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ACIDIZING OF WELLS

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This invention relates generally to the treating of oil and gas wells or the like and, more particularly, to well treating compositions containing acid and to methods utilizing the same in treating or acidizing operations performed to increase or restore the permeability of an underground structure, such as a zone or formation containing oil or gas.

It is believed that the invention will be most widely applied in connection with treating or acidizing operations which are performed on zones or formations partially or completely plugged with paraffin or scale deposits, such as deposits containing iron sulfide, iron oxide, calcium sulfate or the like. It is understood, however, that the invention may be applied elsewhere. In particular, it is anticipated that the invention will provide advantages in acidizing operations where improved results can be obtained if additional heat is present, that is, where a "hot" acid is desired or needed.

Accordingly, a general object of the invention is to provide an improved well treating composition containing acid and an improved method utilizing the same in well treating or acidizing operations.

Another object of the invention is to provide an improved composition and method useful in well treating or acidizing operations wherein it is desired to employ a "hot" acid, such as in removing paraffin or scale deposits tending to obstruct the flow of fluid in a zone or formation penetrated by the bore of an oil or gas well or the like.

The foregoing and additional objects and advantages are attained by the invention, which involves the general concept of improving an acidizing operation by generating additional heat, preferably as nearly as possible to the place of treatment, by reacting together a mineral acid solution, such as an aqueous solution of hydrochloric acid, which may be of the type commonly employed in well acidizing operations, and an agent, such as acetic anhydride, selected to produce heat upon reacting with the acid solution.

In one way of proceeding, quantities of acetic anhydride and an aqueous solution of hydrochloric acid are introduced, while substantially separated, into an oil or gas well or the like and then are allowed to come together at a desired location therein, such as opposite the face of an underground zone or formation to be treated. For example, quantities of the acetic anhydride and acid solution may be separately prepared at the surface of a well equipped with a tubing or the like which extends downwardly to the vicinity of a zone or formation to be treated. The tubing and surrounding annular space thus provide separate paths extending into the well. The acetic anhydride and acid solution are separately introduced and conducted downwardly into the well, each following its separate path until the two are allowed or caused to meet at an interface in the well.

If desired, two liquid streams, each containing one of the treating agents, may be pumped downwardly into the well along the separate paths and the pumping rates of the two streams may be controlled or adjusted at intervals during the treatment to control or adjust the location of the interface at which the acetic anhydride and the acid solution come together in the well.

In another way of proceeding, the acetic anhydride and the acid solution are introduced into the well in substantially separate parts of the same stream. For example, quantities of the treating agents may be alternately pumped downwardly into the well along the same path, such as through the tubing or through the annular space between the tubing and the surrounding surface in the well. A well packer may advantageously be employed in the well at one or both of the upper and lower limits of the zone or formation to be treated, such as to confine the treating agents or to facilitate the injection thereof into the pores and other openings of the surrounding strata.

As in conventional acidizing procedures, the quantities of treating agents required for best results will vary widely from well to well, depending on the particular conditions encountered. In certain wells it may be necessary or desirable to repeat the treatment at relatively frequent intervals, while in other wells repeated treatments may seldom, if ever, be necessary.

As one example, a well in Kansas was treated using 200 gallons of hydrochloric acid solution followed by 200 gallons of acetic anhydride which in turn was followed by 800 gallons of hydrochloric acid solution, with each batch being pumped downwardly into the well along the annular space surrounding the tubing. As another example, a second well in Kansas was similarly treated using 400 gallons of acetic anhydride spaced in 3,000 gallons of hydrochloric acid solution.

In preparing the treating fluids, various other additives and agents may be included, if desired. For example, an acid inhibitor may be included, such as in the stream or portion thereof containing the hydrochloric acid. Also, an agent selected to improve the penetrability of the treating fluids into the well strata may be included in one or both of the separate quantities prepared. If desired, agents may be included to prevent or remove water and emulsion blocks, and for other purposes.

While the invention is not limited to any particular theory of behavior, it is believed that the superior results obtained are due to a combination of advantages resulting from the particular compositions and methods employed. For one thing, the introduction of the acetic anhydride into the well substantially separated from the acid solution results in the development of considerable heat when these ingredients eventually come together in the well bore or in the adjacent well strata.

Where the treatment is performed in a well containing paraffin or scale deposits which are removed more easily in the presence of heat, or by the application of heat in addition to a solvent or treating agent, the development of heat as nearly as possible to the location of the substances to be dissolved or removed is believed to greatly facilitate the treatment. By permitting a more efficient utilization of the higher temperature fluids existing early during the reaction which occurs upon the acetic anhydride and hydrochloric acid solution coming together, the present invention provides greater effectiveness of treatment.

Also, it is believed that the acetic anhydride itself contributes to the acidizing of the well, since the product of its reaction with the aqueous hydrochloric acid solution, or with water which may be otherwise present in the well, is acetic acid which is known in the prior art as an acidizing fluid the use of which affords advantages in many operations, such as in treating wells in which treatments with hydrochloric acid have not always been completely successful.

While the invention has been described with reference to certain particulars and details thereof, it is understood that these are by way of example and that modifications within the spirit of the invention will now present themselves to those skilled in the art. Accordingly, the invention should not be considered limited except by the scope of the claims appended hereto.

What is claimed is:

1. In a well treating operation performed to remove paraffin or scale deposits, the steps of introducing into the well substantially separated treating fluids one of which contains hydrochloric acid and the other of which contains acetic anhydride, causing said treating fluids to come together and remain in the well for a period of time, whereby heat is produced as said mineral acid and acetic anhydride react together during the course of treating the well, and subsequently removing the treating fluids and removed deposits from the well.

2. A method of treating wells for removal of paraffin and scale deposits, comprising the steps of:

(*a*) introducing a quantity of acetic anhydride down an annulus in a well bore;

(*b*) substantially simultaneously therewith, introducing a quantity of an aqueous solution of hydrochloric acid down a separate annulus in the well bore, whereby the acetic anhydride and the hydrochloric acid are each separately introduced and conducted downwardly into the well; and

(*c*) causing the hydrochloric acid and acetic anhydride to meet at a predetermined interface in the well, thereby producing a substantial quantity of heat for removing paraffin and scale deposits therefrom.

3. A method of treating wells for removal of paraffin and scale deposits, comprising the steps of:

(*a*) introducing a quantity of an aqueous solution of hydrochloric acid into a well bore and to the area to be treated;

(*b*) thereafter introducing a quantity of acetic anhydride into the well bore; and

(*c*) causing the acetic anhydride to contact the aqueous solution of hydrochloric acid at the area to be treated in the well bore whereby a quantity of heat is produced for removing paraffin and scale deposits therefrom.

4. The method of claim 3, wherein quantities of aqueous solution of hydrochloric acid and quantities of acetic anhydride are alternately introduced into the well at relatively frequent intervals for producing additional heat as desired.

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