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CORROSION INHIBITOR

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This invention relates to a method for 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 this invention to provide a method for preventing corrosion of ferrous metal surfaces in contact with the production stream of producing oil wells.

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

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

It has now been found that corrosion of ferrous metal 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 a solid, water-soluble, inorganic, arsenous compound into contact with the production stream in the lower portion of the well, and that a pelleted anti-corrosion composition consisting predominantly of a uniform, coherent mixture of sodium arsenite and arsenous oxide and containing sodium arsenite and arsenous oxide in amounts such that the sodium arsenite-arsenic oxide ratio is in the range 10:1 to 1:10 is well adapted for use in the practice of this method. The peculiar advantages and the method of preparing these anti-corrosion pellets 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

15 parts by weight of technical grade arsenous oxide and 50 parts by weight of technical grade sodium meta-arsenite were slurried with 15 parts by weight of water. The resulting slurry was spread in a layer $\frac{1}{4}$ " to $\frac{1}{2}$ " thick in a pan coated with a thin film of petrolatum. The pan was placed in an oven and the paste was dried at 250° F. to 300° F. for a period of 6 hours. The paste dried without shrinkage to form a hard, glassy cake. The cake was ground to form coarse particles, all of which passed through a 12 mesh screen, 50% of which passed through a 30 screen and about 10% of which passed through a 60 mesh screen. This granular product was then mixed with 5 parts of weight of graphite and pelleted in a steel die and plunger mold, $\frac{1}{2}$ " 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 $\frac{1}{2}$ ". The pellets had a crushing strength averaging about 20 pounds and the density averaging about 3 grams per cubic centimeter.

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The pellets do not disintegrate in water at 150° F., but slowly dissolve in it.

Both the procedure followed in the above example and the composition of the pelleted corrosion inhibitor contribute to the production of a solid inhibitor having physical as well as chemical properties making it highly suitable for its intended use.

The pelleted corrosion inhibitor should be a coherent mass which does not readily disintegrate in aqueous media at temperatures in the range 150 to 200° F. which may prevail at the bottom of a well. To this end the pellet should have a reasonably high crushing strength in order that it will not be broken up by the moderately gentle mechanical impact against the well tubing caused by the passage of the production stream through a mass of pellets. The pelleted corrosion inhibitor should have a density above about 2 grams per cubic centimeter, preferably above 2.5, and generally sufficiently large that it will maintain a position close to the bottom of the well and not be carried upward in the tubing by the flow of the production stream. The pelleted corrosion inhibitor should have a relatively slow rate of solution so that a single charge of the inhibitor will remain in the well bottom for an appreciable period of time, for example, for a period of 24 hours. This is especially important where the well requiring treatment is one having a packed off annulus so that the production must be interrupted in order to introduce the charge of corrosion inhibitor.

The active corrosion inhibiting components of the composition of this invention are sodium arsenite and arsenous oxide. Sodium arsenite dissolves rapidly in warm water and has a density below 2 grams per cubic centimeter. Arsenous oxide dissolves slowly in water and has a density of about 4 grams per cubic centimeter. Arsenous oxide, however, cannot be molded by itself to form a pellet having an appreciable mechanical or crushing strength. Pellets produced by subjecting commercial arsenous oxide to pressures of about 40,000 pounds per square inch crumbled readily, breaking down to small particles of sizes such that they could readily be carried upward by the production stream of a producing well. Pellets prepared by slurring arsenous oxide with water, drying in the manner described in the above example, grinding, adding graphite and then compressing, appeared to be little better. It was found that mixtures of sodium arsenite and arsenous oxide could be compressed to form pellets having appreciably higher crushing strength, but even here pellets produced by compressing the dry chemicals in the form in which they are commercially available had little resistance to mechanical fracture. It was found, however, that if mixtures of sodium arsenite and arsenous oxide were slurried with water to produce a fairly thick paste which was then dried and ground pursuant to the above example, the granular product of the grinding could then be compressed to form pellets having a high crushing strength and a very considerable resistance to mechanical fracture. The grinding should be conducted to produce relatively coarse particles generally ranging from about 6 to 60 mesh and preferably about 12 to 60 mesh in size. Mixtures of sodium arsenite and arsenous oxide containing these two components at weight ratios of sodium arsenite to arsenous oxide in the range about 10:1 to 1:10 have crushing strengths such that the pellets are sufficiently resistant to mechanical

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fracture to be used in a producing well without appreciable fragmentation. More desirably, the ratio of sodium arsenite to arsenous oxide is in the range 1:3 to 3:1, while a weight ratio range from 4:6 to 6:4 is especially preferred.

The sodium arsenite and arsenous oxide of the pellets is in the form of a uniform coherent mixture so that the lower solubility of the arsenous oxide controls the rate at which the pellet goes into solution. The exposed sodium arsenite dissolves rapidly, leaving an arsenous oxide surface which dissolves more slowly, exposing more sodium arsenite, and so on, until the pellet has entirely disappeared into solution. This is a very desirable characteristic and variation of the arsenite-arsenous oxide ratio makes it possible to adapt the pellet for use in a particular well. For example, wells having a high daily production of water require treatment with a more rapidly dissolving pellet in order that an inhibiting concentration of arsenic be maintained in the production stream, while wells having a low daily production of water are more economically treated with pellets having a higher content of arsenous oxide and a correspondingly slower rate of solution so that excessive concentrations of arsenic will not be built up in the relatively small volume of produced water. By adding pellets of different solubilities the period between successive treatments can be extended.

As indicated above, the active corrosion inhibiting components of the composition of this invention are sodium arsenite and arsenous oxide; the graphite employed in the above example functions as a lubricant to prolong the life of the dies employed in the pelleting operation and makes the process of pressing easier. While pellets consisting essentially of sodium arsenite and arsenous oxide, and desirably containing a small amount of a lubricant, are excellently suited for the intended use in all respects, it should be noted that small amounts of other materials may be incorporated into the composition if desired. For example, a small amount of a binder may be incorporated into the pellet to increase its coherence and mechanical strength, for example, materials such as sodium silicate, alumina, cane sugar, starch, gelatin, and the like, may be employed for this purpose.

Lubricants other than graphite may be employed; for example, calcium stearate or rosin, may be used.

In some instances it may be desired to increase the average density of the pellets by incorporating an inert weighting agent in the composition. A material such as barium sulfate may be employed for this purpose, or, more desirably, powdered metals such as iron and zinc which have a high density and which are readily dissolved in mildly acid waters may be employed.

It should be noted that the procedure in the illustrative example above may be varied by slurring arsenous oxide and aqueous sodium hydroxide. If this procedure is followed, the sodium hydroxide reacts with a portion of the arsenous oxide to form the arsenite and no sodium arsenite need be employed as such.

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 advantage over aqueous solu-

tions 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 little risk and may be readily and safely stored at the well-head. 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 contents of ferric oxide in parts per million contained in the produced water in the range 9 to 36 during a 12-day observation period. The average daily production of the well was 70 barrels of oil, 349 barrels of water, and 12,000 cu. feet of gas containing about 4% 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 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 for a period of 12 days. On the twelfth day, at noon, pellets were introduced into the annulus, dropped to bottom and mixed with production. 3 pounds of pelleted corrosion inhibitor were introduced. 1½ pounds of the inhibitor introduced had the composition of that prepared in Example 1, above, and the remaining 1½ pounds consisted of pellets containing sodium arsenite, about 5% of graphite as a lubricant, and 15% by weight of metallic zinc based on the weight of sodium arsenite as a weighting agent. Iron counts observed during the observation and test period are tabulated in the following table.

Iron count ¹

First day	16
Second day	10
Third day	9
Fourth day	24
Fifth day	36
Sixth day	14
Seventh day	27
Eighth day	17
Ninth day	14
Tenth day	12
Eleventh day	17
Twelfth day:	
Noon	16
4 p. m.	20
8 p. m.	0
Midnight	0

Thirteenth day:

4 a. m.	0
8 a. m.	0
12 Noon	4
4 p. m.	0
8 p. m.	0
Midnight	0
Fourteenth day	0
Fifteenth day	0
Sixteenth day	11
Seventeenth day	11

¹P. p. m. of Fe₂O₃ determined by the Thiocyanate Colorimetric Method, Scott's Standard Methods of Chemical Analysis, 5th ed., Van Nostrand, 1939, page 486.

²Where the iron count is below 0.5 p. p. m. the value zero is recorded.

From the above table it will be noted that the iron count dropped from 16, the value observed at noon on the twelfth day, to zero at 4 p. m. of the same day following the introduction of the pelleted inhibitor. During a period of four days, following the introduction of 3 pounds of this inhibitor, the iron count remained at zero. During this four-day period the well produced about 1400 barrels or more than 450,000 pounds of brine, nearly 50,000 cubic feet of gas, and 280 barrels of oil. The introduction of the single small charge of the pelleted inhibitor protected the well fully against corrosion for a four-day period. It is evident that the inhibitor is highly effective in small amounts, that production need be interrupted only at infrequent intervals to introduce the charge of corrosion inhibitor and that the time required to implement an anti-corrosion program employing the inhibitor of this invention is obviously very small.

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.

In some wells where an open bottom communicates with the tubing, the pellets are lowered into the well in a mesh basket to prevent pellets from falling into the open bottom zone of little production.

Having described our invention, we claim:

1. A pelleted corrosion inhibiting composition characterized by a high crushing strength consisting essentially of a uniform coherent mixture of sodium arsenite and arsenous oxide, the weight ratio of sodium arsenite to arsenous oxide being in the range 1:10 to 10:1.

2. The composition as defined in claim 1, further characterized by a relatively high rate of solution in brine and by a weight ratio of sodium arsenite to arsenous oxide in the range about 1:1 to 10:1.

3. The composition as defined in claim 1, further characterized by a relatively low rate of solution in brine and by a weight ratio of arsenous oxide to sodium arsenite in excess of 1:1.

4. The method of producing a pelleted corrosion inhibiting composition which comprises mixing one part of sodium arsenite, one-tenth to ten parts of arsenous oxide and sufficient water

to form a thick paste, drying the paste, grinding the dry paste to form coarse particles, and mechanically compressing the coarse particles under a high pressure to form pellets.

5. A pelleted solid corrosion inhibitor characterized by high crushing strength consisting essentially of a uniform coherent mixture of sodium arsenite and arsenous oxide formed by mixing one part of sodium arsenite and one-tenth to ten parts of arsenous oxide with sufficient water to form a thick paste, drying the paste, grinding the dried paste to form coarse

particles, and mechanically compressing the coarse particles under a high pressure to form pellets.

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