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# PREVENTION OF CORROSION USING HETEROCYCLIC NITROGEN COMPOUNDS

Zisis Andrew Foroulis, East Orange, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

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## ABSTRACT OF THE DISCLOSURE

Corrosion of metals by aqueous acidic solutions is markedly inhibited by the presence of a heterocyclic nitrogen compound having a 5-member ring containing 2 or 3 nitrogen atoms. Typical compounds are pyrazole and 1,2,4-triazole. Corrosion of chemical and petroleum process equipment handling hydrocarbon and other chemical streams containing acidic substances is minimized by the presence of a corrosion inhibitor of this invention.

## BACKGROUND OF THE INVENTION

This invention relates to the prevention of corrosion of metals by aqueous acidic solutions, and more particularly to the prevention of corrosion of chemical and petroleum process equipment which is subjected to corrosive attack by aqueous acidic solutions as a result of condensation of water containing dissolved acidic substances.

Various acidic substances which are present in petroleum refining operations cause corrosion of metals with which they come in contact. Examples of destructive inorganic compounds include hydrochloric acid, sulfuric acid, sulfur trioxide, and hydrogen sulfide. Organic compounds causing corrosion include acetic acid, phenolic compounds, naphthenic acids, and aliphatic and naphthenic organic chlorides. Corrosion-causing acids enter the hydrocarbon process streams in pertoleum refineries in various ways. For example, crude oils generally contain naphthenic acids. The organic chlorides do not usually occur naturally in crude oil, but are sometimes added by producers for removal of paraffin deposits in producing wells and pipelines. These tend to hydrolyze in the presence of water to produce hydrochloric acid. Hydrogen sulfide is formed in catalytic desulfurization processes using hydrogen, in which various hydrocarbon feedstocks including virgin and cracked naphthas, as well as gas oils, containing such impurities as mercaptans, disulfides, and thiophenes, are catalytically reacted with hydrogen in order to reduce their sulfur content. Sulfuric acid and sulfur dioxide are both processing reagents, the former being used as an alkylation catalyst and the latter as an extractant for the removal of aromatics from hydrocarbon feedstocks. Hydrochloric acid and hydrogen chloride may result from several sources, including the hydrolysis of organic chlorides, hydrolysis of salt which is mixed with crude oil as a result of the use of brine of oil production operations, and as a result of hydrolysis of chlorine gas which is used in the regeneration of platinum reforming catalysts.

Corrosion caused by acids is also a problem in the chemical industry. For example, concentrated aqueous phosphoric acid, which is widely used in the manufacture of fertilizers as a source of phosphorus, is extremely corrosive to carbon steels. Consequently, expensive alloy steels are widely used in process equipment and in storage and transportation equipment for handling phosphoric acid.

Acidic substances such as the foregoing will cause severe corrosion of the metals from which conventional petroleum refining and chemical process equipment is constructed. Carbon steels, such as 1020 carbon steel containing 0.2% carbon, are used predominantly as materials of construction. While it would be possible to fabricate refinery equipment from steels which are less prone to corrosive attack, such as stainless steel and special alloy steels, the cost of such equipment would be inordinately high and would make any process being conducted with such equipment uneconomical.



Corrosion in petroleum process streams is particularly troublesome in equipment, such as condensers and heat exchangers, where condensation of water takes place. Water vapor is invariably present in hydrocarbon process streams, as is well known. When this water condenses, acidic gases present in the process stream, such as hydrogen chloride, hydrogen sulfide, sulfur dioxide, and carbon dioxide, dissolve in the condensate and attack metal equipment. Such attack occurs in hydrocarbon process streams containing only trace amounts of oxygen or none at all, since the metal is oxidized by the hydrogen ions of the acid.

The overhead stream from an atmospheric pipestill is one example of a petroleum process stream containing acidic gases. Such a stream generally contains hydrogen chloride as well as organic chlorides. Upon condensation of this overhead stream, hydrogen chloride is dissolved in the water condensate and the quantity of hydrogen chloride is ugmented by hydrolysis of a portion of the organic chlorides present. This condensate attacks the condenser surfaces.

One possible technique for inhibiting corrosion of refinery equipment by acids is to neutralize the acid with a base. However, such a solution would not be practical because there is a tremendous daily throughput of feed streams through petroleum or chemical processes which contain acidic materials, thereby requiring a correspondingly large amount of base for neutralization. A further problem arises from the fact that the most likely base for use in such neutralization would be ammonia. However, the neutralization of acidic components such as hydrogen chloride by injection of ammonia in hydrocarbon streams, quite freqeuntly results in extensive fouling of process equipment, such as heat exchangers, towers, etc., due to decomposition of ammonium salt produced by neutralization. In addition, in instances such as the phosphoric acid storage facilities, the use of neutralizers clearly is contraindicated. It is thus evident that a meaningful answer to the problem facing the petroleum and chemical industries would not be based on neutralization or removal of the acidic corrosive agents in the feed stream since such techniques would either be prohibitively expensive or would result in extensive fouling of process equipment. Instead, it is necessary to provide a corrosion inhibitor whose effectiveness does not depend on neutralization of acid present and which does not contribute to fouling.

The use of pyrrole as a corrosion inhibitor for metals exposed to acidic media has been previously suggested. While pyrrole does inhibit corrosion of metals by acids, it tends to polymerize at high temperatures such as those encountered in petroleum processing, and thus produces fouling of process equipment.

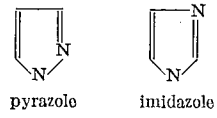
## SUMMARY OF THE INVENTION

It has been found that corrosion of metals by aqueous acids can be markedly inhibited by the presence of a heterocyclic nitrogen compound having a 5-member ring containing 2 or 3 nitrogen atoms. Typical compounds include pyrazole, imidazole, and 1,2,4-triazole.

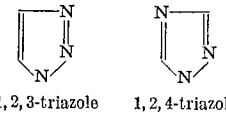
## DETAILED DESCRIPTION

The corrosion inhibitors of this invention are aromatic compounds which have a 5-member heterocyclic ring containing 2 or 3 nitrogen atoms. Among the effective corrosion inhibiting compounds are pyrazole, imidazole,

1,2,3-triazole, 1,2,4-triazole, and derivatives thereof. The parent compounds may be represented by the following structural formulas:

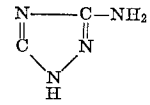


pyrazole imidazole

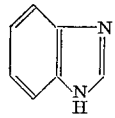


1,2,3-triazole 1,2,4-triazole

Derivatives of the above compounds, as well as the parent compounds themselves, are effective corrosion inhibitors. For example, 3-amino-1,2,4-triazole, which has the structure



is an excellent corrosion inhibitor. The derivative may be a monocyclic compound in which one or more hydrogen atoms of the parent are replaced by substituents, or may be a compound having one or more rings, usually aromatic or alicyclic rings, fused to the heterocyclic ring. For example, benzimidazole, having the formula



is a corrosion inhibitor.

To be good corrosion inhibitors, compounds are preferably moderately soluble in water. The water solubility of the compound must be sufficient to provide an effective corrosion inhibiting concentration. Hence, derivatives having long-chain alkyl substituents, and polycyclic compounds having more than two rings, generally are not effective corrosion inhibitors. Desired water solubility can be achieved in compounds having both solubilizing groups, i.e., hydroxyl, sulfonate salt substituents, and insolubilizing groups such as long-chain alkyl groups.

The inhibitors of this invention may be used effectively in widely varying concentrations. Effective inhibition is obtained in concentrations as low as about $10^{-5}$ moles per liter up to about 0.5 mole per liter of the aqueous acidic phase. Actually, there is no upper limit on the effectiveness of the inhibitors of this invention, and the maximum concentration is limited only by the solubility of the compound. However, concentrations in excess of 0.5 m./l. do not give inhibitory action substantially greater than that obtained at concentrations under 0.5 m./l.

The nitrogen heterocycles of this invention function most effectively in hydrochloric, sulfuric and phosphoric acids. These compounds offer effective protection against corrosion by non-oxidizing acids as well as against corrosion by oxidizing acids.

Any metals which are subject to acid attack can be protected with the inhibitors of this invention. These inhibitors are particularly useful for protection of ferrous metals, and especially low carbon steel, such as 1020 carbon steel (containing 0.2% carbon). Low carbon steels are ideal for construction of petroleum processing equipment from the standpoint of cost and other significant qualities such as strength and their ability to withstand the process stream temperatures. The principal drawback to low carbon steel is its susceptibility to acid corrosion, and problems arising from this are substantially obviated by the use of the inhibitors of this invention.

Corrosion by acids is ordinarily a problem where the pH of the acidic solution is about 4 or lower. The inhibitors of this invention offer excellent protection even in solutions which are decidedly on the acid side, e.g., those having a pH of 1 or lower.



A few types of apparatus used in the petroleum and chemicals processing industry will be cited as examples of apparatus, which as indicated earlier, the presence of aromatic heterocyclic compounds serves to inhibit the corrosion effects of various acid base corrosion causing substances. An area where corrosion is quite serious is the overhead equipment, i.e., condensers and other hardware, in atmospheric distillation towers. Substantial quantities of water vapor and hydrogen chloride distill overhead together with low molecular weight hydrocarbons during atmospheric distillation of crude oil. The hydrogen chloride present in the overhead stream dissolves in the water condensate and attacks the overhead condensers and other related equipment. Corrosion is markedly reduced by injection of a nitrogen heterocyclic compound in the process stream.

Another area where corrosion is widespread and has a deleterious effect is hydrotreating of petroleum fractions. Substantial quantities of hydrogen sulfide are produced in the hydrotreater by reduction of sulfur compounds such as mercaptans, disulfides, and thiophene. This causes severe corrosion, particularly in the presence of water condensate. Also present is hydrogen chloride, which results from the decomposition of organic chlorides such as carbon tetrachloride and trichloroethane in the process stream. In any event, the hydrotreater effluent condenser and other overhead equipment has been plagued with problems instigated by the presence of hydrogen chloride. Again, corrosion is greatly reduced by the injection of a nitrogen heterocycle into the process stream.

Another area where the inhibitors of this invention can be used effectively is to control corrosion in phosphoric acid storage facilities and other related process equipment where phosphoric acid is used in fertilizer manufacture. The nitrogen heterocyclic compound may be directly injected in the process stream.

A significant advantage of the use of corrosion inhibitors is that it is possible to use inexpensive construction materials such as low carbon steel, instead of costly corrosion resistant alloy steels which would render the cost of the process prohibitive.

While ferrous metals have been cited as an illustrative example of metals which can be protected according to this invention, it should be understood that other metals and alloys, such as nickel, zinc, brass, and copper, may also be protected. While copper is more resistant to acid attack in a non-oxidizing atmosphere than the other metals and alloys mentioned, nevertheless it may be prone to slight attack by strong acids, and such attack is mitigated by aromatic heterocyclic nitrogen compounds.

The problem of corrosion attack is most severe in those units, such as condensers, heat exchangers, and transfer lines, where water condenses. The acid gases present in the process stream are dissolved in the condensate, and attack the metal process equipment. It has been found that the corrosion inhibitors herein are effective under the entire temperature range in which water is present in the liquid phase. Since some processes are run at high pressure, the actual temperature may be considerably above the atmospheric boiling point of water; nevertheless, the inhibitors do not lose their effectiveness at such temperatures. Likewise, they remain effective at low temperatures down to 32° F.

The inhibitor is preferably injected into the process stream just a short distance upstream for best results. This mitigates loss of the inhibitor, and also protects the inhibitor from decomposition from high temperatures which prevail in some units of process streams.

While the mechanism for the inhibiting action of aromatic heterocyclic nitrogen compounds is not completely

understood, the following explanation is offered for the purpose of illustration and as an aid in understanding the invention, and should not be taken as limiting the scope of the invention in any manner. The corrosion additive is believed to be adsorbed on the metal surface in the form of a continous or nearly continuous thin film. This film would serve to inhibit any chemical or electrochemical interaction between the acidic corrosive material in solution and the metal surface. The very small quantities of inhibitor that are utilized to form this thin film are not believed to undergo any significant chemical reaction with the acidic corrosive material. Thus, if at all, only small amounts of additional inhibitor would be necessary to maintain long term protection on metal surfaces, these additions being possibly necessitated by attrition losses due to physical interactions of the flowing stream with the film.

As previously noted, the corrosion inhibitor should not be markedly water soluble, nor should it be substantially completely insoluble. In short, the water solubility must be enough to establish an effective concentration, which as earlier noted is generally at least $10^{-5}$ m./l.

The present invention will be more fully understood with reference to the following specific examples. It is understood that these examples are illustrations of specific embodiments of this invention and are not to be taken as limitations.

## EXAMPLE 1

This example illustrates the efficacy of 1,2,4-triazole as an inhibitor of acid induced corrosion of 1020 carbon steel exposed to 0.1 N hydrochloric acid, which has a pH of 1. Corrosion rates were measured by weight loss of carbon steel specimens having a size of approximately 2.5 cm. x 0.6 cm. x 0.3 cm., and a surface area of approximately 15 square centimeters. The specimens were abraded through 4–0 emery paper, degreased in benzene, and washed in distilled water. Immediately after drying, the specimens were weighed and placed in a corrosion cell an immersed in the corrosive solution. Each of the corrosive solutions, except those used for control purposes, contained a predetermined concentration of 1,2,4-triazole. The amount of corroded metal was determined by weight loss. The corrosion cell was basically a 2000 ml. Erlenmeyer flask with a special top to permit entrance and exit for nitrogen for deaeration and to prevent air contamination. The cell had a removable chimney with Pyrex hooks from which the metal surfaces were suspended. The corrosion solution was deaerated with nitrogen before a run. Nitrogen was also bubbled through the solution continuously during a run to prevent contamination with air. A constant temperature was achieved by the use of constant temperature oil bath. All runs were carried out for two days at a constant temperature of 25° C.

The results of representative experiments utilizing the above procedure are summarized below in Table I. In this table, corrosion rate in milligrams per square decimeter per day (mg./dr.$^2$/day or mdd.) and percentage inhibitor efficiency (which equals

$$\frac{Io-Ii}{Io}\times 100$$

where $Io$ is the corrosion rate without inhibitor and $Ii$ is the corrosion rate with inhibitor) are given for various concentrations of inhibitor in moles per liter (m./l.).

TABLE I

| Inhibitor concentration, m./l. | Corrosion rate (mdd.), mg./dm.$^2$/day | Percent inhibitor efficiency |
|---|---|---|
| Blank | 1,555 | |
| $10^{-5}$ | 976 | 37.2 |
| $10^{-4}$ | 753 | 51.7 |
| $5\times10^{-3}$ | 45 | 97.1 |

## EXAMPLE 2

The procedure of Example 1 was followed except that the inhibitor was 3-amino-1,2,4-triazole. Results are summarized in Table II.

TABLE II

| Inhibitor concentration, m./l. | Corrosion rate (mdd.), mg./dm.$^2$/day | Percent inhibitor efficiency |
|---|---|---|
| Blank | 1,555 | |
| $5\times10^{-3}$ | 111 | 92.9 |
| $10^{-1}$ | 7 | 99.5 |

## EXAMPLE 3

The procedure of Example 1 was repeated except that the inhibitor was pyrazole. Results are summarized in Table III.

TABLE III

| Inhibitor concentration, m./l. | Corrosion rate (mdd.), mg./dm.$^2$/day | Percent inhibitor efficiency |
|---|---|---|
| Blank | 1,555 | |
| $1\times10^{-5}$ | 771 | 50.4 |
| $1\times10^{-4}$ | 809 | 48.0 |
| $5\times10^{-3}$ | 242 | 84.4 |
| $1\times10^{-2}$ | 125 | 92.0 |
| $1\times10^{-1}$ | 5.9 | 99.6 |

## EXAMPLE 4

The procedure of Example 1 was repeated except that the inhibotor was 3,5-dimethylpyrazole. Results are summarized in Table IV.

TABLE IV

| Inhibitor concentration, m./l. | Corrosion rate (mdd.), mg./dm.$^2$/day | Percent inhibitor efficiency |
|---|---|---|
| Blank | 1,555 | |
| $1\times10^{-4}$ | 1,243 | 20.1 |
| $1\times10^{-3}$ | 1,017 | 34.7 |
| $1\times10^{-2}$ | 552 | 64.6 |
| $1\times10^{-1}$ | 3.5 | 99.8 |

The corrosion inhibitors described herein give substantial protection against corrosion of metal by acids. These inhibitors are thermally stable, retaining their effectiveness at the elevated temperatures encountered in hydrocarbon process streams.

While this invention has been particularly described with reference to petroleum processing streams, it will be understood that similar acid corrosion problems may also occur in chemical processing equipment and in containers in storage and shipment of acidic materials. Such equipment and containers can also be protected with the corrosion inhibitors of this invention.

What is claimed is:

1. A process for preventing corrosion of a ferrous metal by an aqueous hydrochloric acid solution having a pH not greater than about 4 which comprises adding to said solution a corrosion inhibiting amount of a heterocyclic nitrogen compound having a five-member ring containing 2 or 3 N atoms.

2. A process according to claim 1, in which said compound is 1,2,4-triazole.

3. A process according to claim 1, in which said compound is 3-amino-1,2,4-triazole.

4. A process according to claim 1, in which said compound is pyrazole.

5. A process according to claim 1, in which the concentration of said compound is in the range of about $10^{-5}$ m./l. to about 0.5 m./l.

6. A process according to claim 1, in which said solution and the surrounding atmosphere are non-oxidizing.

7. A process according to claim 1, in which said acidic solution is a condensate in a hydrocarbon process stream.

8. A process according to claim 1, in which said corrosion inhibiting compound is added to a hydrocarbon process stream upstream of the area to be protected.

9. A process for inhibiting corrosion caused by an aqueous hydrochloric acid condensate having a pH less than about 4 in a ferrous metal vessel containing a hydrocarbonaceous fluid, said process comprising adding to said vessel a heterocyclic nitrogen compound having a five-member ring containing 2 to 3 N atoms.

10. A process according to claim 9, in which said vessel carries a hydrocarbon process stream.

11. An aqueous hydrochloric acid solution having a pH less than about 4 and inhibited against corrosive attack on metals, said solution comprising water, an acidic substance normally tending to cause corrosion of metals, and a small but effective corrosion inhibiting amount of a heterocyclic nitrogen compound having a five-member ring containing 2 or 3 N atoms.

12. A solution according to claim 11, having a pH not greater than about 4.

13. A solution according to claim 11, in which said compound is present in a concentration of about $10^{-5}$ m./l. to about 0.5 m./l.

14. A solution according to claim 11, in which said compound is 1,2,4-triazole.



15. A solution according to claim 11, in which said compound is 3-amino-1,2,4-triazole.

16. A solution according to claim 11, in which said compound is pyrazole.


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DELBERT E. GANTZ, Primary Examiner

G. E. SCHMITKONS, Assistant Examiner

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21—2.7; 203—7; 252—390, 394, 396