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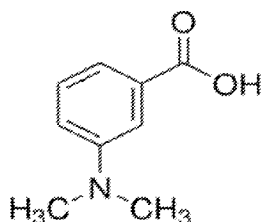


FIG. 1A

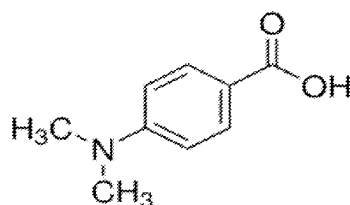


FIG. 1B

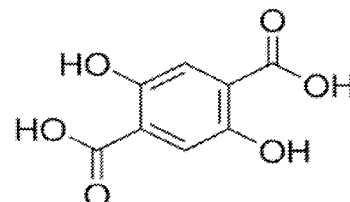


FIG. 1C

(57) Abstract: Corrosion inhibitor compositions and methods for inhibiting corrosion on a metal surface exposed to a hydrocarbon fluid are provided. The corrosion inhibition compositions can include a corrosion inhibitor, such as 3-dimethylamino benzoic acid, 4-dimethylamino benzoic acid, or 2,5-dihydroxyterephthalic acid. The corrosion inhibitor composition can further comprise dimethyl sulfoxide, and heavy aromatic naphtha. The corrosion inhibitor composition can be phosphate-free and can inhibit naphthenic acid corrosion. In the methods, a corrosion inhibitor composition is added to the hydrocarbon fluid exposed to the metal surface to prevent or inhibit corrosion on the metal surface, including naphthenic acid corrosion.

NAPHTHENIC ACID CORROSION INHIBITORS FOR A REFINERY

CROSS-REFERENCE TO RELATED APPLICATION

The present application claims the benefit of and priority to U.S. Patent Application No. 16/901,825, titled NAPHTHENIC ACID CORROSION INHIBITORS FOR A REFINERY,

5 filed on June 15, 2020, which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

The present disclosure is generally related to chemical compositions, and more particularly related to corrosion inhibitor compositions.

10

BACKGROUND OF THE DISCLOSURE

For oil and gas facilities, corrosion is a persistent problem in equipment, piping, and pipelines that are exposed to corrosive fluids, including hydrocarbon feeds. While various types of corrosion can occur throughout these facilities, naphthenic acid corrosion is common in refinery processes that occur at high temperatures (e.g., 200°C to 400°C), for example in refinery processes that process crude oil and its various fractions. For instance, distillation of an acidic crude oil can result in naphthenic acid corrosion. In some circumstances, naphthenic acid corrosion can be predicted in a given refinery apparatus based on the total acid number (TAN) of the fluid that is exposed to the apparatus.

In standard oil and gas facilities, corrosion inhibitors and corrosion-resistant alloys (CRAs) are often used to mitigate naphthenic acid corrosion. For instance, phosphate-based corrosion inhibitors are known to have some effectiveness in controlling naphthenic acid corrosion. However, phosphate-based corrosion inhibitors can have negative effects on downstream refinery units, as these types of inhibitors can result in catalyst poisoning (partial or complete deactivation of the catalyst), for example.

The present application addresses these and other challenges related to mitigating and preventing corrosion in refinery equipment.

SUMMARY OF THE DISCLOSURE

In a first aspect, a corrosion inhibitor composition is provided. The corrosion inhibition composition can comprise 2,5-dihydroxyterephthalic acid (DHTA), dimethyl sulfoxide, heavy aromatic naphtha. In another aspect, the composition comprises approximately: 10-30 weight% of DHTA, 60-80 weight % of dimethyl sulfoxide, and 10-30 weight % heavy aromatic naphtha. In another aspect, the composition comprises approximately: 20 weight % of DHTA; 70 weight % of dimethyl sulfoxide; and 10 weight % heavy aromatic naphtha. In another aspect, the corrosion inhibitor composition inhibits naphthenic acid corrosion. In another aspect, the corrosion inhibitor composition is free of phosphate.

In a second aspect, a corrosion inhibitor composition comprising a corrosion inhibitor, dimethyl sulfoxide, and heavy aromatic naphtha is provided, where the corrosion inhibitor is 3-dimethylamino benzoic acid (3-DMAB) or 4-dimethylamino benzoic acid (4-DMAB). In another aspect, the composition comprises approximately: 10-30 weight% of the corrosion inhibitor, 60-80 weight % of dimethyl sulfoxide, and 10-30 weight % heavy aromatic naphtha. In another aspect, the corrosion inhibitor is 3-DMAB and the composition comprises approximately: 20 weight % of 3-DMAB, 70 weight % of dimethyl sulfoxide, and 10 weight % heavy aromatic naphtha. In another aspect, the corrosion inhibitor is 4-DMAB and the composition comprises approximately: 10 weight % of 4-DMAB, 80 weight % of dimethyl sulfoxide, and 10 weight % heavy aromatic naphtha. In another aspect, the corrosion is caused by naphthenic acid. In another aspect, the corrosion inhibitor composition is free of phosphate.

In a third aspect, a method for inhibiting corrosion on a metal surface exposed to a hydrocarbon fluid is provided. In the method, a corrosion inhibitor composition is added to the hydrocarbon fluid exposed to the metal surface, and the corrosion inhibitor composition comprises 3-DMAB, 4-DMAB, or DHTA. In another aspect of the method, the corrosion inhibitor composition is added to the hydrocarbon fluid in a concentration of approximately 100 ppm to approximately 1000 ppm. In another aspect of the method, the corrosion inhibitor composition comprises 3-DMAB, and further comprises dimethyl sulfoxide, and heavy aromatic naphtha. In a further aspect of the method, the corrosion inhibitor composition comprises approximately: 20 weight % of 3-DMAB, 70 weight % of dimethyl

sulfoxide, and 10 weight % heavy aromatic naphtha, and the corrosion inhibitor composition is added to the hydrocarbon fluid in a concentration of approximately 500 ppm.

In another aspect of the method, the corrosion inhibitor composition comprises 4-DMAB, and further comprises dimethyl sulfoxide, and heavy aromatic naphtha. In a further
5 aspect of the method, the corrosion inhibitor composition comprises approximately: 10 weight % of 4-DMAB, 80 weight % of dimethyl sulfoxide, and 10 weight % heavy aromatic naphtha, and the corrosion inhibitor composition is added to the hydrocarbon fluid in a concentration of approximately 500 ppm.

In yet another aspect of the method, the corrosion inhibitor composition comprises
10 DHTA, and further comprises dimethyl sulfoxide, and heavy aromatic naphtha. In a further aspect of the method, the corrosion inhibitor composition comprises approximately: 20 weight % of DHTA, 70 weight % of dimethyl sulfoxide, and 10 weight % heavy aromatic naphtha, and the corrosion inhibitor composition is added to the hydrocarbon fluid in a concentration of approximately 500 ppm.

15 In another aspect of the method, the corrosion inhibitor composition is added to the hydrocarbon fluid in a refinery process, wherein the refinery process is performed at a temperature of approximately 200°C to approximately 400°C, and wherein the corrosion inhibitor composition inhibits naphthenic acid corrosion on the metal surface.

20 BRIEF DESCRIPTION OF THE DRAWING FIGURES

Figs. 1A-1C display the chemical structures of corrosion inhibitors of the present compositions and methods in accordance with one or more embodiments.

DETAILED DESCRIPTION OF CERTAIN EMBODIMENTS

5 By way of overview and introduction, the present application discloses compositions and methods for inhibiting corrosion on metal surfaces exposed to hydrocarbon fluids. In one or more embodiments, the corrosion inhibitor compositions of the present application are phosphate-free and can comprise a corrosion inhibitor, such as 3-dimethylamino benzoic acid (3-DMAB), 4-dimethylamino benzoic acid (4-DMAB), or 2,5-dihydroxyterephthalic acid
10 (DHTA). Specifically, in one or more embodiments, the corrosion inhibitor composition comprises (i) DHTA, (ii) dimethyl sulfoxide, and (iii) heavy aromatic naphtha. In one or more embodiments, the corrosion inhibitor composition comprises (i) 3-DMAB or 4-DMAB, (ii) dimethyl sulfoxide, and (iii) heavy aromatic naphtha.

In one or more embodiments of the present methods, a corrosion inhibitor
15 composition of the present application can be added to a hydrocarbon fluid in a refinery process in which the hydrocarbon fluid is exposed to one or more metal surfaces. The addition of the corrosion inhibitor composition to the hydrocarbon fluid can mitigate or prevent corrosion on the metal surfaces typically caused by the hydrocarbon fluid. For example, the present compositions and methods can be used to mitigate or prevent
20 naphthenic acid corrosion that is induced during high-temperature (e.g., 200°C to 400°C) refinery processes, such as distillation of an acidic crude oil. In such an embodiment, at least

one of the present corrosion inhibitor compositions is added to the acidic crude oil, thereby reducing the amount of naphthenic acid corrosion that occurs on the metal surfaces exposed to the acidic crude oil.

As such, the present compositions and methods can be used to reduce corrosion—
5 and in particular, naphthenic acid corrosion—in various refinery units, such as crude distillation units, vacuum distillations units, and furnaces, that are exposed to hydrocarbon fluids.

These and other aspects of the present compositions and methods are described in further detail below with reference to the accompany drawing figures, in which one or more
10 illustrated embodiments and/or arrangements of the corrosion inhibitors are shown. The compositions and methods of the present application are not limited in any way to the illustrated embodiments and/or arrangements. It should be understood that the compositions and methods as shown in the accompanying figures are merely exemplary of the compositions and methods of the present application, which can be embodied in various
15 forms as appreciated by one skilled in the art. Therefore, it is to be understood that any structural and functional details disclosed herein are not to be interpreted as limiting the present compositions and methods, but rather are provided as a representative embodiment and/or arrangement for teaching one skilled in the art one or more ways to implement the present compositions and methods.

20 The corrosion inhibitor compositions of the present application generally comprise at least one corrosion inhibitor. Figs. 1A-1C display the chemical structures of various

corrosion inhibitors of the present compositions and methods in accordance with one or more embodiments. Fig. 1A shows the chemical structure of 3-dimethylamino benzoic acid (3-DMAB). Fig. 1B shows the chemical structure of 4-dimethylamino benzoic acid (4-DMAB). Fig. 1C shows the chemical structure of 2,5-dihydroxyterephthalic acid (DHTA). The

5 corrosion inhibitors of the present compositions are free of phosphates, and thus the present compositions are also free of phosphates. As such, the present compositions do not have the same negative effects on downstream refinery units that phosphate-based corrosion inhibitors do. For example, refinery units, such as fluid catalytic cracking (FCC) units and naphtha hydrotreater (NHT) units, are typically downstream of the units that are affected by

10 naphthenic acid corrosion. These FCC and NHT units generally include catalysts that, upon interaction with phosphate groups, become partially or complete deactivated (“catalyst poisoning”), thereby hindering the reactions of the FCC and NHT units. As such, while some phosphate-based corrosion inhibitors mitigate naphthenic acid corrosion, their effectiveness in mitigating corrosion is negated by their downstream effects on catalysts. In

15 contrast, the phosphate-free corrosion inhibitor compositions of the present application are effective at reducing and/or preventing naphthenic acid corrosion, and do not cause catalyst poisoning in downstream operations.

In one or more embodiments, the corrosion inhibitor compositions can comprise one or more additional compounds in addition to the at least one corrosion inhibitor. For

20 instance, in at least one embodiment, the corrosion inhibitor composition can comprise DHTA, dimethyl sulfoxide, and heavy aromatic naphtha. In one or more implementations,

the heavy aromatic naphtha as mentioned herein is the compound identified by CAS #64742-94-5.

In one or more embodiments, the corrosion inhibitor composition can comprise approximately 10-30 weight % of DHTA, approximately 60-80 weight % of dimethyl sulfoxide, and approximately 10-30 weight % heavy aromatic naphtha. In at least one embodiment, the composition can comprise approximately 20 weight % of DHTA, approximately 70 weight % of dimethyl sulfoxide, and approximately 10 weight % heavy aromatic naphtha. In the present application, it should be understood that the term “approximately”, when used in conjunction with a number, refers to any number within 5% of the referenced number, including the referenced number.

In one or more embodiments, the corrosion inhibitor composition can comprise: (i) 3-DMAB or 4-DMAB; (ii) dimethyl sulfoxide; and (iii) heavy aromatic naphtha. In at least one embodiment, the composition comprises approximately 10-30 weight% of either 3-DMAB or 4-DMAB, approximately 60-80 weight % of dimethyl sulfoxide, and approximately 10-30 weight % heavy aromatic naphtha.

In at least one embodiment, the corrosion inhibitor composition can comprise approximately 20 weight % of 3-DMAB, approximately 70 weight % of dimethyl sulfoxide, and approximately 10 weight % heavy aromatic naphtha.

In at least one embodiment, the corrosion inhibitor composition can comprise approximately 10 weight % of 4-DMAB, approximately 80 weight % of dimethyl sulfoxide, and approximately 10 weight % heavy aromatic naphtha.

In one or more embodiments, the present application also discloses methods for inhibiting corrosion on a metal surface that is exposed to a hydrocarbon fluid. The present methods utilize one or more of the corrosion inhibitor compositions discussed above. In one or more embodiments, the method can comprise adding at least one of the corrosion inhibitor compositions of the present application to a hydrocarbon fluid exposed to the metal surface. The hydrocarbon fluid can be in-use in a metal refinery unit, such as a crude distillation unit, vacuum distillation unit, or furnace. The addition of the at least one corrosion inhibitor composition to the hydrocarbon fluid can reduce corrosion on the metal surfaces typically caused by the hydrocarbon fluid.

In one or more embodiments of the present methods, the corrosion inhibitor compositions can mitigate or prevent naphthenic acid corrosion that is induced during high-temperature (e.g., 200°C to 400°C) refinery processes, such as distillation of an acidic crude oil. For example, in one or more embodiments, at least one of the present corrosion inhibitor compositions can be added to an acidic crude oil that is used in a high-temperature refinery unit, such as a crude distillation unit. Acidic crude oil typically causes naphthenic acid corrosion on the metal surfaces of a crude distillation unit over time. However, the addition of the at least one corrosion inhibitor composition to the acidic crude oil mitigates the occurrence naphthenic acid corrosion or, in certain implementations, prevents naphthenic acid corrosion from occurring on the metal surfaces exposed to the acidic crude oil.

In one or more embodiments, the at least one corrosion inhibitor composition is added to the hydrocarbon fluid (e.g., acidic crude oil) after it enters the refinery unit. As such, in one or more embodiments, the corrosion inhibitor composition(s) of the present

application can be continuously added in the hydrocarbon fluid at a selected amount, measured in parts per million (ppm) for example, to protect the refinery equipment from naphthenic acid corrosion.

In one or more embodiments of the present methods, the corrosion inhibitor
5 composition can be added to the hydrocarbon fluid in a concentration of approximately 100 ppm to approximately 1000 ppm. In one or more embodiments, the corrosion inhibitor composition can be added to the hydrocarbon fluid in a concentration of approximately 500 ppm.

For example, in at least one embodiment, a corrosion inhibitor composition
10 comprising approximately 20 weight % of DHTA, approximately 70 weight % of dimethyl sulfoxide, and approximately 10 weight % heavy aromatic naphtha can be added to a hydrocarbon fluid in a concentration of approximately 500 ppm. Similarly, in one or more embodiments, a corrosion inhibitor composition comprising approximately 20 weight % of 3-DMAB, approximately 70 weight % of dimethyl sulfoxide, and approximately 10 weight %
15 heavy aromatic naphtha can be added to the hydrocarbon fluid in a concentration of approximately 500 ppm. Likewise, in at least one embodiment, a corrosion inhibitor composition comprising approximately 10 weight % of 4-DMAB, approximately 80 weight % of dimethyl sulfoxide, and approximately 10 weight % heavy aromatic naphtha.

Additional aspects and advantages of the present compositions and methods are
20 further described in the Example Section below, in which one or more illustrated embodiments and/or arrangements of the compositions and methods are shown and discussed.

Example – Corrosion Test

In the present example, three formulations of the present corrosion inhibitor compositions were tested to show their ability to inhibit naphthenic acid corrosion on metal coupons exposed to a hydrocarbon stream in accordance with one or more embodiments herein.

Specifically, a rotating cage autoclave corrosion test was performed to measure the corrosion inhibition efficiency of the various formulations. The test was performed in accordance with ASTM standard G170. A hydrocarbon fluid comprising 310 gm (about 350 mL) of mineral oil heavy (CAS # 8042-47-5) was provided to the rotating cage autoclave cell and 4.2 gm (about 4.56 mL) of naphthenic acid (CAS # 1338-24-5; commercial grade with acid value of 230 mg KOH/g) was added to the fluid to make a test solution having a TAN value of 3 mg KOH/g.

Three formulations (formulations 1, 2, and 3) of corrosion inhibitor compositions in accordance with one or more embodiments of the present application were tested. The respective compositions of the three formulations are shown in Table 1 below:

Table 1

Corrosion inhibitor composition	Chemical composition (in weight %)				
	3-Dimethylamino benzoic acid (3-DMAB)	4-Dimethylamino benzoic acid (4-DMAB)	2,5-dihydroxy-terephthalic acid (DHTA)	Dimethyl sulfoxide (DMSO)	Heavy aromatic naphtha (HAN)
Formulation 1	20			70	10
Formulation 2		10		80	10

Formulation 3			20	70	10
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The three formulations of corrosion inhibitor compositions were added separately in the test solution in separate runs as shown in results of Table 2, below. The mixture of the test solution and the respective formulations were exposed metal coupons in the test cell. A control run was also done in which no corrosion inhibitor composition was added to the test solution. Nitrogen gas purging was performed to remove the oxygen content in the test solution as well as in the test cell. The experimental conditions were as follows:

Test temperature: 300 °C

Rotating speed: 1000 rpm

Atmosphere: Nitrogen

Corrosion specimen: Carbon Steel (C1018).

These conditions were maintained for three hours. After the procedure, the metal coupons (corrosion specimens) were removed, excess oil was rinsed away, and the excess corrosion product was removed from the surface of the metal coupons using Clarke's solution (ASTM G1). Each metal coupon was then weighed, and the corrosion rate was calculated in mils per year (MPY). The detailed steps of the rotating cage autoclave corrosion test are shown below:

1. Add 310 gm (350 ml) of mineral oil heavy in the autoclave.

2. Add the naphthenic acid to the mineral oil heavy to achieve a test solution having an acid value of TAN 3.0 mg KOH/g (the naphthenic acid is 4.2 gm with acid value of 230 mg KOH/g).
3. Add desired dosage of corrosion inhibitor formulation (formulation 1, 2, or 3) to the test solution and mix well.
4. Mount pre-weighed metal coupons in the autoclave, and set the temperature to 100°C.
5. Close the autoclave, start heating and keep the stirring the solution at 500 rpm with continuous nitrogen gas purging for about 30 - 45 minutes and, after that, increase the rpm of cage speed to 1000 rpm.
6. Increase temperature of heating to 150°C and stop nitrogen gas purging.
7. Begin raising the temperature to a test temperature 300°C.
8. Continue heating to raise the temperature to the test temperature of 300°C, and mix the mixture at 1000 rpm, for 3 hours.
9. Cool the autoclave temperature to 60°C.
10. Remove the metal coupons and clean them initially with toluene/acetone and then with Clarke's solution (ASTM G1) to remove the corrosion product.
11. Dry and weigh the metal coupons.
12. Calculate the naphthenic acid corrosion inhibition efficiency.

The corrosion inhibition efficiency was calculated using the below equations. For each of the test formulations, corrosion inhibition efficiency was calculated by comparing

weight loss of the metal coupon due to the respective test formulations with weight loss of metal coupon in the test run without a corrosion inhibitor formulation.

Corrosion inhibition efficiency = {(weight loss for coupon without corrosion inhibitor) - (weight loss for coupon with corrosion inhibitor) / (weight loss for coupon without corrosion inhibitor)} × 100.

The corrosion rate in MPY (mils per year) was calculated by the following formula:

$$\text{MPY} = \{534 \times \text{Weight loss in mg}\} / (\text{Density in gm / cc}) \times (\text{Area in inch}^2) \times (\text{Test duration in hours}).$$

The results obtained from the rotating cage experiments with and without a corrosion inhibitor are presented in Table 2 below. Specifically, the corrosion inhibition efficiencies of the various formulations are provided in Table 2. The corrosion rate of the control experiment (i.e., run 1, without a corrosion inhibitor) was 221 MPY. The results of Table 2 also showed that each of formulations 1-3 at a concentration of 500 ppm exhibited substantial decreases in corrosion rate relative to control (run 1). Notably, formulation 3 exhibited 99% corrosion inhibition efficiency at 5000 ppm concentration (run 4). Formulation 1 exhibited 67% corrosion inhibition efficiency at 500 ppm concentration (run 2), and formulation 2 exhibited 87% corrosion inhibition efficiency at 1000 ppm concentration (run 3).

Table 2

Run	Hydrocarbon fluid	Total Acid Number (TAN) mg KOH/g	Corrosion inhibitor formulation	Concentration (ppm)	Corrosion Rate (MPY)	Corrosion Inhibition (%)
1	Mineral Oil (Heavy)	3	None	0	221	NA
2	Mineral Oil (Heavy)	3	Formulation 1	500	74	67
3	Mineral Oil (Heavy)	3	Formulation 2	500	28	87
4	Mineral Oil (Heavy)	3	Formulation 3	500	3	99

Accordingly, based on the experimental results, corrosion inhibitor formulations 1, 2 and 3 each showed corrosion inhibition efficiency in high-temperature naphthenic acid conditions (i.e., 300°C and 3 TAN mineral oil solution). Formulation 3 exhibited 99% corrosion inhibition and formed a protective barrier layer on the metals surface of the coupons in contact with the corrosive fluids. Formulations 1 and 2 were still effective at forming a protective barrier layer on the metal surfaces of the coupons in contact with the corrosive fluids. As such, the present experimental runs show that the metal surfaces in refinery piping (e.g., furnaces, pump arounds) and equipment (e.g., crude distillation unit, vacuum distillation unit) are protected from naphthenic acid corrosion by adding the corrosion inhibitor compositions of the present application to the corrosive fluids (e.g., 3 TAN mineral oil heavy).

Although much of the foregoing description has been directed to compositions and methods for inhibiting corrosion on metal surfaces in refineries or pipelines, the compositions and methods disclosed herein can be similarly deployed and/or implemented

in scenarios, situations, and settings far beyond the referenced scenarios. It should be further understood that any such implementation and/or deployment is within the scope of the composition and methods described herein.

It is to be further understood that like numerals in the drawings represent like
5 elements through the several figures, and that not all components and/or steps described and illustrated with reference to the figures are required for all embodiments or arrangements. Further, the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms "a", "an" and "the" are intended to include the plural forms as well,
10 unless the context clearly indicates otherwise. It will be further understood that the terms "including," "comprising," or "having," "containing," "involving," and variations thereof herein, when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components,
15 and/or groups thereof.

It should be noted that use of ordinal terms such as "first," "second," "third," etc., in the claims to modify a claim element does not by itself connote any priority, precedence, or order of one claim element over another or the temporal order in which acts of a method are performed, but are used merely as labels to distinguish one claim element having a certain
20 name from another element having a same name (but for use of the ordinal term) to distinguish the claim elements.

Notably, the figures and examples above are not meant to limit the scope of the present disclosure to a single implementation, as other implementations are possible by way of interchange of some or all of the described or illustrated elements. Moreover, where certain elements of the present disclosure can be partially or fully implemented using known components, only those portions of such known components that are necessary for an understanding of the present disclosure are described, and detailed descriptions of other portions of such known components are omitted so as not to obscure the disclosure. In the present specification, an implementation showing a singular component should not necessarily be limited to other implementations including a plurality of the same component, and vice-versa, unless explicitly stated otherwise herein. Moreover, applicants do not intend for any term in the specification or claims to be ascribed an uncommon or special meaning unless explicitly set forth as such. Further, the present disclosure encompasses present and future known equivalents to the known components referred to herein by way of illustration.

The foregoing description of the specific implementations will so fully reveal the general nature of the disclosure that others can, by applying knowledge within the skill of the relevant art(s), readily modify and/or adapt for various applications such specific implementations, without undue experimentation, without departing from the general concept of the present disclosure. Such adaptations and modifications are therefore intended to be within the meaning and range of equivalents of the disclosed implementations, based on the teaching and guidance presented herein. It is to be understood that the phraseology or terminology herein is for the purpose of description and

not of limitation, such that the terminology or phraseology of the present specification is to be interpreted by the skilled artisan in light of the teachings and guidance presented herein, in combination with the knowledge of one skilled in the relevant art(s). It is to be understood that dimensions discussed or shown are drawings are shown accordingly to one example
5 and other dimensions can be used without departing from the disclosure.

The subject matter described above is provided by way of illustration only and should not be construed as limiting. Various modifications and changes can be made to the subject matter described herein without following the example embodiments and applications illustrated and described, and without departing from the true spirit and scope of the
10 invention encompassed by the present disclosure, which is defined by the set of recitations in the following claims and by structures and functions or steps which are equivalent to these recitations.

What is claimed is:

1. A corrosion inhibitor composition, comprising:

2,5-dihydroxyterephthalic acid (DHTA);

dimethyl sulfoxide; and

5 heavy aromatic naphtha.

2. The corrosion inhibitor composition of claim 1, wherein the composition comprises approximately:

10-30 weight% of DHTA;

10 60-80 weight % of dimethyl sulfoxide; and

10-30 weight % heavy aromatic naphtha.

3. The corrosion inhibitor composition of claim 1, wherein the composition comprises approximately:

15 20 weight % of DHTA;

70 weight % of dimethyl sulfoxide; and

10 weight % heavy aromatic naphtha.

4. The corrosion inhibitor composition of claim 1, wherein the corrosion inhibitor
20 composition inhibits naphthenic acid corrosion.

5. The corrosion inhibitor composition of claim 1, wherein the corrosion inhibitor composition is free of phosphate.

6. A corrosion inhibitor composition, comprising:

5 a corrosion inhibitor, wherein the corrosion inhibitor is 3-dimethylamino benzoic acid (3-DMAB) or 4-dimethylamino benzoic acid (4-DMAB);

dimethyl sulfoxide; and

heavy aromatic naphtha.

10 7. The corrosion inhibitor composition of claim 6, wherein the composition comprises approximately:

10-30 weight% of the corrosion inhibitor;

60-80 weight % of dimethyl sulfoxide; and

10-30 weight % heavy aromatic naphtha.

15 8. The corrosion inhibitor composition of claim 6, wherein the corrosion inhibitor is 3-DMAB and wherein the composition comprises approximately:

20 weight % of 3-DMAB;

70 weight % of dimethyl sulfoxide; and

20 10 weight % heavy aromatic naphtha.

9. The corrosion inhibitor composition of claim 6, wherein the corrosion inhibitor is 4-DMAB and wherein the composition comprises approximately:

10 weight % of 4-DMAB;

80 weight % of dimethyl sulfoxide; and

5 10 weight % heavy aromatic naphtha.

10. The corrosion inhibitor composition of claim 6, wherein the corrosion is caused by naphthenic acid.

10 11. The corrosion inhibitor composition of claim 6, wherein the composition is free of phosphate.

12. A method for inhibiting corrosion on a metal surface exposed to a hydrocarbon fluid, the method comprising:

15 adding a corrosion inhibitor composition to the hydrocarbon fluid exposed to the metal surface, wherein the corrosion inhibitor composition comprises 3-DMAB, 4-DMAB, or DHTA.

13. The method of claim 12, wherein the corrosion inhibitor composition is added to the
20 hydrocarbon fluid in a concentration of approximately 100 ppm to approximately 1000 ppm.

14. The method of claim 12, wherein the corrosion inhibitor composition comprises 3-DMAB, and further comprises dimethyl sulfoxide, and heavy aromatic naphtha.

15. The method of claim 14, wherein the corrosion inhibitor composition comprises
5 approximately: 20 weight % of 3-DMAB, 70 weight % of dimethyl sulfoxide, and 10 weight % heavy aromatic naphtha, and

wherein the corrosion inhibitor composition is added to the hydrocarbon fluid in a concentration of approximately 500 ppm.

10 16. The method of claim 12, wherein the corrosion inhibitor composition comprises 4-DMAB, and further comprises dimethyl sulfoxide, and heavy aromatic naphtha.

17. The method of claim 16, wherein the corrosion inhibitor composition comprises
15 approximately: 10 weight % of, 4-DMAB, 80 weight % of dimethyl sulfoxide, and 10 weight % heavy aromatic naphtha, and

wherein the corrosion inhibitor composition is added to the hydrocarbon fluid in a concentration of approximately 500 ppm.

18. The method of claim 12, wherein the corrosion inhibitor composition comprises
20 DHTA, and further comprises dimethyl sulfoxide, and heavy aromatic naphtha.

19. The method of claim 18, wherein the corrosion inhibitor composition comprises approximately: 20 weight % of DHTA, 70 weight % of dimethyl sulfoxide, and 10 weight % heavy aromatic naphtha, and

wherein the corrosion inhibitor composition is added to the hydrocarbon fluid in a
5 concentration of approximately 500 ppm.

20. The method of claim 12, wherein corrosion inhibitor composition is added to the hydrocarbon fluid in a refinery process, wherein the refinery process is performed at a temperature of approximately 200°C to approximately 400°C, and wherein the corrosion
10 inhibitor composition inhibits naphthenic acid corrosion on the metal surface.

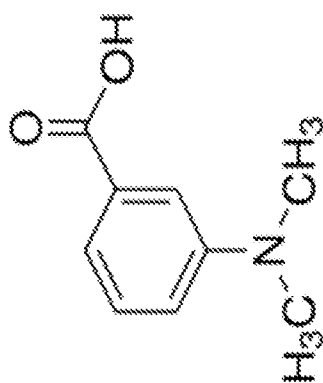


FIG. 1A

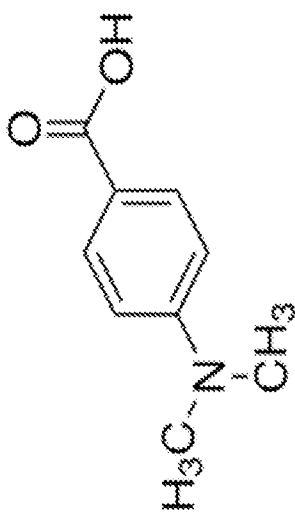


FIG. 1B

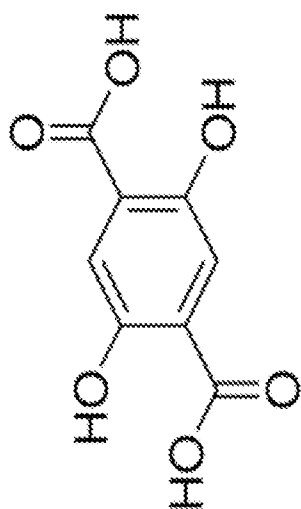


FIG. 1C

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2021/037201

A. CLASSIFICATION OF SUBJECT MATTER INV. C10G7/10 C10G9/16 C23F11/10 C10G75/02 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C10G C23F C10L C09K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2003/013621 A1 (SARTORI GUIDO [IT] ET AL) 16 January 2003 (2003-01-16) the whole document	12,13,20 1-11, 14-19
A	----- US 2003/012681 A1 (BLUM S C; DALRYMPLE D C ET AL.) 16 January 2003 (2003-01-16) the whole document	1-20
A	----- US 6 583 091 B2 (EXXONMOBIL RES & ENG CO [US]) 24 June 2003 (2003-06-24) the whole document -----	1-20
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 10 September 2021		Date of mailing of the international search report 21/09/2021
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Handrea-Haller, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2021/037201

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