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METHOD OF TREATING WELLS

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This invention relates to a process of restoring or increasing the flow from wells sunk in calcareous formations.

It is well known that the flow of oil from oil wells sunk in calcareous formations may be sufficient for some time to permit profitable working of the well, but that eventually the flow becomes hindered or completely stopped before the oil-bearing strata have been exhausted by the formation of calcareous deposits in and around the cavity of the well. These calcareous deposits may partially or wholly fill the cavity of the oil well and may also settle in the passages leading to the oil well through the calcareous rock, thereby preventing oil from passing from the oil-bearing strata into the cavity of the oil well.

To restore or increase the production of oil wells sunk in calcareous formations, from which the flow of oil has ceased or substantially diminished, it has been proposed to introduce mineral acids such as hydrochloric acid into the wells to dissolve the calcareous deposits causing the stoppage of the flow. However, such mineral acids corrode the metal equipment of the well and hence are obviously undesirable. The use of hydrochloric acid containing an inhibitor has also been proposed with the idea that the inhibitor would prevent the acid from corroding the metal equipment of the well. However, the incorporation of inhibitors in hydrochloric acid used in the treatment of oil wells of the type under consideration does not remove other serious objections to the use of such acid, namely, that the acid reacts vigorously with the calcareous deposits in the well, creating violent disturbances therein, and may thereby cause injury to the well cavity as well as to the metal equipment; and further, if the calcareous deposits are covered with films of oil the mixture of hydrochloric acid and inhibitor does not contact the calcareous deposits as rapidly as may be desired, since the oil film is not readily penetrated or removed by this composition.

It is the object of this invention to provide a process for rapidly restoring or increasing the flow of oil in wells sunk in calcareous formations without causing injury to the well cavity.

I have now discovered that by introducing into oil wells sunk in calcareous formations the flow of oil from which has ceased or substantially diminished, an aqueous solution of a composition comprising a compound selected from the group consisting of free organic sulfonic acids and organic acid esters of sulfuric acid, which acids and acid esters contain at least one alkyl group of at least 3 carbon atoms, and particularly a compound selected from the above group containing at least one alkyl group having 3 to 16 carbon atoms, said compound being present in amounts sufficient to form soluble salts with calcareous deposits in and around the cavity of the well, whereby such deposits are removed, and then removing the spent solution from the oil well, the flow of oil from the well is quickly restored or substantially increased. The rapid action of the compositions used in accordance with my invention I believe to be due to the marked emulsifying properties of the organic sulfonic acids and organic esters of sulfuric acid present in such compositions, since any oil films present on the calcareous deposits are emulsified and removed therefrom, thereby permitting ready access of the acidic compositions to the deposits. Preferred compositions for use in accordance with my invention are those comprising free organic sulfonic acids or organic acid esters of sulfuric acid, which acids and acid esters contain at least one alkyl group of not less than 10 nor more than 16 carbon atoms. These compositions display particularly effective emulsifying properties, so that oil films covering the calcareous deposits are quickly removed. They also rapidly disperse any finely-divided insoluble material which may be present in the well, thus permitting removal of this material along with the spent treating solution.

The compositions used in accordance with my invention may be used alone in aqueous solutions, or, if desired, admixed with sulfuric acid which may be added to aid in effecting dissolution of the calcareous deposits in the well. I have found that the free organic sulfonic acids and the organic acid esters of sulfuric acid, when used in conjunction with sulfuric acid, inhibit the corrosive action of the mineral acid. I have found further, that mixtures of sulfonic acid with the compositions above described react with calcareous deposits in an oil well in a much less violent manner than do hydrochloric acid or sulfuric acid alone; moreover, the organic compounds of my invention disperse any insoluble material formed by reaction of sulfuric acid with the calcareous material, thus maintaining contact between the treating acid and the calcareous deposits. If it is desired further to inhibit the corrosive action of the sulfuric acid on the metal parts of the well when using solutions containing sulfuric acid, small amounts of inhibitors such as phosphine bases or nitrogenous bases, e. g. thiocarbanilide, quinaldine, acridines, etc., may be added thereto.

In carrying out the process of my invention, an aqueous solution of a composition comprising a compound selected from the group consisting of free organic sulfonic acids and organic acid esters of sulfuric acid, which acids and esters contain at least one alkyl group having at least 3 carbon atoms, in amounts sufficient to form soluble salts with calcareous deposits in and around the cavity of the well, is first prepared. The amount of the compound present in the solution may vary widely depending upon the particular compound employed. Generally it may be said that the amount of acid or acid ester present in the solution may vary between about 1 and about 50% and is preferably maintained in the range of from about 5 to about 20% of the solution. Thus, I have found that an approximately 10% aqueous solution of isopropyl naphthalene sulfonic acid may be used in accordance with this invention. When operating in accordance with the preferred embodiment of my invention, i. e. when using a solution of a composition comprising free organic sulfonic acids or organic acid esters of sulfuric acid, which acids and esters contain at least one alkyl group having not less than 10 nor more than 16 carbon atoms, the concentration of the acid or acid esters may be maintained within the above-mentioned range of about 1 to about 50%, but is preferably maintained in the range from about 5 to about 20% of the solution. Examples of such compositions are: hexadecyl phenol sulfonic acid; lauryl sulfonic acid; mono-lauryl sulfuric acid ester; or a mixture comprising alkyl aryl sulfonic acids such as may be prepared by chlorinating petroleum fractions, for example kerosene, until the organically combined chlorine therein is from about 75% to about 150% of that required theoretically for monochlorination, condensing the chlorinated kerosene with an aromatic compound such as benzene, naphthalene, diphenyl, phenol, phenetole, etc. by a Friedel-Crafts type of reaction to obtain mixtures of alkylated aryl compounds, and sulfonating the latter mixtures.

The solution prepared as above described may be introduced into the oil well to be treated in any desirable manner. For example, the solution may be forced into the well cavity and the surrounding calcareous formation by other solutions which are introduced into the mouth of the oil well after introduction thereinto of the treating solution. Preferably, the treating solution is forced into the well by the gas which is released from the well by action of the solution upon the calcareous formation, since this method avoids reintroduction of oil and emulsification thereof in the cavity of the well. The compounds present in the solutions used in accordance with this invention react readily with the calcareous deposits in the oil well to form soluble calcium and magnesium salts; thus, substantially no insoluble salts are deposited in the well in the practice of this phase of my invention. Furthermore, the corrosive action of these solutions is negligible, so that they may be introduced into the well without removal of any of the metal equipment; for example, a piece of freshly prepared wrought iron lost only about 0.1% of its weight upon immersion for one hour in a 10% aqueous solution of isopropyl naphthalene sulfonic acid. The same sulfonic acid solution, on the other hand, dissolved 2% of its weight of powdered calcium carbonate in less than 3 seconds. The time of contact necessary substantially to exhaust the treating solution by reaction with calcareous deposits will vary widely with different wells and conditions. The temperature at which the treating solution is introduced into the well is preferably, though not necessarily, about atmospheric temperature. After the solution has remained in contact with the calcareous deposits until its action is substantially exhausted, it is removed from the well and pumping resumed.

When employing solutions of compositions containing sulfuric acid, in the practice of this invention, the aqueous solution should preferably contain not less than 5% of its weight and not more than 50% of its weight as acid, and the organic sulfonic acids or organic sulfuric acid esters therein should be not less than one-half and preferably equal to the weight of 100% sulfuric acid in the solution. The sulfonic acids and the organic acid esters inhibit the action of the mineral acid upon the metal equipment of the well and if present in quantities here specified they also diminish the violence of the action of the mineral acid upon the calcareous deposits in the well. When using such solutions, it may be desired to further inhibit the action of the sulfuric acid by incorporating between about 0.01 and about 1% of an inhibitor such as phosphine bases or nitrogenous bases, e. g. thiocarbanilide, quinaldine, etc. This phase of my invention possesses the particular advantage over prior processes employing mineral acids for treating depleted oil wells in calcareous formations in that the sulfonic acids and organic acid esters of sulfuric acid used in accordance with this invention remove the oil from the surfaces of the calcareous formations and disperse the oil as well as any finely-divided insoluble deposits which may be formed by the action of the sulfuric acid upon the calcareous formation, thereby permitting the removal of such oil and insoluble deposits from the well cavity along with the spent treating solution. Thus, the process of my invention permits the use of inexpensive sulfuric acid which could not advantageously be used in prior processes because it forms insoluble calcium sulfate upon contacting the calcareous deposits.

The following examples are illustrative of the process of my invention:

Example 1.—5000 pounds of a 10 per cent solution of di-isopropyl naphthalene sulfonic acid are introduced into an oil well through the iron pump tube. Sufficient crude oil is then introduced into the tube to fill it and thereby force the acid solution through the tube into the well. The acid solution is permitted to remain in the well until its activity is substantially exhausted. It is then pumped out and regular pumping of the well resumed. The flow of oil is substantially increased by this treatment.

Example 2.—5000 pounds of a 6 per cent solution of lauryl sulfonic acid are introduced into an oil well through the iron pump tube. Sufficient crude oil is then introduced into the tube to fill it and thereby force the acid solution through the tube into the well. The acid solution is permitted to remain in the well until its activity is substantially exhausted. It is then pumped out and regular pumping of the well resumed. The flow of oil is substantially increased by this treatment.

Example 3.—The parts are by weight.

A Pennsylvania kerosene fraction which is characterized by a sp. gr. of 0.788 at 24° C. and boiling range 185° to 275° C. is treated with 4×10^{-4} of its weight of iodine, and chlorine gas

is passed through the agitated hydrocarbon mixture which is maintained between 60° and 70° C. until the sp. gr. of the mixture has reached a value between 0.910 and 0.918 at 24° C., and corresponds to an organically combined chlorine content of about 115 per cent of the amount theoretically required to monochlorinate the hydrocarbons (average molecular weight correlated with boiling range=$C_{14}H_{30}$) in the mixture. The mixture may conveniently be termed keryl chloride, i. e. a mixture of alkyl chlorides in which the aliphatic residues are derived from kerosene hydrocarbons.

50 parts of the resulting keryl chloride are added slowly to a rapidly agitated mixture of 100 parts dry benzene and 2½ parts anhydrous aluminum chloride, while the temperature of the mixture is maintained at about 35° C. The mixture is warmed to about 45° C. and agitated for about 1½ hours; then it is allowed to stand and cool for about 2 hours, before the upper layer of oil is withdrawn. The oil contains the condensation product which is formed from the keryl chloride and benzene, which may conveniently be called keryl benzene, i. e. alkyl substituted benzene in which the aliphatic residues are derived from kerosene hydrocarbons.

The oil is distilled at atmospheric pressure until the vapor temperature reaches about 150° C. The remaining distilland is distilled in vacuo at about 3 to 4 inches of mercury pressure without heating until the distilland has a temperature of about 120° C. The distilland is stripped in this manner of uncondensed benzene and low-boiling constituents. To the remaining distilland about 2 parts of caustic soda are added; the distillation is continued until the temperature in the vapor is 250° C. at 14 mm. mercury pressure, and the distillate after the caustic soda addition is collected separately as the fraction which is chiefly keryl benzene.

The keryl benzene is given a sulfuric acid wash by stirring it for about one hour at 40° C. with about 15 per cent of its weight of 100 per cent sulfuric acid, then permitting the mixture to stand and to stratify, and separating the lower layer of washing acid from the upper layer of oil.

The latter is mixed with 1.25 times its weight of 100 per cent sulfuric acid at a temperature between 30° and 35° C. The mixture is warmed to 55° C. and agitated at that temperature for one hour. It is then allowed to stand and to stratify for about 2 hours, and the middle layer of sulfonated material is separated from the top layer which is chiefly unsulfonated material, and from the bottom layer which is chiefly spent sulfuric acid.

The middle keryl benzene sulfonic acid layer is drowned in ice and ice water, and adjusted to a desired content of keryl benzene sulfonic acid. (One method of determining the content of sulfonic acid and sulfuric acid in the resulting aqueous solution is to neutralize a sample with caustic soda, and thus ascertain the total content of inorganic sulfates and organic sulfonates in the neutral solution, then to remove the organic sulfonates from the solution with alcohol in which they are soluble, and ascertain the amount of organic sulfonates therein. From the results, the proportions and content of sulfonic acid and sulfuric acid in the original solution may be calculated.) 5000 pounds of a 10 per cent solution of keryl benzene sulfonic acid prepared in the manner described above are introduced into an oil well through the pump tube. The solution is forced through the tube into the well, and is permitted to remain therein until the activity of the solution is substantially exhausted. The solution is then pumped out and regular pumping of the well is resumed. The flow of oil is substantially increased by this treatment.

Other keryl aryl sulfonic acids, i. e. alkyl-substituted aryl sulfonic acids in which the aliphatic residues are derived from keroene hydrocarbons, may be prepared in the manner similar to that described in this example by substituting for the benzene other mono- and dinuclear hydrocarbons, such as naphthalene or diphenyl, or nuclearly substituted derivatives of the hydrocarbons, such as the hydroxy, halogen, lower alkyl or alkoxy derivatives, for example, phenol, phenetole, naphthol, chlorbenzene, toluene, etc., and by substituting for the Pennsylvania kerosene fraction described other petroleum fractions of the kerosene boiling range.

The keryl aryl sulfonic acids so prepared can be used instead of keryl benzene sulfonic acid.

Example 4.—5000 pounds of a 15 per cent solution of mono-butyl sulfuric acid ester are introduced into an oil well through the iron pump tube. Sufficient crude oil is then introduced into the tube to fill it and thereby to force the acid solution through the tube into the well. The acid solution is permitted to remain in the well until its activity is substantially exhausted. It is then pumped out and regular pumping of the well resumed. The flow of oil is substantially increased by this treatment.

In place of the acids mentioned in the above examples, other compounds such as the following may be used in the practice of my invention:

Isopropyl naphthalene sulfonic acid
Hexadecyl phenol sulfonic acid
Mono-propyl sulfuric acid ester
Mono-isopropyl sulfuric acid ester
Mono-lauryl sulfuric acid ester
Alkyl benzene sulfonic acids having at least one alkyl group of at least 3 and not more than 16 carbon atoms
Tertiary butyl phenol sulfonic acid
Capryl sulfonic acid
Glycol dioleate disulfuric acid
Glycol dioleate mono-sulfuric acid
Palmitic toluidide sulfonic acid
Mono-amyl sulfuric acid ester.

In place of the above compounds further substituted derivatives may be used, such as disulfonic acids for the corresponding mono-sulfonic acids. The sulfuric acid derivatives may be used in relatively pure or in crude condition.

It is to be understood that the term "process of increasing the flow of oil" used in the claims is intended to refer not only to a process of increasing the flow of oil in a well which is producing oil at a diminished rate, but also to a process of restoring the flow of oil in a well which before treatment was producing substantially no oil.

While the invention has been described above in connection with the treatment of oil wells in calcareous formations, it will be understood that it is applicable to the treatment of other wells, such as gas or other fluid-supplying wells in calcareous formations.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that

all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. In a process of increasing the flow of fluid in a well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous solution of a composition comprising an organic compound containing an acid residue of sulfuric acid and at least one alkyl group having at least 3 carbon atoms, said compound being present in concentration of at least 1% in said aqueous solution, and constituting at least one-third of the total acid present in the solution, whereby said organic compound reacts to remove calcareous deposits in and around the cavity of the well by forming soluble salts with such deposits.

2. In a process of increasing the flow of oil in an oil well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous solution of a composition comprising mineral acid and an organic compound containing an acid residue of sulfuric acid and at least one alkyl group having 3 to 16 carbon atoms, said compound being present in concentration of at least 1% in said aqueous solution, and constituting at least one-third of the total acid present in the solution, whereby said organic compound reacts to remove calcareous deposits in and around the cavity of the well by forming soluble salts with such deposits.

3. In a process of increasing the flow of oil in an oil well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous solution of a composition comprising an organic compound containing an acid residue of sulfuric acid and at least one alkyl group having 10 to 16 carbon atoms, said compound being present in concentration of at least 1% in said aqueous solution and constituting at least one-third of the total acid present in the solution, whereby said organic compound reacts to remove calcareous deposits in and around the cavity of the well by forming soluble salts with such deposits.

4. In a process of increasing the flow of oil in an oil well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous solution of a composition comprising a compound selected from the group consisting of isopropyl naphthalene sulfonic acid, di-isopropyl naphthalene sulfonic acid, hexadecyl phenol sulfonic acid, mono-propyl sulfuric acid ester, mono-isopropyl sulfuric acid ester, mono-butyl sulfuric acid ester, mono-lauryl sulfuric acid ester, alkyl benzene sulfonic acids having at least one alkyl group of 3 to 16 carbon atoms, tertiary butyl phenol sulfonic acid, capryl sulfonic acid, lauryl sulfonic acid, glycol dioleate disulfuric acid, glycol dioleate mono-sulfuric acid, palmitic toluidide sulfonic acid, and monoamyl sulfuric acid ester, said compound being present in concentration of at least 1% in said aqueous solution, and constituting at least one-third of the total acid present in the solution, whereby said organic compound reacts to remove calcareous deposits in and around the cavity of the well by forming soluble salts with such deposits.

5. In a process of increasing the flow of oil in an oil well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous acid solution containing not less than 5% nor more than 50% of acid comprising sulfuric acid and an organic compound containing an acid residue of sulfuric acid and at least one alkyl group having 10 to 16 carbon atoms.

6. In a process of increasing the flow of oil in an oil well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous solution comprising between about 1% and about 50% of an organic compound containing an acid residue of sulfuric acid and at least one alkyl group having 3 to 16 carbon atoms, said solution containing no substantial amount of inorganic acid, whereby the organic compound reacts with calcareous deposits in and around the cavity of the well to form soluble salts with such deposits.

7. In a process of increasing the flow of oil in an oil well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous solution comprising between about 5% and about 20% of an organic compound containing an acid residue of sulfuric acid and at least one alkyl group derived from a petroleum oil, the boiling range of which indicates it predominates in hydrocarbons of 10 to 16 carbon atoms, said solution containing no substantial amount of inorganic acid, whereby the organic compound reacts with calcareous deposits in and around the cavity of the well to form soluble salts with such deposits.

8. In a process of increasing the flow of oil in an oil well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous solution comprising between about 1% and about 50% of mixed alkyl aryl sulfonic acids in which the alkyl groups contain 3 to 16 carbon atoms, said solution containing no substantial amount of inorganic acid, whereby the organic compound reacts with calcareous deposits in and around the cavity of the well to form soluble salts with such deposits, and removing the spent solution from the well.

9. In a process of increasing the flow of oil in an oil well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous acid solution containing between about 5 and about 50 parts total acid per 100 parts aqueous solution, said acid comprising sulfuric acid and not less than one-half part per part sulfuric acid in the solution of an organic compound containing an acid residue of sulfuric acid and at least one alkyl group having at least 3 carbon atoms.

10. In a process of increasing the flow of oil in an oil well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous acid solution containing between about 5 and about 50 parts total acid per 100 parts aqueous solution, said acid comprising approximately equal parts by weight of sulfuric acid and mixed alkyl aryl sulfonic acids in which the alkyl groups contain 10 to 16 carbon atoms and are derived from kerosene hydrocarbons.

11. In a process of increasing the flow of oil in an oil well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous solution comprising between about 5 and about 20% di-isopropyl naphthalene sulfonic acid, said sulfonic acid constituting at least about one-third of the total acid in said solution, whereby said sulfonic acid reacts with calcareous deposits in and around the cavity of the well to form soluble salts with such deposits, and removing the spent solution from the well.

12. In a process of increasing the flow of oil in an oil well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous solution comprising between about 5 and about 20% mono-propyl sulfuric acid ester, said sulfuric acid ester constituting at least about one-third of the total acid in said solution, whereby said sulfuric acid ester reacts with calcareous deposits in and around the cavity of the well to form soluble salts with such deposits, and removing the spent solution from the well.

13. In a process of increasing the flow of oil in an oil well sunk in a calcareous formation, the improvement which comprises introducing into said well an aqueous solution comprising between about 5 and about 20% of mixed alkyl benzene sulfonic acids prepared by chlorinating a kerosene of boiling range 185° to 275° C. until the organically combined chlorine therein is from about 75% to about 150% of that required theoretically for monochlorination, condensing the chlorinated kerosene with benzene by a Friedel-Crafts type of reaction to obtain mixed alkyl benzenes, and sulfonating the latter mixture, said sulfonic acids constituting at least about one-third of the total acid in said solution, whereby said sulfonic acids react with calcareous deposits in and around the cavity of the well to form soluble salts with such deposits, and thereafter removing the spent solution from the well.

LAWRENCE H. FLETT.

CERTIFICATE OF CORRECTION.

Patent No. 2,338,282. January 4, 1944.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 40, for "sulfonic acid" read --sulfuric acid--; page 3, second column, line 11, for "keroene" read --kerosene--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of February, A. D. 1944.

Leslie Frazer
Acting Commissioner of Patents.

(Seal)

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