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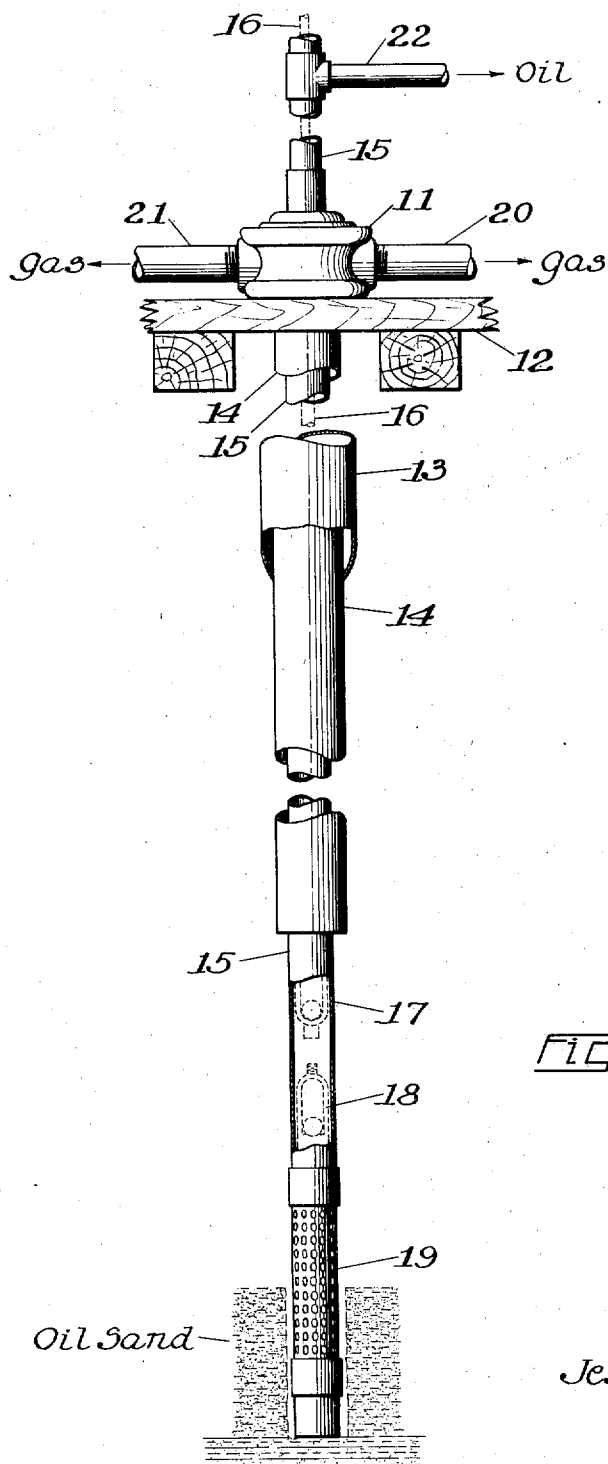
J. R. WILSON

1,990,969

WELL TREATMENT

Filed March 16, 1933

2 Sheets-Sheet 1



INVENTOR
Jesse Russell Wilson
BY
Bruce K. Brown
ATTORNEY

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J. R. WILSON

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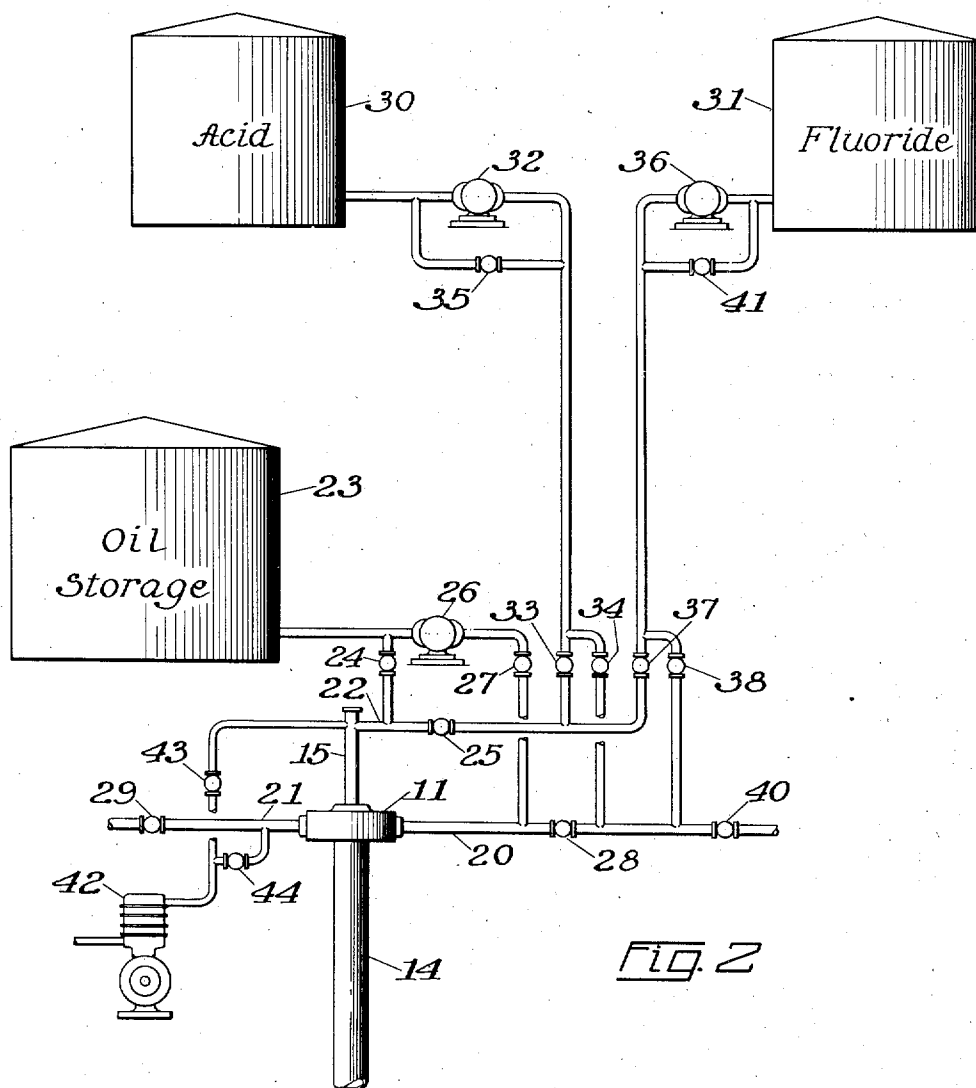


Fig. 2

INVENTOR
Jesse Russell Wilson
BY *Bruce K. Brown*
ATTORNEY

UNITED STATES PATENT OFFICE

1,990,969

WELL TREATMENT

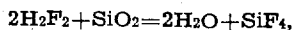
Jesse Russell Willson, Chicago, Ill., assignor to
Standard Oil Company, Chicago, Ill., a corpo-
ration of Indiana

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29 Claims. (Cl. 166—21)

My invention pertains to the treatment of wells, particularly deep wells for the production of oil, gas, water, brine, or other fluids, with chemicals to decrease the resistance to flow encountered by the fluid in the geological formation at the base of the well. The principal object of my invention is to make it possible to treat wells with hydrofluoric acid or other reagents, particularly reagents of a poisonous, corrosive or dangerous nature without actually handling the reagent. This is done by introducing into the well two or more materials capable of interacting to form the desired reagent. Detailed objects of my invention will become apparent as the description thereof proceeds.

In the operation of wells, particularly oil wells producing from a sand or other silicious geological formation, the original rate of flow tends to decrease with greater or less rapidity after the well is first "brought in" and even if the well produced freely at first it is ultimately necessary to start pumping in order to maintain a reasonable rate of production. Furthermore, even after pumping is resorted to the rate of production tends to decline until it ultimately reaches a point at which it is no longer economical to continue the operation of the well. This point is very often reached long before the oil or other fluid in the subterranean reservoir is exhausted. This phenomenon is occasioned by the fact that finely divided sand, other silicious material and miscellaneous debris tend to be deposited by the fluid flowing toward the base of the well, thereby clogging up the pores or passages in the geological formation immediately surrounding the base of the well with the result that the resistance to flow is greatly increased. It has occurred to me that one method of rectifying this situation is to dissolve out this deposited material by the use of a suitable reagent. In the case of sand, one suitable reagent is hydrofluoric acid or hydrogen fluoride which reacts with the sand in accordance with the following equation:

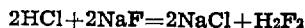


producing water and silicon tetrafluoride, the latter being a gas. The principal difficulty with this procedure is that hydrofluoric acid is an extremely dangerous material to handle. The risk encountered in introducing it into an oil well would be so great that I do not believe it has ever actually been attempted.

My invention solves this problem by introducing into the well two or more harmless or rela-

tively harmless reagents which by their interaction generate hydrofluoric acid within the well and/or within the geological formation at the base of the well. The hydrofluoric acid in turn interacts with the sand or other silicious material deposited in the pores of the formation and constituting a portion of it. In some cases the hydrofluoric acid may react with the bulk of the formation itself, thereby tending to increase the size of the cavity at the base of the well with consequent reduction of the resistance to flow, but, in general, the acid is forced back into the pores of the formation, by means hereafter discussed, and serves to clean out these pores or passages.

Various materials can be used for this purpose, since, as is well known, hydrofluoric acid can be generated by a variety of materials. In general, however, I prefer to use as one of my materials an acid, preferably a strong mineral acid such as hydrochloric, sulfuric or nitric and as the other of my materials an aqueous solution or suspension of an inorganic fluoride such as an alkali fluoride, an alkaline earth fluoride, or a mixed fluoride. The principal requirement is that none of the products of the reaction should be insoluble so as to clog up the pores of the formation. One of the pairs of materials which I prefer to use is hydrochloric acid and sodium fluoride which interact in accordance with the following equation to generate hydrofluoric acid and sodium chloride:



Care should be taken to use the hydrochloric acid in quantities somewhat in excess of the stoichiometrical equivalent of the sodium fluoride used. This is done for the purpose of maintaining an excess of acid at all times within the geological formation during the treatment. If this is not done the silicon tetrafluoride formed tends to react with the water present to form insoluble or gelatinous silicic and hydrofluosilicic acids which clog up the formation. For the same reason, it is highly preferably that at least a portion of the acid reach the geological formation before the fluoride since this will prevent any hydrofluoric acid being generated except in a sufficiently strongly acid solution to substantially prevent the deposition of insoluble or gelatinous materials.

The amount of the two reagents introduced will, of course, vary greatly with the condition and nature of the well to be treated. However, in the treatment of deep oil wells producing from sand formations I prefer to use amounts of materials adapted to produce from 500 to 10,000 lbs. of

hydrofluoric acid. The amount of the acid material introduced should be at least 5% and preferably from 10% to 100% in excess of that required to react with the fluoride according to the above equation.

The method of introducing these materials into a well can best be described by reference to the accompanying drawings in which:

Figure 1 represents an elevation of an oil well partially in section; and

Figure 2 represents a diagrammatic elevation of the well head together with means for introducing the various materials used.

In Figure 1, casinghead 11 rests on the derrick floor 12. Drive pipe 13 extends a short distance down into the ground and within it is the customary casing 14 which extends up to casinghead 11. Inside of casing 14 is the usual tubing 15 through which the oil is produced. The gas produced along with the oil is normally recovered from the annular space between casing 14 and tubing 15. Within tubing 15 are the pump rods 16, working valve 17 and standing valve 18, which are shown in dashed lines, since, in general, it is preferable to remove them prior to treatment in accordance with my invention. At the bottom of tubing 15 is any desired form of screen and anchor 19. Gas produced from the well flows out through pipes 20 and/or 21 and oil similarly produced flows or is pumped out through pipe 22.

Referring now more particularly to Figure 2, when it is desired to treat the well in accordance with my invention, it is desirable, as previously indicated, to remove elements 16, 17 and 18. It is then desirable to flow oil back into the well from oil storage tank 23. This can be done by opening valve 24, valve 25 being closed. Simultaneously, oil can be flowed or pumped into the casing 14. This can conveniently be accomplished by means of pump 26 and valve 27, valves 28 and 29 being closed. When casing 14 and tubing 15 have been filled with oil to a point sufficient to counterbalance the pressure exerted by the fluid reservoir at the base of the well, the next step is to introduce the materials necessary to generate the hydrofluoric acid. This can be done in a variety of ways. Thus, the acid contained in storage tank 30 (for instance hydrochloric acid of 18° Bé.) and the fluorine-containing material contained in storage tank 31 (for instance a concentrated aqueous suspension of sodium fluoride pulverized to pass a 200 mesh screen) can be introduced into tubing 15 in alternate "slugs" or they can similarly be introduced into casing 14 in alternate slugs or either of them can be introduced into tubing 15 and the other simultaneously into casing 14. It is also possible to introduce both of these materials simultaneously into tubing 15 or casing 14, thereby allowing the mixture to take place at the well head. This last method is in general not the most desirable since generation of the hydrofluoric acid takes place above ground which is attended with some danger. It is, however, greatly preferable to direct introduction of hydrofluoric acid.

In general, I prefer to put both materials into the well through tubing 15. This is done by first pumping acid by means of pump 32 from storage tank 30 through valves 33 and 25 into tubing 15 (valves 24, 34, 35, 37 and 43 being closed). When the desired amount of acid has thus been introduced into the well, valve 33 is closed and the fluoride slurry contained in storage tank 31 is then introduced into tubing 15 by means of pump 36 and valves 37 and 25 (valves 24, 33, 38, 41 and

43 being closed). When the desired amount of fluoride has been introduced, valve 37 is closed and acid is again introduced by means of pump 32 and valves 33 and 25. In operating by this method, which I may refer to as the "slug method," I prefer to introduce as the first slug from 10 to 25% of the total acid to be used and then to introduce alternate slugs of fluoride and acid, each slug being between 2 or 3% and 10 or 15% of the total amount of each of these materials to be introduced.

In order to avoid any intermixing of the two materials being introduced until they reach the geological formation, "spacers" may be introduced into tubing 15 between the "slugs" of acid and fluoride previously described. As such "spacers" small slugs of oil (from tank 23) or water (from a source not shown) are appropriate. Other inert fluids can be used.

When the hydrostatic pressure of the acid and fluoride is sufficient to blow these materials into the well at a satisfactory rate, pumps 32 and 36 can be dispensed with and the introduction can be accomplished by means of valves 35 and 41. Pumping is usually more practical, however.

As aforementioned, a satisfactory alternative to the "slug method" is to introduce either the acid or the fluoride through tubing 15 and the other of these two materials through casing 14 (i. e. through the annular space between tubing 15 and casing 14). Thus, acid can be introduced into tubing 15 through valves 33 and 25 and fluoride can simultaneously be introduced into casing 14 through valves 38 and 28. Alternatively acid can be introduced into the casing through valves 34 and 28 and fluoride into the tubing through valves 37 and 25. Also, as aforementioned, both of these two materials can be introduced into tubing 15 or into casing 14 by obvious manipulations of the various valves shown, but this is not a preferred method. In any event, a considerable amount of acid is introduced prior to the introduction of fluoride in order to prevent the precipitation of silicic acids.

When one material is introduced through the casing and the other through the tubing it is generally desirable to omit the step of introducing oil prior to introducing the acid and fluoride since this avoids the necessity of allowing these materials to settle through a large head of oil.

A still further alternative not shown in the drawings is to use two tubings in place of tubing 15 within casing 14, putting the acid down through one tubing and the fluoride through the other. This is a satisfactory method but entails the use of special equipment.

Regardless of how the two materials are introduced into the well it is desirable, after the introduction is completed, to force them back into the geological formation at the base of the well. This can be done by flowing in or pumping in an additional amount of oil, or better, it can be accomplished by blowing the materials down with a blast of air or gas. This can be accomplished by means of compressor 42 which is equipped to blow air or gas into tubing 15 and/or casing 14 through valves 43 and/or 44 (valves 24, 25, 27, 28 and 29 being closed). The air or gas thus blown in not only serves to blow the materials introduced and their reaction products back into the geological formation where they will do the most good, but also serves to agitate the two materials introduced which promotes a thorough reaction with maximum formation of hydrofluoric acid. Furthermore, it tends to blow the gaseous silicon

tetrafluoride formed by the reaction of the hydrofluoric acid on the silicious material in the geological formation back away from the base of the well. This is desirable since, if silicon tetrafluoride encounters water, or an aqueous solution, which is not strongly acid, near the base of the well it tends to precipitate silicic and hydrofluosilicic acids, as previously described, which clog up the pores of the formation. On the other hand, if this silicon tetrafluoride is blown well back into the formation before reacting with water, it can do relatively little harm.

While Figure 2 illustrates a permanent set-up it will readily be understood that tanks 30 and 31, pumps 32, 36 and possibly 26, as well as compressor 42 can be mounted on trucks or otherwise rendered portable and moved from well to well, the necessary connections being made to the well head as desired.

Although I have described my invention in connection with the use of hydrochloric acid and an aqueous suspension of sodium fluoride, other alternative materials capable of generating hydrofluoric acid can be used. Thus, for example, sulfuric acid can be used in place of hydrochloric. The sulfuric acid has the advantage of being a stronger acid, less volatile and considerably cheaper. Its use is dangerous, however, if there is likely to be any limestone or other calcareous material in the formation. If the formation contains both silicious and calcareous substances it is well to use hydrochloric acid and to use it in considerable excess, allowing some of it to react with the calcareous material to form carbon dioxide, water and soluble chlorides, and the rest to react with the fluoride, forming hydrofluoric acid which in turn reacts with the silicious matter present. Thus, both silicious and calcareous substances can be converted into soluble materials and gases.

Nitric acid and other acids, particularly strong mineral acids, can be used. Similarly, in place of sodium fluoride, other alkali fluorides, alkaline earth fluorides or mixed fluorides can be used. In fact, any two or more materials which will interact to form hydrofluoric acid and which will not cause precipitation of other reaction products can be used.

In introducing strong mineral acids into a well it is desirable to use an inhibitor which will retard or prevent the action of the acid on the metal of the tubing or casing. Such inhibitors are well known in the art. As an example, when sulfuric acid is used it is desirable to use purified sludge acid recovered by the process of U. S. Patent No. 1,793,146 from the reaction products formed in the treating of raw cracked gasolines with sulfuric acid. This sludge acid contains certain nitrogen bases which are very potent inhibitors.

Although I have described my invention in connection with the generation of hydrofluoric acid within a well (which term includes for the purposes of the claims the geological formation at the base of the well), it will be understood that my invention also comprises the introduction into a well of any two or more materials which will interact therein to form a different material which is of value in treating the well. The methods which I have described are particularly useful where it is desired to treat a well with a reagent which is poisonous, corrosive or toxic. It is also useful where it is desired to treat a well

with an unstable substance which must be formed in situ in order to be effective.

The words "generate a reagent within said well" and similar words as used in the appended claims refer to the generation of the reagent within the well proper and/or within the geological formation at the base of the well.

I claim:

1. A process for the treatment of a well to increase the rate of fluid production therefrom comprising the introduction into said well of at least two materials adapted by their interaction to generate a reagent within said well capable of dissolving a portion of the geological formation at the base of said well.

2. A process for the treatment of a well to increase the rate of fluid production therefrom comprising the introduction into said well of at least two materials adapted by their interaction to generate an acid reagent within said well capable of dissolving a portion of the geological formation at the base of said well.

3. A process for the treatment of a well to increase the rate of fluid production therefrom comprising the introduction into said well of at least two materials adapted by their interaction to generate hydrofluoric acid within said well.

4. A process for the treatment of a well to increase the rate of fluid production therefrom comprising the introduction into said well of an acid and a fluorine compound adapted by their interaction to generate hydrofluoric acid within said well.

5. A process for the treatment of a well to increase the rate of fluid production therefrom comprising the introduction into said well of a strong acid and a fluoride adapted by their interaction to generate hydrofluoric acid within said well.

6. A process according to claim 5 in which the acid is hydrochloric acid.

7. A process according to claim 5 in which the acid is sulfuric acid.

8. A process according to claim 5 in which the acid is nitric acid.

9. A process for the treatment of a well to increase the rate of fluid production therefrom comprising the introduction into said well of a strong mineral acid and an alkali fluoride adapted by their interaction to generate hydrofluoric acid within said well.

10. A process for the treatment of a well to increase the rate of fluid production therefrom comprising the introduction into said well of an acid substance followed by the introduction into said well of a substance adapted to react with said acid substance to generate hydrofluoric acid within the geological formation at the base of said well.

11. A process for the treatment of a well to increase the rate of fluid production therefrom, comprising introducing into said well through segregated conduits, a strong acid and a fluoride adapted to react with said acid to generate hydrofluoric acid within said well.

12. A process for the treatment of a well to increase the rate of fluid production therefrom, comprising the introduction into said well of alternate slugs of a strong mineral acid and an alkali fluoride, adapted to react with said acid to generate hydrofluoric acid within the geological formation at the base of said well.

13. A process for the treatment of a well to increase the rate of fluid production therefrom,

comprising the introduction into said well of a relatively large slug of a strong mineral acid, followed by the introduction of alternate slugs of an alkali fluoride in aqueous dispersion and said strong mineral acid.

14. A process according to claim 13 in which said slugs are separated by a spacer of an inert fluid.

15. A process for the treatment of a well to increase the rate of fluid production therefrom comprising introducing into said well through separate conduits at least two materials adapted by their interaction to generate hydrofluoric acid within said well.

16. A process for the treatment of a well to increase the rate of fluid production therefrom comprising introducing into said well alternate fluid and a slug of a second reagent adapted to react with said first reagent to generate hydrofluoric acid within said well.

17. A process for the treatment of a well to increase the rate of fluid production therefrom comprising introducing into said well in succession through a conduit extending into said well a slug of a first reagent, a spacer of an inert fluid and a slug of a second reagent adapted to react with said first reagent to generate hydrofluoric acid within said well.

18. A process according to claim 17 in which said inert fluid comprises water.

19. A process according to claim 17 in which said inert fluid comprises oil.

20. A process for the treatment of a well to increase the rate of fluid production therefrom comprising the introduction into said well of a fluoride and a stoichiometrical excess of a strong acid adapted by their interaction to generate hydrofluoric acid within said well.

21. A process for the treatment of a well to increase the rate of fluid production therefrom comprising the introduction into said well of a fluoride and an amount of a strong mineral acid at least 5% in excess of the amount required to interact completely with said fluoride to form hydrofluoric acid within said well.

22. A process for the treatment of a well to increase the rate of fluid production therefrom comprising the introduction into said well of an aqueous dispersion of an alkali fluoride and an amount of a mineral acid, selected from the group comprising hydrochloric acid, sulfuric acid and nitric acid, at least 10% in excess of the amount required to interact completely with said fluoride to form hydrofluoric acid within said well.

23. A process according to claim 22 in which at least a substantial portion of said mineral acid reaches the base of said well before any substantial portion of said alkali fluoride reaches the base of said well.

24. A process for the treatment of a well to increase the rate of fluid production therefrom comprising introducing into said well a strong acid and a fluoride adapted by their interaction to generate hydrofluoric acid within said well and blowing said acid, said fluoride and their reaction products back into the geological formation at the base of said well.

25. A process for the treatment of an oil well to increase the rate of oil production therefrom comprising introducing into said well an aqueous dispersion of an acid and an aqueous dispersion of a fluorine compound adapted by their interaction to generate hydrofluoric acid within said well.

26. A process for the treatment of an oil well to increase the rate of oil production therefrom comprising introducing into said well an aqueous solution of a strong mineral acid and an aqueous dispersion of an alkali fluoride to generate hydrofluoric acid within said well.

27. A process for dissolving material deposited in the passage of a geological formation at the base of a well, comprising introducing an acid and a fluoride into said well to generate hydrofluoric acid within said well and forcing said acid and said fluoride to the base of said well and into contact with said geological formation to dissolve at least a portion of said material.

28. A process for dissolving silicious material deposited in the passages of a geological formation at the base of a well, comprising introducing an acid and a fluoride into said well to generate hydrofluoric acid within said well and forcing said acid and said fluoride to the base of said well and into contact with said silicious material to dissolve at least a portion of said silicious material.

29. A process for dissolving finely divided sand deposited in the passage of a predominately silicious geological formation at the base of an oil well comprising introducing a strong mineral acid and a soluble fluoride into said well to generate hydrofluoric acid within said well and forcing said acid and said fluoride to the base of said well and into said passages of said geological formation to dissolve at least a portion of said finely divided sand.

JESSE RUSSELL WILSON.