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PROCESS FOR TREATING OIL WELLS

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This invention pertains to the art of treating oil wells to increase their production, and relates more specifically to the removal of clogging deposits of paraffinic, asphaltic, waxy, and similar nature by means of an exothermic process carried out in acid reaction.

Many processes have already been proposed to melt and remove obstructing paraffin wax deposits from oil wells by the heat-generating interaction of such agents as, for example, a strong acid and a caustic alkali, or a comminuted metal, an oxidizing compound and a caustic alkali.

These processes, however, often fail to generate an amount of heat sufficient to clean the well. When carried out in neutral reaction, as, for example when generating heat by the interaction of a strong acid and a caustic alkali, these processes are furthermore ineffective either to remove inorganic scale deposits from the bottom of the hole, or to dissolve calcareous deposits from the formation adjacent the borehole.

When carried out in alkaline reaction, these processes have also the disadvantage of causing the formation of insoluble precipitates by the interaction of the reagents used with the calcium and magnesium ions usually present in a well and formation brines whereby the formation is often further plugged and the production of the well reduced.

It is therefore an object of this invention to provide a method for treating clogged oil-wells by means of reagents capable of developing an amount of heat sufficient for a complete removal of the obstructing deposits of paraffinous, asphaltic or waxy nature.

It is another object of this invention to provide for the above treatment a process capable of being carried out in acid reaction, whereby the formation of insoluble precipitates by the interaction between the reagents used and the salts present in the well and adjacent formations is eliminated.

It is a further object of this invention to provide for said treatment a heat-generating process involving the use of reagents having a sufficiently acid character to attack the scaly and calcareous deposits within the well and adjacent formation, whereby said deposits are disintegrated and removed from the well simultaneously with the paraffinous deposits melted by the effect of the heat-generating reaction.

It is another object of this invention to provide for said treatment a heat generating process carried out in the presence of, or immediately followed by the application of a solvent capable of readily dissolving the paraffin wax at temperatures near its melting point, whereby said wax is removed from the well and is prevented from clogging the formation by solidifying on cooling.

The process of the present invention consists broadly in generating heat within a well by means of an exothermal reaction involving the reduction of oxidizing compounds by the nascent hydrogen evolved by the action of an acid on an electropositive metal, according, for example, to the following reaction

$$Mg(metal)+2HCl=MgCl_2+H_2(nascent)+heat$$

$$3H_2(nascent)+Na_2Cr_2O_7+8HCl=2NaCl+2CrCl_3+7H_2O+heat$$

As oxidizing compounds suitable for the present process, the following inorganic substances may be used: water soluble metal nitrates, chlorates, perchlorates, chromates, dichromates, permanganates and persulphates.

As acids suitable for the present process, aqueous solutions of any strong inorganic acid may be used, such as hydrochloric, sulfuric or nitric acid, which may be suitably inhibited to prevent corrosion of the equipment.

As metals suitable for the present process, any electropositive metal such as aluminum, zinc, magnesium, calcium etc., may be used. The metal should be used in suitably comminuted form, for example, in the form of mossy zinc, magnesium turnings, or aluminum ground, for example, to pass a 20 mesh screen.

As solvents suitable for use in conjunction with the present process, the following solvents may be used: carbon tetrachloride, benzol, gasoline, kerosene, kerosene extract, tetralin, methyl ethyl ketone, etc.

In treating a well by the process of the present invention, the following procedure may be followed:

A sample of the paraffin wax deposits is obtained from the well and subjected to tests to determine its melting point and the type of solvent especially effective in dissolving it at temperatures near its melting point. The melting points of paraffin waxes from oil wells usually fall within a temperature range of from 50° to 95° C.

The well is then bailed or pumped until free of liquid, and a suitable amount of oil is placed in the well. A desired solvent may be added to

the oil at this or any later stage of the process, the quantity of said solvent being preferably considerably in excess of that anticipated as necessary for dissolving the wax deposits which it is desired to remove from the well. The heat generating reagents are then introduced into the well in any desired manner. For example, a preferred method consists in pumping down the well or placing thereinto by means of a bailer an aqueous solution of an acid together with one of the oxidizing compounds listed above, dissolved therein, followed by lowering the desired comminuted metal in suitable containers. Another method may comprise pumping down the well an aqueous solution of one of the oxidizing compounds listed above, lowering the desired comminuted metal in suitable containers, and then introducing an aqueous solution of an acid into the well, etc. The amount of the reagent used is calculated so as to raise the fluid level above the top of the producing formation, and so as to generate an amount of heat in excess by at least 50% over that necessary to give the desired raise in temperature, whereby the effect of heat losses due to conduction into the formation is neutralized, and the temperature of the fluid in the well is raised above the melting point of the paraffin wax. In calculating the amount of the reagents and of the solvent used, reference may be had to Tables I and II, given hereinbelow.

The hot solution is allowed to remain in the well for a sufficiently long time, for example, from 2 to 8 hours, to insure that all the paraffin wax has been melted and has been dissolved by the solvent and is then removed by bailing, swabbing or pumping, before the temperature becomes low enough to cause the paraffin wax to solidify again.

It is inadvisable to force the hot solvent into the formation by applying pressure at this stage, since the resulting cooling of the solvent, more or less saturated with the wax, may cause a plugging of the formation. It is therefore preferable to remove the wax together with the hot solvent from the well, and to follow this procedure by a second treatment with a cold wax solvent to be forced into the formation, if the latter step appears necessary.

The aqueous acid used in the process of the present invention may be of any desired concentration from about 5 to 25 per cent or more. In cases where the well contains scaly or calcareous deposits, which may sometimes be intermingled with wax deposits and prevent the solvent from reaching and dissolving the heated wax, the acid in the present treating composition attacks and disintegrates said mineral deposits, whereby the effectiveness of the process is greatly increased. An excess of acid over that required for condensing the comminuted metal used in this process is usually employed for effecting the disintegration of calcareous formations in addition to the removal of wax. The formation of insoluble precipitates which often occurs in heat generating processes carried out in alkaline reaction due to the interaction of the reagents used with calcium and magnesium salts usually present in wells, is precluded due to the acid character of the present composition.

The amounts of heat generated by using varying proportions and concentrations of reagents are shown in Table I, and may be used in calculating the actual quantities of said reagents necessary for an effective treatment.

Table I

Composition No.	Regents by weight	Heat evolved in B. t. u./lb. of composition
1	1 gr. Al 8 gr. NaOH 1 gr. $NaNO_3$ 100 ml. H_2O	102.6
2	1.35 gr. Mg 100 ml. 7.5% HCl	96.4
3	1.35 gr. Mg 3 gr. $NaNO_3$ 100 ml. 7.5% HCl	106.8
4	1.35 gr. Mg 3 gr. $NaNO_3$ 100 ml. 5% HCl	122.0

Table I shows that compositions Nos. 3 and 4, used according to the present invention, evolve a considerably greater amount of heat per pound of composition used than, for example, composition No. 2, where the reaction between the acid and the metal is not carried out in the presence of an oxidizing agent, or composition No. 1, where the generation of heat is carried out in alkaline reaction.

The amounts of reagents which may actually be used according to the present invention to obtain a desired increase of temperature in a well are shown in Table II, which refers, by way of example, to the treatment, throughout about 125 feet of a producing sand, of a well having a 6 inch casing.

Table II

Weight of reagents in pounds		Volume in barrels		Temperature increase, °C.
Mg	$NaNO_3$	Acid: 15% HCl	Solvent: gasoline	
8	16	1	4	30
11	22	1	4	40
14	28	1	4	50
20	40	1.5	4	60

Although, for the sake of brevity, magnesium, sodium nitrate and hydrochloric acid have been used to illustrate the application of the present process to the removal of paraffin wax deposits from oil wells, it may be shown by laboratory and field tests that the same results are obtainable by the use of the other metals, acids and oxidizing substances specified for use in the present process.

We claim as our invention:

1. In the process of cleaning wells from high-melting organic deposits comprising paraffinic matter, the steps of introducing thereinto a comminuted electropositive metal, an aqueous solution of an inorganic acid, and an inorganic oxidizing agent selected from the group consisting of water-soluble metal nitrates, chlorates, perchlorates, chromates, dichromates, permanganates, and persulfates, causing nascent hydrogen to be evolved by the action of the acid on the electropositive metal, causing the oxidizing compound to be reduced by the nascent hydrogen in acid reaction, allowing the heat generated by the interaction of said agents to melt the paraffinic deposits within said wells and removing from the wells the matter melted by said heat.

2. In the process of cleaning wells from high-melting organic deposits comprising paraffinic matter, the steps introducing thereinto a comminuted electropositive metal, an aqueous solution of an inorganic acid, an inorganic oxidizing agent selected from the group consisting of wa-

ter-soluble metal nitrates, chlorates, perchlorates, chromates, dichromates, permanganates, and persulfates, and a solvent, causing nascent hydrogen to be evolved by the action of the acid on the electropositive metal, causing the oxidizing compound to be reduced by the nascent hydrogen in acid reaction, allowing the heat generated by the interaction of said agents to melt the paraffinic deposits within said wells, causing the paraffinic matter melted by the heat to dissolve in said solvent, and removing from the wells the matter melted by said heat and said solvent.

3. In the process of cleaning wells from deposits comprising mixed paraffinic and inorganic matter, the steps of introducing thereinto a liquid comprising a comminuted electropositive metal, an aqueous solution of a strong inorganic acid capable of reacting with said metal and said inorganic obstructing matter, an inorganic oxidizing compound selected from the group consisting of water-soluble metal nitrates, chlorates, perchlorates, chromates, dichromates, permanganates, and persulfates, and a solvent causing heat to be generated within the well by the interaction of said agents, causing the paraffinic matter melted by the heat to dissolve in the solvent, causing the inorganic matter to dissolve in the acid, and removing the dissolved deposits from the well.

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