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PROCESS FOR PREVENTING CORROSION
AND CORROSION INHIBITOR

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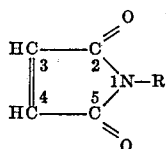
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This invention relates to the inhibition of corrosion of metals and particularly to a composition for use in preventing corrosion of iron, steel and ferrous alloys. The corrosion inhibitors contemplated herein are characterized by their solubility in aromatic or aliphatic hydrocarbon solvents and their very slight solubility in water or brines. They find special utility in the prevention of corrosion of ferrous pipe or equipment which is in contact with a corrosive, oil-containing medium, as, for example, in oil wells producing corrosive oil or oil-brine mixtures, in refineries, and the like. Our inhibitors may, however, be used in other systems or applications. They appear to possess properties which impart to iron or steel resistance to attack by a variety of corrosive agents, such as brines, weak inorganic acids, organic acids, CO₂, H₂S, etc.

The compounds which we have found to be effective for the purpose described belong to the general class of N-aliphatic-2,5-pyrrolinediones.

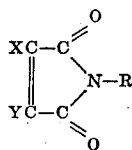
Various simple derivatives obtained by substituting halogen or aliphatic radicals for hydrogen attached to the carbon atoms in the 3, and 4 position for the pyrrolinedione ring are equally effective.

The N-aliphatic pyrrolinedione compounds may be represented by the structural formula below in which the conventional ring numbering system is shown:



where R represents an aliphatic radical as described below.

Where the pyrrolinedione is substituted on the carbon atoms in the 3 and/or 4 position, such compounds may be represented by the following formula:



where X and Y are members selected from the class consisting of hydrogen, halogen and simple hydrocarbon groups; and R has its previous significance.

In the prevention of corrosion of iron and other ferrous metals, these products may be applied

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to the metal surface in the molten state or as solutions in suitable solvents. When they are employed in the prevention of corrosion of tubing or casing in oil or gas wells, a number of methods of application may be used. When the oil or gas well is equipped with tubing surrounded by casing the corrosion preventing compound in liquid form or dissolved in a suitable solvent may be dumped down the casing where it becomes intermingled with the oil or gas being produced and is subsequently carried up the flow tube with the fluid and thus contacts all of the pipe which is to be protected. In other cases the liquid composition may be pumped continuously into the annular space between tubing and casing after it falls to the bottom of the well and is intermingled with the oil or gas as previously described. In some wells the tubing is packed off against the casing near the bottom of the tubing string, thus preventing the addition of the corrosion preventing compound down the annular space. Where this is done, particularly in gas wells or so-called gas condensate wells, it is desirable to perforate the tubing string at a point just above the packer to permit the added corrosion preventive to enter the gas stream opposite the perforations. Where it is impractical to perforate the tubing or for other reasons this is undesirable, the corrosion preventing compound may be dumped into the tubing of the well by means of a suitable lubricating device. When this is done the flow of fluid is either shut off at the well head, or in the case of pumping wells, the pump is shut down. The corrosion preventive composition is preferably one incorporating a heavy solvent which will cause the solution to fall rapidly through the oil contained in the tubing. In some cases the tubing will not be full of oil when the flow is stopped and the fall of the corrosion preventive composition will take it rapidly to the oil surface. In some cases the reagent may be formed into solid sticks by incorporating into a soluble, solid composition, such as asphalt, waxes or various resins. When in this form, the sticks may be dropped down the tubing in a manner similar to that employed in adding a liquid material. The addition of the corrosion preventive compound by these methods involving dumping of the material down the tubing is, of course, less satisfactory than those methods involving the addition of the reagent to the annular space of the well, since in the former case only the interior of the flow tube would be protected. However, in many wells the most severe corrosion occurs at this point and treatment is justified even when the reagent cannot

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be applied to all of the well equipment. It is often desirable to protect surface flow lines even when corrosion is absent in the well. In this case the corrosion preventive compound may be introduced into the flow line at an up-stream point so it may become intermingled and mixed with the flowing fluid to protect the pipe carrying the fluid.

As pointed out above, the compounds which we have found to be particularly effective in preventing the corrosion of iron and ferrous materials are the N-aliphatic 2,5 pyrrolinediones. The aliphatic group in these compounds includes arylalkyl, cycloaliphatic and branch chain aliphatic as well as straight chain aliphatic groups. Arylalkyl amines in which the amino group is attached to the alkyl radical are included since they are essentially substituted alkyl amines and due to their strong basic character appear to be equally effective to unsubstituted aliphatic amines in the present use. In addition, the aliphatic group may be saturated or unsaturated. The primary amines from which the N-aliphatic groups are derived may be obtained from vegetable oils, fish oils, from naphthenic acids or synthetic acids obtained by oxidation of petroleum fractions or other hydrocarbons. We have found that the best results are obtained when the N-aliphatic group is a saturated aliphatic group. Furthermore, we have found that for effective corrosion preventive action, these reagents must contain an N-aliphatic group containing at least 7 carbon atoms. In order that the reagents may be readily soluble in oils it is desirable that the N-aliphatic group contain less than about 33 carbon atoms. Particularly outstanding corrosion preventive compounds are those derived from saturated aliphatic amines containing from 12 to 20 carbon atoms.

The 3,4 carbon atoms of our pyrrolinediones may be substituted by simple hydrocarbon or halogen groups, such as chlorine, bromine, iodine, methyl, ethyl, butyl, cyclohexylphenyl and the like. Particularly effective corrosion preventives are prepared from 3,4 substituted maleic anhydride where the substituent is hydrogen or methyl. Identical products are, of course, derivable from 3,4 substituted fumaric acid derivatives. The simplest N-aliphatic 2,5 pyrrolinedione may be pictured as compounds derived by the reaction of maleic anhydride with an aliphatic primary amines. However, we obtain equally effective compounds if a substituted maleic anhydride compound is used in place of the maleic anhydride in forming the final imide. Samples of suitable substituted maleic anhydrides for use in synthesis of these materials include ethyl maleic acid, citraconic anhydride, dimethyl maleic anhydride, dimethyl fumaric acid, citraconic acid, fumaric acid, monochlormaleic acid, phenyl maleic acid, dichlormaleic acid, and the like.

Samples of suitable N-aliphatic 2,5 pyrrolinediones which are effective in inhibiting corrosion of materials include N-octadecyl chloromaleimide, N-hexadecyl citraconimide, N-octadecylmaleimide, N-lauryl maleimide, N-octylmaleimide, N-benzyl maleimide, N-naphthenylmaleimide, N-tetradecyl-citraconimide, N-2 ethylhexylcitraconimide, N-abietylcitraconimide, N-docosylchloromaleimide, N-oleylbromomaleimide.

In general, the desired pyrrolinedione may be readily prepared by heating a suitable primary amine and the maleic acid or substituted maleic acid at temperature between 95° C. and 250° C.,

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preferably in the presence of a stream of inert gas, until water evolution ceases.

The following examples show typical methods of manufacture of such products, the parts used being by weight:

Example 1

20 parts of maleic anhydride and 54 parts of an equal molal mixture of octadecenyl and octadecylamine were placed in a reaction vessel equipped with gas inlet tube, stirrer, heater and take-off tube. The mixture was brought to a temperature of 180° C. and held for six hours. During the last hour a slow stream of nitrogen was passed through the reaction mixture to complete removal of water of reaction. About 3.3 parts of water were obtained. On cooling, the product was a hard resinous solid, readily soluble in benzol, and other hydrocarbon solvents.

Example 2

54 parts of octadecyl amine were substituted for the mixture of amines of Example 1. Otherwise the procedure is identical with that of Example 1 immediately preceding.

Example 3

37 parts of dodecyl amine were substituted for the amine mixture of Example 1. 28 parts of monochloromaleic anhydride were substituted for the maleic anhydride in Example 1. Otherwise procedure is identical with that of Example 1.

Example 4

112 parts of citraconic anhydride and 129 parts of octyl amine were reacted in the apparatus of Example 1. Temperature was brought to 195° C. and maintained for 6 hours. During the last hour a slow stream of nitrogen was passed through the mixture to complete removal of water of reaction. About 18 parts of water were obtained from the condensate.

Example 5

112 parts of citraconic anhydride and 284 parts of dihydroabietylamine were reacted as in Example 4. Otherwise the procedure is identical with that of Example 4 immediately preceding.

If desired, our products may be made by employing mixtures of suitable amines and maleic acid or simple maleic acid derivatives. Also, in the application of these materials they may be employed in mixtures containing other corrosion preventives such as, for example, organic phosphites, chromates, sulfonates, etc. We have already pointed out that these materials may be applied in the pure form to the metal to be protected, but in many instances it is desirable to form a solution having fluid properties which will permit easy application of the reagent or more efficient application. Particularly where the reagent is to be used for the protection of oil wells, or gas well, by dropping or dumping down the annular space between tubing and casing, it is desirable that the compound be of such viscosity as to permit easy pumping even at quite low temperatures. In preparing fluid compositions, hydrocarbon or halogenated hydrocarbons are particularly useful although other organic solvents such as higher molecular weight alcohols, ketones, ethers, etc., may be employed. For solid compositions, waxes and resins are particularly useful as blending agents and modifiers. As examples of suitable corrosion preventive compositions of this type, the following are presented, where the parts are by weight.

Corrosion preventive composition No. 1

	Parts
Product of Example 2	25
Aromatic naphtha	50
S. A. E. 30 low V. I. oil	25

Corrosion preventive composition No. 2

	Parts
Product of Example 1	30
Commercial xylene	20
Crude petroleum oil	50

Corrosion preventive composition No. 3

	Parts
Product of Example 3	50
Mahogany sulfonate	20
Gas oil	30

Corrosion preventive composition No. 4

	Parts
Product of Example 2	70
Ozokerite wax	30

The above were melted together and cast into cylinders 1 1/4 inch in diameter by 18 inches long. These are suitable for dropping down the tubing of wells.

Corrosion preventive composition No. 5

	Parts
Product of Example 1	50
Petroleum resin ("Velsicol")	25
High melting paraffin wax	25

The above were melted together and cast into sticks as in composition No. 4.

Corrosive preventive composition No. 6

	Parts
Product of Example 1	35
Carbon tetrachloride	30
Methylnaphthalene	35

Corrosion preventive composition No. 7

	Parts
Product of Example 1	5
Kerosene	85
S. A. E. 30 lubricating oil	5
Petrolatum	5

In the corrosion preventive compositions, the concentration of pyrrolinedione will usually be between 10% and 90% of the total composition weight. The use of more dilute compositions entails the use of excessive volumes of reagent, and more concentrated solution approach, in physical properties, the pure pyrrolinedione.

Examples of the field application of corrosion preventives as described herein are given below:

Application No. 1

A gas-condensate well was chosen in the West Tuleta pool of Bee County, near Pettus, Texas, as being representative of a corrosive gas well. This well, producing at 7850 feet from the Wilcox horizon, has suffered two tubing failures due to corrosion over the 35-month period prior to the application of the corrosion preventive. A description of the well before treatment follows:

Gas produced per day	mmcf	4.6
Distillate produced per day	bbl	175
Brine produced per day	do	2
Tubing pressure	p. s. i.	2050
Well head temperature	° F.	157

Corrosion preventive composition No. 1 was continuously fed down the casing of this well by chemical feed pumps, and the corrosive condition of the well was determined by the iron content of the brine and by the rate of corrosion in I. P. Y.

(inches penetration per year) of mild steel test coupons inserted in pairs at the well head.

The effect of treatment of this well over a period of several months is recorded in the table below:

16-day test period No. —	1	2	3	4	5	6
Ratio chemical/distillate	0	1/2700	1/5546	0	1/14,300	1/30,000
Iron, P. P. M., content of brine	43	3.4	2.2	7.6	4.9	15.0
IPY	0.038	0.0045	0.0034	0.019	0.0024	0.0033

Application No. 2

A second representative gas-condensate well was chosen in the Placedo field of South Texas. A description of the well before treatment is as follows:

Gas produced per day containing	
0.4 mole per cent CO ₂	mmcf 2.7
Distillate produced per day	bbl 8
Brine produced per day	do 1/2

Corrosion preventive composition No. 1 was batch dumped down the casing of this well once a day. The effect of treatment of this well as indicated by the I. P. Y. of steel test coupons and iron content of the brine is tabulated below:

14-day test period No.	1	2	3
Ratio Chemical/distillate	0	1/896	1/1300
Iron content of brine, P. P. M.	75	3	3
IPY	0.0086	0.00034	0.00036

Results similar to the above were obtained by the use of corrosion preventive composition #2 in an oil well producing sour crude oil in a New Mexico field.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. In the process of preventing corrosion of metals, the step of applying to the metal surface a N-aliphatic 2,5 pyrrolinedione; said aliphatic radical containing at least 7 and not more than 32 carbon atoms.

2. In the process of preventing corrosion of metals, the step of applying to the metal surface a member of the class consisting of N-aliphatic maleimide and 3,4 methyl derivatives thereof; said aliphatic radical containing at least 7 and not more than 32 carbon atoms.

3. In the process of preventing corrosion of iron and ferrous alloys, the step of applying to the metal surface a member of the class consisting of N-aliphatic maleimide and 3,4 methyl derivatives thereof; said aliphatic radical containing at least 7 and not more than 32 carbon atoms.

4. In the process of preventing corrosion of iron and ferrous alloys, the step of applying to the metal surface a member of the class consisting of N-alkyl maleimide and 3,4 methyl derivatives thereof; said alkyl radical containing at least 7 and not more than 32 carbon atoms.

5. In the process of preventing corrosion of iron and ferrous alloys, the step of applying to the metal surface a member of the class consisting of N-alkyl maleimide and 3,4 methyl derivatives thereof; said alkyl radical containing at least 12 and not more than 20 carbon atoms.

6. In the process of preventing corrosion of iron and ferrous alloys, the step of applying to the metal surface N-dodecyl 2,5 pyrrolinedione.

7. In the process of preventing corrosion of

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iron and ferrous alloys, the step of applying to the metal surface N-cetyl 2,4 pyrrolinedione.

8. In the process of preventing corrosion of iron and ferrous alloys, the step of applying to the metal surface N-octadecyl 2,5 pyrrolinedione.

9. A composition of matter comprising a N-aliphatic 2,5 pyrrolinedione dissolved in a solvent selected from the class consisting of hydrocarbons and halogenated hydrocarbons; the concentration of said N-aliphatic 2,5 pyrrolinedione in said composition being within the range of 10% to 90%.

10. A composition of matter comprising a member of the class consisting of N-aliphatic maleimide and 3,4 methyl derivatives thereof, dissolved in a solvent selected from the class consisting of hydrocarbons and halogenated hydrocarbons; the concentration of said member in said composition being within the range of 10% to 90%.

11. A composition of matter comprising a member of the class consisting of N-alkyl maleimide and 3,4 methyl derivatives thereof, dissolved in a solvent selected from the class consisting of hydrocarbons and halogenated hydrocarbons; the concentration of said member in said composition being within the range of 10% to 90%.

12. A composition of matter comprising a member of the class consisting of N-alkyl maleimide and 3,4 methyl derivatives thereof, in which said alkyl radical is one containing at least 12 and not more than 20 carbon atoms, dissolved in a solvent selected from the class consisting of hydrocarbons and halogenated hydrocarbons; the concentration of said member in said composition being within the range of 10% to 90%.

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13. A composition of matter comprising N-dodecyl 2,5 pyrrolinedione dissolved in a solvent selected from the class consisting of hydrocarbons and halogenated hydrocarbons; the concentration of said N-dodecyl 2,5 pyrrolinedione in said composition being within the range of 10% to 90%.

14. A composition of matter comprising N-cetyl 2,5 pyrrolinedione dissolved in a solvent selected from the class consisting of hydrocarbons and halogenated hydrocarbons; the concentration of said N-cetyl 2,5 pyrrolinedione in said composition being within the range of 10% to 90%.

15. A composition of matter comprising N-octadecyl 2,5 pyrrolinedione dissolved in a solvent selected from the class consisting of hydrocarbons and halogenated hydrocarbons; the concentration of said N-octadecyl 2,5 pyrrolinedione in said composition being within the range of 10% to 90%.

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