

UNITED STATES PATENT OFFICE

2,024,718

TREATMENT OF WELLS

Leonard C. Chamberlain, Midland, Mich., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Michigan

No Drawing. Application March 14, 1934,
Serial No. 715,475

11 Claims. (Cl. 166—21)

The invention relates to the treatment with acids of wells yielding fluid products, more particularly oil or gas wells, to increase the production therefrom.

sealed permanently thereby. Thus the usual acid treatment in such a case may result either in sealing the well permanently against further production or in so greatly reducing the rate of production as to make operation economically impractical.

5 In prevailing methods of treatment, a charge of acid is led into the well and forced therefrom into the surrounding earth or rock by the application of fluid pressure. After the acid is neutralized as a result of its action upon the acid-soluble constituents of the earth formation, the spent acid is withdrawn from the well. I have observed, however, that in some cases the spent acid can be withdrawn out of the earth formation with difficulty, or not at all even though the well be put under vacuum by long continued pumping. When this occurs, the spent acid holds back the oil or gas behind it, so that resumption of production is slow or cannot be had at all.

10 I have found that the cause of such difficulties seems to be due largely to the fact that the capillary pores of the earth formation become filled with both gas and liquid, thereby giving rise to a phenomenon which is similar to, if not identical with, what is known as the "Jamin action". The Jamin action may be demonstrated readily in a capillary tube, the surface of the bore of which bears a slight oil film or is not entirely clean, by introducing into such bore alternately a globule of aqueous liquid and a bubble of gas, so as to form a chain of liquid globules separated by gas bubbles. Jamin discovered that if the bubbles in such a chain be sufficiently numerous, very high pressures are required to force the chain out of the tube. A report of Jamin's experiments is found in Compt. Rend., vol. 50, 1860, pp. 172-176, 311-314, and 385-389. The magnitude of the pressure required to discharge the chain of alternate liquid globules and gas bubbles from the tube depends upon the following factors: (1) the diameter of the capillary bore, (2) the surface tension of the liquid in contact with the gas, (3) the degree of adhesion between the liquid and the walls of the tube, i. e. the ability of the liquid to "wet" the bore of the tube.

45 The above effect may be produced in an oil-bearing sand, the surface of the particles of which are more or less coated with oily material. The interstices between the particles act like capillaries, and when gas is present or is formed therein, as by the action of acid upon a carbonate constituent of the sand to produce carbon dioxide, a mixture of gas bubbles and liquid droplets is formed in the passages which produces the Jamin action and requires a high pressure to force the gas and liquid out of the capillaries. If the rock pressure does not exceed that necessary to overcome the resistance to flow caused by the Jamin action, the aqueous solutions resulting from an acid treatment cannot be discharged from the well and the same may be

The problem of bringing about a resumption of production of a well under the aforementioned circumstances involves, therefore, reducing the pressure necessary to cause a flow of aqueous solutions through the interstices of the earth or rock formation toward the well. For this the usual treatments do not provide.

15 Of the three factors previously enumerated which determine the magnitude of the resistance to flow resulting from the Jamin action only the surface tension and adhesion are susceptible of direct control in the treatment. Since the degree of adhesion between the oil covered earth particles and the spent acid depends upon the surface tension of the latter, lowering its surface tension also reduces the degree of adhesion and consequently the Jamin action. On the other hand, merely reducing the degree of adhesion without substantially reducing the surface tension of the spent acid such as by the use of colloidal solutions in flooding processes does not suffice to overcome the effect of the Jamin action. This is due to the fact that the range of action of the adhesive forces is practically limited to the contacting surfaces. The spent acid does not exist in the earth formation as mere tenuous films adhering to oil coated earth particles. It exists as discontinuous portions of liquid having large enough dimensions to exhibit the properties of liquids in bulk. In order to reduce the effect of the Jamin action it is necessary therefore to substantially change the surface tension of the bulk of the aqueous liquid involved by dissolving therein a sufficient quantity of a soluble surface tension lowering agent.

Among the objects of the invention is to provide a method of treating wells with an acid whereby the porosity of the surrounding earth may be increased and the rate of production thereby improved with reduced risk of closing the pores of the producing stratum with alternating bubbles of gas and globules of spent acid or aqueous liquid which would prevent the resumption of production. Other objects and advantages will appear as the description proceeds.

My invention is predicated upon the discovery that the tendency for aqueous solutions, and more particularly the spent acid, to remain in the earth formation and obstruct or hinder the resumption of production may be overcome or at least substantially reduced by incorporating with the solution a water-soluble agent capable of substantially lowering the surface tension of aqueous solutions. For example, I have found

that, when water-soluble liquids having a lower surface tension than water, as well as soluble solids whose aqueous solutions possess a lower surface tension than water, are added to the acid used for treating the well, they are effective to reduce the pressure required to overcome the head created by the Jamin action. It is possible by employing such liquids or solutions in admixture with acid to treat successfully wells in which the rock pressure is too low to discharge the spent acid after the conventional acid treatment.

The invention, then, consists of the method hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain modes of carrying out the invention, such modes illustrating, however, but various ways in which the principle of the invention may be used.

Broadly stated, the treatment contemplated by my process comprises introducing into the earth formation surrounding the well, in connection with an acid treatment thereof, a sufficient quantity of an agent capable of lowering the surface tension of the aqueous solution resulting from the action of acid upon acid-soluble constituents of the formation, so that the head created by the Jamin action is reduced to a point where the rock pressure will overcome the same. Agents that lower the surface tension of aqueous solutions of calcium or magnesium salts are effective to lower the surface tension of the spent acid solution resulting from the aforementioned acid treatment. Such agents also will lower the surface tension of water. However, the choice of such agent must be restricted to those which dissolve in the spent acid without the formation of a precipitate with salts present in the solution, generally calcium and magnesium salts. The proportion of such agent that is most effective to lower the surface tension is that which forms a saturated solution with water or the spent acid, while proportions lower than the saturating amount have a correspondingly lesser effect.

The following substances are illustrative of agents suitable for the purpose: water-soluble alcohols such as methyl, ethyl, normal- and isopropyl-alcohol; allyl alcohol; normal-, primary-, and secondary-butyl alcohol; primary and tertiary butyl alcohol; normal, iso-primary and active secondary amyl alcohol, tertiary hexyl alcohol; tertiary amyl phenol; hexyl resorcinol; tertiary butyl catechol; ethylene glycol; water-soluble ketones, such as acetone and methyl ethyl ketone; water-soluble ethers, such as dimethyl, methyl ethyl ether, para-hydroxy phenetole; water-soluble aldehydes, such as acetaldehyde, propionic, and normal butyric aldehyde; the water-soluble halogen derivatives of all of the above may be used; water-soluble aliphatic acids, such as valeric, propionic, and butyric acid and their chlor-derivatives, such as mono-, di-, and trichloroacetic acid and alpha-chloropropionic acid. Such agents are sufficiently soluble in aqueous solutions of alkali and alkaline earth metal salts to bring about an effective degree of lowering of the surface tension thereof.

The agent and the acid may be mixed together before their introduction into the well or may be introduced thereinto separately. It is generally preferable to make a mixture of the acid and the surface tension lowering agent, so that the latter may be introduced into the well in a single operation, although if desired the agent may be introduced into the well ahead of the acid, in which

case they may become mixed together within the earth formation.

In carrying out the treatment of a well, oil and water standing therein may be removed if desired by bailing, pumping or the like and then after removing the pump, pump rods, and standing valve, if such are there, a predetermined amount of acid is introduced into the well, the amount being dependent upon the particular well under treatment and may be varied to suit conditions peculiar to it. It has been found that a suitable charge may be from 1500 to 10,000 pounds or more of the acid. The amount of surface tension lowering agent employed may be from 3 or 5 per cent up to 25 or 50 per cent or more of the weight of the acid charge, depending upon the solubility of the same in the resulting spent acid and the degree of reduction of the pressure head resulting from the Jamin action thereof that is desired. Water soluble alcohols, such as methyl, ethyl, and isopropyl alcohol, on account of their relatively low cost may be employed preferably. For example, 500 gallons (4500 lbs.) of 15 per cent hydrochloric acid solution (1.075 sp. gr. and 50 gallons of ethyl alcohol (330 lbs.) may be employed. Another example of a suitable mixture is that formed from 1000 gallons of hydrochloric acid (9000 lbs.) and 200 gallons (1290 lbs.) of isopropyl alcohol.

A suitable charge of acid and surface tension lowering agent such as given in the previous examples by way of illustration is introduced directly into a well in any convenient manner, as by pumping through the well tube. In order to extend its action beyond the immediate vicinity of the well bore, pressure may be applied to the acid mixture, for example, by means of gas introduced into the well under pressure or by filling the well bore with oil or water, so as to create a hydrostatic head upon the charge. A convenient method for introducing the solution of acid and surface tension lowering agent, that insures forcing the charge into the earth surrounding the base of the well, is described in U. S. Patent No. 1,891,667.

Any acid capable of attacking and dissolving the earth formation so as to form water-soluble salts therewith and increase its porosity may be employed. Hydrochloric acid is generally suitable for the purpose. For use in contact with metal pipes and other parts of well equipment it is best to add an inhibitor to the acid, as described in U. S. Patent No. 1,877,504. A suitable concentration is between 5 and 25 per cent of HCl by weight, although other concentrations may be used, if desired, to which from 0.5 to 5 per cent of an inhibitor is added.

After the surface tension lowering agent and acid have been introduced into the well and the acid has become partly or substantially neutralized by action upon the acid soluble constituents of the earth formation, the spent acid may be withdrawn. If the surface tension of the spent acid is lowered sufficiently by the presence therein of a surface tension lowering agent, relatively low rock pressures will suffice to cause a movement of the spent acid toward the well, from which it may be removed readily by pumping, bailing or the like. Since the back pressure resulting from the Jamin action is substantially reduced by my treatment, in most instances a substantially complete withdrawal of spent acid may be had so that the production of oil may be resumed soon after a treatment. I have found also that the oil produced immediately following a

treatment is usually not contaminated with spent acid as is frequently the case in prior methods of treatment.

5 The effect of water soluble surface tension lowering agents on the head required to overcome the Jamin action has been ascertained experimentally by the use of a capillary tube having a bore 0.33 mm. in diameter. In these experiments the solution to be tested was introduced into the bore as drops of solution alternately with bubbles of air thereby forming a Jamin chain therein. Any convenient number of drops may be introduced into the tube. Air was then forced into one end of the tube, the other being open, and the air pressure required to force the chain out of the tube was ascertained with a mercury manometer. It was found that so long as each liquid drop was large enough to contact the surface of the bore, that is, form a closure therein, the pressure required to force the drops along the bore was independent of the lengths of the drops and directly proportioned to the number of drops in the chain. By dividing the pressure required to force a chain out of the tube (expressed in centimeters of mercury) by the number of drops in the chain, the pressure required per drop is obtained, which value serves to compare the head required to overcome the Jamin action of various liquids. In the case of aqueous liquids that are ordinarily found in wells such as water, solutions of calcium, magnesium and sodium chloride and the like of various concentrations, as well as acids formerly used to treat a well, the pressure head per drop is between about 0.28 and 0.48 cm.

35 The reduction in the Jamin pressure head that can be had in my process may be shown by comparing the pressure required to overcome the Jamin action of aqueous calcium chloride solution resulting from the action of say 15.2 per cent hydrochloric acid on limestone with the pressure required with the solution resulting when alcohol is first added to the acid. Aqueous hydrochloric acid containing 15.2 per cent of hydrochloric acid forms 20.7 per cent calcium chloride solution on being neutralized by acting upon limestone. The pressure required to overcome the Jamin action of this solution is about 0.3 cm. per drop in a capillary tube having a bore of 0.33 mm. If alcohol be added to the acid before acting upon limestone in amount say as given above in the illustrative examples of suitable acid mixtures, then on neutralizing the acid with limestone, the solutions resulting contain 21.3 and 18.2 per cent of calcium chloride and 55 7.0 and 11.5 per cent of ethyl and iso-propyl alcohol respectively. The pressure now required to overcome the Jamin action of these neutralized solutions is only 0.067 and 0.0021 cm., respectively, per drop in the same capillary tube. Thus the reduction in pressure required to overcome the Jamin action is reduced about 80 per cent and 99 per cent, respectively, as a result of the presence of alcohol in the spent acid.

65 Other equally striking reductions in the Jamin pressure head may be had by dissolving a suitable amount of a soluble surface tension lowering agent in the liquid involved. Tests of the kind described also furnish a guide in selecting the amount and kind of agents for the purpose and gives a means for distinguishing operative agents from those that do not bring about a reduction in the Jamin pressure head. Colloidal

solutions for example that do not contain a soluble agent capable of lowering the surface tension of aqueous solutions are inoperative as well as agents which are completely coagulated or precipitated by electrolytes or other substances which may be present in the liquids encountered in the earth formation.

Other modes of applying the principle of my 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.

I therefore particularly point out and distinctly claim as my invention:—

1. In a method of treating a well, the steps which consist in introducing thereinto a water-soluble agent capable of substantially lowering the surface tension of water and an acid capable of forming water-soluble salts with the earth formation.

2. In a method of treating a well, the step which consists in introducing thereinto an aqueous solution of an agent capable of substantially lowering the surface tension of water and an acid capable of forming water-soluble salts with the earth formation.

3. In a method of treating a well, the steps which consist in forming a solution of an acid capable of producing water-soluble salts with the earth formation and an agent, soluble in said acid, capable of substantially lowering the surface tension of water, and introducing the so formed solution into a well.

4. In a method of treating a well, the steps which consist in introducing thereinto an acid solution capable of forming water-soluble salts with the earth formation, to which solution is added from 3 to 50 per cent of a water-soluble alcohol.

5. In a method of treating a well, the step which consists in introducing thereinto an aqueous solution of hydrochloric acid and an alcohol selected from the group consisting of methyl alcohol, ethyl alcohol, normal and iso-propyl alcohol and butyl alcohols.

6. In a method of treating a well to increase the output therefrom, the steps which consist in introducing thereinto an acid capable of forming water-soluble salts with the earth formation and a water-soluble liquid agent having a lower surface tension than water.

7. In a method of treating a well to increase the output therefrom, the steps which consist in introducing thereinto an acid capable of forming water-soluble salts with the earth formation and a water-soluble liquid agent capable of lowering the surface tension of water.

8. A method of treating a well which comprises introducing thereinto a water-soluble alcohol and hydrochloric acid.

9. In a process of cleaning wells the step comprising charging thereinto a composition comprising inhibited hydrochloric acid and N-butyl alcohol.

10. In a process of cleaning wells the step comprising charging thereinto a composition comprising inhibited hydrochloric acid and acetone.

11. In a process of cleaning wells the step comprising charging thereinto a composition comprising inhibited hydrochloric acid and ethyl alcohol.

LEONARD C. CHAMBERLAIN.