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(54) **COMPOSITION FOR CORROSION INHIBITION IN A FUEL MIXTURE AND ITS METHOD OF PREPARATION THEREOF**

(57) The present disclosure relates to a composition for corrosion inhibition in a fuel mixture, the composition comprising: 0.1-4 w/w % of an amine; 0.1-4 w/w % of a quaternary ammonium salt; 0.1-3 w/w % of an antioxidant; 30-60 w/w % of a polar solvent; and 30-60 w/w % of a hydrocarbon-based solvent, wherein the w/w % is based on the total weight of the composition. The present disclosure also relates to a method for preparing a composition for corrosion inhibition in a fuel mixture. The corrosion inhibitor of the present invention delivered excellent corrosion resistance, minimum dosage levels & good stability and miscibility which can be used for mitigating corrosion issues in neat Ethanol and Gasohol.

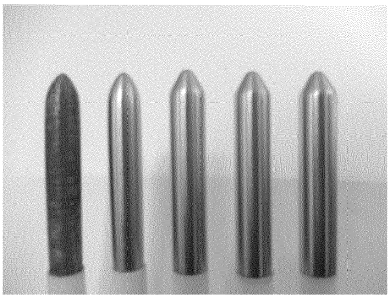

Fig. 1

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Description

FIELD OF THE INVENTION

[0001] The present disclosure relates to a composition for corrosion inhibition in a fuel mixture. The present disclosure also relates to a method for preparing a composition for corrosion inhibition in a fuel mixture.

BACKGROUND OF THE INVENTION

[0002] Background description includes information that may be useful in understanding the present invention. It is not an admission that any of the information provided herein is prior art or relevant to the presently claimed invention, or that any publication specifically or implicitly referenced is prior art.

[0003] US20100187481A1 relates to the use of ionic liquids for improving the lubricating effect of synthetic, mineral and native oils. The invention relates in particular to an improved lubricating composition that is protected from thermal and oxidative attack.

[0004] WO2015183929A1 relates to a concentrated multi-functional additive that can be continuously dosed in internal combustion engines. The multi-functional additive package comprising: A) about 2.4 to about 90% by weight of a blend of: I) at least one oxygen-containing compound, II) at least one nitrogen-containing compound, B) about 2.5 to about 90% by weight of at least one lubricity, and C) about 2.5 to less than about 50% by weight of at least one solvent.

[0005] Ethanol is a clean, reliable, and sustainable energy candidate for meeting the growing demands of alternate fuels. The major challenge in implementing the higher ethanol blended fuel is corrosion issues. Ethanol has a high affinity for absorbing moisture and this causes general and localized corrosion. Interestingly, under some conditions, dissolved oxygen initiates the oxidation of ethanol into acid, leading to an increase in the acidity of the medium.

[0006] It has been observed that ethanol has a superior tendency to increase the octane number and it is an eco-friendly fuel. It is being blended regularly with MS. The corrosiveness of the ethanol-blended fuel depends on the hygroscopic property of the medium. Small amounts of water ingress and dissolved oxygen are expected to be present in gasoline and this increases the susceptibility of materials to general and localized corrosion. The cost-effective method to mitigate corrosion in gasohol is the addition of a suitable corrosion inhibitor. The key performance indicator of the corrosion inhibitor is to meet a NACE Standard method rating of B+ (less than 5% surface rust) or better for the recommended treat rate. Considering the mandate for increasing ethanol blending in Gasoline and market demand for corrosion inhibitors for gasohol blends, thus there is a need to develop corrosion inhibitors exclusively for ethanol storage and gasohol blends.

OBJECTS OF THE INVENTION

[0007] An objective of the present invention is to provide a composition for corrosion inhibition in a fuel mixture.

[0008] Another objective of the present invention is to provide a method for preparing a composition for corrosion inhibition in a fuel mixture.

[0009] Yet another objective of the present invention is to provide a fuel composition.

[0010] Another objective of the present invention is to provide use of a composition for corrosion inhibition.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

Figure 1: Pictorial representation of coupons (left to right) (i) in ethanol - in the absence of corrosion inhibitor, (ii) E5 blend (iii) E10 blend (iv) E20 blend (v) in ethanol - presence of corrosion inhibitor.

Figure 2: Electrochemical impedance spectroscopy of carbon steel with inhibitor in (a) E10 and (b) E20. Inset figure shows the reference medium without inhibitor addition.

Figure 3: Tafel polarization curve of carbon steel in (a) E10 and (b) E20 blends in the absence and presence of corrosion inhibitor.

Figure 4: Image of the NACE tested sample for ethanol taken from Tank 6, Tank 12, Tank 19, Tank 20 and Tank 21 after 1-month addition of corrosion inhibitor.

SUMMARY OF THE INVENTION

[0012] This summary is provided to introduce a selection of concepts in a simplified form that are further described below in Detailed Description section. This summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used as an aid in determining the scope of the claimed subject matter.

[0013] The present disclosure discloses a composition for corrosion inhibition in a fuel mixture having 0.1-4 w/w % of an amine; 0.1-4 w/w % of a quaternary ammonium salt; 0.1-3 w/w % of an antioxidant; 30-60 w/w % of a polar solvent; and 30-60 w/w % of a hydrocarbon-based solvent, wherein the w/w % is based on the total weight of the composition.

[0014] The present disclosure discloses a method for preparing a composition for corrosion inhibition in a fuel mixture having a) mixing 30-60 w/w % of a polar solvent, 0.1-3 w/w % of an antioxidant, 0.1-4 w/w % of a quaternary ammonium salt and 0.1-4 w/w % of an amine to obtain a first mixture; and b) mixing 30-60 w/w % of hydrocarbon-based solvent to the first mixture to obtain a corrosion inhibitor in a fuel mixture, wherein the w/w % is based on the total weight of the composition.

[0015] The present disclosure also discloses a fuel composition having a fuel mixture, and 10 to 200 ppm of a composition comprising: 0.1-4 w/w % of an amine; 0.1-4 w/w % of a quaternary ammonium salt; 0.1-3 w/w % of an antioxidant; 30-60 w/w % of a polar solvent; and 30-60 w/w % of a hydrocarbon-based solvent, wherein the w/w % is based on the total weight of the composition.

[0016] The present disclosure also discloses the use of a composition having 0.1-4 w/w % of an amine; 0.1-4 w/w % of a quaternary ammonium salt; 0.1-3 w/w % of an antioxidant; 30-60 w/w % of a polar solvent; and 30-60 w/w % of a hydrocarbon-based solvent, wherein the w/w % is based on the total weight of the composition, as a corrosion inhibitor in a fuel mixture of ethanol and gasoline.

[0017] Various objects, features, aspects and advantages of the inventive subject matter will become more apparent from the following detailed description of preferred embodiments.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The following is a detailed description of embodiments of the disclosure. The embodiments are in such detail as to clearly communicate the disclosure. However, the amount of detail offered is not intended to limit the anticipated variations of embodiments; on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the present disclosure as defined by the appended claims.

[0019] Unless the context requires otherwise, throughout the specification which follow, the word "comprise" and variations thereof, such as, "comprises" and "comprising" are to be construed in an open, inclusive sense that is as "including, but not limited to."

[0020] As used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the content clearly dictates otherwise. It should also be noted that the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

[0021] In some embodiments, the numbers expressing quantities of ingredients, properties such as concentration, reaction conditions, and so forth, used to describe and claim certain embodiments of the invention are to be understood as being modified in some instances by the term "about." Accordingly, in some embodiments, the numerical parameters set forth in the written description are approximations that can vary depending upon the desired properties sought to be obtained by a particular embodiment. In some embodiments, the numerical parameters should be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of some embodiments of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as practicable.

[0022] The recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each individual value is incorporated into the specification as if it is individually recited herein.

[0023] All processes described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g. "such as") provided with respect to certain embodiments herein is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention otherwise claimed. No language in the specification should be construed as indicating any non-claimed element essential to the practice of the invention.

[0024] The headings and abstract of the invention provided herein are for convenience only and do not interpret the scope or meaning of the embodiments.

[0025] The following discussion provides many example embodiments of the inventive subject matter. Although each embodiment represents a single combination of inventive elements, the inventive subject matter is considered to include all possible combinations of the disclosed elements. Thus if one embodiment comprises elements A, B, and C, and a second embodiment comprises elements B and D, then the inventive subject matter is also considered to include other

remaining combinations of A, B, C, or D, even if not explicitly disclosed.

[0026] All publications herein are incorporated by reference to the same extent as if each individual publication or patent application were specifically and individually indicated to be incorporated by reference. Where a definition or use of a term in an incorporated reference is inconsistent or contrary to the definition of that term provided herein, the definition of that term provided herein applies and the definition of that term in the reference does not apply.

[0027] Groupings of alternative elements or embodiments of the invention disclosed herein are not to be construed as limitations. Each group member can be referred to and claimed individually or in any combination with other members of the group or other elements found herein. One or more members of a group can be included in, or deleted from, a group for reasons of convenience and/or patentability. When any such inclusion or deletion occurs, the specification is herein deemed to contain the group as modified thus fulfilling the written description that follows, and the embodiments described herein, is provided by way of illustration of an example, or examples, of particular embodiments of the principles and aspects of the present disclosure. These examples are provided for the purposes of explanation, and not of limitation, of those principles and of the disclosure.

[0028] It should also be appreciated that the present invention can be implemented in numerous ways, including as a system, a method or a device. In this specification, these implementations, or any other form that the invention may take, may be referred to as processes. In general, the order of the steps of the disclosed processes may be altered within the scope of the invention.

[0029] Various terms as used herein are shown below. To the extent a term used in a claim is not defined below, it should be given the broadest definition persons in the pertinent art have given that term as reflected in printed publications and issued patents at the time of filing.

[0030] Ethanol is a clean, reliable, and sustainable energy candidate for meeting the growing demands of alternate fuels. Ethanol blending with gasoline provides superior combustion and socio-economic benefits. The transition from 10% ethanol blended fuel to 20 % ethanol blended fuel in future as aimed to bring added advantages to the refinery and automation industries. As mentioned in background section that the major challenge in implementing the E20 blended fuel is corrosion issues. Ethanol has a high affinity for absorbing moisture and this causes general and localized corrosion. Interestingly, under some conditions, dissolved oxygen initiates the oxidation of ethanol into acid, leading to an increase in the acidity of the medium. The efficacy of a novel chemical formulation has been extensively analyzed for mitigating the corrosion issues in neat ethanol, E10 and E20 blends using international standards. These formulations do not alter any of the properties of the gasoline and can be used in various marketing and distribution areas.

[0031] The novel corrosion inhibitor delivers excellent corrosion resistance, minimum dosage levels & good stability and miscibility which can be used for mitigating corrosion issues in neat Ethanol and Gasohol.

[0032] In the present context, "gasohol" refers to a blend of ethanol and gasoline. Further, gasoline may be alternately referred to as motor spirit in the description to follow.

[0033] An aspect of the present disclosure relates to a composition for corrosion inhibition in a fuel mixture.

[0034] In an embodiment, the composition comprises: 0.1-4 w/w % of an amine; 0.1-4 w/w % of a quaternary ammonium salt; 0.1-3 w/w % of an antioxidant; 30-60 w/w % of a polar solvent; and 30-60 w/w % of a hydrocarbon-based solvent, wherein the w/w % is based on the total weight of the composition.

[0035] In an embodiment of the present disclosure, the weight ratio between the polar solvent and the hydrocarbon-based solvent is in the range of 1:4 to 4: 1, or 1:3 to 3:1, or 1:2 to 2:1. Preferably, the weight ratio between the polar solvent and the hydrocarbon-based solvent is 1: 1.

[0036] In an embodiment of the present disclosure, the amine is derived from an aliphatic base having 4 to 18 carbon atoms, or 4 to 16 carbon atoms, or 4 to 12 carbon atoms, or 4 to 8 carbon atoms. Preferably, the amine is derived from aliphatic base having 4 to 6 carbon atoms.

[0037] In an embodiment of the present disclosure, the quaternary ammonium salt is selected from a group consisting of tetraalkyl ammonium halide, trialkylmethyl ammonium halide, dialkyldimethyl ammonium halide, tetrabutyl ammonium halide, and combinations thereof. Preferably, chloride and/or bromide are used as halide in the above quaternary ammonium salt.

[0038] In an embodiment of the present disclosure, the antioxidant is selected from a group consisting of amine antioxidants, sterically hindered phenolic antioxidants, polyhydroxy phenolic antioxidants, derivatives and mixtures thereof. The sterically hindered phenolic antioxidant is selected from a group consisting of 2-methyl-6-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol, 4-(N,N-di-methylaminomethyl)-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tertbutylphenol, 2,6-bis(1,1-dimethylethyl)-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, and combinations thereof.

[0039] In an embodiment of the present disclosure, the sterically hindered phenolic antioxidant is selected from the group consisting of 4-ethyl-2,6-di-tertbutylphenol, 2,6-bis(1,1-dimethylethyl)-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n- butylphenol, and combinations thereof.

[0040] In an embodiment of the present disclosure, the sterically hindered phenolic antioxidant is selected from the

group consisting of 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, and combinations thereof.

[0041] In an embodiment of the present disclosure, the polar solvent is selected from a group consisting of acetone, methanol, ethanol, ethylacetate, butanol, isopropyl alcohol, and combination thereof. In another embodiment of the present disclosure the polar solvent is selected from the group consisting of ethanol, ethylacetate, butanol, isopropyl alcohol, and combination thereof.

[0042] In an embodiment of the present disclosure, the hydrocarbon-based solvent is selected from a group consisting of kerosene, toluene, xylene, hexane, petroleum ether, heptane, and combinations thereof. In another embodiment of the present disclosure the hydrocarbon-based solvent is selected from a group consisting of kerosene, toluene, xylene, petroleum ether, and combinations thereof.

[0043] In an embodiment, the corrosion inhibitor is effective for gasohol blends comprising 5 to 100 volume % of ethanol.

[0044] In an embodiment, the present disclosure discloses that the composition is capable of attaining a B++(<0.1 %) rating for carbon steel in accordance with NACE standards for E5-E50 blends and neat ethanol.

[0045] In an embodiment, the present disclosure discloses that the composition works for the gasohol blends and neat ethanol where conductivity values are as high as 2.4 μS/sec. The composition works effectively for different temperature regimes for carbon steel was investigated using pHe (ASTM D 6423) for a wide range of temperature, which varies from subzero temperature 50 °C. The composition provides the increment of charge transfer resistance (R_{ct} value) deduced from the electrochemical impedance spectroscopy (EIS) improves by 92.32%.

[0046] Another aspect of the present disclosure relates to a method for preparing the above composition. Accordingly, the embodiments described hereinabove in respect of the composition are applicable here as well.

[0047] In an embodiment, the method comprises: a) mixing 30-60 w/w % of a polar solvent, 0.1-3 w/w % of an antioxidant, 0.1-4 w/w % of a quaternary ammonium salt and 0.1-4 w/w % of an amine to obtain a first mixture; and b) mixing 30-60 w/w % of hydrocarbon-based solvent to the first mixture to obtain a corrosion inhibitor in a fuel mixture, wherein the w/w % is based on the total weight of the composition.

[0048] In an embodiment, the present disclosure discloses that the stirring in step a) and b) are carried out for a period in the range of 45-50 minutes and 25-35 minutes respectively, preferably at 45 and 30 minutes respectively. The stirring is carried out at a speed in the range of 50-150 rpm, preferably at 100 rpm.

[0049] Another aspect of the present disclosure relates to a fuel composition comprising a fuel mixture, and the composition described above. Accordingly, the embodiments described hereinabove in respect of the composition are applicable here as well.

[0050] In an embodiment of the present disclosure, the fuel composition comprises: the fuel mixture, and 10 to 200 ppm of the composition comprising 0.1-4 w/w % of an amine; 0.1-4 w/w % of a quaternary ammonium salt; 0.1-3 w/w % of an antioxidant; 30-60 w/w % of a polar solvent; and 30-60 w/w % of a hydrocarbon-based solvent, wherein the w/w % is based on the total weight of the composition.

[0051] In an embodiment of the present disclosure, the fuel mixture comprises ethanol and gasoline.

[0052] Another aspect of the present disclosure relates to the use of the composition, described herein above. Accordingly, the embodiments described hereinabove in respect of the composition are applicable here as well.

[0053] An embodiment of the present disclosure discloses the use of the composition comprising: 0.1-4 w/w % of an amine; 0.1-4 w/w % of a quaternary ammonium salt; 0.1-3 w/w % of an antioxidant; 30-60 w/w % of a polar solvent; and 30-60 w/w % of a hydrocarbon-based solvent, wherein the w/w % is based on the total weight of the composition, as a corrosion inhibitor in a fuel mixture of ethanol and gasoline.

[0054] While the foregoing describes various embodiments of the disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof. The invention is not limited to the described embodiments, versions or examples, which are included to enable a person having ordinary skill in the art to make and use the invention when combined with information and knowledge available to the person having ordinary skill in the art.

EXAMPLES

[0055] The present invention is further explained in the form of following examples. However, it is to be understood that the following examples are merely illustrative and are not to be taken as limitations upon the scope of the invention.

General synthesis of corrosion inhibitor

[0056] To prepare corrosion inhibitor formulations, 0.1-4 w/w% of polar solvent, 0.1-3 w/w% of antioxidant and 0.1-4 w/w% of quaternary ammonium salt, suitably selected from the above table, were stirred for 45 minutes at 100 rpm to obtain the first mixture. Subsequently, 30-60 w/w % of the hydrocarbon-based solvent, suitably selected from the above table, was added to the first mixture and stirred for 25 minutes at 100 rpm to obtain different corrosion inhibitor formulations. Table A below summarizes the formulations and their ingredients:

Table A: Inventive and comparative examples

Examples	Amine	Quaternary amm. Salt	Sterically hindered phenolic antioxidant	Polar solvent:HC solvent
Inv. Ex. 1	4-5 w/w%			1:1
Comp. Ex. 1	6 w/w%	6 w/w%	4 w/w%	5:1
Comp. Ex. 2	1-2 w/w%	1-2 w/w%	1-2 w/w%	5:1

NACE TM0172 Rust Prevention Test

[0057] Antirust performance of the formulations was determined according to "NACE standard TM-01-72-Antirust Properties of petroleum products Pipeline Cargoes". The test method is essentially the ASTM D665 method modified to determine antirust properties of gasoline and distillate fuels in movement through pipelines. The method involves immersing a cylindrical carbon steel test specimen in 300 mL of the test fuel (ethanol/gasohol), which is stirred for 4 hours at 38-40 °C. 30 mL of distilled water is added to the test fuel after 30 minutes. The antirust rating is based on the portion of the test specimen that has changed after the 4 hours and is represented using the following rating scale along with the corrosion rate (Table 1). The same procedure is repeated with a corrosion inhibitor added to ethanol/gasohol.

Table 1: Corrosion rating as per NACE standards.

Rating	The proportion of the test surface rusted
A	0
B++	Less than 0.1% (2 or 3 spots of no more than 1 mm diameter
B+	Less than 5%
B	5-25
C	25-50
D	50-75
E	75-100

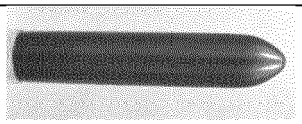
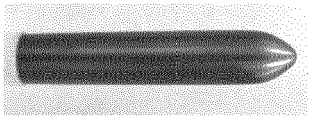
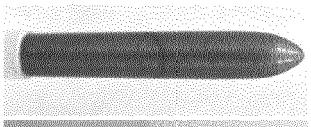
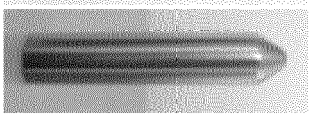
[0058] The fuel blend with corrosion inhibitor must meet a NACE Standard Test rating of B+ (less than 5% surface rust) or better for the recommended treat rate to be acceptable.

Rust Prevention Test

Ethanol system

[0059] Based on the different combinations of amines, antioxidants, and quaternary ammonium salts, several formulations were made. Carbon steel coupon is severely corroded in the absence of either one of these above components in the formula. As a result, single package of efficient constituents made an excellent inhibitor. The formulations have been found suitable for the ethanol systems and gasohol, meeting the B++ rating. Table 2, showed the corrosion percentage, rating and metal image of the coupon in NACE test in-where the necessity of each ingredient in the formula has been found out.

Table 2: Corrosion rating as per NACE standards for formula different component at 200 ppm in ethanol.

Formulation	C %	Rating	Metal Image
Absence of amine	72.1	D	
Absence of antioxidant	56.2	D	
Absence of quaternary ammonium salts	63.4	D	
Inv. Ex.1	0.03	B++	

[0060] Without any inhibitor addition, the ethanol system shows a rating of D, with ~56-72% corrosion percentage. As can be seen from above table, ethanol with the present formulation exhibited a rating of B++ with corrosion percentage of 0.03 %.

Gasohol system

[0061] After the performance evaluation of the above formulations in ethanol medium as shown in Table 2, these formulations were evaluated for their performance with different weight percentage in different blends to measure the potential inhibition towards hindering the corrosion of metal (E5 with 10 ppm of and E10 with 20 ppm of inhibitor). These observations are tabulated in Table 3.

[0062] Table 3: Corrosion rating as per NACE standards for different formulations in gasohol blends (E5 and E10)

Formulation	E5		E10	
	C%	Rating	C%	Rating
Comp. Ex.1	11	C	57.2	**D**
Inv. Ex.1	**0.03**	**B++**	**0.08**	**B++**
Comp. Ex.2	7	B	8.6	B

[0063] It was observed that except for Inv. Ex. 1, the remaining formulations have failed to meet the KPI of B+. In view of the same, Inv. Ex. 1 was shortlisted for further studies.

Optimization of the dosage

[0064] The composition was further optimized for the concentration of its active components and the impact of various dosage of the inhibitor on different blends (E5, E10, and E20) was studied. The minimum NACE standard test rating requirement is B+. The formulations were optimized for a rating of B++ for longer life of structures at the operations and distribution networks. The observations are tabulated in Table 4 for both neat ethanol and different gasohol blends.

Table 4: Corrosion rating as per NACE standards for different concentrations of Corrosion Inhibitor formulation.

Inhibitor dosage (ppm)	E5		E10		E20		Ethanol	
	C%	Rating	C%	Rating	C%	Rating	C%	Rating
10	24.1	B	-	-	-	-	-	-
11	1.2	B+						

(continued)

Inhibitor dosage (ppm)	E5		E10		E20		Ethanol	
	C%	Rating	C%	Rating	C%	Rating	C%	Rating
12	**0.03**	**B++**	-	-	-	-	-	-
15	0.03	B++	-	-	-	-	-	-
16			12.8	B				
17	-	-	0.1	B+	-	-	-	-
18	-	-	**0.04**	**B++**	-	-	-	-
20	-	-	0.09	B++	-	-	-	-
25	-	-	-	-	20.8	B	-	-
28					2.9	B+		
30	-	-	-	-	**0.06**	**B++**	-	-
40	-	-	-	-	0.03	B++		
150	-	-	-	-	-	-	20	B
180	-	-	-	-	-	-	5.6	B
200	-	-	-	-	-	-	**0.04**	**B++**
300	-	-	-	-	-	-	0.3	B+

[0065] The concentration optimization studies show the required inhibitor dosage of the inhibitor. Dosage requirement for neat ethanol protection was 200 ppm of corrosion inhibitor. For E5, E10 and E20 blends, the optimum dosage of corrosion inhibitor was 12, 18 and 30 ppm respectively, with B++ rating. However, Corrosion % was less in all cases for corrosion inhibitor.

Electrochemical Characterization

[0066] The electrochemical property of the corrosion inhibitor in E10 and E20 were studied for carbon steel. Fig. 2 shows the Nyquist plots of the sample in the absence and presence of inhibitor varies from 18 ppm and 30 ppm for E10 and E20 blends, respectively. Figure shows the clear observation of single time constant, confirms the double layer formed between solution and metal substrate. It can be observed from Table 5 that R_{ct} values are increasing with decrease of CPE value as the concentration of corrosion inhibitor increased. Inhibitor adsorbed on the metal surface which protects the metal from further dissolution in corrosive medium. As a result, less surface will be exposed and maximum protection efficiency of 91 and 92 % and corresponding charge resistance value of 502 and 404 ohm attained for E10 and E20 respectively.

Table 5: Electrochemical impedance parameter of carbon steel in E10 and E20 blends in the absence and presence of corrosion inhibitor.

Blend	Inhibitor Concentration (ppm)	R_s (ohm)	CPE, Y_0 ($\mu F/cm^2$)	n	R_{ct} (ohm)	IE (%)
E10	Blank	7.9	372.4	0.88	44.6	-
	18	169	176.9	0.81	502	91
E20	Blank	5.9	238	0.82	31	-
	30	198	186.8	0.85	404	92

[0067] Fig.3 shows the Tafel plot of the carbon steel in E10 and E20 blended medium in the absence and presence of corrosion inhibitor. The polarization parameters were derived from the extrapolation of the anodic and cathodic curve and exhibited in the Table 6. The value of the βa reduced with corrosion inhibitor concentration, denotes the reduction of anodic reaction at the metal surface. The inhibited system showed lower corrosion potential, corrosion current, slope values and higher corrosion resistance value. The E_{corr} value shift from negative to positive potential in the inhibited medium revealed that corrosion inhibitor was passivating effectively on the metal surface in both E10 and E20 blended medium. Hence, the i_{corr} value decreased as shown in the following Table 6.

Table 6: Tafel polarization parameter of carbon steel in E10 and E20 blends in the absence and presence of corrosion inhibitor.

Blend	Inhibitor Concentration (ppm)	$-E_{corr}$ (mV)	βa (mV/dec)	βc (mV/dec)	i_{corr} ($\times 10^{-4}$ A/cm^2)	Inhibitor Efficiency (%)
E10	Blank	513	108	91	3.0	-
	18	406	82	98	0.18	94
E20	Blank	497	126	110	3.80	-
	30	435	101	132	0.13	96.5

Temperature effect:

[0068] Corrosion Inhibitor efficacy over temperature was evaluated using NACE test. The corrosion inhibitor was mixed up with ethanol and blends E5 and E10 and stored at different temperature -4, 10, 30 and 50 °C for 24h. Later, the density and corrosion parameters were studied from different standards. Density of the ethanol and blends did not change with temperature as seen from the Table 7. The corrosion rating of coupon in ethanol, E10 and E20 for the different temperature exposed B++ rating and density of ethanol, E10 and E20 were 0.7941, 0.7578 and 0.77112 g/cc respectively in all temperature.

Table 7: Temperature effect on density of ethanol and blends and NACE

Sample	Temperature(°C)	Density (g/cc)	NACE Coupon	
			C%	Rating
Ethanol	-4	0.7941	0.09	B++
	10	0.7941	0.07	B++
	30	0.7941	0.1	B++
	50	0.7941	0.08	B++
E10	-4	0.7578	0.07	B++
	10	0.7578	0.06	B++
	30	0.7578	0.03	B++
	50	0.7578	0.05	B++
E20	-4	0.7712	0.07	B++
	10	0.7712	0.05	B++
	30	0.7712	0.01	B++
	50	0.7712	0.08	B++

pHe study

[0069] To observe the change of pHe in ethanol and E10 and E20 blends are determined using pHe (Ethanol electrode). The pHe of the medium was verified after the addition of the corrosion inhibitor and the pHe values were varied from 7.1-7.5. As observed from Table 8, the pHe values are not varying much in different medium, thereby inferring that the composition has not neither performed a pH booster role nor a neutralizer role, but an inhibitor. In addition, NACE corrosion test also exhibited the rating and corrosion percentage, wherein B++ rating was observed for all blended medium with different corrosion percentage.

Table 8: pHe effect on ethanol and blends in the presence of corrosion inhibitor.

Medium	pHe	NACE	
		Rating	C%
Ethanol	7.3	B++	0.01
Ethanol + corrosion inhibitor	7.5	B++	0.03
E10	7.2	B++	0.08
E10 + corrosion inhibitor	7.1	B++	0.06
E20	7.4	B++	0.07
E20 + corrosion inhibitor	7.5	B++	0.05

Stability study

[0070] The inhibition effect of corrosion inhibitor after six months of storage was evaluated using NACE Test TM0172. Corrosion inhibitor was stored in ambient temperature and pressure at chemical store room. Before and after storage of corrosion inhibitor, NACE test was performed and the results are shown in Table 9. The corrosion rating for ethanol, E10 and E20 before and after was B++. On the other hand, the C% values have not changed significantly.

Table 9: Stability (Time effect) of corrosion inhibitor in ethanol and blends.

Corrosion inhibitor after 6 months of storage	NACEtestingTM0172			
	Before		After	
	Rating	C%	Rating	C%
Neat ethanol	B++	0.07	B++	0.08
E10	B++	0.04	B++	0.06
E20	B++	0.03	B++	0.07

Field study and analysis:

[0071] The formulated corrosion inhibitor was sent to refinery locations and mixed up with ethanol stored in different underground tanks for field study and evaluation. Samples were collected from the terminal after a month of supply and the following parameters were evaluated and tabulated in Table 10. Various parameters like NACE rating, conductivity of ethanol, pHe of ethanol, and CHNS analysis of corrosion inhibitor were studied. NACE analysis reported B+ rating for all different tanks with the C% ranging between 0.8-2.8%. The quality of the ethanol was varied after a month-long addition of corrosion inhibitor. The conductivity of ethanol is expected to be in the range of 0.3-2.6 μS/cm after addition of corrosion inhibitor.

[0072] As seen in Table 10 it is evident that for all tanks the conductivity ranges between 1.4-2.4 μS/cm. The presence of corrosion inhibitor was confirmed with the CHNS analysis wherein nitrogen percentage was monitored and it was inferred that all tanks contain 0.3 % of nitrogen with acidity (pHe) of the ethanol also being monitored. The acidity reduction in between 5.3-7.3 infers that ethanol oxidation process is less after the addition of corrosion inhibitor.

[0073] It can be observed from the above parameters that the property of ethanol remained unaffected by the corrosion inhibitor during storage. Fig 4 shows the metal coupon after NACE test in ethanol collected from different tanks.

Table 10: Field study evaluation of corrosion inhibitor after a month of supplied to terminal.

Sample withdrawn from tank	NACE testing TM0172		Conductivity (μS/cm)	pHe	CHNS (%)
	Rating	C%			
Tank 6	B+	2.4	1.4	7.1	0.3
Tank 12	B+	1.2	2	7.3	0.3
Tank 19	B+	2.5	2.2	7.0	0.3
Tank 20	B+	0.8	2.4	6.9	0.3

(continued)

Sample withdrawn from tank	NACE testing TM0172		Conductivity (μS/cm)	pHe	CHNS (%)
	Rating	C%			
Tank 21	B+	1.7	2.3	5.3	0.3

MS properties

[0074] The gasohol properties and quality was verified using different standards after injection of the corrosion inhibitor in ethanol. The MS properties before and after addition of corrosion inhibitor in different blend like E5, E10 and E20 are tabulated in Table 11. It is observed from the Table that the quality and parameter of the gasohol remain unchanged in the presence of corrosion inhibitor.

Table 11: Motor Gasoline - Specification (MS- BS VI specification)

Characte ristics	Unit s	Test Metho d	Specificati ons for E10		MS	E5	E5 with CI (15 ppm dosag e)	E10	E10 with CI (18 ppm dosag e)	E20	E20 with CI (30 ppm dosag e)
			Mi n	Max							
Appearan ce	-	Visual	-		Bright & clear	Bright & clear	Bright & clear	Bright & clear	Bright & clear	Bright & clear	Bright & clear
Color	-	Visual	-		Orang e	Orang e	Orang e	Orang e	Orang e	Orang e	Orang e
Density @ 15°C	g/cm 3	IS 1448 P: 16	0.7 2	0.77 5	0.74	0.74	0.74	0.74	0.74	0.7635	0.7633
Distillatio n Recovery @ 70 °C	% vol	IS 144 8P:18/ ISO34 05	10	55	30	39	39	50	50	50	50
Distillatio n Recovery @ 100 °C	% vol	IS 144 8P:18/ ISO34 05	40	70	57	58	58	61	61	70	70
Distillatio n Recovery @ 150 °C	% vol	IS 144 8P:18/ ISO34 05	75	95	89	89	88	88	89	90	90
Distillatio n FBP	°C	IS144 8P: 18/ISO34 05	-	210	182	181.2	182.3	182.2	182.1	183.7	182.6
Distillatio n Residue	% vol	IS144 8P: 18/ISO34 05	-	2.0	0.6	0.6	1.1	1.2	1.1	0.6	0.4
Existent Gum	g/m^3	IS144 8P29	-	40	22	18	20	32	34	20	24
Total Sulphur	Mg/ Kg	ISO-20846	-	10	4	2	3	3	3	3	3
Cu Strip Corrosion for 3 hrs @ 50 °C	-	IS144 8P: 15	-	1A	1A	1A	1A	1A	1A	1A	1A

[0075] A skilled artisan will appreciate that the quantity and type of each ingredient can be used in different combinations or singly. All such variations and combinations would be falling within the scope of present disclosure.

[0076] The foregoing examples are merely illustrative and are not to be taken as limitations upon the scope of the invention. Various changes and modifications to the disclosed embodiments will be apparent to those skilled in the art. Such changes and modifications may be made without departing from the scope of the invention.

Claims

1. A composition for corrosion inhibition in a fuel mixture, the composition comprising:

   0.1-4 w/w % of an amine;
   0.1-4 w/w % of a quaternary ammonium salt;
   0.1-3 w/w % of an antioxidant;
   30-60 w/w % of a polar solvent; and
   30-60 w/w % of a hydrocarbon-based solvent,
   wherein the w/w % is based on the total weight of the composition.

2. The composition as claimed in claim 1, wherein the weight ratio between the polar solvent and the hydrocarbon-based solvent is in the range of 1:4 to 4:1.

3. The composition as claimed in claim 1, wherein the amine is derived from an aliphatic base having 4 to 18 carbon atoms.

4. The composition as claimed in claim 1, wherein the quaternary ammonium salt is selected from a group consisting of tetraalkyl ammonium halide, trialkylmethyl ammonium halide, dialkyldimethyl ammonium halide, tetrabutyl ammonium halide and combination thereof.

5. The composition as claimed in claim 1, wherein the antioxidant is selected from a group consisting of amine antioxidants, sterically hindered phenolic antioxidants, polyhydroxy phenolic antioxidants, derivatives and mixtures thereof.

6. The composition as claimed in claim 5, wherein the sterically hindered phenolic antioxidant is selected from a group consisting of 2-methyl-6-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol, 4-(N,N-di-methylaminomethyl)-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tertbutylphenol, 2,6-bis(1,1-dimethylethyl)-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-n-butylphenol and combination thereof.

7. The composition as claimed in claim 1, wherein the polar solvent is selected from a group consisting of acetone, methanol, ethanol, ethylacetate, butanol, isopropyl alcohol and combination thereof.

8. The composition as claimed in claim 1, wherein the hydrocarbon-based solvent is selected from a group consisting of kerosene, toluene, xylene, hexane, petroleum ether, heptanes and combination thereof.

9. The composition as claimed in claim 1, wherein the corrosion inhibitor is effective for gasohol blends comprising 5 to 100 volume % of ethanol.

10. The composition as claimed in claim 1, wherein the composition is capable of attaining a B^{++}(<0.1 %)rating for carbon steel in accordance with NACE standards for E5-E50 blends and neat ethanol.

11. A method for preparing a composition for corrosion inhibition in a fuel mixture, said method comprising:

    a) mixing 30-60 w/w % of a polar solvent, 0.1-3 w/w % of an antioxidant, 0.1-4 w/w % of a quaternary ammonium salt and 0.1-4 w/w % of an amine to obtain a first mixture; and
    b) mixing 30-60 w/w % of hydrocarbon-based solvent to the first mixture to obtain a corrosion inhibitor in a fuel mixture,

    wherein the w/w % is based on the total weight of the composition.

12. A fuel composition comprising:

a fuel mixture, and
10 to 200 ppm of a composition comprising:

0.1-4 w/w % of an amine;
0.1-4 w/w % of a quaternary ammonium salt;
0.1-3 w/w % of an antioxidant;
30-60 w/w % of a polar solvent; and
30-60 w/w % of a hydrocarbon-based solvent,
wherein the w/w % is based on the total weight of the composition.

13. The fuel composition as claimed in claim 11, wherein the fuel mixture comprises ethanol and gasoline.

14. Use of a composition comprising

0.1-4 w/w % of an amine;
0.1-4 w/w % of a quaternary ammonium salt;
0.1-3 w/w % of an antioxidant;
30-60 w/w % of a polar solvent; and
30-60 w/w % of a hydrocarbon-based solvent,
wherein the w/w % is based on the total weight of the composition,
as a corrosion inhibitor in a fuel mixture of ethanol and gasoline.

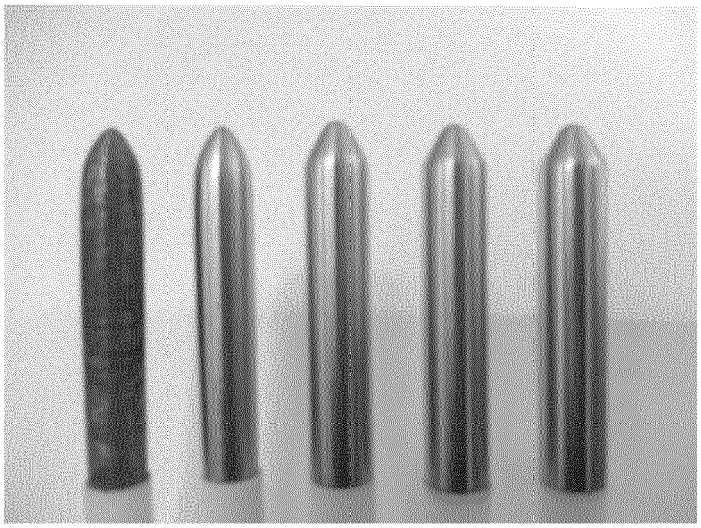


Fig. 1

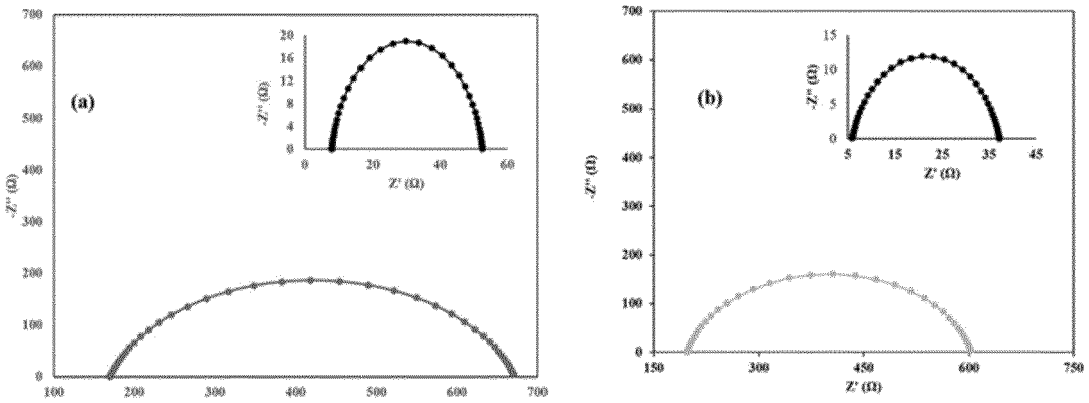


Fig. 2

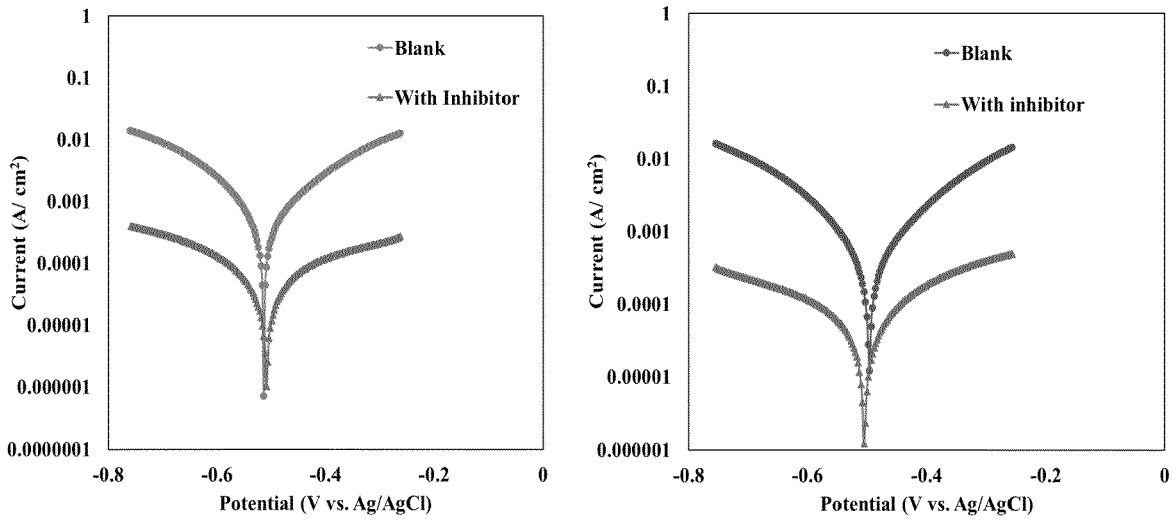

1
0.1
0.01
0.001
0.0001
0.00001
0.000001
0.0000001
Current (A/ cm²)
Blank
With Inhibitor
-0.8
-0.6
-0.4
-0.2
0
Potential (V vs. Ag/AgCl)
1
0.1
0.01
0.001
0.0001
0.00001
0.000001
Current (A/ cm²)
Blank
With inhibitor
-0.8
-0.6
-0.4
-0.2
0
Potential (V vs. Ag/AgCl)

Fig. 3

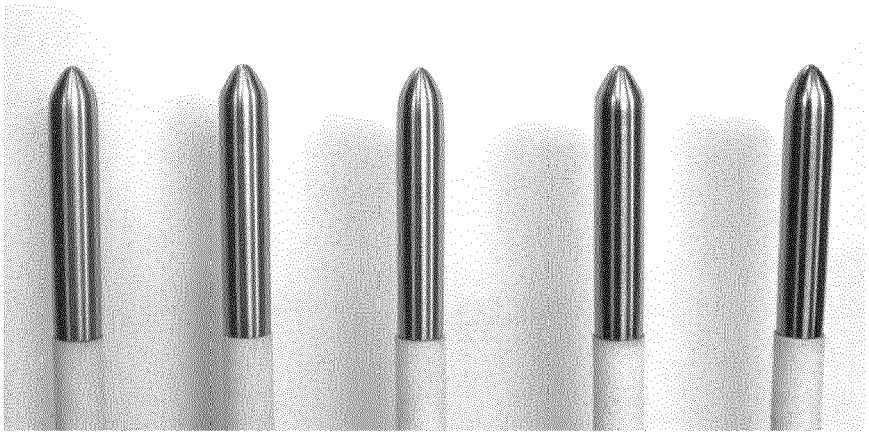


Fig. 4

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EUROPEAN SEARCH REPORT

Application Number
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A	* paragraphs [0001], [0006] - [0016], [0047] - [0073], [0080], [0081], [0090] - [0109] * * claims; example 3 *	4,13,14	C10L1/223
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	14 August 2024	Keipert, Olaf

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