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CORROSION INHIBITION

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10 Claims. (Cl. 252—8.55)

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This invention relates to the prevention of corrosion of metals. In one aspect it relates to the prevention of corrosion of metallic well equipment used in the production of hydrocarbon well fluids such as oil wells and gas wells, but more especially gas-condensate wells.

The prevention of corrosion of metals is an extremely serious problem. This problem is particularly serious in connection with the production of oil, gas and hydrocarbon well fluids generally. The problem is especially serious in the production of gas-condensate (so-called distillate) wells wherein the gas is present in the reservoir under extremely high pressures, generally at least 1500 pounds per square inch. The well fluid produced from such gas-condensate wells is very frequently extremely corrosive resulting in serious damage to or destruction of the well tubing and associated metallic equipment employed in producing the well. This equipment is almost invariably composed of ferrous metals, especially steel. Attempts have been made to eliminate the corrosion of such equipment by constructing it from corrosion-resisting alloys but the expense of using such alloys is prohibitive and in many cases it is impossible to find an available alloy which will satisfactorily resist the corrosion. A more satisfactory solution of the problem of corrosion would seem to reside in the use of a corrosion inhibitor. See for example Walker 1,829,705; 1,873,083 and 1,873,084. However thus far no completely satisfactory inhibitor has been found.

The general problem of preventing corrosion in gas-condensate wells and previous proposals for solution of this problem are discussed in detail in my article "Corrosion in High-Pressure Gas-Condensate Wells" which appeared in The Oil and Gas Journal, vol. 45, No. 33, page 81 et seq. (December 21, 1946). Another discussion of the problem is given by T. S. Bacon on pages 5–13 of the Proceedings, 25th Anniversary Convention, of the Natural Gasoline Association of America, Dallas, Texas (April, 1946.) See also Menaul "Causative Agents of Corrosion in Distillate Field," The Oil and Gas Journal, vol. 43, No. 33, pages 80–81 (November 11, 1944).

It has been proposed to use sodium chromate as a corrosion inhibitor in gas-condensate wells. See for example the articles by C. K. Eilerts, applicant and others appearing in the "Oil Weekly," vol. 123, No. 5, pages 17–22 (September 30, 1946) and No. 6, pages 30–34 (October 7, 1947). However sodium chromate has not proven completely satisfactory primarily for the reason that when it is used it tends to form an obstruction in the

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flowstring resulting in plugging of the well which is very serious.

It has been proposed by Menaul et al. to use formaldehyde as an inhibitor of corrosion caused by hydrogen sulfide. See Petroleum Technology, vol. 9, Technical Publication No. 1970 (January, 1946). However this inhibitor is not effective in all types of corrosion but is limited in its application to corrosion caused by hydrogen sulfide. Hydrogen sulfide is seldom an important factor in the corrosion encountered in the production of gas-condensate wells.

The principal object of the present invention is to provide an improved method of inhibiting corrosion of metal. Another object is to provide an improved method of inhibiting corrosion of well tubing and associated metallic equipment during the production of hydrocarbon well fluids. Another object is to provide an improved method of inhibiting corrosion of well tubing and associated metallic equipment used in the production of gas-condensate wells. Another object is to provide a method of inhibiting corrosion as set forth in the foregoing objects wherein no obstruction of the well as a result of precipitation caused by the inhibitor is possible. Another object is to provide an improved method of inhibiting the corrosion of steel by mixtures of water and carbon dioxide under elevated pressure. Numerous other objects will more fully hereinafter appear.

I have discovered that the corrosion of metals by substances normally manifesting a corroding action upon same may be inhibited by an alkyl sulfenamide. My invention involves having present with the metal and the corrosive material an alkyl sulfenamide in an amount sufficient to effectively inhibit corrosion of the metal by the corrosive material. My invention is particularly applicable to the problem of inhibiting corrosion of well tubing and associated metallic equipment used for the production of hydrocarbon well fluids such as gas, oil, and especially gas-condensate or distillate. In applying the invention to production of such hydrocarbon well fluids, the alkyl sulfenamide is introduced in any suitable way into contact with the metallic equipment which is undergoing contact with the normally corrosive well fluid being produced.

In applying my invention to the prevention of corrosion of well tubing and similar well equipment, I usually prefer to introduce the alkyl sulfenamide into the annular space between the well casing and the well tubing, allowing the alkyl sulfenamide to descend in the annulus by the force

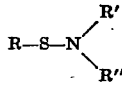
of gravity and at the bottom of the well to be caught by the upflowing fluid and carried thereby upwardly through the tubing string. In this way intimate contact of the inhibitor of my invention with the well tubing over the area where the corrosion generally occurs is effected.

The alkyl sulfenamide may be introduced to the well in any suitable form, either as a solid, as a slurry in a suitable liquid, or as a solution in a suitable solvent. Water-soluble or water-dispersible alkyl sulfenamides are often preferred and are often added as a water solution or colloidal suspension. A solid alkyl sulfenamide which is water-soluble or water-dispersible may be introduced, say in the form of a powder or as a suspension in a non-aqueous solvent. Use of water-soluble or water-dispersible alkyl sulfenamides is preferred because they go into the water phase which is often present in the well and which frequently contains the corrosive material such as carbon dioxide, lower fatty acids, such as acetic, propionic, and the like, and hydrogen sulfide.

If the annular space between the tubing and the casing is packed off, it may be necessary to introduce the alkyl sulfenamide inhibitor of the present invention through an extra string of pipe such as that known as "macaroni tubing." Alternatively it may be desired to introduce lumps or sticks of the inhibitor into the tubing against the flow of the fluid being produced. If desired such lumps or sticks may be surrounded with a suitable soluble substance such as sodium silicate to add strength and delay disintegration and solution of the lumps or sticks until they approach the bottom of the well. Alternatively the powdered or granular inhibitor may be enclosed in a soluble capsule, this capsule being dropped down the tubing string in any suitable manner and the capsule being dissolved by the well fluid as it attains the bottom of the well.

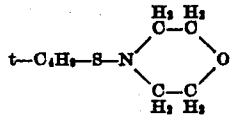
The tertiary alkyl sulfenamides are particularly preferred for use in the present invention. Examples of tertiary alkyl groups which may be attached to the sulfur atom in the sulfenamide are tertiary butyl, tertiary amyl, tertiary hexyl, tertiary octyl, tertiary dodecyl, etc.

The alkyl sulfenamides used in accordance with the present invention have the following general formula:



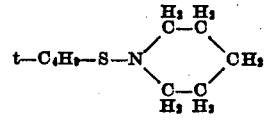
where R is an alkyl group, preferably unsubstituted and preferably a tertiary alkyl group and where R' and R'' are either hydrogen, an alkyl group, an aryl group, an aralkyl group, a cycloalkyl group, etc. R' and R'' may be the same or different. As will hereinafter more fully appear, particularly suitable alkyl sulfenamides are those wherein the R' and the R'' groups form with the nitrogen atom a heterocyclic ring. Examples are the alkyl sulfenamides derived from morpholine, thiomorpholine, piperidine, piperazine, etc.

Any alkyl sulfenamide may be used as the inhibitor in accordance with the present invention. However as indicated above I prefer to use the tertiary alkyl sulfenamides especially tertiary butyl sulfenamides made by reacting a tertiary butyl sulfenyl halide with a secondary heterocyclic amine such as morpholine or piperidine. The sulfenamide prepared from tertiary butyl sulfenyl halide and morpholine has the structural formula



and may be designated N-t-butyl sulfenyl morpholine.

The sulfenamide made from tertiary butyl sulfenamide halide and piperidine has the structural formula



and may be denoted N-t-butyl sulfenyl piperidine.

Other examples of tertiary butyl sulfenamides are those prepared from N-methyl aniline and from phenyl beta-naphthylamine and designated N-phenyl-N-methyl-t-butyl sulfenamide and N-phenyl-N-beta-naphthyl-t-butyl sulfenamide respectively.

Other tertiary alkyl sulfenamides may be those prepared from aliphatic amines such as methyl, ethyl, propyl, butyl and higher mono-amines, dimethyl, diethyl, dipropyl, dibutyl and higher dialkyl amines, methylethylamine, and any other primary or secondary amine including ammonia.

One preferred method of preparing alkyl sulfenamides is set forth in detail in the copending application of C. M. Himel, Serial No. 617,871, filed September 21, 1945, now abandoned, which is hereby incorporated in this specification by reference. This copending application discloses a simple and economical method of preparing the alkyl sulfenamides from cheap and readily available raw materials, namely alkyl mercaptans or disulfides and amines, by reacting the mercaptan or disulfide with a halogen to form a sulfenyl halide, and then reacting the alkyl sulfenyl halide, with an amine to form a corresponding alkyl sulfenamide.

The method of the present invention is particularly applicable to the prevention or inhibition of that type of corrosion which is encountered in the production of gas-condensate or distillate wells which present the most serious corrosion problem because of the high pressure and temperature prevailing which promote corrosion. This type of corrosion is believed to be largely attributable to the presence of lower fatty acids and of carbon dioxide which is extremely corrosive in the presence of an aqueous phase and under the high pressure and temperature encountered.

Actual laboratory corrosion tests made in confirmation of the present invention show that a preferred alkyl sulfenamide namely N-t-butyl sulfenyl morpholine reduced the corrosion rate of mild steel in carbonic acid by 54 per cent. N-t-butyl sulfenyl morpholine is a clear liquid, slightly soluble in water. The tests were made using SAE 1020 steel coupons. One coupon was suspended in distilled water as a comparison standard, and the second coupon was suspended in distilled water containing 400 parts per million of N-t-butyl sulfenyl morpholine (by weight based on the weight of water). The sulfenamide was uniformly dispersed throughout the aqueous phase. Both samples were placed under 55 lbs. per square inch absolute pressure of carbon dioxide for 48 hours. The corrosion rate

of the steel coupon in distilled water saturated with carbon dioxide without the inhibitor was 0.015,4 inches penetration per year, while the corrosion rate of the steel coupon with 400 parts per million of N-t-butyl sulfenyl morpholine was 0.007,1 inches penetration per year, a reduction of 54 per cent in the corrosion rate. The tests were carried out at room temperatures (approximately 75° F.) in containers made of "Lucite" (polymerized methyl methacrylate). At 55 pounds per square inch pressure absolute, the pH of the resulting carbonic acid is 3.4.

The amount of the alkyl sulfenamides employed in practicing the present invention may vary within wide limits and will depend upon the degree of corrosion encountered and degree of inhibition of corrosion desired. In general the extent of reduction of corrosion is proportional to the amount of the inhibitor employed. Those skilled in the art will be able to readily select a suitable amount of the inhibitor.

From the foregoing many advantages of the present invention will be apparent to those skilled in the art. The principal advantage is that it provides an effective method of preventing corrosion by materials which cause corrosion in production of oil, gas, and gas-condensate wells. Another advantage is that the present invention accomplishes prevention of that type of corrosion which takes place in the absence of oxygen such as that encountered in the production of hydrocarbon well fluids particularly of gas-condensate. Another advantage is that the inhibitor of the present invention is readily available from cheap and available raw materials. Another advantage is that the inhibitor of the present invention presents no problem of precipitation or obstruction of the tubing string which has been the most serious objection to the use of sodium chromate. Numerous other advantages will be apparent to those skilled in the art.

I claim:

1. The method of inhibiting the corrosion of steel by mixtures of water and carbon dioxide under elevated pressure which comprises introducing an alkyl sulfenamide to the system and thereby substantially reducing corrosion of said steel.

2. The method of inhibiting the corrosion of steel by mixtures of water and carbon dioxide under elevated pressure which comprises introducing N-tertiary butyl sulfenyl morpholine to the system in amount equal to 400 parts per million of the water present and thereby substantially reducing corrosion of said steel.

3. The method of inhibiting corrosion of ferrous well tubing and associated ferrous metallic equipment by carbon dioxide under elevated pressure in an oil well during the production of hydrocarbon well fluids which comprises introducing an alkyl sulfenamide into contact with said ferrous metallic equipment which is contacted by the well fluid being produced thereby substantially reducing corrosion of said equipment.

4. The method of protecting steel in an oil well from corrosion by mixtures of water and carbon dioxide, under elevated pressures, which comprises introducing an alkyl sulfenamide to the system thereby substantially reducing corrosion of said steel.

5. The method of protecting steel from corrosion by a mixture of water and carbon dioxide in contact therewith under elevated pressure, which comprises incorporating an alkyl sulfenamide with said mixture of water and carbon dioxide, thereby substantially reducing corrosion of said steel.

6. The method of inhibiting corrosion of a ferrous metal caused by a mixture of water and carbon dioxide in contact therewith under pressure, which comprises introducing an alkyl sulfenamide into said water-carbon dioxide mixture, thereby substantially reducing corrosion of said ferrous metals.

7. The method of protecting ferrous metals in an oil well from corrosion by mixtures of water and carbon dioxide, under elevated pressures, which comprises introducing an alkyl sulfenamide to the system thereby substantially reducing corrosion of said ferrous metal.

8. The process of claim 4 wherein said alkyl sulfenamide is N-tertiary-butyl-sulfenyl morpholine.

9. The process of claim 4 wherein said alkyl sulfenamide is N-tertiary-butyl-sulfenyl piperidine.

10. The process of claim 4 wherein said alkyl sulfenamide is N-phenyl-N-methyl-tertiary-butyl sulfenamide.

HENRY A. CARLSON.

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