

1

3,108,635

FOAM INHIBITING METHOD AND COMPOSITION
FOR OIL WELLSJoseph F. Chittum, Whittier, Calif., assignor to California
Research Corporation, San Francisco, Calif., a corpo-
ration of Delaware

No Drawing. Filed July 15, 1960, Ser. No. 42,958

8 Claims. (Cl. 166-41)

The present invention relates to improving the productivity of oil wells, and pertains more particularly to improving productivity of pumping oil wells which produce petroleum having a tendency to foam within the well.

All too often it is found that when a well reaches the stage of having to be produced by pumping, the oil entering the annulus in the borehole surrounding the producing string of tubing from the pump to the surface tends to form an altogether too stable foam. When it is desired to withdraw gas from the annulus of the well, the column of foam rises sometimes to a height of 5,000 ft. and often to a height of 1,000 to 2,000 ft. in the annulus. Such a column of foam exerts a considerable back pressure on the producing zones and, hence, tends to reduce the amount of oil which is produced from said zones into the borehole. Further, the formation of foam in the borehole reduces the accumulation of the liquid petroleum in the portion of the borehole from which the pump takes suction. Hence, the pump often takes suction on foam rather than liquid petroleum, thereby greatly reducing the efficiency of the pump. Both these effects result in a decreased oil production of the well.

Therefore, an object of my invention is to provide an improved process for increasing the productivity of oil wells in which the oil tends to foam. A further object is to provide a method of controlling foaming in an oil well in a manner that requires less foam inhibitor than heretofore considered practical. Another object of my invention is to provide an improved foam inhibitor stick composition which is especially suited for use in controlling excessive foaming of oil in pumping wells.

With the above objects in mind, I have found that the productivity of the well can be appreciably increased by controlling the foam in the annulus while pumping the well and withdrawing gas from the annulus as desired. I have further found that oil well foams are generally of two different types differing primarily in the orientation of the charge in the electrical double layer in the foam bubbles. One type has a negative charge on the inner surface of the electrical double layer of the foam bubble. The other type has a positive charge. Such charged foams can be controlled and the productivity of the well maintained at a relatively high level by a simple procedure of properly placing within the annulus of a well my foam inhibitor of a composition suited to the type of foam. By the use of the present invention, excessive amounts of such foams in an oil well can be avoided in a convenient manner without much interference with normal operations and with less foam inhibitor than heretofore considered practical.

Heretofore it has been proposed to suppress foaming by the use of silicone foam inhibitors in oil solutions. Greatly diluted solutions of silicones have been tried in both the laboratory and the field, but without practical success. If, for instance, a dilute kerosene solution of silicone is introduced into the well annulus, it probably flows down the casing or tubing with channels or fingers of decreasing concentrations as it enters the foam. This can be readily observed by a laboratory test simulating

2

the condition. Obviously, an expensively large amount of diluted silicone would be required to provide a reasonable chance for the foam inhibitor to get to the whole surface of the foam without being erratically held up along the length of the casing and producing string. Intrinsic in such a method are the difficulties of fingering and waste of chemical by diversion into ineffective areas.

In contrast to the above, the present method efficiently reduces charged foams with a minimum consumption of expensive chemicals. While I do not wish to be bound by theory, the success of my method appears to result from fulfilling several criteria simultaneously. The foam inhibitor is specifically compounded with a surfactant which tends to form a surface charge opposite to the charge of the foam in the well. Thus, the foam inhibitor is compounded with a cationic amine when the foam charge is negative and with an anionic sulfonate when the charge is positive. Another important feature of the invention is that the inhibitor is quite concentrated at its point of action. Consequently, the rate of use of the concentrated inhibitor is very low. Also, the inhibitor tends to disperse over the whole surface of the foam after contact, and hence, fingering is minimized. Moreover, these efficient conditions are set up more or less automatically by the nature of the process. These advantages and objects follow from the practice of the invention, as described hereinafter.

To determine the charge of the foam in the well annulus, any suitable method can be used. One test uses an H-shaped electrophoretic cell and the test oil is placed in both legs of the cell. Foam is generated by bubbling gas through the oil until a steady state with pressure-temperature equilibrium is reached. Then a medium high strength is placed across the cell by applying a D.C. current to the electrodes placed in the cell legs. If the bubbles are positively charged, they will move toward the negative electrode. If they are negatively charged, they tend to move toward the positive electrode. This movement can be detected easily by viewing the bubbles through a microscope trained at the cross channel of the H-cell.

Another procedure is to make foams in two test tubes with the oil from the well. This can be done by placing in each tube 10 ml. of the test oil plus 5 ml. of distilled water. The water is boiled until several inches of foam are produced. Then to one tube of foam is added 0.25 gram of an oil-soluble alkali metal sulfonate such as the sodium salt of mahogany sulfonic acid of about 450 molecular weight. To another foam sample is added a similar amount of the imidazoline of ricinoleic acid. If the foam is more rapidly broken with the sulfonate, the foam is positively charged. If it is more rapidly broken with the imidazoline, the foam is negatively charged.

After determining the charge on the foam, the preferred step in the process of the present invention is to substantially depress the column of foam in the annulus of the well to a reasonable level. One suitable method consists of temporarily discontinuing the withdrawal of gas from the annulus of the well, whereby the pressure within the well is allowed to build up and the column of foam reduced. Other means of obtaining the initial reduction of the foam column can also be used, such as by injecting into the annulus a large slug of liquid foam inhibitor.

After the foam column is initially depressed, a mixture of particular proportions of proper surfactant and silicones, as described later, are added at or near the upper surface of the foam column. This is done most efficiently as well as most conveniently by dropping my preferred new foam inhibitor stick into the annulus so that it comes to rest at a point above the producing zone and

near, but spaced above, the top of the depressed column of foam. If a tubing anchor is not positioned within the annulus so that the foam inhibitor sticks are properly placed, then a suitable catcher or porous barrier of some kind is placed in the well to cause the foam inhibitor sticks to come to rest in the desired position.

The composition of the foam inhibiting sticks is such that they slowly melt and/or are leached with condensate of petroleum vapors. In this way foam inhibitor in relatively high concentration is continually added to the top portion of the foaming liquid in sufficient amount to control the foaming tendency. Thus, hydrocarbon condensing on the inhibitor sticks dissolves or liquifies silicone and surfactant. The drops of condensate become concentrates of silicone plus the proper surfactant by the time they fall onto the foam surface. The surfactant aids in dispersing the agents rapidly over the foam surface. In this way a high silicone concentration is mainly in the surface layer of foam only. This concentration on the surface is desirably above 100 p.p.m., and may be 300-400 p.p.m. of the oil, but in the layers below the foam surface the silicone concentration may be 5-15 p.p.m. or less. Since the foam contains only a relatively small amount of oil, the total silicone requirement is extremely low. For example, where the foam height is depressed from 4,000 ft. down, and stabilized at, 500 feet and oil production is 150-200 barrels per day, the silicone required is probably less than 0.1 p.p.m. of the total oil produced.

After the foaming is brought under control, the withdrawal of gas from the annulus at the top of the well may be re-established. The supply of foam inhibitor sticks in position in the well annulus is maintained by introducing additional sticks from time to time.

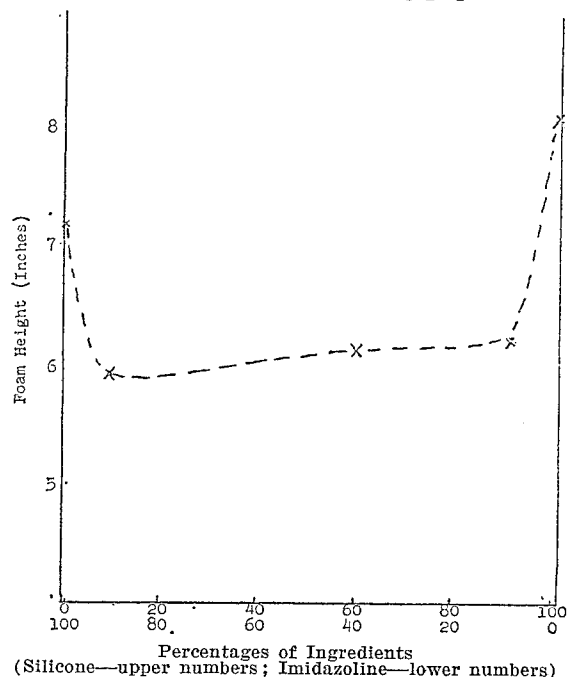
By the present invention foaming is controlled and the productivity of the well can be increased substantially. For example, in an extreme instance of high foaming tendency in a well where a column of foam rose to 5,000 ft. in the annulus, it was found that the productivity of the well could be increased by about 50% to 100% by means of the above-described treatment of the present invention.

Preferably, my foam-inhibiting sticks consist essentially of three ingredients. The first ingredient is a petroleum wax having a melting point in the range of 150 to 200° F. which is satisfactory for use in wells of relatively normal temperatures. Higher melting point waxes are used where extremely high temperatures are encountered. Preferably the melting point of the wax is sufficiently high to provide a stick composition having a melting point ranging from 5-25° F. above the temperature of the liquid petroleum produced into the borehole. So-called micro-crystalline waxes are preferred because they combine the desirable properties of relatively high melting point and compatibility with the other ingredients. The wax normally comprises 50 to 80% of the foam-inhibiting stick composition.

The remainder of the foam inhibiting stick composition is a mixture consisting of 10 to 90%, preferably 20 to 80%, of dimethyl silicone polymer having a viscosity in the range of 500 to 100,000 centistokes. Preferably the dimethyl silicone polymer has a viscosity in the range of 25,000 to 75,000 centistokes. The other 90-10% of the mixture is a preferentially oil-soluble surfactant which tends to form a surface charge opposite to the charge of the foam in the well. When the foam is negatively charged, the surfactant is an amine which preferably has, for high surface activity, a molecular weight above about 260. Such amines are higher molecular weight aliphatic and cycloaliphatic amines or amides. Preferred because of effectiveness and stability are the imidazolines of higher fatty acids, particularly those acids of at least ten carbon atoms. Suitable imidazolines include those of ricinoleic acid, oleic acid, stearic acid and like fatty acids, with those having hydroxyl substituents like ricinoleic acid being preferred. Imidazolines having molecular weights

above 290 are most effective. Also, higher alkyl (having at least ten carbon atoms) amines such as lauryl, oleyl, and octadecyl amines can be used. Various other amines include fatty polyamines derived from fatty acids such as oleic and stearic acids as well as soya bean oil, coconut oil and tallow oil acids. Such polyamines have two or more amine groups located at one end of at least one long oleophilic hydrocarbon chain. An example is N-tallow-1,3-diamino propane. When the charge on the foam is positive, the surfactant to be combined with silicones in the mixture is a preferentially oil-soluble alkali metal sulfonate such as sodium mahogany sulfonate, potassium mahogany sulfonate, and like anion surface-active salts of various oil-soluble alkylated aromatic or naphthenic sulfonic acids. The sulfonates can be obtained by neutralizing the sulfonic acids such as mahogany sulfonic acids having molecular weights of 400 to 500 which are recovered in the sulfuric acid treatment of lubricating oil stocks.

The effect of the desired ratios of silicone and amine in controlling crude oil foaming in a vertical tube like in an oil well is shown in the following graph:



These results were obtained from tests run with a crude oil giving a negatively charged foam and having a high foaming tendency as observed from a 5,000-foot foam column in the well producing the oil. In the test, a vertical tube 12 inches high with an internal diameter of 0.95 inch was used. The crude oil was poured into the tube to a height of 2 inches. Foam was produced up to the 10-inch level by dispersing nitrogen gas in the oil. Then a rod with the inhibitor material on the end was lowered into the surface of the foam. The effect of each material after one minute was noted, and the percentage of the original foam height was determined. The graph shows these percentages for various proportions of polymethylsiloxane of about 12,500 centistoke viscosity and imidazoline of ricinoleic acid. The graph shows that in the test silicone imidazoline mixtures gave effective reductions in foam, greater than either 100% silicone or 100% imidazoline.

With a positively charged foam, a similar series of tests were run with various proportions of polymethylsiloxane of about 30,000 centistoke viscosity and sodium mahogany sulfonate of about 475 molecular weight. The silicone-sulfonate mixtures, especially mixtures of 20-80% of silicone plus sulfonate as the remainder gave

strikingly effective reductions in foam, whereas either 100% silicone or 100% sulfonate increased the foam height. In a further series of tests, polymethylsiloxanes of different viscosities were substituted for that used above. Those with viscosities of 12,500 and 60,000 centistokes were as effective as the silicone of 30,000 centistoke viscosity, while a silicone of 1,000 centistoke viscosity was about 90% as effective.

The overall composition of the foam-inhibiting sticks is adjusted where possible to provide a melting point for the composition of about 5 to 25° F. above the temperature of the liquid oil accumulated at the bottom of the well. For example, a foam inhibiting stick which is formed as a cylinder weighing about one-half pound and has a melting point of about 180° F., when placed in position in a well having a bottom hole liquid temperature of 170° F., will have a life of about 100 hours.

The foam inhibitor composition above described may be formed into shapes suitable for introduction into the annulus of a well and easy placement in position above the top of the depressed foam column in the well. One desirable shape is a relatively thin cylinder of about one-half or three-quarters of an inch up to one or two inches in diameter and a length of five to twenty inches. A convenient size is a stick of one inch diameter by twelve inches long which for a composition of 10% dimethyl silicone polymer of 12,500 centistokes viscosity, 10% imidazoline of ricinoleic acid, and 80% of a petroleum paraffin wax having a melting point of 190 to 195° F., weighs about one-half pound. Although the number of such sticks that will be used depends primarily on the particular foaming tendency of the petroleum being produced, it has been found that for a particularly severely foaming well the initial treatment may comprise 25 to 30 sticks of the aforesaid composition with the addition of 6 to 10 sticks twice a week to maintain the foaming tendency under control.

While the above-described stick compositions are the preferred means of controlling foams in oil wells, the invention also contemplates injecting into the top of a depressed column of such foam the mixture of 10 to 90% dimethyl silicone polymer with 500 to 100,000 centistoke viscosity and the remainder a preferentially oil-soluble cationic amine surfactant or anionic sulfonate. The mixture can be injected at the proper level in the well annulus by any suitable means such as a small reservoir fitted with a drip valve or a string of small tubing from the well surface.

The following examples are given to further illustrate the present invention.

Example 1

Solid foam inhibitor sticks one inch in diameter and 14 inches in length can be prepared to weigh about ½ pound with a composition of 10% of polymethyl silicone material of about 12,500 centistoke viscosity, 80% of a microcrystalline wax with a melting point of about 190–195° F. and 10% ricinoleic acid imidazoline. The sticks are prepared by melting the wax, adding the other ingredients and stirring until the mixture was homogeneous. Then this melted mixture is poured into cardboard tubes and allowed to cool.

Example 2

Other solid foam inhibitor sticks of the dimensions and weight of those in Example 1 can be prepared with a composition of 80% of a microcrystalline wax with a melting point of about 190–195° F., 10% of polymethyl silicone material of about 12,500 centistoke viscosity and 10% of octadecyl amine.

Sticks of the compositions of Examples 1 and 2 should last about 100 hours in a hydrocarbon condensate atmosphere at about 165° F. Thus, they would last for a long time and slowly release concentrated inhibitor when placed in a well at about this temperature. If the sticks were properly positioned above a negatively-charged foam

column in a well, they would be very effective in controlling the foam.

Example 3

Solid foam sticks one inch in diameter and 14 inches in length were prepared with a composition of 50% of polymethyl silicone material of about 60,000 centistoke viscosity, 25% of a microcrystalline wax with a melting point of about 150° F. and 25% sodium mahogany sulfonate of molecular weight of about 475. The sticks were prepared by melting the wax, adding the other ingredients and stirring until the mixture was homogeneous. Then this melted mixture was poured into cardboard tubes and allowed to cool. The sticks had a melting point of about 145° F.

Example 4

In the test well a 4,900 foot column of foam stood in the annulus between the casing and tubing. Before the test the well was producing at about 120 barrels of crude oil per day. Then the sticks prepared in Example 3 were dropped into the casing of the well, which contained a tubing anchor about 500 feet above the producing zone. Ten sticks were dropped into the well the first day, six each the second and third day, ten the fourth day, and twenty the fifth day. The production from the well increased by about 50 barrels per day after a five-day period.

Example 5

Sticks of about the same shape as those in Example 3 but of a higher melting point by containing 70 parts of a petroleum paraffin wax of 190/195° F. melting point, 15 parts polymethylsiloxane of 60,000 centistoke viscosity and 15 parts of sodium mahogany sulfonate of about 450 molecular weight. These sticks have a life span in a hydrocarbon condensate atmosphere at 170° F. of about 110 hours. Thus, they would last for a long time and slowly give up concentrated inhibitor in a normal well at about this temperature.

Obviously, modifications—some less desirable than others—of the above examples of the method and compositions of the present invention can be made. All percentages given herein are percentages by weight, except where specifically indicated to be otherwise.

I claim:

1. In a method of operating a pumping oil well in which the oil tends to foam within the well and wherein oil is produced by a pump near the bottom of the well up through a producing string of tubing, gas is withdrawn from the annulus of the well outside of the producing string, and a negatively-charged foam tends to accumulate in the annulus, thereby generating a back pressure on the producing zones and tending to reduce the efficiency of said pump, the improvement of increasing the productivity of said oil well which comprises the steps of temporarily discontinuing said removal of gas from the annulus of the oil well to cause the column of said foam in the annulus to be substantially depressed, then positioning in said annulus near but spaced above the top of the depressed column of foam standing in the annulus of the well a solid foam-inhibiting composition consisting essentially of 50–80% wax having a melting point above 150° F. and the remainder consisting of at least 10% each of dimethyl silicone polymer having a viscosity of 500 to 100,000 centistokes and preferentially oil-soluble amine surfactant, said solid inhibiting composition having a melting point of from 5 to 25° above the temperature of the well at the point therein in which the said composition is placed, thereafter re-establishing the withdrawal of gas from the annulus of the well and maintaining within said annulus a sufficient quantity of said solid foam-inhibiting composition to keep the column of foam depressed below the point at which said foam-inhibiting composition is placed in said annulus.

2. In a method of operating a pumping oil well in which the oil tends to foam within the well and wherein

7

oil is produced by a pump near the bottom of the well up through a producing string of tubing, gas is withdrawn from the annulus of the well outside of the producing string, and a negatively-charged foam tends to accumulate in the annulus, thereby generating a back pressure on the producing zones and tending to reduce the efficiency of said pump, the improvement of increasing the productivity of said oil well which comprises the steps of initially depressing substantially the column of said foam in the well annulus, and then maintaining said foam column depressed by adding to the top of the depressed foam column a mixture consisting essentially of at least 10% each of dimethyl silicone polymer having a viscosity of 500 to 100,000 centistokes and preferentially oil-soluble amine surfactant.

3. In a method of operating a pumping oil well in which the oil tends to foam in the well and wherein oil is produced by a pump in the bottom of the well up through a producing string of tubing, gases are withdrawn from the annulus of the well outside of the producing string and a negatively-charged foam tends to accumulate in such annulus, thereby generating a back pressure on the producing zones and tending to reduce the efficiency of said pump, the improvement of offsetting the tendency of said foam to accumulate and of increasing thereby the productivity of said oil well by adding to the top of the column of foam in said annulus a mixture consisting essentially of at least 10% each of dimethyl silicone polymer having a viscosity of 500 to 100,000 centistokes and preferentially oil-soluble amine surfactant.

4. An improved foam inhibitor stick composition

8

adapted to control foaming in the annulus of oil wells, said composition consisting essentially of 50 to 80% by weight of a petroleum wax having a melting point in the range of 150 to 200° F. and the remainder consisting of at least 10% each of dimethyl silicone polymer having a viscosity of 500 to 100,000 centistokes and preferentially oil-soluble amine surfactant.

5. The composition of claim 4, wherein said composition is cast into elongated shapes adapted for insertion into the annulus of oil wells.

6. The composition of claim 4, wherein said wax is a microcrystalline wax.

7. The composition of claim 4, wherein said amine surfactant is in imidazoline of a higher fatty acid.

8. The composition of claim 4, wherein said amine is an alkyl amine having at least 10 carbon atoms in an alkyl group.

References Cited in the file of this patent

UNITED STATES PATENTS

2,416,503	Trautman et al.	Feb. 25, 1947
2,453,352	Tremain et al.	Nov. 9, 1948
2,585,522	Watts et al.	Feb. 12, 1952
2,698,295	Cardwell et al.	Dec. 28, 1954
2,824,059	Chamot	Feb. 18, 1958
2,993,223	Krammes	July 25, 1961
3,033,789	Asseff	May 8, 1962

OTHER REFERENCES

Silicones, by R. N. Meals and F. M. Lewis, Reinhold Pub. Co., New York, 1959, page 87.