Patented Nov. 12, 1929 1,734,990

UNITED STATES PATENT OFFICE

ALBERT H. ACKERMAN, OF CHICAGO, ILLINOIS, ASSIGNOR TO CATALYTIC CHEMICAL COMPANY, OF CHICAGO, ILLINOIS, A CORPORATION OF COLORADO

PROCESS AND MATERIAL FOR TREATING OIL WELLS TO ENHANCE THEIR PRODUCTIVITY

No Drawing. Application filed December 31, 1926, Serial No. 158,418. Renewed April 15, 1929.

This invention is a continuation in part of copending applications, Serial No. 75,472 and Serial No. 76,901.

My invention relates to the treatment of mineral oils and it has special reference to a composition of materials that may be employed for the purpose of substantially precluding the congealing of such oils whereby they may be kept flowing from the wells, or out of the tanks, or in the pipe-lines, and to a process of treating oil-wells for the purpose herein specified.

Certain crude mineral oils possess high cold-tests which render it very difficult, especially in cold weather, to handle the oils in such manner that they can be readily pumped from the wells or the tanks without the pumps or the pipe-lines becoming clogged. In other instances, wells that have been flowing for a considerable period of time have their production substantially reduced because of the accumulation of the paraffin or other heavy non-flowable substances in the oil-bearing sands which seriously impedes the flow of the oil to the pump which removes the oil from the well.

Heretofore it has been proposed to apply heat in various forms, to prevent the oil from congealing or from becoming clogged in the oil-bearing sands, but my present invention contemplates adding a new composition of materials to the oil which will enhance the flow of the oil or to the well to minimize the clogging of the oil-bearing sands, and I explain the results that I obtain by the theory that my combination of materials breaks up the carbon clusters, binders, etc. so that the petroleum remains more fluid and minimizes the tendency of the oil to clog the pipe-lines or pump barrel or to become obstructed in the interstices of the oil-bearing sands.

In some wells which are adapted to be treated by my present invention, paraffin rapidly accumulates therein in cold weather. The quantity of paraffin increases rapidly toward the top of the hole of the well because of the chilling as a result of the expanding gas. As the paraffin accumulates, pumping becomes more and more difficult and, consequently, it becomes necessary to pull the rods and tubing and to clean them out in order that the well may produce oil at a sufficiently high rate to warrant the pumping of the well. Cleaning out a well as described above is a very expensive process and adds greatly to the cost of the crude oil procured therefrom. My present invention, in addition to other uses, is particularly adapted to treat oil-wells that have had their production lowered as I have pointed out above.

I have found that by placing my composition of material in proper amounts in an oil well, as I will describe hereinafter, I have been able to increase greatly the productivity of the well for a substantial period of time, thereby eliminating the necessity of pulling the rods and tubing and cleaning out the well for the purpose of resuming economical production of oil therefrom.

I have found that the following composition of materials, when added in adequate amounts to an oil well whose production has been retarded as described above, enhances greatly the flow of oil from the well without cleaning the well. I make use of the following chemicals or their equivalents:

Anthracene ($C_{14}H_{10}$), preferably the usual 40% commercial green powdered variety; sulfuric acid (H_2SO_4) 93% commercial; oil of mirbane (nitrobenzene, $C_6H_5NO_2$); sodium hydroxide (NaOH); and naphthalene ($C_{10}H_8$), preferably in the flake form.

I have found that the following proportions of the foregoing chemicals give very good results, but obviously I do not wish to be bound to these particular proportions for the ingredients, as other proportions of them or their equivalents may give very satisfactory results.

	Per cent
Anthracene (40% commercial, powdered)	3.25
Sulfuric acid (concentrated, 93%)	0.65
Oil of mirbane (nitrobenzene)	1.30
Naphthalene, flake	66.00
Sodium hydroxide, granular or powder	28.80

In making up my composition of materials I proceed preferably in the following manner.

The anthracene is treated for some time in the cold with the sulfuric acid. This causes an action upon the anthracene which appears to render it considerably more reactive. The mixture resulting from the anthracene and the sulfuric acid is practically dry. The purpose of treating the commercial anthracene, referred to above, with the sulfuric acid is to render the same more reactive by destroying some of the impurities in the commercial anthracene. If, however, 85% pure anthracene is used in the composition this sulfuric acid treatment becomes unnecessary. For reason of expense, however, the common 40% green anthracene is preferred, and this requires the sulfuric acid treatment. The sodium hydroxide added later is for the purpose of removing or neutralizing any excess of sulfuric acid that may remain after the action of the latter on the anthracene since the sulfuric acid, as such, is not needed in the final composition. The oil of mirbane is then incorporated and, because of its oily nature covers the anthracene with an oily film and also dissolves a certain amount of the anthracene. The resultant mass is pasty. The napthalene is next incorporated by thoroughly grinding the materials already enumerated in a ball mill or similar machine. The sodium hydroxide is preferably ground to a fine powder before being incorporated with the materials already in the ball-mill. After adding the sodium hydroxide to the mill, all of the materials are thoroughly ground together to obtain a complete mixing of them. The small residual amount of sulfuric acid thus becomes neutralized by the sodium hydroxide forming sodium sulfate, but it will be noted that the sulfuric acid is not neutralized by the sodium hydroxide until the former has had its desired action upon the anthracene with which it is first admixed, as described above.

In employing my composition of materials which, for convenience, I will hereinafter refer to as the "reagent," I introduce sufficient quantities of the reagent into the bottom of the oil-well to be treated. It is obvious, of course, that many methods are available for introducing the reagent into the oil-well but I found the following to be in actual practice a very suitable method. The reagent is placed into a suitable container having a removable bottom, which container is so constructed that it can be lowered to the bottom of the oil-well by means of a "sand-line." As the container comes into forcible contact with the bottom of the well, the bottom of the container will open and will allow the charge of reagent to drop out.

Another method by means of which the reagent may be placed in the well is to dissolve a suitable quantity of the reagent in a mixture of water and oil, thus forming what is technically known in the art as a "lubricator." This lubricator comprising the reagent, may then be discharged into the well from the top and, if desired, washed down into the well with additional oil, such as the crude-oil naturally produced by the well or other oil. In treating wells it may sometimes be desirable to place the reagent by means of the container as aforesaid and, in addition thereto, place further quantities of the reagent in a "lubricator." When the reagent is placed in the well, it is allowed to act for some time upon the material in the well and in the shot-hole of the well, if one is present, and also upon its surrounding oil-bearing sand at the bottom of the well. The reagent appears to "cut" or dissolve the paraffin-like waxes and the other heavy portions of the crude-oil in the oil-sand, as a result of which the paraffin-like waxes and the other hard or heavy viscous materials become softened and, in some instances, dissolved. The fluidity of the crude-oil in the well is thus increased while, at the same time, more crude-oil can flow from the surrounding oil-bearing sand into the bottom of the well or the shot-hole. As a consequence, an increase in the oil-flow or in the oil pumped from the well per given period of time is attained.

While I am not able at this time to set forth a theory of operation for my composition of materials, or the reagent herein referred to, I have demonstrated by treating oil-wells as described above, that my reagent is highly effective in increasing the production of such oil-wells when employed in accordance with the process that I have outlined. A theory as to the action of my reagent is incapable of being definitely formulated because the conditions existing at the bottom of an oil-well, deep down in the earth where pressure and temperature conditions are unknown, render an explanation of the operation of my invention not only difficult but, at the present state of our knowledge of oil-geology, almost impossible. Suffice it to say that the beneficial action of my reagent and the process of employing the same have been fully demonstrated as I will now set forth in several specific illustrative examples, each of which describes a particular treatment for an oil-well that has been in production for a considerable period of time prior to the time of treating it in accordance with my invention.

A certain oil-well which had been in production for many years has decreased until the average daily yield was approximately one barrel, one-half being water and the other half being oil. The well had a shot-hole at the bottom of it, and was practically dry because the oil did not stand very high in the well casing. Enough water and oil were poured down the well to fill the shot-hole and to provide enough fluid to reach about 150 feet up into the well-casing. Substan-

tially 7½ barrels of oil and 13½ barrels of water or a total of 21 barrels of fluid were poured into the well. The rods and tubing had been pulled from the well and substantially 250 to 300 pounds of my reagent were placed at the bottom of the well by means of the container mentioned above. The rods and tubing were then replaced in the well, and about 24 hours after the reagent had been placed in the well, pumping was commenced. After pumping was resumed, thirteen barrels of oil were pumped to the surface during the first day of operation. The following day four barrels of oil were pumped from the well, and this well then continued to produce from 2½ to 3 barrels of oil per day for a period of over thirty days.

In the treatment of another oil-well in accordance with my present invention, the well in question had been pumping about 40 barrels daily for a year prior to the time that the reagent was added. The well was found to have about 1400 feet of oil standing in the hole. Previous to treating the well, it was necessary to "pull" the well every four or five days as it became impossible to pump it on account of the accumulation of paraffin therein. Substantially 100 pounds of the reagent were placed into the bottom of the well by means of the container hereinbefore mentioned. In addition, sixty pounds of the reagent were dumped into the well from the top, and this was washed down with about 5 barrels of oil from the same well, taken from the stock-tank. The well was then allowed to stand, with the reagent in it, for about 40 hours, and then pumping was resumed. A production of 170 barrels of oil was secured during the first 18 hours of pumping, and for two weeks following the treatment of the well the production of the same was 140 barrels of oil daily. Several months thereafter the well in question was still producing over 100 barrels of oil per day. In a short time subsequent to the treatment of the well its total production had exceeded by more than 5000 barrels of oil the normal production of the well prior to the time that it was treated in accordance with my invention.

While I have herein described my composition of materials or reagent and the process of treating oil-wells therewith in order to increase their production, all without applying external heat, it is to be understood that my process is also applicable to be used with heat treatment of the wells, I do not desire to be limited to the specific reagent and processes herein described inasmuch as only such limitations are to be imposed upon my invention as are set forth in the appended claims.

I claim:

1. A composition of materials for treating oil-wells comprising the reaction product resulting from the admixture of anthracene with sulfuric acid, oil of mirbane, naphthalene, and sodium hydroxide.

2. A composition of materials for treating oil-wells comprising anthracene which has been treated with sulfuric acid, to which has been subsequently added oil of mirbane, naphthalene, and sodium hydroxide.

3. A composition of materials for treating oil-wells comprising substantially 3.25% commercial anthracene that has been treated with sulfuric acid, 1.30% oil of mirbane, 66% naphthalene, and 28.80% sodium hydroxide.

4. A composition of materials for treating oil-wells, consisting of anthracene, sodium sulphate, oil of mirbane, naphthalene, and sodium hydroxide, the same being the reaction product resulting from the admixture of anthracene, sulfuric acid, oil of mirbane, naphthalene, and sodium hydroxide.

5. A composition of materials for treating crude oil comprising substantially 3.25% commercial anthracene that has been treated with sulfuric acid, 1.30% oil of mirbane, 66% naphthalene, and 28.80% sodium hydroxide.

6. The process of treating oil-wells by placing into the said wells a composition of materials comprising the reaction product resulting from the admixture of anthracene, sulfuric acid, oil of mirbane, naphthalene, and sodium hydroxide.

7. The process of treating oil-wells by placing into the said wells a composition of materials comprising the reaction products resulting from the admixture of substantially 3.25% anthracene, 0.65% sulfuric acid, 1.30% oil of mirbane, 66% naphthalene, and 28.80% sodium hydroxide.

8. The process for increasing the fluidity of crude oils which constitutes treating them with a composition of materials comprising the reaction products resulting from the admixture of anthracene, sulfuric acid, oil of mirbane, naphthalene, and sodium hydroxide.

9. The process for increasing the fluidity of crude oils which constitutes treating the same with a composition of materials comprising the reaction products resulting from the admixture of substantially 3.25% anthracene, 0.65% sulfuric acid, 1.30% oil of mirbane, 66% naphthalene, and 28.80% sodium hydroxide.

10. The process for treating oil-wells which comprises adding to the oil and other fluids at the bottom of said wells a composition of materials comprising anthracene that has been treated with sulfuric acid, oil of mirbane, naphthalene, and sodium hydroxide.

11. The process for treating oil-wells which comprises adding to the oil and other fluids at the bottom of said wells a composition of materials comprising substantially 3.25% anthracene that has been treated with substantially 0.65% sulfuric acid, 1.30% oil of mirbane, 66% naphthalene, and 28.80% sodium hydroxide.

12. The process of treating oil wells which comprises dissolving in a mixture of crude oil and water a composition of materials containing the reaction products resulting from the admixture of anthracene, sulfuric acid, oil of mirbane, naphthalene, and sodium hydroxide, and then pouring the solution thus obtained into the oil-well for the purpose of increasing the fluidity of the crude oil in said well.

13. The process of increasing the production of oil-wells which consists in placing into oil-wells a composition of materials comprising the reaction products resulting from the admixture of 3.25% of anthracene, 0.65% sulfuric acid, 1.30% oil of mirbane, 66.00% naphthalene and 28.80% sodium hydroxide.

In witness whereof, I have hereunto subscribed my name.

ALBERT H. ACKERMAN.