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CORROSION INHIBITING COMPOSITION

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This invention relates to a method of inhibiting the corrosion of ferrous metals constituting the flow lines of producing oil wells, to a corrosion inhibiting composition suitable for use in the process, and to a method for preparing the corrosion inhibiting composition.

Corrosion of ferrous metal surfaces in contact with the production streams of producing oil wells has long been recognized as a serious operating problem by petroleum producers. A considerable research effort has been directed to this problem, and several methods of reducing corrosion rates and thereby reducing the frequency of replacement of well tubing, sucker rods, etc. have been proposed. In the present state of the art it appears that the attack upon any given corrosion problem must of necessity be in a very considerable degree empirical. To illustrate, corrosion inhibitors which have been found effective in the acid media of pickling baths cannot be expected to exhibit an equivalent inhibiting effect in a different corrosive environment. Many of the inhibitors which are effective in pickling baths are found to accelerate corrosion under the conditions which exist in a producing oil well. Further, a corrosion inhibitor which is effective in a particular well or field is frequently found to be entirely ineffective and even to accelerate corrosion in a different well or field.

Where a particular inhibitor is found effective to prevent corrosion in a particular well, the usual method of applying it is to introduce a solution of the inhibitor into the annulus between the well liner and the tubing. The inhibitor solution is mixed with the production stream at the bottom of the well and flows through the tubing together with the produced oil and water. An appreciable number of wells cannot be treated in this manner since a section of the annulus between the liner and tubing has been packed or cemented to control gas pressure. Attempts to treat these wells with an inhibiting solution are usually unsuccessful since the production must be stopped in order to introduce the solution into the tubing and permit it to gravitate to the well bottom, and then upon resumption of production the solution is very rapidly carried from the well together with the production stream.

It is an object of the present invention to provide a corrosion inhibitor which is well adapted for use in oil wells having a packed annulus.

It is a further object of this invention to provide a corrosion inhibiting composition which is highly effective in reducing corrosion rates in producing oil wells, especially in oil wells in which the production stream comprises crude oil, brine, and carbon dioxide gas.

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It has now been found that corrosion of tubing, sucker rods, etc. in producing oil wells discharging a production stream comprising crude oil and brine (predominantly aqueous sodium chloride), especially brine containing dissolved or dispersed gaseous carbon dioxide, can be effectively controlled by introducing coherent solid pellets consisting predominantly of sodium arsenite into contact with the production stream in the lower portion of the well and that a pelleted corrosion inhibitor consisting entirely, except for small amounts of a binder and a lubricant, of sodium arsenite and a weighting agent is excellently adapted for use in this method of corrosion control. The advantages of this pelleted composition and the method of preparing it are described in detail hereinafter.

The following Example 1 illustrates the manner in which the corrosion inhibiting compositions of this invention may be prepared.

EXAMPLE 1

80 parts by weight of technical grade sodium meta-arsenite were slurried with 15 parts by weight of water to produce a paste. The paste was spread in a layer ¼'' to ½'' thick in a pan coated with petrolatum. The pan was placed in an oven and dried at a maximum temperature of about 300° F. The dry paste had the appearance of a glassy cake and was quite hard. The cake was ground to form coarse particles, all of which passed through a 12 mesh screen, 40 to 50% of which passed through a 30 mesh and about 10% of which passed through a 60 mesh screen. This granular product was then intimately mixed with 20 parts by weight of finely divided dried alumina gel, 15 parts by weight of powdered metallic zinc and 5 parts by weight of graphite and pelleted in a steel die and plunger mold, ½'' in diameter, by exerting a force of 5 tons on the plunger. The resulting pellets were in the form of a cylinder capped at each end by a spherical segment. Both the diameter of the cylinder and the height of the cylindrical pellet were approximately ½''. The pellets had a crushing strength averaging about 15 lbs. and a density averaging about 2.6 grams per cubic centimeter. The pellets disintegrated and dissolved in water at 150° F. in less than 1 hour.

Both the procedure followed in the above ex-

ample and the composition of the pelleted corrosion inhibitor contribute to the production of a product having physical and chemical properties, making it highly suitable for its intended use.

The pelleted corrosion inhibitor of this invention should be a solid mass which disintegrates and dissolves in aqueous media at temperatures in the range 150° to 200° F. which may prevail at the bottom of a well in a short time, desirably substantially less than 1 hour. The pellet, however, should have a reasonably high crushing strength in order that it may be able to withstand the mechanical forces and impacts to which it is subjected in packaging and handling so that it may arrive at the wellhead substantially intact, the pellets being sufficiently large to settle rapidly through a standing production stream in the well tube when this method of introducing the pellets into the well is necessary. The pelleted corrosion inhibitor should have a density above about 2.5 grams per cubic centimeter and, generally, a density sufficiently high that it will sink rapidly to the bottom of the well. The corrosion inhibitor of this invention should have a relatively high rate of solution so that an effective inhibiting concentration of arsenic can rapidly be built up in the produced water. The property of dissolving rapidly is especially important in wells having a high daily production of water.

The active corrosion inhibiting component of the compositions of this invention is sodium arsenite. Sodium arsenite dissolves rapidly in warm water and has a density slightly less than 2 grams per cubic centimeter. Sodium arsenite alone cannot easily be molded to form a pellet having an appreciable mechanical strength, and even if such a pellet had a sufficient mechanical strength, its density would be too low to permit advantageous use for its intended purpose, particularly in wells having packed off annuli where the pellets must be introduced through the tubing more or less filled with the liquid effluent of the well.

In order to increase the resistance of the pellets to mechanical fracture, in other words, to increase the crushing strength of the pellets, a binder is desirably employed. The binder in the above example is alumina gel. Other materials, for example sodium silicate, cane sugar, starch, gelatin, and the like, may be mixed with sodium arsenite in the manner described in Example 1 to function as a binder which increases the mechanical strength of the pellet. The alumina employed in the above example is unique in its binding action in that it permits the production of a pellet having a high crushing strength, but one which disintegrates rapidly in warm water to permit the sodium arsenite to go into solution. In the above example, powdered metallic zinc was employed as a weighting agent. Other metals having a density above 6 and readily soluble in mildly acid waters, for example, iron, may be employed as the weighting agent. Zinc, however, is preferred since it has an additional advantage over other weighting agents. It is more electropositive (higher in electromotive series) than iron and therefore will corrode sacrificially to iron when two are in contact and iron is protected. Similarly, inert solids having fairly high densities, for example, barium sulfate, may be employed as the weighting agent.

The graphite in the above example functioned as a lubricant to prolong the life of the dies used

in pelleting the dried granules and to facilitate the pressing operation. Other lubricants, for example, calcium stearate or rosin, may be employed.

The procedure followed in the above example in preparing the pellets, i. e., slurrying the active solid component with a small amount of water, drying, grinding to produce a coarse granular solid, and pelleting the coarse granules mixed with the binder, weighting agent and lubricant is followed in order to impart a sufficient degree of mechanical strength to the pellets. Attempts to pellet mixtures of sodium arsenite, powdered zinc, finely divided alumina, and graphite, after simply mixing the dry materials in the form in which they are commercially available, produced pellets of low mechanical strength insufficient to resist the forces to which they were subjected during handling and packaging.

The procedure followed in the above example may be varied, if desired, by using arsenous oxide and concentrated aqueous sodium hydroxide instead of sodium arsenite and water, the sodium hydroxide and arsenous oxide reacting to produce the sodium arsenite.

The pellets are desirably of some substantially regular geometric shape which is characterized by a ratio of area to volume which is low, preferably below about 5. Spherical or spheroidal pellets are suitable and the cylindrical pellets described in the example are desirable.

The pelleted inhibitor of this invention has a very considerable practical advantage over aqueous solutions of arsenous compounds in practical field use. Water-soluble arsenic compounds are highly toxic and can cause severe skin irritation. Under field conditions the likelihood of accidental ingestion of arsenic, should working precautions be relaxed, constitutes a serious hazard as to aqueous arsenical solutions. The pelleted inhibitor may be handled with a little risk and may be readily and safely stored at the wellhead. The pellets may be made practically foolproof by coating them with a protective film of an inert water-soluble coating. Gelatin and water-soluble gums are well adapted for use as the coating material.

The effectiveness of the method and composition of the invention in the inhibiting corrosion of ferrous metal tubing in a producing well is illustrated in the following Example 2.

EXAMPLE 2

The well selected for test had consistently exhibited a moderate corrosion rate as indicated by iron counts, that is, by the content of ferric oxide in parts per million contained in the produced water in the range 14 to 48 during a three-week observation period. The average daily production of the well was 3 barrels of oil, 80 barrels of water, and 600 cubic feet of gas containing about 3% carbon dioxide. This production was delivered through a 2½" steel pipe. The essential features of the corrosive environment of this well included a ferrous metal in contact with oil, brine, and gas containing carbon dioxide, gas liquid interfaces in contact with the metal, and areas of turbulent liquid flow in contact with the metal surfaces. The metal in this environment is corroded away by direct attack of carbonic acid which is markedly accelerated by electrochemical phenomena arising out of the contact of phase interfaces with the metal and out of the contact of turbulent flowing liquid with the metal surface. The iron count of the well was observed over a period of three weeks.

On the twenty-third day, at noon, 1 pound of pelleted corrosion inhibitor having the composition of that prepared in Example 1, above, was introduced into the well. Iron counts, indicating the corrosion rate, observed during the observation and test period are tabulated in the following table:

Iron count [1]

First day	34
Second day	20
Third day	20
Fourth day	18
Seventh day	48
Eighth day	27
Eleventh day	20
Twelfth day	14
Thirteenth day	20
Fourteenth day	20
Fifteenth day	43
Nineteenth day	34
Twenty-third day:	
Noon	22
4 p. m.	[2] 0
8 p. m.	4
Midnight	20
Twenty-fourth day:	
4 a. m.	20
8 a. m.	14
12 noon	10
4 p. m.	10
8 p. m.	16
Midnight	20
Twenty-fifth day	27

[1] P. P. M. of Fe_2O_3 determined by the Thiocyanate Colorometric Method, Scott's Standard Methods of Chemical Analysis, 5th ed., Van Nostrand, 1939, page 486.
[2] Below 0.5 P. P. M.

From the above table it will be noted that the iron count dropped very rapidly after the introduction of the pelleted inhibitor, from a value of 22 observed at noon on the twelfth day to zero at 4 p. m. of the same day. The rapid reduction of the iron count results from the effects of the quick dissolving pelleted inhibitor of this invention.

The equipment required to introduce the corrosion inhibitor of this invention into the well is of the simplest. A lubricator having a valve at either end is connected to the well tubing. The valve adjacent to the tubing is closed, the pellets are introduced into the lubricator, the upper valve is then closed, and the valve adjacent to the tubing is opened permitting the pellets to drop into the tubing through the standing oil to the base of the well. In treating a well having an open annulus, the lubricator is attached to communicate with the annulus and the pellets are dropped through the annulus to the base of the tubing.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A pelleted corrosion inhibiting composition having a density of at least 2.5 grams per cubic centimeter consisting predominantly of a uniform coherent mixture of a major proportion of sodium arsenite and a minor proportion of metallic zinc.

2. A pelleted corrosion inhibiting composition having a density of at least 2.5 grams per cubic centimeter consisting essentially of a major proportion of sodium arsenite as the active inhibiting component, and minor proportions of metallic zinc, alumina, and a lubricant.

3. The method of producing a pelleted corrosion inhibiting composition, which comprises slurrying sodium arsenite with sufficient water to form a thick paste, drying the paste, grinding the dry paste to coarse particles, mixing the particles with small amounts of metallic zinc, a binder and a lubricant, and compressing the mixture under a high pressure to form pellets, the amount of metallic zinc being sufficient to give the pellet a density of at least 2.5 grams per cubic centimeter.

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