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ACID COMPOSITION FOR TREATMENT OF DEEP WELLS

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The invention relates to the treatment of deep wells and is more especially concerned with the treatment of wells in which the producing stratum comprises a silicate rock formation of which serpentine is representative.

The treatment of deep wells in a limestone formation with aqueous hydrochloric acid containing various inhibiting agents to prevent the attack of the raw acid upon the metal parts of the well is disclosed in United States Patent 1,877,504. The use of hydrochloric acid in wells drilled into a serpentine formation has not given satisfactory results as to increasing the output of fluid product from the well. We have now found that the use of an aqueous oxidizing acid solution, containing hydrochloric acid and nitric acid, and more particularly, the use of an aqueous solution containing hydrochloric acid, nitric acid, and hydrofluoric acid, gives satisfactory results in the treatment of wells in a serpentine formation. However, such a solution is oxidizing in nature, and the inhibiting agents normally employed in solutions of hydrochloric acid alone are not effective to inhibit sufficiently the attack of such oxidizing acid solution upon the metal parts of the well.

It is therefore an object of the present invention to provide materials suitable for use as inhibiting agents, which will effectively prevent the attack of a raw oxidizing acid solution upon the metal parts of a deep well, particularly at the elevated temperatures encountered at the base of the bore of such wells.

There are a number of inhibiting agents which are suitable for use at room temperature, and which at such temperatures are capable of substantially inhibiting the attack of oxidizing acid solutions upon metal, for example, alpha-naphthyl-amine, para-phenylenediamine, benzidine, phenyl-hydrazine, pyrrole, and quinoline. However, the temperature conditions encountered in a deep well make it imperative that the inhibitor be effective at 100° F. and slightly higher. For instance, in the Michigan oil field the temperature in the producing stratum is about 104° F., and in the main producing stratum of the Texas field it is approximately 150° F. We have determined that the aforesaid inhibitors, although effective at ordinary temperatures, e. g. about 70° lose their effectiveness at 100° F., and therefore are not suitable to inhibit oxidizing acid solutions in the treatment of deep wells.

We have now discovered, however, that the diamino derivatives of benzophenone and diphenyloxide, when added to aqueous oxidizing acid solutions, are effective at the temperature encountered in deep wells to inhibit the attack of such acid solutions upon the well tubing, etc.

The following examples show the effectiveness of diamino-diphenyloxide and of diaminobenzophenone to inhibit the attack upon mild steel by aqueous oxidizing acid solutions maintained at elevated temperatures. Weighed strips of sand-blasted, clean mild steel of like surface area were immersed in solutions of the composition shown, and after 18 hours the strips were removed, rinsed, and weighed. All percentages of acid and inhibitor are by weight based on the total weight of solution.

Example 1

15 per cent HCl—5 per cent HNO_3. Temperature—100° F.

	Grams loss
Blank	10.587
0.4% diaminodiphenyloxide	0.509
0.4% diaminobenzophenone	0.494

Example 2

15 per cent HCl—3 per cent HNO_3—2 per cent HF. Temperature—100° F.

	Grams loss
Blank	7.806
0.4% diaminodiphenyloxide	0.5
0.2% diaminobenzophenone	0.606

Example 3

15 per cent HCl—5 per cent HNO_3. Temperature—151° F.

	Grams loss
Blank	18.903
1% diaminodiphenyloxide	2.587
1% diaminobenzophenone	2.540

At a temperature of 68° F. aqueous oxidizing acid solutions containing the diamino derivatives of diphenyloxide and benzophenone have substantially no action upon the metals ordinarily employed in wells and in apparatus for the treatment of wells.

The treatment of a deep well with aqueous oxidizing acid solutions containing the diamino derivatives of diphenyloxide or benzophenone may be accomplished according to the known procedures. We incorporate between about 0.1 and 1.0 per cent by weight of such a derivative with an aqueous solution containing preferably between about 5 and about 20 per cent of hydrochloric acid, and between about 1 and about 10 per cent of nitric acid, with or without the addition of small amounts of hydrofluoric acid, e. g.

between about 1 and about 10 per cent thereof.

The inhibited aqueous oxidizing acid solution can then be introduced into the well through the pump tube so that the latter need not be withdrawn prior to the treatment. It is sufficient merely to pull the pump rod and valves and pour the acid solution in through the tube. The acid solution is preferably added in amount calculated to fill the bore of the well to a depth not exceeding the thickness of the fluid producing stratum. In order to force the charge of acid out of the pump tube into the producing stratum it may be followed by a charge of oil, water, or other liquid, or pressure may be applied by other suitable means, e. g. by air pressure or by means of a pump. When introduced into the bottom of the well the acid attacks the rock structure and dissolves or disintegrates it, thereby enlarging the pores or channels in the rock or opening up new channels. After the action of the acid has practically ceased, the spent solution may be pumped or bailed out. In many cases it may be desirable to repeat the treatment one or more times.

Another method which may be used in treating a deep well with our aqueous oxidizing acid solution employing our inhibitors is to introduce into the well in concentrated form, ahead of the main oxidizing acid charge, a quantity of the diamino derivative of diphenyloxide or benzophenone thereby forming protective surfaces over the metal equipment within the well before said main charge of acid is contacted with such surfaces.

The diamino derivative may be employed in the form of a solution or emulsion thereof with any vehicle which does not react therewith to destroy its inhibiting properties. Among the various vehicles which may be employed we mention particularly ethyl alcohol. Having in this manner substantially immunized the metal surfaces within the well, we may then introduce the acid charge into the well and follow the general procedure outlined above for treatment with inhibited acid.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the materials employed, provided the ingredients stated by any of the following claims or the equivalent of such stated ingredients be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. An aqueous oxidizing solution containing nitric acid and a relatively small amount of a diamino derivative of a compound selected from the group consisting of diphenyloxide and benzophenone.

2. An aqueous oxidizing solution containing nitric acid, hydrochloric acid, and a relatively small amount of a diamino derivative of a compound selected from the group consisting of diphenyloxide and benzophenone.

3. An aqueous oxidizing solution containing nitric acid, hydrofluoric acid, and a relatively small amount of a diamino derivative of a compound selected from the group consisting of diphenyloxide and benzophenone.

4. An aqueous oxidizing solution containing nitric acid, hydrochloric acid, hydrofluoric acid, and a relatively small amount of a diamino derivative of a compound selected from the group consisting of diphenyloxide and benzophenone.

5. An aqueous oxidizing solution containing between about 1.0 and about 10.0 per cent by weight of nitric acid and a relatively small amount of a diamino derivative of a compound selected from the group consisting of diphenyloxide and benzophenone.

6. An aqueous oxidizing solution containing between about 1.0 and about 10.0 per cent by weight of nitric acid, between about 5.0 and about 20.0 per cent by weight of hydrochloric acid, and a relatively small amount of a diamino derivative of a compound selected from the group consisting of diphenyloxide and benzophenone.

7. An aqueous oxidizing solution containing between about 1.0 and about 10.0 per cent by weight of nitric acid, between about 1.0 and about 10.0 per cent by weight of hydrofluoric acid, and a relatively small amount of a diamino derivative of a compound selected from the group consisting of diphenyloxide and benzophenone.

8. An aqueous oxidizing solution containing between about 1.0 and about 10.0 per cent by weight of nitric acid, between about 5.0 and about 20.0 per cent by weight of hydrochloric acid, between about 1.0 and about 10.0 per cent by weight of hydrofluoric acid, and between about 0.1 and 1.0 per cent by weight of a diamino derivative of a compound selected from the group consisting of diphenyloxide and benzophenone.

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