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TREATMENT OF WELLS

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The invention relates to the treatment of wells. It more particularly concerns an improved method of treating wells with hydrochloric acid to dissolve calcareous matter therein.

In treating wells with hydrochloric acid wherein the acid is introduced into the well and forced into the surrounding formation to react with the calcareous rock and increase the permeability thereof, thus allowing the oil to flow into the well more readily, it has been proposed to introduce the acid emulsified with oil or the like to prevent the acid from attacking the metal parts of the well. In the proposed method, an emulsion of the water-in-oil type in which the aqueous acid phase is surrounded by the oil phase is employed and since each droplet of acid is surrounded by oil the acid is prevented from coming into direct contact with the metal parts of the well which it would ordinarily attack. However, the proposed method has the disadvantage that it is very difficult to produce an emulsion of the above type even when emulsifying agents are employed. In addition, once the emulsion is produced, it is extremely difficult, if not impossible in many instances, to force the emulsified mixture into the formation through the smaller pores and flow channels, since these emulsions are usually of a highly viscous nature. In the relatively open pores of the formation where such an emulsion can be injected, it may not break in which case the acid is unable to attack the calcareous rock.

We have discovered that it is unnecessary to introduce the acid and oil as an emulsion in order to protect the metal parts of the well, but instead if a relatively small quantity of an oil such as crude oil is simultaneously introduced into the well along with the acid, whereby the oil distributes itself in the acid without becoming emulsified therewith, the oil forms a film on the metal parts of the well as the acid is introduced thus protecting the metal surfaces contacted. Ordinarily an oil film formed upon a metal surface is not effective to prevent the corrosive attack of hydrochloric acid upon the metal since the acid rapidly destroys such a film as is well known in the pickling industry where acids are used to remove not only metal oxide and scale coatings but oily and greasy films as well. In the present invention, however, a single oil film is not formed and then destroyed but rather the film first formed as the oil and acid are caused to flow over the metal surfaces is constantly renewed or reformed by the oil present with the acid and continuously entering the well so that the acid never completely destroys the film protecting the metal surfaces.

By our improved method, unemulsified hydrochloric acid may be introduced into the well and forced into the surrounding formation while the metal parts of the well are effectively protected without the difficulties involved in emulsifying the acid in oil, thus giving improved results as regards the ease with which the acid may be forced into the formation. Employing our improved method also insures that the acid will readily attack the calcareous rock, since each acid droplet is not surrounded by an oil film as is the case when an emulsion such as has been previously proposed is employed.

In carrying out the method of the invention in a well equipped with the usual casing and tubing, the charge of acid is preferably introduced into the well through the tubing and at the same time a small quantity of oil is introduced into the tubing along with the acid where it distributes itself with the acid due to the turbulence of flow and coats the inside of the tubing and any other metal parts of the well contacted with a protective film. The oil coating the metal parts of the well protects them so that the corrosive effects of the acid are substantially prevented. After the desired quantity of acid has been introduced into the well, pressure may be applied, if necessary, as by pumping, to force the acid from the tubing and the well bore into the surrounding formation. The acid is held in place for a period of time to allow it to react with the formation, after which the spent solution may be withdrawn, as by bailing, and the well returned to production.

The amount of hydrochloric acid to employ depends upon the extent of the formation to be treated, for example, from 500 to 5000 gallons or more may be satisfactorily employed.

The amount of oil to use to give protection of the metal parts of the well may be relatively small. In general, we have found that from 0.1 to 5 per cent or more by volume, and preferably 1.0 per cent, of an oil such as crude oil, based on the volume of acid solution to be used, gives generally satisfactory results. Although crude oil is preferably used because of its cheapness and ready availability, derivatives thereof, such as for example, fuel oil, lubricating oil, and the like may be suitably used. Vegetable oils, such as castor oil, linseed oil, and the like may also be used. While it is preferable to introduce the oil continuously along with the acid in those instances when the oil is being distributed throughout the

acid as it enters the well, the oil may be added in small quantities at frequent intervals as the acid is introduced, it being necessary, however, to add the oil often or continually to insure the constant renewal of the oil film on the metal parts. The distribution or mixing of the oil in the acid may be brought about by bringing the oil and acid together in a single pipe connection at the well head and allowing them to flow together into the well, or in those instances where a pump is used to introduce the acid into the well and force it therefrom into the surrounding formation, the oil may be lubricated or fed into the pump intake, where it becomes distributed throughout the acid and thus forms an oil film on the metal parts, protecting them from the action of the acid.

In the foregoing manner the metal parts of a well may be protected during a treatment with hydrochloric acid, the degree of protection afforded being in the order of about 80 to 95%. This protection we have found can be even further improved. We have discovered that by including in the acid solution an inhibitor of the action of acids on metals, said inhibitor being selected from the group consisting of the acid soluble compounds of arsenic, antimony and bismuth, and then using this solution in combination with oil in the manner above described substantially 100% protection is afforded the metal parts of the well even though these be of various metals. For example, while comparative tests show that members of the above group of acid soluble compounds such as sodium arsenite are only about 80 per cent effective in preventing the attack of hydrochloric acid on iron, hydrochloric acid containing a similar amount of sodium arsenite and used in combination with crude oil in the manner set forth does not substantially attack iron, the effectiveness of the protection afforded being 99.9 per cent or more. Thus the protection obtained by employing the combination of oil and inhibitor is very markedly greater than can be obtained by employing inhibitor alone or by employing oil alone regardless of the amounts of each employed.

In using an inhibitor of the action of hydrochloric acid on metals in addition to introducing the acid in the presence of a relatively small amount of oil, the inhibitor is preferably first dissolved in the acid and thereafter the oil and the acid containing the inhibitor can be introduced into the well in the manner previously described. The amount of inhibitor to employ may vary widely although between about 0.1 to 5 per cent or more generally gives satisfactory results.

By use of the improved method, protection is afforded the metal parts of the well without the necessity of forming an emulsion as has been previously proposed, and, in addition the acid which is in a continuous phase instead of being in oil encased drops, readily and rapidly penetrates and attacks the calcareous rock of the formation. The acid also readily dissolves calcium carbonate scale deposits in the well bore tubing and like locations for the same reason.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed:

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

1. In a method of treating a well with hydrochloric acid, the step which consists in introducing the acid into the well and together therewith a relatively small amount of an oil, the acid being in continuous phase.

2. In a method of treating a well with hydrochloric acid, the steps which consist in mixing the acid with between about 0.1 to 5 per cent of crude oil and introducing the mixture into the well.

3. In a method of treating a well with hydrochloric acid, the step which consists in introducing into the well simultaneously and continuously along with the acid a relatively small quantity of oil, the acid being in continuous phase and having dissolved therein a relatively small amount of an arsenic compound.

4. In a method of treating a well with hydrochloric acid containing an agent selected from the group consisting of the acid soluble salts of bismuth, arsenic and antimony, the step which consists in introducing the acid containing said agent into the well and thence into the surrounding formation and together therewith a relatively small amount of an oil, the acid being in continuous phase.

5. In a method of treating a well with hydrochloric acid containing between about 0.1 to 5 per cent of an acid soluble arsenic compound, the step which consists in introducing the acid containing said arsenic compound into the well and thence into the surrounding formation and together therewith between about 0.1 to 5 per cent of crude oil.

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