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INTERNAL CORROSION PREVENTION IN FERROUS METAL CONTAINERS FOR LIGHT LIQUID PETROLEUM DISTILLATES

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7 Claims. (Cl. 44—72)

This invention relates to a means for preventing internal corrosion and scale formation in pipe lines and the like, particularly those which are used for transporting hydrocarbons, as for example gasoline, and has also been found useful for removing rust, scale, or other corrosion product deposits when such exist as a precondition in pipe lines. The invention provides a practical and economical process for preventing the formation of rust internally in vessels which are constructed of steel or iron-containing alloys and which are used in the transportation or storage of fluids which are substantially immiscible with water.

Conditions in pipes used in the transportation of gasoline in particular are usually highly favorable to corrosion, which results in the formation of rust on the inner pipe wall. The two important factors which give rise to this corrosion are water and free oxygen. Water is carried into the pipe as entrained droplets and as dissolved water in the gasoline which enters the pipe from sweetening treaters, washers, or the like. This water maintains the inner pipe wall in a substantially wet or moistened condition. Since the gasoline may contain as much as 0.006 wt. per cent or more of free oxygen which was dissolved in it during treating operations or in storage before the gasoline entered the pipe, the basic conditions for the formation of scale and rust on steel pipe will be present. The extent or rate of corrosion is aggravated by the usually rapid flow of the gasoline over the metal surface and by the presence of corrosive constituents in the gasoline or water associated with the gasoline.

It is an object of this invention to provide means whereby such scale and rust formation will be presented, and in the case where such conditions already exist, to expedite the removal of such deleterious material and prevent further formation thereof. A further object of the present invention is to produce a hydrocarbon oil composition, through addition of a relatively small proportion of an aqueous solution of certain inhibitors to that oil, which imparts corrosion resistance to steel or other iron-containing alloys with which it is in contact. Further, it is an object of the present invention to attain these ends by chemical treatment in such a manner that no unfavorable effects upon the non-corroded portions of the pipe line or upon the hydrocarbon oil will be had.

Internal rusting and corrosion in pipe lines used in transportation of hydrocarbon oils, a field wherein economy is a vitally necessary consideration, is a problem of prime importance even when occurring only to a minor degree, since it seriously decreases the volume of liquid which will flow under constant pressure. This decrease in throughout capacity of pipe is brought about by internal rusting, since one volume of iron will increase approximately thirty times in forming rust, with resulting restriction of internal pipe diameter, and further, since the rust scale is rough and irregular and usually grows in the form of blisters or tubercles, with resulting increase of skin friction. Eliminating this internal corrosion results in increased satisfactory operation and life of hydrocarbon oil containers.

According to the present invention, solutions, preferably aqueous, of alkali metal nitrites, particularly sodium nitrite, are introduced into the vessel or conduit together with with hydrocarbon oil in controlled amounts and under controlled conditions in order to inhibit corrosion and formation of rust.

It has been found that water-soluble inhibitors other than the alkali metal nitrites which are known to be suitable for inhibition of corrosion in systems with substantially aqueous phase fluids are inapplicable, inefficient, or impracticable for use in systems with substantially hydrocarbon oils.

In order to determine the practicable limits for use in pipe line practice, numerous experiments were made with representative samples of the commercial finished gasoline and entrained water associated with it which were found to be corroding a pipe line through which the gasoline was passing. Mixtures of the gasoline and of the pipe line water, to which sodium nitrite and sodium hydroxide were added to give aqueous solutions of various concentrations and hydrogen ion concentration (pH), were shaken in contact with weighed pieces of polished steel for a period usually of two weeks. The pH of the water was adjusted at the start of the experiments because it was found to be a critical factor. At the end of the test period, the steel pieces were removed from the test mixture, examined to determine the extent and severity of corrosion then they were cleaned to remove rust and/or corrosion scale only, and weighed to determine the total weight loss. From the weight difference thus obtained, the corrosion rate in terms of inches penetration per year is calculated.

The following examples, which are taken from experiments made in the manner outlined above, illustrate the permissible lower limit of sodium nitrite concentration that will satisfactorily pre-

vent corrosion and rust scale formation. The results are summarized in the following table:

$NaNO_2$ concentration as wt. percent of H_2O present	Corrosion rate
Percent	*Inches/year*
0.08	0.0000
0.06	0.0000
0.04	0.0006
0.02	0.0030

From the above results, it will be seen that between 0.04% and 0.06% sodium nitrite concentration, a sudden change in the degree of protection afforded occurs. It has also been found that for sodium nitrite at 0.06% concentration, which appears to be the lowest concentration that it is desirable to use, best results are obtained when the pH of the water is held to a minimum value of at least 8, no additional advantage being gained above a pH of 12. A pH of 6 or lower appears to negative the inhibiting action of the sodium nitrite entirely. In practice, the desired pH is maintained when necessary by injecting a water-soluble alkaline compound, as for example sodium hydroxide, into the pipe line along the sodium nitrite.

In addition to inhibiting the rate of attack on uncorroded surfaces, experiments have revealed the fact that the sodium nitrite possesses the further advantage of effectively stopping corrosion after the metal surface is already rusted. An additional valuable advantage is derived then from the practice of the present invention, since the cessation of further rusting in a pipe when rust exists as a precondition permits the normal turbulent flow of liquid and the occasional use of mechanical cleaning operations gradually to loosen, remove, and carry off the rust scale from the pipe wall, so that a smooth and unrestricted conduit is attained in a relatively short time. I believe that the usefulness of the present invention in removing corrosion products results in part from the prevention of additional formation of rust which would tend to cement rust projections or loosened corrosion product particles to the pipe wall, and in part from interaction of the already formed rust with the sodium nitrite.

The quantity of inhibitor used is dependent upon the extent to which it is desired corrosion be decreased, the severity of corrosion encountered, the amounts and kinds of materials present in the hydrocarbon fluid, on the amount of corrosion which has already occurred, and on the rate at which it is desired to remove corrosion product previously formed on the metal walls. Although a concentration of 0.04% by weight sodium nitrite in solution in the aqueous phase has been found to be sufficient for substantially complete inhibition of corrosion under optimum conditions, the preferable concentration for application in actual practice also being dependent upon the factors named above, it may be desirable to employ a higher concentration which can be determined experimentally in each case. The quantity of inhibitor present must be sufficient to maintain the concentration of inhibitor at not less than 0.04% by weight in every portion of the aqueous phase which may come into contact with a corrodible metal surface. Preferably a quantity of sodium nitrite amounting to not more than 0.01% weight of the hydrocarbon oils is used in achieving the desired beneficial effects.

The present invention may be executed in an intermittent or continuous manner, the corrosion inhibitor being introduced into the substantially water-immiscible fluid in the form of an aqueous solution, or as a slurry or paste made by mixing the powdered inhibitor with oil, or as a substantially dry salt bed or cartridge through or over which the whole or a part of the fluid is passed, or in the form of a powder added directly to the gasoline. Further, if desired, the inhibitor may be added in other than aqueous solution, as for example in an alcohol, particularly methyl, or ether solution or in ammonia or in any other liquid in which the particular alkali metal nitrite to be used is soluble.

The following detailed example is for the purpose of illustrating a mode of executing my invention and the beneficial effects which result from its use. It is to be understood that the invention is not to be considered as limited to the specific modes or conditions of operation disclosed. By a suitable modification of conditions and materials, the inhibition of corrosion also may be achieved. Following is a description of an application of my invention to 115 miles of 8-inch gasoline pipe line.

The new pipe, it was determined, had a "C" factor of 144. At present, pipe line flow efficiency is usually considered in terms of a coefficient "C" as calculated from the Massachusetts Institute of Technology modification of the Williams and Hazen equation, which is as follows:

$$q = \frac{Cd^{2.63}P^{0.54}}{66g^{0.54}}$$

wherein

q=flow rate in barrels per hour
C=coefficient
d=internal diameter of the pipe line in inches
P=friction loss in pounds per square inch per 1000 feet of pipe
g=specific gravity of material being transported

Gasoline was pumped through this line for a period of seventeen months, at which time the "C" factor was again determined and found to be 128, indicating a decrease in efficiency of 11.1% even though mechanical methods of cleaning the pipe had been used regularly over this period.

Aqueous sodium nitrite solution was then injected into the gasoline stream entering the pipe line in quantities sufficient to bring the concentration of inhibitor to at least 2.0% weight in the total aqueous phase entering the line, and sufficient to amount to 0.000016% (0.16 part per million) by weight of the gasoline entering the pipe line. Sodium hydroxide was also added in sufficient quantities to maintain a pH of 8 to 10 in the aqueous phase. This application of my invention actually amounted to injecting in a continuous manner 5 gallons of 2.5% by weight sodium nitrite solution per 24 hours.

The above treatment was continued for four months, at the end of which period the "C" factor was again determined and found to be 144; in other words, all of the rust scale had been removed within this period and the pipe line brought back to its original efficiency. The cost of such treatment at the present price of sodium nitrite (approximately 240 pounds at $0.08 per pound) is negligible, whereas the loss resulting from an 11% decrease in pipe line efficiency is a

matter of thousands of dollars for a similar period.

When applying the present method to pipe lines already in a corroded condition, full benefits along the entire length of pipe line cannot be expected immediately following the inception of minimum quantity inhibitor treatment suitable for uncorroded pipe, owing to absorption or reaction of the alkali metal nitrites with constituents of the corrosion product. If it is desirable to obtain complete cessation of corrosion immediately, it has been found necessary to add further sodium nitrite in quantities sufficient to react stoichiometrically with said corrosion products, in addition to amounts sufficient to inhibit further corrosion. The amounts of inhibitor necessary must be experimentally determined in each case. Often, however, it is preferable to avoid full immediate attainment of the corrosion inhibitor benefits in a corroded pipe line of long standing, since too rapid release of the large accumulations of corrosion products from the pipe wall may interfere seriously with normal operation of the pipe line.

Although the above description of the invention has particular reference to the application of sodium nitrite to pipe lines used for the transportation of gasoline, other alkali metal nitrites may be as well applied to inhibition of internal corrosion in other hydrocarbon or similar substantially water-immiscible fluid-carrying lines.

The use of sodium nitrite according to the present invention does not appear to have any deleterious effect upon gasoline, tests having shown that no change in appearance, octane number, gun content, or other commercially important properties occurs after contact with the inhibitor.

The present process embodies numerous advantages over existing systems for similar use, as for example the costs of sodium nitrite is negligible considering the small quantities necessary for complete corrosion protection, no special or complicated systems for controlling conditions during injection are required, and no after-treatment of the material in contact with the inhibitor is necessary. Further, contaminants often contained in the hydrocarbon phase, such as complex organic compounds of oxygen, nitrogen, and sulfur, and contaminants contained in the aqueous phase, such as metal salts or compounds entrained from sweetening treaters, have little or no effect upon the life or efficacy of the inhibitor.

This application is a division of U. S. Patent No. 2,297,666, issued September 29, 1942.

I claim as my invention:

1. The process of inhibiting internal corrosion in a ferrous metal container in contact with light liquid petroleum distillates comprising subjecting the interior of the container to the inhibiting action of a solution of an alkali metal nitrite, the concentration of said alkali metal nitrite solution being less than approximately 0.01% by weight of the light liquid petroleum distillates in said container and the pH of said alkali metal nitrite solution being in excess of 6 and not exceeding approximately 12.

2. The process of inhibiting internal corrosion in a ferrous metal container in contact with light liquid petroleum distillates comprising subjecting the interior of the container to the action of a solution of an alkali metal nitrite, the concentration of said alkali metal nitrite solution being less than approximately 0.01% by weight of the light liquid petroleum distillates in said container and the pH of said alkali metal nitrite solution being in excess of approximately 8 and not exceeding approximately 12.

3. The process according to claim 2 wherein the alkali metal nitrite is in aqueous solution.

4. The process according to claim 2 wherein the alkali metal nitrite is sodium nitrite.

5. The process of inhibiting internal corrosion in a ferrous metal container in contact with light liquid petroleum distillates comprising subjecting the interior of the container to the inhibiting action of an aqueous solution of an alkali metal nitrite, the concentration of alkali metal nitrite in said inhibiting solution being at least 0.04% by weight of the total available water in said container and the pH of said inhibiting solution being in excess of 6 and not exceeding approximately 12.

6. The process according to claim 5 wherein the alkali metal nitrite is sodium nitrite.

7. The process of inhibiting internal corrosion in a ferrous metal container in contact with light liquid petroleum distillates comprising subjecting the interior of the container to the inhibiting action of an aqueous solution of sodium nitrite, the concentration of sodium nitrite in said inhibiting solution being at least 0.04% by weight of the total available water in said container and the pH of said sodium nitrite solution being at least approximately 8 and not exceeding approximately 12.

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