is 12.8 at 138° F.

Thus, at ambient temperatures such as commonly encountered at the earth's surface, an aqueous solution of either salt can be prepared having densities up to between 11–12 pounds per gallon. At increased temperatures slightly higher density salt solutions can be obtained.

Of course, lesser amounts of the salt per gallon of solution will produce proportionate reductions in the resultant density of such solution.

It has been found that mixtures of the monosodium and disodium salts of orthophosphoric acid as the solute from which salt solution is prepared allow greater amounts of salt to be dissolved per gallon of salt solution with the solution having a resultant higher density. For example, it has been found that with mixtures of monosodium and disodium phosphates a solution can be prepared at 77° F. having a density of over 14 pounds per gallon of salt solution.

At higher temperatures, greater amounts of the mixed salt can be dissolved to produce higher-density salt solutions.

The use of these mixed-salt solutions in accordance with the present invention provides higher densities than can be obtained with solutions of the individual salts. The advantage of employing high density salt solutions from solutions of such mixed sodium salts of orthophosphoric acid will be evident from the drawing.

Conventional liquids employed in a well, when subjected to high pressure gases, will entrain sufficient quantities of the gases to reduce to an appreciable degree the densities and viscosities of the liquids. These effects caused by the solution of the gases in the liquids is known as "gas cutting" and greatly reduces the effectiveness of the well fluids. The use of the high-density salt solutions of the present invention in a well is of particular advantage since such solutions do not serve as solvents for gaseous hydrocarbons to any significant extent and therefore are not readily "gas cut."

It has been found that when mixtures of the salts of monosodium and disodium phosphate are used having about 62 percent by weight of monosodium phosphate and 38 percent by weight of disodium phosphate not only can a mixed-salt solution be prepared having higher density than that of either salt individually but, additionally, a mixed-salt solution can be prepared having a density

higher than the density of the individual salt solution for the same total salt concentration per volume of salt solution. Table III sets forth the concentrations and densities of a number of such mixed-salt solutions.

TABLE III

[62% NaH_2PO_4—38% Na_2HPO_4 (by weight at 77° F.]

Salt concentration	5.37	7.23	7.32	[1] 8.61
Density	11.9	13.0	13.1	14.1

[1] Saturated solution.

At increased temperatures (shown in the drawing by the chain-line portion of the curve for this mixed-salt solution) greater amounts of the mixed salt can be dissolved to produce higher density salt solutions.

Other solutions having varying amounts of the monosodium and disodium phosphate salts can be prepared and used. In Table IV, a number of such mixed-salt solutions are set forth. From the following Table IV and the drawing it is apparent that advantageous results can be obtained when the mixture of the salts of monosodium and disodium phosphates are used in the range of between 50–80 percent by weight of monosodium phosphate and between 20–50 percent by weight of disodium phosphate.

TABLE IV

[Mixtures of NaH_2PO_4 and Na_2HPO_4 at 77° F.]

Reference Point on Drawing	Percent (wt.) NaH_2PO_4	Percent (wt.) Na_2HPO_4	Salt Concentration	Density
A	75.2	24.8	6.72	12.7
B	31.0	69.0	2.39	10.0
C	50.0	50.0	6.69	13.3

Trisodium phosphate can also be used along with monosodium and disodium phosphate and also in mixtures of such salts. However, the low solubility of trisodium phosphate and the lower density of the resultant salt solutions compared with those of the other mentioned salt solutions in most instances will not make its use as advantageous as that of the monosodium and disodium phosphate salts.

The similarity between the sodium and potassium salts of orthophosphoric acid permits the use of the latter salts in accordance with the advantageous use of the sodium orthophosphoric acid salts to form high density salt solutions. Thus, the monopotassium, dipotassium and tripotassium salts of orthophosphoric acid, and mixtures of such salts, can be used to great advantage. Dipotassium phosphate has the greatest solubility of the potassium salts and can be used to prepare salt solutions having densities up to between 14–15 pounds per gallon at approximately 95° F. In the following Table V, a number of such solutions are set forth.

TABLE V

[K_2HPO_4]

Salt concentration	3.48	6.43	9.41	[1] 10.
Density	11.5	12.9	14.5	14.
Temperature,° F	80	80	86	95

[1] Saturated solution.

At increased temperatures, greater amounts of this salt can be dissolved to provide salt solutions having proportionally higher densities.

The potassium salts can be mixed with the sodium salts to prepare high-density, sodium-potassium-containing salt solutions of orthophosphoric acid. For example, an aqueous mixture having 53.5 percent of dipotassium phosphate and 46.5 percent monosodium phosphate by weight in the amount of 7.69 pounds of such salt mixture per gallon of salt solution at 100° F. has a density of 13.2 pounds per gallon. Such salt solution is indicated by point "D" on the drawing, and has a density greater than that ob-

tained for a saturated solution of the monosodium phosphate salt at such temperature.

Thus, as will be seen from the foregoing, the aqueous liquid used to provide a high-density fluid for use in the process of the present invention comprises a mixture of water as a solvent with a solute selected from the group consisting of the monosodium, disodium and trisodium and monopotassium, dipotassium and tripotassium salts of orthophosphoric acid and mixtures of such salts. By selection of a given salt or mixture of salts and adjustment of concentration, aqueous liquid solutions containing salt concentrations up to about 11 pounds per gallon of salt solution and having densities from that of water 8.35 pounds per gallon up to about 15 pounds per gallon can be obtained at the ambient temperatures commonly encountered at the earth's surface.

Because the solubility of the mentioned sodium and potassium salts of orthophoshoric acid increases with increased temperature, greater salt concentrations can be obtained at elevated temperatures to provide correspondingly higher densities. This is an important advantage in very deep wells where high temperatures are encountered. Further the aqueous liquid solutions of these salts are stable both to pressure and temperature.

The aqueous liquid solution of the individual and mixed salts, both the sodium and potassium salts of orthophosphoric acid, can be prepared in various ways as will be apparent to one skilled in the art. For example, the salt or salts can be dissolved directly in water. Alternatively, orthophosphoric acid can be reacted with a solution of sodium or potassium hydroxide in proper amounts to obtain the aqueous liquid salt solution desired. Further, a solution of orthophosphoric acid can be reacted with solid sodium or potassium hydroxide, or a solution thereof, in proper amounts to obtain the aqueous liquid salt solution desired. Additionally, sodium or potassium hydroxide can be reacted in aqueous media in proper amounts with monosodium or disodium or potassium phosphate to obtain the aqueous liquid salt soltuion desired.

The salt solutions can be prepared at the earth's surface or in the well bore as desired. The salts can be dissolved in water, in amounts less than saturation or at saturation, or can be made into supersaturated solutions. Because high-density salt solutions are viscous, even slurries of the solid salts may be formed having large amounts of undissolved salts suspended therein and introduced by pumping or the like through the well to a position adjacent the formation desired to be sealed by the resultant aqueous liquid salt solution. Also, the salts can be added to brine to increase the obtainable density above 10 pounds per gallon.

Corrosion inhibitors such as sodium arsenite may be added to the aforementioned salt solutions if desired.

The mechanical manner in which the salt solution having the desired density is prepared or the equipment with which such aqueous liquid salt solution is introduced through the well to a position adjacent the desired formation is not deemed critical within the process of the present invention. Various arrangements therefore will be apparent to one skilled in the art.

The essentials of the present process are as follows:

(1) The prevention of the unintentional expulsion of formation fluids, particularly petroleum hydrocarbons, from a subterranean formation containing the same at pressures greater than atmospheric into a well formed into the earth and penetrating such formation by introducing the aqueous liquid salt soltuion, heretofore described in detail, through the well to a position adjacent the formation containing the petroleum hydrocarbons, the aqueous liquid having a density sufficient to provide a hydrostatic pressure on such formation of a magnitude sufficient to prevent expulsion of the petroleum therefrom into the well.

(2) The aqueous liquid salt solution, as previously described, comprising a mixture of water as a solvent with a solute selected from the group consisting of the monosodium, disodium, and trisodium and the monopotassium, dipotassium, and tripotassium salts of orthophosphoric acid, and mixtures of such salts.

The aqueous liquid salt solution is maintained within the well adjacent the petroleum hydrocarbon-containing formation for whatever time interval is necessary and desired to prevent the expulsion of the petroleum hydrocarbons from the formation. The aqueous liquid can be readily removed from the well by pumping or by other methods when expulsion of petroleum hydrocarbons from the mentioned formation is desired.

It will be readily appreciated from the foregoing that all of the objects of this invention have been attained in providing a process using a stable high-density aqueous liquid salt solution to prevent the unintentional expulsion of hydrocarbons from underground formations. These aqueous liquid salt solutions are stable and relatively noncorrosive, and are readily prepared and can be used during the drilling and completion of a well or as packer fluids. They do not have the deficiencies of heretofore known fluids used in similar processes.

This invention may be embodied in other forms without departing from the spirit or essential characteristics thereof. Such other forms are intended to be within the spirit of this invention and it is intended to protect by this Letters Patent all forms of the invention falling within the scope of the following claims.

The invention having been described, what is claimed is:

1. A process for preventing the unintentional expulsion of formation fluids from a subterranean formation containing the same at pressures greater than atmospheric into a well penetrating such formation comprising the steps of introducing through the well to a position adjacent the formation containing formation fluids an aqueous liquid having a density sufficient to provide a hydrostatic pressure on said formation of a magnitude sufficient to prevent expulsion of said formation fluids therefrom into said well, said aqueous liquid comprising a mixture of water and a mixture of at least two solutes selected from the group consisting of the mono-, di-, and trisodium and the mono-, di-, and tripotassium salts of orthophosphoric acid, the amounts of the solutes selected being such as to provide said aqueous liquid with a density greater than the densities of solutions of the selected solutes individually at the same conditions, and maintaining said aqueous liquid within said well adjacent said formation.

2. The process of claim 1 wherein said aqueous liquid contains said mixture of solutes up to an amount sufficient to saturate the liquid with said mixture of solutes at a temperature between the ambient temperature at the earth's surface and the temperature within said well adjacent said formation.

3. The process of claim 1 wherein said aqueous liquid contains said mixture of solutes in an amount up to 11 pounds in each gallon of aqueous liquid.

4. A process for preventing the unintentional expulsion of formation fluids including the petroleum hydrocarbons from a subterranean formation containing same at pressures greater than atmospheric upon penetration of such formation by a well formed into the earth comprising the steps of introducing through the well to a position adjacent the formation containing formation fluids, an aqueous liquid having a density sufficient to provide a hydrostatic pressure on said formation of a magnitude sufficient to prevent expulsion of said formation fluids therefrom into said well, said aqueous liquid comprising a mixture of water and a mixture of at least two solutes selected from the group consisting of mono- and disodium salts of orthophosphoric acid, the amounts of the solutes selected being such as to provide said aqueous liquid with a density greater than the densities of solutions of the

selected solutes individually at the same conditions, and maintaining said aqueous liquid within said well adjacent said formation.

5. The process of claim 4 wherein said aqueous liquid contains said mixture of solutes consisting of a mixture of the mono- and disodium salts of orthophosphoric acid in quantities of said mixture up to an amount sufficient to saturate said liquid with said mixture of solutes at a temperature between the ambient temperature at the earth's surface and the temperature within the well adjacent said formation.

6. The process of claim 4 wherein said aqueous liquid contains said mixture of solutes consisting of a mixture of between 50 to 80 percent by weight of the monosodium salt and between 20 to 50 percent by weight of the disodium salt of orthphosphoric acid.

7. The process of claim 4 wherein said aqueous liquid contains said mixture of solutes consisting of a mixture of 62% by weight of the monosodium salt and 38% by weight of the disodium salt of orthophosphoric acid.

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