HIGH TEMPERATURE CORROSION INHIBITOR

FIELD OF INVENTION

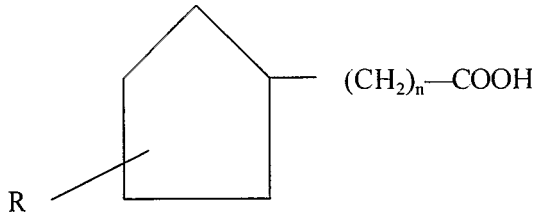
This invention relates generally to a process for inhibiting corrosion in refining operations. It is specifically directed toward the inhibition of corrosion caused by naphthenic acids which are present in the crude oil.

BACKGROUND OF THE INVENTION

Corrosion problems in petroleum refining operations associated with naphthenic acid constituents in crude oils have been recognized for many years. Such corrosion is particularly severe in atmospheric and vacuum distillation units at temperatures of between about 350°F and 790°F. Other factors that contribute to the corrosivity of crudes containing naphthenic acids include the amount of naphthenic acid present, the concentration of sulfur compounds, the velocity and turbulence of the flow stream in the units, and the location in the unit (e.g., liquid/vapor interface).

In the distillation refining of crude oils, the crude oil is passed successively through a furnace and one or more fractionators such as an atmospheric tower and a vacuum tower. In most operations, naphthenic acid corrosion is not a problem at temperatures below about 350°F. Traditional nitrogen-based filming corrosion inhibitors are not effective at temperatures above 350°F, and the other approaches for preventing naphthenic acid corrosion such as neutralization present operational problems or are not effective.

It should be observed that the term "naphthenic acid" includes mono- and di-basic carboxylic acids and generally constitutes about 50% by weight of the total acidic components in crude oil. Many of the naphthenic acids may be represented by the following formula:



where R is an alkyl or cycloalkyl group and n ranges generally from 2 to 10.

Many variations of this structure and molecular weight are possible. Some practitioners include alkyl organic acids within the class of naphthenic acids.

Naphthenic acids are corrosive between the range of about 350°F (180°C) to about 790°F (420°C). At the higher temperatures, the naphthenic acids are in the vapor phase and the rate of decarboxylation increases. At the lower temperatures, the corrosion rate is not serious. The corrosivity of crude oils and distillates is also affected by the presence of sulfide compounds, such as hydrogen sulfide, mercaptans, elemental sulfur, sulfides, disulfides, polysulfides and thiophenols. Corrosion due to sulfur compounds becomes significant at temperatures as low as 450°F. The catalytic generation of hydrogen sulfide by thermal decomposition of mercaptans has been identified as a cause of sulfidic corrosion.

Efforts to minimize or prevent the naphthenic acid corrosion have included the following approaches:

a) blending of higher naphthenic acid content oil with oil low in naphthenic acids;

b) neutralization and removal of naphthenic acids from the oil; and

c) use of corrosion inhibitors.

Because these approaches have not been entirely satisfactory, the accepted approach in the industry is to construct the distillation unit, or the portions exposed to naphthenic acid corrosion, with the resistant metals such as high quality stainless steel or alloys containing higher amounts of chromium and molybdenum. However, in units not so constructed, there is a need to provide inhibition treatment against this type of corrosion. The prior art corrosion inhibitors for naphthenic acid environments include nitrogen-based filming corrosion inhibitors. However, these corrosion inhibitors are relatively ineffective in the high temperature environment of naphthenic acid oils.

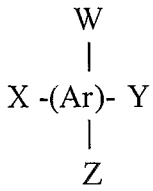
Atmospheric and vacuum distillation systems are subject to naphthenic acid corrosion when processing certain crude oils. Currently used treatments are thermally reactive at use temperatures. In the case of phosphorus-based inhibitors, these are thought to lead to a metal phosphate surface film that is more resistant to naphthenic acid corrosion than the base steel. These inhibitors are relatively volatile and exhibit fairly narrow distillation ranges. They are fed into a column above or below the point of corrosion depending on the temperature range. Polysulfide inhibitors decompose into complex mixtures of higher and lower polysulfides and perhaps, elemental sulfur and mercaptans. Thus, the volatility and protection offered is not predictable.

DETAILED DESCRIPTION

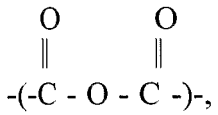
The present invention provides a method for inhibiting the corrosion of the internal metallic surfaces of the equipment used in processing crude oil or the high temperature petroleum distillates derived therefrom. It comprises adding to the crude oil or distillate an effective amount, sufficient to inhibit corrosion, of a tetra functional substituted aromatic compound (I) and/or a trimellitic acid ester or trimellitic anhydride (II).

The tetra functional substituted aromatic compounds (I) as defined above may be represented by the general formula:

I.



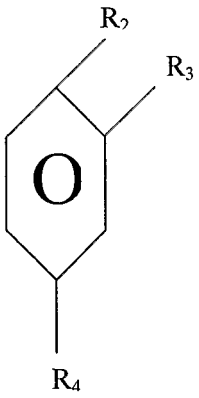
wherein W, X., Y, and Z are all present and may be the same or different and are individually selected from the groups consisting of (OH); (COOH); and $COOR_1$, with the proviso that vicinal pairs of W, X, Y, Z can be



i.e., anhydride function. R_1 in the formula is an alkyl moiety having from about 1 to about 16 carbon atoms; Ar is an aromatic moiety.

The esters or anhydrides of trimellitic acid (II) are represented by the formula (II)

II.





wherein R_2 and R_3 are – (-C-)- or – (-C-O-)- with the proviso that when one of

R_2 or R_3 is $-(-\overset{\overset{O}{\|}}{C}-)-$ or $-(-\overset{\overset{O}{\|}}{C}-O-)-$ then the other is either $-(-\overset{\overset{O}{\|}}{C}-)-$ or $-(-\overset{\overset{O}{\|}}{C}-O-)-$ sufficient to form an anhydride group i.e., $-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-$ linking the 1 and 2 position on the aromatic moiety; R_2 and R_3 may also be $COOR_5$ wherein each R_5 is independently selected from alkyl groups of from about 1 to about 16 carbon atoms. R_4 is $COOR_6$ wherein R_6 is a C_1-C_{16} alkyl group.

Representative compounds falling within formula I above include propyl gallate, gallic acid, pyromellitic acid (i.e., 1,2,4,5 – benzenetetracarboxylic acid); 1,2,4,5 – benezenetetracarboxylic dianhydride; octyl gallate;, and tetra octyl pyromellitate. Pyromellitic acid is presently preferred.

With regard to compounds encompassed by formula (II) above, 1,2,4 benzenetricarboxylic anhydride and trioctyltrimellitate may be mentioned.

In accordance with one aspect of the present invention, the treatment i.e., compounds I and/or II above may be fed directly to the crude charge, e.g., and provide protection in the lower crude tower and vacuum column. Conversely, the inhibition treatment can be fed anywhere to the process stream wherein it will be brought into contact with the process medium, e.g., crude or distillate fraction thereof.

The most effective amount of the corrosion inhibitor to be used in accordance with this invention can vary, depending on the local operating conditions and the particular hydrocarbon being processed. Thus, the temperature and other characteristics of the acid corrosion system can have a bearing on the amount of the inhibitor or mixture of inhibitors to be used. Generally, where the operating temperatures and/or the acid concentrations are higher, a proportionately higher amount of the corrosion inhibitor will be required. It has been found that the concentration of the corrosion inhibitor added to the crude oil may range from about

1 ppm to 5000 ppm, by volume. It has also been found that it is preferred to add the inhibitor at a relatively high initial dosage rate of 2000-3000 ppm and to maintain this level for a relatively short period of time until the presence of the inhibitor induces the build-up of a corrosion protective coating on the metal surfaces. The corrosion inhibitor may be added either neat or diluted. Once the protective surface is established, the dosage rate needed to maintain the protection maybe reduced to a normal operational range of about 100-1500 ppm without substantial sacrifice of protection.

EXAMPLES

The invention will now be further described in conjunction with the following examples, which are provided for illustration purposes and are not intended to act as a limitation thereof.

A weight loss coupon autoclave test was used to evaluate compounds for naphthenic acid corrosion. Test specimens were cleaned, preweighed, mild steel or 5Cr corrosion coupons that were provided with a glass bead surface finish. A paraffinic hydrocarbon oil was dosed with naphthenic acids to give a Total Acid Number of 6.0 and placed into the test autoclave. Candidate treatments, which were solids at room temperature, were added to the autoclaves and mixed. The oil was deareated with argon. In some experiments, the effect of sulfide on corrosion and inhibition was determined by the addition of a sulfur containing compound, namely n-dodecylmethylsulfide in Example 2 and dibutylsulfide in Example 5, which resulted in 0.5% sulfide in those experiments. The autoclaves were heated to the desired test temperature of either 600°F or 500°F. After 20 hours exposure, the coupons were removed, cleaned, and reweighed. Test results are shown below. In the experiments with n-dodecylmethylsulfide, corrosion inhibition was only determined with the mild steel coupons since corrosion rates were quite low, <10 mpy, with the 5Cr coupons.

Example 1

316C, No Sulfide Added

Untreated Corrosion Rates: Mild Steel = 108.2 MPY, 5Cr = 153.9 MPY

Inhibitor	Dosage	% Corrosion Inhibition	
		MS	5Cr
Gallic Acid	100	-32	40
Gallic Acid	1000	92	93
1,2,4,5-Benzenetetracarboxylic Acid	100	95	99
1,2,4,5-Benzenetetracarboxylic Acid	1000	98	99
Propyl Gallate	100	30	97
Propyl Gallate	1000	96	99

Example 2

316C, 0.5% sulfide added as n-Methyldodecylsulfide

Untreated Corrosion Rates: Mild Steel = 39.9 MPY

Inhibitor	Dosage	% Corrosion Inhibition
		MS
Gallic Acid	100	25

Gallic Acid	1000	78
1,2,4,5-Benzenetetracarboxylic Acid	100	78

Example 3

216C No sulfide added

Untreated Corrosion Rates: Mild Steel = 45.5 MPY, 5Cr = 36.3 MPY

Inhibitor	Dosage	% Corrosion Inhibition	
		MS	5Cr
Gallic Acid	100	32	91
Gallic Acid	1000	98	84

Example 4

316C, No Sulfide Added

Untreated Corrosion Rate: 1010 Mild Steel = 143 MPY

Test Compound	Dosage ppm	% Corrosion Inhibition
1,2,4,5-benzenetetracarboxylic acid	25	84
1,2,4,5-benzenetetracarboxylic acid	100	82
1,2,4,5-benzenetetracarboxylic acid	250	93

1,2,4,5-benzenetetracarboxylic dianhydride	25	31
1,2,4,5-benzenetetracarboxylic dianhydride	100	84
1,2,4,5-benzenetetracarboxylic dianhydride	250	93
Octyl Gallate	25	-21
Octyl Gallate	100	-12
Octyl Gallate	250	-15
Propyl Gallate	25	27
Propyl Gallate	100	9
Propyl Gallate	250	41
Tetra-octyl pyromellitate	25	-30
Tetra-octyl pyromellitate	100	50
Tetra-octyl pyromellitate	250	60
Tri-octyl trimellitate	25	-9
Tri-octyl trimellitate	100	34
Tri-octyl trimellitate	250	23
1,2,4-benzenetricarboxylic anhydride	100	35
1,2,4-benzenetricarboxylic anhydride	250	58

Example 5

316C, 0.5% sulfide added as dibutylsulfide

Untreated Corrosion Rate: 1010 MS = 76 MPY

Test Compound	Dosage ppm	% Corrosion Inhibition
1,2,4,5-benzenetetracarboxylic acid	100	35
1,2,4,5-benzenetetracarboxylic acid	250	43
1,2,4,5-benzenetetracarboxylic acid	1000	52
1,2,4,5-benzenetetracarboxylic anhydride	100	22
1,2,4,5-benzenetetracarboxylic anhydride	250	34
1,2,4,5-benzenetetracarboxylic anhydride	1000	57
Gallic acid	250	40
Gallic acid	1000	82
Octyl Gallate	250	57
Octyl Gallate	1000	72
Propyl Gallate	250	38
Propyl Gallate	1000	54
Tetra-octyl pyromellitate	250	45
Tetra-octyl pyromellitate	1000	21
Tri-octyl trimellitate	250	0
Tri-octyl trimellitate	1000	0
1,2,4-benezenetricarboxylic anhydride	250	14

1,2,4-benezenetricarboxylic anhydride	1000	58

Example 6

A high temperature autoclave was used to evaluate a number of comparative and prospective corrosion inhibitors in a dearated HVG0 derived from a Venezuelan crude oil. One static carbon steel coupon was hung in the vapor space. Two carbon steel coupons were rotated at about 2 fps in the liquid phase. Liquid phase temperature was controlled at 600°F for approximately 20 hours. The weight loss, surface area, and exposure time were used to calculate the general corrosion rate in mpy for untreated and treated coupons. Results are shown below.

Test Compound	Dosage ppm	Corrosion mpy
Blank		14.2
Phenyl didecylphosphite C-1	50	13.4
Phenyl didecylphosphite C-1	100	7.2
ammonium salt of dinonyl phenyl sulfonic acid C-2	100	11.8
gallic acid	100	9.8
gallic acid	200	10.7
pyrogallol C-3	100	11.9
catechol C-4	100	11.5
salicylic acid C-5	100	12.2
benzoic acid C-6	100	15.2

phthalic acid C-7	100	11.2

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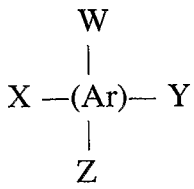
Test compound identification above having a C letter prefix designates a comparative example. As shown above in the examples, the tetra acidic aromatic compounds (I) and trimellitic acid esters and anhydrides II are effective in reducing corrosion of metallic surfaces in contact with high temperature crudes, particularly naphthenic acid containing crudes. The treatments of the invention also do not contain phosphorous or sulfide moieties which have proven problematic with regard to possible catalyst poisoning and thermal instability respectively.

It is also noted that the treatments of the invention are effective corrosion inhibitors in those crude oil and petroleum distillate containing systems in which both naphthenic acids and sulfur compounds are present. As is known in the art, naphthenic acid corrosion appears to be exceptionally serious in the presence of sulfur compounds, especially hydrogen sulfide.

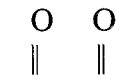
What is claimed is:

CLAIMS

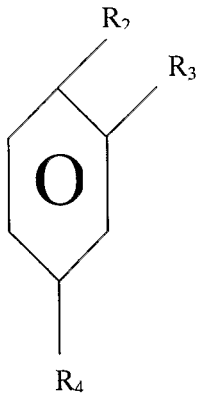
1. A method for inhibiting corrosion of the internal metallic surfaces of equipment used in the processing of crude oil or high temperature distillates heated to temperatures of between about 350°F and about 790°F comprising adding to the crude oil or high temperature petroleum distillate a corrosion inhibiting amount of a corrosion inhibitor selected from the groups (I) and (II) and mixtures thereof, wherein said corrosion inhibitor (I) has the formula:



wherein W, X, Y, and Z are all present and are the same or different and are individually selected from the groups consisting of OH; COOH; and $COOR_1$, with the

proviso that vicinal pairs of W, X, Y, and Z may be selected from  ; R_1 is an alkyl moiety having from about 1 to 16 carbon atoms and Ar is an aromatic compound;

said corrosion inhibitor (II) having the formula



wherein R_2 and R_3 are $COOR_5$, $-(-\overset{O}{\overset{\|}{C}}-)-$; or $-(-C-\overset{O}{\overset{\|}{C}}-O-)-$ with the proviso that when one of R_2 or R_3 is $-(-\overset{O}{\overset{\|}{C}}-)-$ or $-(-C-\overset{O}{\overset{\|}{C}}-O-)-$ then the other is either $-(-\overset{O}{\overset{\|}{C}}-)-$ or $-(-C-\overset{O}{\overset{\|}{C}}-O-)-$ sufficient to form an anhydride group linking the R_2 and R_3 functions, each R_5 is individually selected from alkyl groups having from about 1 to about 16 carbon atoms; R_4 is $COOR_6$ wherein R_6 is an alkyl group having from about 1 to about 16 carbon atoms.

2. The method as recited in claim 1 wherein Ar is substituted benzene.

3. The method as recited in claim 2 wherein said corrosion inhibitor (I) is selected from the group consisting of gallic acid, pyromellitic acid, propyl gallate, octyl gallate, tetra octyl pyromellitate, and 1,2,4,5-benzenetetracarboxylic dianhydride.

4. The method as recited in claim 3 wherein said corrosion inhibitor (I) is pyromellitic acid.

5. The method as recited in claim 2 wherein the corrosion inhibitor (II) is selected from 1,2,4-benzenetricarboxylic anhydride and trioctyltrimellitate.

6. The method as recited in claim 3 wherein said crude oil or petroleum distillate comprises naphthenic acid and said corrosion inhibitor is naphthenic acid induced corrosion.

7. The method as recited in claim 6 wherein said crude oil or petroleum distillate further comprises a sulfur containing compound.

8. The method as recited in claim 1 wherein the amount of corrosion inhibitor (I) and/or (II) added to the crude oil or distillate is an amount sufficient to generate a concentration of from about 1-5,000 ppm by volume.

9. The method as recited in claim 8 wherein the concentration is from about 100 to about 1500 ppm.

10. The method as recited in claim 3 wherein said corrosion inhibitor is 1,2,4,5-benzenetetracarboxylic dianhydride.