METHOD AND COMPOSITION FOR CONTROLLING FOAMING IN OIL WELLS

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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 which interferes with pumping the oil away from the annulus of the well. The column of oil 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 oil 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 foamy in an oil well in a manner that requires less foam inhibitor than heretofore considered practical. Another object of my invention is to provide a process of foam inhibitor 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. One widely occurring type is that which has a positive charge on the inner surface of the electrical double layer of the foam bubble. Such positively-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 new foam-inhibiting composition. By the use of the present invention, excessive amounts of such positively-charged 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 control 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, with little or no 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 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 positively-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. Thus, the foam inhibitor is specifically compounded with anionic sulfonates to break up positively-charged foams. Further, the inhibitor is quite concentrated at its point of action. That which gets into the bulk of the well is substantially carried downward by the breaking foam. 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 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 whether the foam in the well annulus is positively charged, and hence, susceptible to treatment by the present invention, any suitable method can be used to test the charge on the inner layer of the foam bubbles. 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 field 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. 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 one to tube of foam is added 0.25 g. of an oil-soluble alkali metal sulfonate such as the sodium salt of mahogany sulfonic acid of about 450 molecular weight. To another tube 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.

As a first step in the process of the present invention, the column of foam in the annulus of the well is substantially depressed 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 positively-charged foam column is initially depressed, a mixture of particular proportions of certain
sulfonates 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 condensate on the inhibitor sticks dissolves silicone and sulfonate. The drops of condensate become concentrated solutions of silicone plus sulfonate by the time they fall on to the foam surface. The sulfonate 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 desirable about 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 foaming-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, the remainder of said mixture being a preferentially oil-soluble alkali metal sulfonate such as sodium mahogany sulfonate, potassium mahogany sulfonate, and like union surface-active salts of various oil-soluble alkylated aromatic or naphthenic sulfonates. Preferably the dimethyl silicone polymer has a viscosity in the range of 25,000 to 75,000 centistokes. 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 sulfonate in controlling crude oil foaming in a vertical tube like in an oil well is shown in the following graph:

**EFFECTIVENESS OF SULFONATE-SILICONE MIXTURES TO INHIBIT POSITIVELY-CHARGED FOAMS**

These results were obtained from tests run with a crude oil giving a positively-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 30,000 centistoke viscosity and sodium mahogany sulfonate of about 475 molecular weight. The graph shows that in the test either 100% silicone or 100% sulfonate increased the foam height, but that silicon and sulfonate mixtures, especially mixtures of 20-80% silicone plus sulfonate as the remainder, gave effective reductions in foam.

In another 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 over-all 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 described above 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 15% dimethyl
silicone polymer of 30,000 centistokes viscosity, 15% sodium mahogany sulfonate derived from a mahogany sulfonic acid of 450 molecular weight, and 70% 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 composition is the preferred means of controlling positively-charged foams in oil wells, the invention also contemplates injecting into the top of 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 alkali metal sulfonate as an anionic surfactant. 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 sticks one inch in diameter and 14 inches in length were prepared with a composition of 50% of polyethylene 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 2**

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 stocks prepared in Example 1 were dropped into the top of this column. After a number of hours the foam was observed to accumulate to about 500 feet above the producing zone. Ten sticks were dropped into the well the first day, six 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 3**

Sticks of about the same shape as those in Example 1 but of a higher melting point by containing 70 parts of a petroleum paraffin wax of 190°/195°F melting point, 15 parts polyethyleneoxide 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. Then 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 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 positively-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 alkali metal sulfonate, said solid inhibiting composition having a melting point of from 5 to 25° above the temperature of the well at the point wherein in 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 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 positively-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 alkali metal sulfonate.

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 near 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 positively-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 20% each of dimethyl silicone polymer having a viscosity of 500 to 100,000 centistokes and preferentially oil-soluble alkali metal sulfonate.

4. An improved foam inhibitor stick composition 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 130 to 200°F and the remainder consisting essentially of a mixture of at least 20% each of dimethyl silicone polymer having a viscosity of 500 to 100,000 centistokes and preferentially oil-soluble alkali metal sulfonate.

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.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION
Patent No. 3,108,634
October 29, 1963
Joseph F. Chittum

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 25, for "about" read -- above --;
line 58, for "helting" read -- melting --.

Signed and sealed this 28th day of April 1964.

(SEAL)
Attest:
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