Patented May 30, 1933

1,911,446

# UNITED STATES PATENT OFFICE

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## METHOD OF TREATING DEEP WELLS

No Drawing. Application filed October 17, 1932. Serial No. 638,182.

The present invention concerns a method of treating deep wells, such as oil, gas, brine, or water wells to increase the output therefrom and is an extension and improvement over the invention disclosed in a prior application of John J. Grebe and Ross T. Sanford, Serial No. 620,292, filed June 30, 1932, issued as Patent No. 1,877,504 on September 13, 1932.

In said prior application it is disclosed that a deep well, in which the mineral-bearing stratum either consists of limestone or of other formation subject to chemical attack by a strong mineral acid or is contiguous to such formation, may be treated with hydrochloric acid containing an agent capable of inhibiting attack of said acid on metals to increase the output of the well. The acid solution is forced into channels and pores of the mineral-bearing stratum under high pressure, such as that created by following the acid charge with a charge of oil, water, or other liquid, by creating still added pressure by means of a pump, or by capping the entrance to the well and creating a high gas pressure within the same. The acid, upon being forced into channels or pores of the mineral-bearing stratum, attacks the calcareous rock, dissolving or disintegrating the same, thereby enlarging said channels and pores or opening new channels through which the mineral may flow to the well. The inhibiting agent present in the acid solution substantially prevents attack of the acid upon metal equipment within the well so that it is unnecessary to withdraw the pump tubing or other metal equipment from the well prior to introducing the acid thereto.

Although the above method is an improvement over all other methods for the chemical treatment of wells to increase the output therefrom, said method comprises a disadvantageous feature. Some of the more effective agents for inhibiting attack of hydrochloric acid upon metals (e. g. mercaptans, thio-phenols, etc.) art but slightly soluble in aqueous hydrochloric acid. In addition, such agents are less dense and more viscous than is the acid solution. During introduction of a hydrochloric acid solution containing such inhibitor into a well, the inhibitor tends to rise to the upper surface of the acid solution and to follow the acid solution downward into the well at a relatively slow rate. During the course of such treatment, there is danger that the acid which first strikes a given metal surface within a well may contain the inhibiting agent in a quantity insufficient to prevent some corrosion and that metal equipment located near the bottom of the well may be corroded to considerable extent during the time required for the relatively viscous inhibiting agent to follow the flow of the acid and form a protective surface on the equipment.

We have now found that an inhibiting agent which is but slightly soluble in the acid to be employed in treating an oil, gas, brine, water, or other deep well may be introduced into the well in concentrated form ahead of the main acid charge, thereby forming protective surfaces over metal equipment within the well before said main charge of acid is contacted with such surfaces. Through such improved mode of operation, the possibility of attack on the metal equipment within a well by the acid is practically avoided.

To the accomplishment of the foregoing and related ends, the present invention, then, consists of the method hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail but certain of the various ways in which the principle of our invention may be employed.

In treating an oil well according to our improved method, the pump rod and valves are first withdrawn from the well. An inhibiting agent, such as a mercaptan (e. g. propyl mercaptan, normal butyl mercaptan, isobutyl mercaptan, tertiary butyl mercaptan, normal hexyl mercaptan, etc.) or a thio-phenol, (e. g. thio-phenol, 2-methyl-thio-phenol, 4-ethyl-thio-phenol, etc.) which is but sparingly soluble in the acid with which the well is to be treated, is introduced into the well, preferably, through the pump

tubing. Such agent, if liquid, may be employed alone, but ordinarily we prefer to employ a solution or emulsion containing said agent in the quantity and concentration found most desirable.

The inhibiting agent may be employed in the form of a solution or emulsion thereof with any vehicle which does not react with said agent to destroy its inhibiting properties. Among the various vehicles which may be employed are water, aqueous soap solution, sulphuric acid, and organic solvents such as gasoline, naphtha, benzene, carbon tetrachloride, trichlorethane, etc.

Due to the possibility of equipment within a well having previously been rusted or otherwise corroded, we prefer first to treat the well with a solution or emulsion of an inhibiting agent which also contains an acid, such as sulphuric acid, chloro-acetic acid, etc., capable of dissolving or scaling corrosion products from the metal equipment within the well. An intimate mixture of 1 gallon of a mercaptan (e. g. butyl-mercaptan, hexyl-mercaptan, etc.) and 1 gallon of 25 per cent aqueous sulphuric acid (which emulsifies quite readily with mercaptan) is well adapted to the purpose. The proportion and concentration of the acid present in the inhibitor mixture may be varied between wide limits. Such mixture, however, should contain a substantial quantity of the inhibiting agent. In practice we prefer to employ the inhibiting agent in concentration representing at least 30 per cent of the total weight of said mixture.

In addition to containing an acid capable of removing corrosion products from the surfaces of metal equipment within a well, the inhibitor solution may advantageously contain an organic solvent capable of loosening or dissolving wax and other organic solids which may be lodged in the channels and pores of the mineral-bearing rock strata. Among the many organic solvents which may be employed in such manner are gasoline, naphtha, benzene, trichloro-ethane, tetrachloroethane, etc. Through first treating a well with a mixture containing:—

(1) At least 30 per cent its weight of an agent which is but slightly soluble in aqueous hydrochloric acid and which is capable of inhibiting attack of hydrochloric or other strong mineral acid on metals.

(2) Sulphuric or other acid capable of removing corrosion products from metal surfaces, and

(3) An organic solvent capable of loosening or loosening and dissolving waxes and other solid organic deposits inside the well, metal equipment within the well is simultaneously cleaned and provided with surfaces which protect such equipment against the corrosive action of the main charge of acid subsequently added.

The quantity of inhibiting agent to be employed in treating a well is dependent upon the particular agent selected for use and upon both the depth of, and quantity of metal equipment within, the well under treatment. Ordinarily we find an inhibitor mixture containing about 1 gallon of a mercaptan, such as butyl mercaptan, etc., to be ample for the treatment of a well containing 3500 feet of 2 inch tubing.

After the inhibiting agent has been introduced into a well it is followed up by a charge of a strong mineral acid such as hydrochloric acid, hydrobromic acid, dilute nitric acid (e. g. 6 per cent nitric acid), etc., which is capable of reacting with limestone and other calcareous rock to form water-soluble products. The acid is employed in such manner and quantity that it preferably does not fill the bore of the well to a depth greater than the thickness of the mineral-bearing stratum. We prefer to use hydrochloric acid for such treatment. The acid may be employed in any desired concentration, but we find a between 5 and 20 per cent aqueous hydrochloric acid solution to be best adapted to the purpose.

After charging the well with acid, pressure is applied to force the acid into the channels and pores of the mineral-bearing rock. Such pressure may be applied by following the acid with a charge of oil, water, brine, or other liquor, by auxiliary action of a pump, or by capping the well and creating a gas pressure therein. The acid, upon being forced into the channels and pores of the mineral-bearing stratum, dissolves or disintegrates the calcareous rock and enlarges said channels and pores or opens new channels through which the oil may flow into the well. The action of the acid upon limestone formation causes the evolution of a considerable volume of carbon dioxide gas. This gas may be allowed to escape up the casing or the latter may be capped off, thereby creating a gas pressure in the well which assists in forcing the acid into the pores and crevices of the rock.

After the action of the acid has practically ceased, the spent solution containing the dissolved salts may be pumped or bailed from the well.

Our invention may be practiced in ways other than those hereinbefore described. It is not necessary, for instance, to add the inhibiting agent and acid solution through the pump tubing, as any other convenient method may be used. The pump tubing may be withdrawn, the inhibiting agent be poured down the inner surfaces of the well casing, and the acid charge may be poured down the well hole or a dump bailer may be

used to lower the charge of acid into the base of the bore. As has previously been pointed out, it is important that surfaces of metal equipment within a well be treated with the inhibiting agent before contacting the main acid charge with such surfaces.

While the foregoing description has been directed particularly to the treatment of oil wells, our method may be employed similarly to increase the flow of gas wells and brine or water wells in cases where the mineral or water-bearing stratum, or the immediately adjacent strata, are of a limestone or calcareous formation, or of a nature such as to be acted upon and dissolved by hydrochloric, hydrobromic, or dilute nitric acid.

Throughout the claims, where it is specified that a liquid body shall contain a corrosion inhibitor in relatively high concentration, the expression "relatively high concentration" is intended to cover any concentration, by weight, of said corrosion inhibitor greater than is required in a 12.5 per cent aqueous hydrochloric acid solution in order to substantially inhibit attack of said acid upon a metal such as iron. Also, in the claims, where it is specified that a liquid body, containing a corrosion inhibitor and an acid, shall contain said corrosion inhibitor in relatively high concentration with respect to the acid, it shall be understood that the claim covers any such liquid body containing the corrosion inhibitor in concentration greater than that required to substantially inhibit attack of the acid present in said liquid body upon a metal such as iron and that the liquid body as a whole may contain any suitable proportion of a non-acid diluent.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. In a method of increasing the output of a well for producing a fluid mineral product such as oil, gas, water, or brine, the steps which consist in treating metal equipment within the well with a liquid mixture containing at least 30 per cent its weight of a corrosion inhibitor selected from the class consisting of mercaptans and thio-phenols and containing an acid capable of removing corrosion products from such metal equipment, and thereafter introducing a 5 to 20 per cent hydrochloric acid solution into the base of the well in such manner that only metal surfaces inside the well which have been treated with the corrosion inhibitor are exposed to contact with the acid.

2. In a method of increasing the output of a well for producing a fluid mineral product such as oil, gas, water, or brine, the steps which consist in treating metal equipment within the well with a liquid mixture consisting of sulphuric acid, an organic solvent capable of dissolving solid paraffins, and a corrosion inhibitor selected from the class consisting of mercaptans and thio-phenols, said mixture containing at least 30 per cent of its weight of the corrosion inhibitor, thereafter introducing a 5 to 20 per cent hydrochloric acid solution into the base of the well in such manner that only metal surfaces inside the well which have been treated with the corrosion inhibitor are exposed to contact with the acid, permitting the acid to act upon the rock formation surrounding the well cavity, and withdrawing the spent acid.

3. In a method of treating a well with acid, the steps which consist in treating metal equipment within the well with a liquid body containing a relatively high concentration of a corrosion inhibitor capable of inhibiting attack of a strong acid upon metals and thereafter introducing an acid, capable of reacting with calcareous rock to form water-soluble products, into the base of the well.

4. In a method of treating a well with acid, the steps which consist in treating metal equipment within the well with a liquid body containing a relatively high concentration of a corrosion inhibitor selected from the class consisting of mercaptans and thio-phenols and thereafter introducing an acid, capable of reacting with calcareous rock to form water-soluble products, into the base of the well in the usual manner.

5. In a method of treating a well with acid, the steps which consist in treating metal equipment within the well with a liquid body containing a corrosion inhibitor capable of inhibiting attack of a strong acid upon metals and an acid capable of removing corrosion products from such metal equipment, the corrosion inhibitor being present in relatively high concentration with respect to the quantity of the acid present in said liquid body, and thereafter introducing an acid, capable of reacting with calcareous rock to form water-soluble products, into the base of the well in the usual manner.

6. In a method of treating a well with acid, the steps which consist in treating metal equipment within the well with a liquid body containing a corrosion inhibitor selected from the class consisting of mercaptans and thio-phenols, and also containing an acid capable of removing corrosion products from such metal equipment, the corrosion inhibitor being present in relatively high concentration with respect to the quantity of acid present in said liquid

body, and thereafter introducing an acid, capable of reacting with calcareous rock to form water-soluble products, into the base of the well in the usual manner.

7. In a method of treating a well with acid, the steps which consist in treating metal equipment within the well with a liquid body containing at least 30 per cent its weight of a corrosion inhibitor capable of inhibiting attack of a strong acid upon metals, and thereafter introducing an acid, capable of reacting with calcareous rock to form water-soluble products, into the base of the well in the usual manner.

8. In a method of treating a well with acid, the steps which consist in treating metal equipment within the well with a liquid body containing at least 30 per cent its weight of a corrosion inhibitor selected from the class consisting of mercaptans and thio-phenols, and thereafter introducing an acid, capable of reacting with calcareous rock to form water-soluble products, into the base of the well in the usual manner.

9. In a method of treating a well with acid, the steps which consist in treating metal equipment within the well with a liquid body containing a relatively high concentration of a corrosion inhibitor capable of inhibiting attack of a strong acid upon metals and thereafter introducing aqueous hydrochloric acid into the base of the well.

10. In a method of treating a well with acid, the steps which consist in treating metal equipment within the well with a liquid body containing a relatively high concentration of a corrosion inhibitor selected from the class consisting of mercaptans and thio-phenols and thereafter introducing aqueous hydrochloric acid into the base of the well in the usual manner.

11. In a method of treating a well with acid, the steps which consist in treating metal equipment within the well with a liquid body containing a corrosion inhibitor selected from the class consisting of mercaptans and thio-phenols, and also containing an acid capable of removing corrosion products from such metal equipment, the corrosion inhibitor being present in relatively high concentration with respect to the quantity of acid present in said liquid body, and thereafter introducing aqueous hydrochloric acid into the base of the well in the usual manner.

Signed by us this 14th day of October, 1932.

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