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ACIDIZING WELLS

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This invention relates to the art of acidizing wells and more particularly to the use of sulfamic acid for such purposes.

In recent years the treatment of oil and gas wells with acid to open up producing formations has achieved great importance. This work has been done almost exclusively by the use of hydrochloric acid although other acids have been used or proposed. Hydrochloric acid is by no means ideal for this purpose since for one thing it attacks iron and steel very vigorously and therefore can be used successfully only in the presence of an inhibitor or by the use of some other expensive procedure for minimizing corrosion difficulties. Furthermore, hydrochloric acid for many purposes is too rapid in its action and it must be blended with other materials to slow down this action so that it will penetrate deep into the geological formations adjacent the well before becoming spent.

It is an object of my invention to provide an acid or acid mixture which will not corrode iron and steel to the extent that hydrochloric acid and other conventional strong mineral acids do and which will give a more advantageous action on the formations being acidized. Other and more detailed objects, advantages and uses of my invention will become apparent as the description thereof proceeds.

Sulfamic acid (HSO_3NH_2) is a strong inorganic acid which is solid at all ordinary temperatures and which has a fairly high water solubility. Its acid strength on an equi-molal basis is slightly less than that of such mineral acids as hydrochloric, nitric and sulfuric but, on the other hand, it is far stronger than phosphoric acid or such relatively strong organic acids as acetic acid. This acid strength results in its being sufficiently powerful for efficient acidizing but, on the other hand, makes its action slightly slower than that of hydrochloric acid and this is definitely advantageous since it permits the acid to penetrate further back in the formation before it is completely spent by chemical action on the calcium and magnesium carbonates and other constituents of typical limestone producing formations.

A marked advantage of sulfamic acid is that it can be injected into the well with minimum corrosion of the tubing and other iron and steel members with which it necessarily comes in contact. This fact is illustrated by the following experiments:

Steel strips 1" by 6 by $\frac{3}{32}$ inches containing approximately 0.2% carbon were polished with emery cloth and steel wool, weighed and immersed in various acid solutions at 80° F. to determine corrosion. A slow stream of air was bubbled through each solution and after twenty-four hours the strips were removed, cleaned and weighed. The following results were obtained:

	Corrosion in gms./sq. in./day
1N hydrochloric acid	0.460
0.5N hydrochloric acid	0.438
1N sulfamic acid	0.218
0.5N sulfamic acid	0.166

Thus for acids of a given strength on a molal basis, sulfamic acid causes far less corrosion than hydrochloric acid and it is apparent that this striking difference remains even if the acids are compared at strengths for equal hydrogen ion concentration rather than for equi-molal concentrations since 1N sulfamic acid gives far less corrosion than 0.5N hydrochloric acid. While I do not know the reason for this markedly lower rate of corrosion with sulfamic acid, it may be due to the presence of the amine group in the molecule which gives an inhibiting influence or, in other words, it may be a case in which the acid and inhibitor are united in a single molecule. In any event, the rate of corrosion is so much lower than with hydrochloric acid that the use of sulfamic acid without inhibitors becomes practical.

Another advantage of sulfamic acid is that its salts are, practically without exception, highly water soluble and this eliminates much of the difficulty heretofore encountered in the plugging of formations due to the precipitation of insoluble substances.

While sulfamic acid can be used alone very satisfactorily, various addition agents can be added to it for purposes known to the art including further reduction of corrosiveness, inhibition of the precipitation of iron and aluminum hydroxides, control of the rate of acid action and control of the rate of penetration. However, the use of such addition agents is in general much less important with sulfamic acid than with acids such as hydrochloric.

Moreover, while sulfamic acid can be used alone it can also be used together with conventional strong mineral acids such as hydrochloric and nitric, particularly the former, and so used has many of the advantages above described.

If sulfamic acid is used alone the acid strength can suitably be from about 20% to about 40% on

a weight basis while if used with hydrochloric acid or the like, the total acid concentration can be from about 10% to about 40% by weight and any desired portion of this can be sulfamic acid. The total mixed acid can suitably be from about 5% to about 50% sulfamic and from about 95% to about 50% hydrochloric. If the hydrochloric acid predominates, acid strengths in the higher portion of the 10 to 40% range above mentioned are to be avoided.

Amongst the addition agents which can be used in sulfamic acid or in mixed acids containing sulfamic acid are the mono- and di-nitrogen substituted alkyl, aryl, aralkyl and alkaryl derivatives of sulfamic acid itself since these materials in minor amounts are of value in assisting the penetration of the acid through oil films and in the further inhibition of the corrosion of iron and steel parts. Furthermore, it is believed that these materials reduce the tendency of iron and aluminum hydroxides to precipitate.

My invention has been described with reference to the introduction of acids to react on and open up the geological formations at the base of a well. It is, however, likewise applicable to other closely related uses involving the introduction of an acid into a well to react with materials in fluid communication with the well. For instance, my invention can be used in the removal of mud sheaths from producing formations. Thus calcium carbonate can be incorporated in the drilling mud when drilling into a production formation and sulfamic acid or a mixture of sulfamic and hydrochloric acids can later be introduced to generate carbon dioxide within the sheath and cause it to break away. Alternatively such sheaths can be removed by successive treatment with a carbonate solution and a solution containing sulfamic acid.

Also sulfamic acid solutions can be used to remove cement from oil wells by acidization or to make a porous well strainer in the base of the well by dissolving out a soluble material such as lime from a concrete well strainer.

I claim:

1. A method of treating a well comprising introducing a solution comprising sulfamic acid into said well to react with substances in fluid communication with said well.

2. A method of treating an oil well comprising introducing into said well a solution comprising sulfamic acid and an acid selected from the group consisting of hydrochloric and nitric acids to react with substances in fluid communication with said well.

3. A method of acidizing an oil well comprising forcing a solution comprising sulfamic acid into said well and into geological formations adjacent said well to react with and open up said geological formations.

4. A method according to claim 3 in which said solution contains from about 20% to about 40% sulfamic acid.

5. A method according to claim 3 in which said solution contains in addition to sulfamic acid a minor amount of a substance selected from the group consisting of the mono- and di-nitrogen substituted alkyl, aryl, aralkyl and alkaryl derivatives of sulfamic acid.

6. A method of acidizing an oil well comprising forcing a solution comprising sulfamic acid and hydrochloric acid into said well and into geological formations adjacent said well to react with and open up said geological formations.

7. A method according to claim 6 in which the total acid strength is from about 10% to about 40% and in which the sulfamic acid constitutes at least 5% of the total acid.

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DISCLAIMER

2,148,006.—*Maurice H. Arveson*, Flossmoor, Ill. ACIDIZING WELLS. Patent dated February 21, 1939. Disclaimer filed March 4, 1940, by the assignee, *Standard Oil Company*.

Hereby enters this disclaimer to claims 1, 3, and 4 of said Letters Patent.

[*Official Gazette April 2, 1940.*]