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(54) Title: A NEUTRALIZING AMINE FORMULATION AND PROCESS OF PREPARATION THEREOF

(57) Abstract: The instant disclosure provides formulation for corrosion inhibition. The formulation comprising: a) at least one first amine; and b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1. The instant disclosure also provides a process for preparing the formulation. Also, the instant disclosure provides a method of reducing fouling in a petroleum refinery.

A NEUTRALIZING AMINE FORMULATION AND PROCESS OF PREPARATION THEREOF

FIELD OF THE INVENTION

5 **[001]** The present disclosure generally relates to the field of inhibiting corrosion in the crude distillation units of refineries. In particular the present disclosure discloses a formulation which combats the problem associated of condensing hydrocarbons which contain water and chlorides

BACKGROUND OF THE INVENTION

10 **[002]** Refineries employ neutralizing amines to guard their crude distillation unit overhead systems from corrosion due to hydrochloric acid (HCl) or acidic sulfur species and fouling due to build-up of sublimating species. The amines are usually organic amines (such as di-ethanol amine, monoethanol amine, triethanolamine, morpholine, piperazine, etc.) which function by neutralizing acidic contaminants, thereby increasing
15 the pH to an appropriate level for minimizing corrosion of the various system. Unfortunately, some of the best amines for refinery steam system protection are the least compatible with the crude unit processes.

[003] US 4,062,764 discloses that alkoxylated amines are useful in neutralizing the initial condensate. US 3,472,666 suggests that alkoxy substituted aromatic amines in
20 which the alkoxy group contains from 1 to 10 carbon atoms are effective corrosion inhibitors in petroleum refining operations. Representative examples of these materials are aniline, anisidine and phenetidines.

[004] US 4,430,196 discloses the utility of hydroxylated amines. Representative examples of these neutralizing amines are dimethylisopropanolamine and
25 dimethylaminoethanol.

[005] US 3,981,780 suggests that a mixture of the salt of a dicarboxylic acid and cyclic amines are useful corrosion inhibitors when used in conjunction with traditional neutralizing agents, such as ammonia.

[006] Many problems are associated with traditional neutralizing amines, i.e.,
30 formation of hydrochloride or sulfide salts of those neutralizing amines which will

condense at the water dew point on metallic surfaces. The salts appear before the dew point of water is reached and result in fouling and under-deposit corrosion.

[007] Accordingly, there is a need in the art for a neutralizing formulation/agent which can effectively neutralize the acidic species and as a result combat the primary corrosion problem encountered in crude distillation unit overhead systems.

SUMMARY OF THE INVENTION

[008] In an aspect of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8:

1 – 10: 1.

[009] In an aspect of the present disclosure, there is provided a process for preparing the formulation comprising: (a) at least one first amine; and (b) at least one second amine, the process comprising: (a) obtaining the at least one first amine; (b) obtaining the at least one second amine; (c) contacting the at least one first amine, the at least one second amine, and optionally the at least one additive to obtain the formulation, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1.

[0010] In an aspect of the present disclosure, there is provided a method of reducing fouling in a petroleum refinery comprising, adding the formulation comprising: (a) at least one first amine; and (b) at least one second amine to a water system.

[0011] These and other features, aspects, and advantages of the present subject matter will be better understood with reference to the following description and appended claims. This summary is provided to introduce a selection of concepts in a simplified form. This summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter.

DETAILED DESCRIPTION OF THE INVENTION

[0012] Those skilled in the art will be aware that the present disclosure is subject to variations and modifications other than those specifically described. It is to be understood that the present disclosure includes all such variations and modifications.

The disclosure also includes all such steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any or more of such steps or features.

Definitions:

5 **[0013]** For convenience, before further description of the present disclosure, certain terms employed in the specification, and examples are collected here. These definitions should be read in the light of the remainder of the disclosure and understood as by a person of skill in the art. The terms used herein have the meanings recognized and known to those of skill in the art, however, for convenience and completeness, particular
10 terms and their meanings are set forth below.

[0014] The articles “a”, “an” and “the” are used to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article.

[0015] The terms “comprise” and “comprising” are used in the inclusive, open sense, meaning that additional elements may be included. It is not intended to be construed as
15 “consists of only”.

[0016] The term fouling and/or corrosion problem refers to aqueous corrosion due to hydrochloric acid (HCl) or acidic sulfur species, or the build-up of sublimating species such as ammonium chloride under deposit corrosion in distillation units.

[0017] The term “surfactant amine” refer to fatty acid amines which can be used as
20 surfactants. Such surfactant amines include, by way of example C₁₋₁₀ alkyl ammonium chloride, alkyldimethyl ammonium chloride. The term alkyl herein refers to a branched or unbranched chain having 1-10 carbon atoms. Additionally, the surfactant amines in the present disclosure are those which are known to a person skilled in the art.

[0018] The term “ionic liquid” are used to refer quaternary ammonium compounds
25 known to a person skilled in the art.

[0019] Throughout this specification, unless the context requires otherwise the word “comprise”, and variations such as “comprises” and “comprising”, will be understood to imply the inclusion of a stated element or step or group of element or steps but not the exclusion of any other element or steps.

[0020] The term “including” is used to mean “including but not limited to”, “including” and “including but not limited to” are used interchangeably.

[0021] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the disclosure, the preferred methods, and materials are now described. All publications mentioned herein are incorporated herein by reference.

[0022] Ratios, concentrations, amounts, and other numerical data may be presented herein in a range format. It is to be understood that such range format is used merely for convenience and brevity and should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a weight percentage of about 50 % to 90 % should be interpreted to include not only the explicitly recited limits of about 50% and 90 %, but also to include sub-ranges, such as 55-85 %, 65-75%, and so forth, as well as individual amounts, including fractional amounts, within the specified ranges, such as 90 %, 85 %, for example.

[0023] The present disclosure is not to be limited in scope by the specific embodiments described herein, which are intended for the purposes of exemplification only. Functionally equivalent products, compositions, and methods are clearly within scope of the disclosure, as described herein.

[0024] As discussed in the background section, to counter the problems associated with the traditional neutralizing amines, the formulation of the present disclosure provides a neutralizing formulation/agent comprising: (a) at least one first amine; and (b) at least one second amine. The at least one first amine to the at least one second amine present in the formulation can have a weight ratio is in the range of 8: 1 – 10: 1. The neutralizing formulation effectively neutralizes the acidic species and as a result combat the primary corrosion problem encountered in crude distillation unit overhead systems.

[0025] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8:1 – 10: 1.

5 [0026] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8.5: 1 – 9.5: 1.

[0027] In an embodiment of the present disclosure, there is provided a formulation
10 comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is 9:1.

[0028] In an embodiment of the present disclosure, there is provided a formulation as described herein, wherein the at least one first amine has a weight percentage in the range of 50 to 95 % with respect to the formulation.

15 [0029] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8:1 – 10: 1 and the at least one first amine has a weight percentage in the range of 50 to 95 % with respect to the formulation.

20 [0030] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8.5: 1 – 9.5: 1 and the at least one first amine has a weight percentage in the range of 50 to 95 % with respect to the formulation.

25 [0031] In an embodiment of the present disclosure, there is provided a formulation as described herein, wherein the at least one first amine has a weight percentage in the range of 60 to 95 % with respect to the formulation. In another embodiment the at least one first amine has a weight percentage in the range of 75 to 92 % with respect to the formulation. In yet another embodiment the at least one first amine has a weight
30 percentage in the range of 80 to 90 % with respect to the formulation.

[0032] In an embodiment of the present disclosure, there is provided a formulation as described herein, wherein the at least one first amine is selected from the group consisting of diethanolamine, morpholine, monoethanolamine, triethanolamine, cyclohexylamine, piperazine, diethylaminoethanol, methyldiethanolamine, ethyl ethanolamine, aminoethyl piperazine, and combinations thereof.

[0033] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1 and the at least one first amine is selected from the group consisting of diethanolamine, morpholine, monoethanolamine, triethanolamine, cyclohexylamine, piperazine, diethylaminoethanol, methyldiethanolamine, ethyl ethanolamine, aminoethyl piperazine, and combinations thereof.

[0034] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8.5: 1 – 9.5: 1 and the at least one first amine is selected from the group consisting of diethanolamine, morpholine, monoethanolamine, triethanolamine, cyclohexylamine, piperazine, diethylaminoethanol, methyldiethanolamine, ethyl ethanolamine, aminoethyl piperazine, and combinations thereof.

[0035] In an embodiment of the present disclosure, there is provided a formulation as described herein, wherein the at least one first amine is selected from the group consisting of diethanolamine, morpholine, monoethanolamine, triethanolamine, cyclohexylamine, piperazine, diethylaminoethanol, and combinations thereof. In another embodiment the at least one first amine is selected from the group consisting of diethanolamine, morpholine, monoethanolamine, triethanolamine, cyclohexylamine, piperazine, and combinations thereof. In yet another embodiment the at least one first amine is selected from diethanolamine or morpholine. In yet another embodiment the at least one first amine is selected from the group consisting of diethanolamine, morpholine, diethylaminoethanol, and combinations thereof.

[0036] In an embodiment of the present disclosure, there is provided a formulation as described herein, wherein the at least one second amine has a weight percentage in the range of 5 to 15 % with respect to the formulation.

5 [0037] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1 and the at least one second amine has a weight percentage in the range of 5 to 15 % with respect to the formulation.

10 [0038] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8.5: 1 – 9.5: 1 and the at least one second amine has a weight percentage in the range of 5 to 15 % with respect to the formulation.

15 [0039] In an embodiment of the present disclosure, there is provided a formulation as described herein, wherein the at least one second amine has a weight percentage in the range of 6 to 15 % with respect to the formulation. In another embodiment the at least one second amine has a weight percentage in the range of 8 to 12 % with respect to the formulation. In yet another embodiment the at least one second amine has a weight percentage of 10 % with respect to the formulation.

20 [0040] In an embodiment of the present disclosure, there is provided a formulation as described herein, wherein the at least one second amine is a product of epichlorohydrin and the at least one first amine.

25 [0041] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1 and the at least one second amine is a product of epichlorohydrin and the at least one first amine and the at least one first amine.

30 [0042] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of

8.5: 1 – 9.5: 1 and the at least one second amine is a product of epichlorohydrin and the at least one first amine and the at least one first amine.

[0043] In an embodiment of the present disclosure, there is provided a formulation as described herein, wherein the at least one second amine is a product of epichlorohydrin and the at least one first amine, and has a weight percentage in the range of 5 to 15 % with respect to the formulation. In another embodiment the at least one second amine is a product of epichlorohydrin and the at least one first amine, and has a weight percentage in the range of 6 to 15 % with respect to the formulation. In one another embodiment the at least one second amine is a product of epichlorohydrin and the at least one first amine, has a weight percentage in the range of 8 to 12 % with respect to the formulation. In yet another embodiment the at least one second amine is a product of epichlorohydrin and the at least one first amine, and has a weight percentage of 10 % with respect to the formulation.

[0044] In an embodiment of the present disclosure, there is provided a formulation as described herein, wherein the at least one second amine is a product of epichlorohydrin and the at least one first amine selected from the group consisting of diethanolamine, morpholine, monoethanolamine, triethanolamine, cyclohexylamine, piperazine, diethylaminoethanol, methyldiethanolamine, ethyl ethanolamine, aminoethyl piperazine, and combinations thereof.

[0045] In an embodiment of the present disclosure, there is provided a formulation as described herein, wherein the at least one second amine has a weight percentage in the range of 5 to 15 % with respect to the formulation, and is a product of epichlorohydrin and the at least one first amine selected from the group consisting of diethanolamine, morpholine, monoethanolamine, triethanolamine, cyclohexylamine, piperazine, diethylaminoethanol, methyldiethanolamine, ethyl ethanolamine, aminoethyl piperazine, and combinations thereof.

[0046] In an embodiment of the present disclosure, there is provided a formulation as described herein, wherein the at least one second amine has a weight percentage in the range of 5 to 15 % with respect to the formulation, and is a product of epichlorohydrin and the at least one first amine selected from the group consisting of diethanolamine,

morpholine, monoethanolamine, triethanolamine, cyclohexylamine, piperazine, diethylaminoethanol, methyldiethanolamine, ethyl ethanolamine, aminoethyl piperazine, and combinations thereof and the at least one first amine has a weight percentage in the range of 50 to 95 % with respect to the formulation.

5 [0047] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1 and the at least one first amine is selected from the group consisting of diethanolamine, morpholine, monoethanolamine, triethanolamine, cyclohexylamine,
10 piperazine, diethylaminoethanol, methyldiethanolamine, ethyl ethanolamine, aminoethyl piperazine, and combinations thereof and the at least one second amine is a product of epichlorohydrin and the at least one first amine.

[0048] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the
15 at least one first amine to the at least one second amine weight ratio is in the range of 8.5: 1 – 9.5: 1 and the at least one first amine is selected from the group consisting of diethanolamine, morpholine, monoethanolamine, triethanolamine, cyclohexylamine, piperazine, diethylaminoethanol, methyldiethanolamine, ethyl ethanolamine, aminoethyl piperazine, and combinations thereof and the at least one second amine is a
20 product of epichlorohydrin and the at least one first amine.

[0049] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; (b) at least one second amine; and (c) at least one additive having a weight percentage in the range of 0 to 5 % with respect to the formulation; and is selected from the group consisting of surfactant amines, ionic
25 liquids, and combinations thereof.

[0050] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; (b) at least one second amine; and (c) at least one additive having a weight percentage in the range of 0 to 5 % with respect to the formulation, and is selected from the group consisting of surfactant amines, ionic

liquids, and combinations thereof, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1.

[0051] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine; (b) at least one second amine; and (c) at least one additive having a weight percentage in the range of 0 to 5 % with respect to the formulation, and is selected from the group consisting of surfactant amines, ionic liquids, and combinations thereof, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8.5: 1 – 9.5: 1.

[0052] In an embodiment of the present disclosure, there is provided a formulation as described herein, wherein the formulation optionally comprises at least one additive having a weight percentage in the range of 0 to 5 % with respect to the formulation and selected from the group consisting of surfactant amines, ionic liquids, and combinations thereof. In another embodiment the at least one additive has a weight percentage in the range of 0.5 to 4.5 % with respect to the formulation. In one another embodiment the at least one additive has a weight percentage has a weight percentage of 3 % with respect to the formulation. In yet another embodiment the at least one additive is surfactant amine. In another embodiment the at least one additive is ionic liquid. In another embodiment of the present disclosure, the additive is an ionic liquid, i.e. 1-decyl-3-methylimidazolium chloride having a weight percentage of 2 % with respect to the formulation.

[0053] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine having a weight percentage in the range of 50 to 90 % with respect to the formulation; (b) at least one second amine having a weight percentage in the range of 5 to 10 % with respect to the formulation; and (c) at least one additive having a weight percentage in the range of 0 to 5 % with respect to the formulation.

[0054] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine having a weight percentage in the range of 50 to 90 % with respect to the formulation; (b) at least one second amine having a weight percentage in the range of 5 to 10 % with respect to the formulation; and (c) at least one

additive having a weight percentage in the range of 0 to 5 % with respect to the formulation, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1.

[0055] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine having a weight percentage in the range of 50 to 90 % with respect to the formulation; (b) at least one second amine having a weight percentage in the range of 5 to 10 % with respect to the formulation; and (c) at least one additive having a weight percentage in the range of 0 to 5 % with respect to the formulation, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8.5: 1 – 9.5: 1.

[0056] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine having a weight percentage in the range of 50 to 90 % with respect to the formulation; (b) at least one second amine having a weight percentage in the range of 5 to 10 % with respect to the formulation; and (c) at least one additive having a weight percentage in the range of 0 to 5 % with respect to the formulation, wherein the at least one first amine to the at least one second amine weight ratio is 9:1.

[0057] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine having a weight percentage in the range of 50 to 90 % with respect to the formulation; and (b) at least one second amine having a weight percentage in the range of 5 to 10 % with respect to the formulation, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1.

[0058] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine having a weight percentage in the range of 50 to 90 % with respect to the formulation; and (b) at least one second amine having a weight percentage in the range of 5 to 10 % with respect to the formulation, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8.5: 1 – 9.5: 1.

[0059] In an embodiment of the present disclosure, there is provided a formulation comprising: (a) at least one first amine having a weight percentage in the range of 50 to 90 % with respect to the formulation; and (b) at least one second amine having a weight percentage in the range of 5 to 10 % with respect to the formulation, wherein the at least one first amine to the at least one second amine weight ratio is 9:1.

[0060] In an embodiment of the present disclosure there is provided a process for preparing the formulation comprising: (a) at least one first amine; and (b) at least one second amine, the process comprising: (a) obtaining the at least one first amine; (b) obtaining the at least one second amine; and (c) contacting the at least one first amine, the at least one second amine to obtain the formulation.

[0061] In an embodiment of the present disclosure there is provided a process for preparing the formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1, the process comprising: (a) obtaining the at least one first amine; (b) obtaining the at least one second amine; and (c) contacting the at least one first amine, the at least one second amine, and optionally the at least one additive to obtain the formulation.

[0062] In an embodiment of the present disclosure there is provided a process for preparing the formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8.5: 1 – 9.5: 1, the process comprising: (a) obtaining the at least one first amine; (b) obtaining the at least one second amine; and (c) contacting the at least one first amine, the at least one second amine, and optionally the at least one additive to obtain the formulation.

[0063] In an embodiment of the present disclosure there is provided a process for preparing the formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1, the process comprising: (a) obtaining the at least one first amine; (b) obtaining at least one second amine, i.e., a reaction product obtained by contacting epichlorohydrin, and at least one first amine at a temperature in the range of

40 – 60 °C for a period in the range of 2 – 4 hours; and (c) contacting the at least one first amine, the at least one second amine, and optionally the at least one additive to obtain the formulation.

[0064] In an embodiment of the present disclosure there is provided a process for
5 preparing the formulation as described herein, wherein at least one second amine is a reaction product obtained by contacting epichlorohydrin, and at least one first amine at a temperature in the range of 40 – 60 °C for a period in the range of 2 – 4 hours. In another embodiment reaction product is obtained by contacting epichlorohydrin, and at least one first amine at a temperature in the range of 42 – 58 °C for a period in the range
10 of 2.5 – 3.5 hours. In one another embodiment reaction product is obtained by contacting epichlorohydrin, and at least one first amine at a temperature in the range of 50 °C for a period in the range of 3 hours.

[0065] In an embodiment of the present disclosure there is provided a process as described herein, wherein contacting the at least one first amine, the at least one second
15 amine, and optionally the at least one additive to obtain the formulation is carried out at a temperature in the range of 25 °C - 60 °C for a period in the range of 10 minutes – 120 minutes. In another embodiment contacting the at least one first amine, the at least one second amine, and optionally the at least one additive to obtain the formulation is carried out at a temperature in the range of 35 °C - 55 °C for a period in the range of 20 minutes
20 – 100 minutes. In another embodiment contacting the at least one first amine, the at least one second amine, and optionally the at least one additive to obtain the formulation is carried out at a temperature in the range of 40 °C for a period in the range of 20 minutes.

[0066] In an embodiment of the present disclosure there is provided a process for preparing the formulation comprising: (a) at least one first amine; and (b) at least one
25 second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1, the process comprising: (a) obtaining the at least one first amine; (b) obtaining the at least one second amine; and (c) contacting the at least one first amine, the at least one second amine, and optionally the at least one additive to obtain the formulation is carried out at a temperature in the range of 25 °C - 60 °C for a
30 period in the range of 10 minutes – 120 minutes.

[0067] In an embodiment of the present disclosure there is provided a process for preparing the formulation comprising: (a) at least one first amine; and (b) at least one second amine, the process comprising: (a) obtaining the at least one first amine; (b) obtaining the at least one second amine is carried out by contacting epichlorohydrin, and
5 at least one first amine at a temperature in the range of 40 – 60 °C for a period in the range of 2 – 4 hours; and (c) contacting the at least one first amine, the at least one second amine carried out at a temperature in the range of 25 °C - 60 °C for a period in the range of 10 minutes – 120 minutes to obtain the formulation.

[0068] In an embodiment of the present disclosure there is provided a process for
10 preparing the formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1, the process comprising: (a) obtaining the at least one first amine; (b) obtaining at least one second amine, i.e., a reaction product obtained by contacting epichlorohydrin, and at least one first amine at a temperature in the range of
15 40 – 60 °C for a period in the range of 2 – 4 hours; and (c) contacting the at least one first amine, the at least one second amine carried out at a temperature in the range of 25 °C - 60 °C for a period in the range of 10 minutes – 120 minutes to obtain the formulation.

[0069] In an embodiment of the present disclosure there is provided a process for
20 preparing the formulation comprising: (a) at least one first amine; (b) at least one second amine; and (c) at least one additive, the process comprising: (a) obtaining the at least one first amine; (b) obtaining the at least one second amine; (c) obtaining at least one additive; and (c) contacting the at least one first amine, the at least one second amine, and the at least one additive to obtain the formulation.

[0070] In an embodiment of the present disclosure there is provided a process for
25 preparing the formulation comprising: (a) at least one first amine; (b) at least one second amine; and (c) at least one additive, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1, the process comprising: (a) obtaining the at least one first amine; (b) obtaining at least one second amine, i.e., a
30 reaction product obtained by contacting epichlorohydrin, and at least one first amine at

a temperature in the range of 40 – 60 °C for a period in the range of 2 – 4 hours; (c) obtaining at least one additive; and (c) contacting the at least one first amine, the at least one second amine, and the at least one additive is carried out at a temperature in the range of 25 °C - 60 °C for a period in the range of 10 minutes – 120 minutes to obtain the formulation.

[0071] In an embodiment of the present disclosure there is provided a method of reducing fouling in a petroleum refinery comprising, adding the formulation comprising: (a) at least one first amine; (b) at least one second amine; and (c) at least one additive, to a water system.

[0072] In an embodiment of the present disclosure there is provided a method of reducing fouling in a petroleum refinery comprising, adding the formulation comprising: (a) at least one first amine; and (b) at least one second amine to a water system, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1.

[0073] In an embodiment of the present disclosure there is provided a method of reducing fouling in a petroleum refinery comprising, adding the formulation comprising: (a) at least one first amine; and (b) at least one second amine to a water system, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1, wherein the at least one second amine is a product of epichlorohydrin and the at least one first amine.

[0074] In an embodiment of the present disclosure there is provided a method of reducing fouling in a petroleum refinery comprising, adding the formulation comprising: (a) at least one first amine; (b) at least one second amine; and (c) at least one additive, to a water system, wherein the water system is an oil refinery overhead system.

[0075] In an embodiment of the present disclosure there is provided a method of reducing fouling in a petroleum refinery as described herein, wherein the water system is in an oil refinery overhead system.

[0076] In an embodiment of the present disclosure there is provided a method of reducing fouling in a petroleum refinery comprising, adding the formulation comprising: (a) at least one first amine; and (b) at least one second amine to a water system, wherein

the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1 and the water system is an oil refinery overhead system.

[0077] In an embodiment of the present disclosure there is provided a formulation comprising: (a) at least one first amine; and (b) at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1, wherein the formulation can act as a film forming neutralizing amine for reducing fouling in a petroleum refinery.

[0078] Although the subject matter has been described in considerable detail with reference to certain preferred embodiments thereof, other embodiments are possible.

10 EXAMPLES

[0079] The disclosure will now be illustrated with working examples, which is intended to illustrate the working of disclosure and not intended to take restrictively to imply any limitations on the scope of the present disclosure. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice of the disclosed methods and compositions, the exemplary methods, devices and materials are described herein. It is to be understood that this disclosure is not limited to particular methods, and experimental conditions described, as such methods and conditions may apply.

[0080] It is well recognized that corrosion will occur on the internal surfaces of refinery equipment when amine salts condense above the temperature of the water dewpoint. The neutralization formulation of the present disclosure neutralizes the acidic components at the point of initial condensation and minimizes/ eliminates deposits of salts on metal surfaces of distillation columns and thereby avoids formation of fouling and under-deposit corrosion.

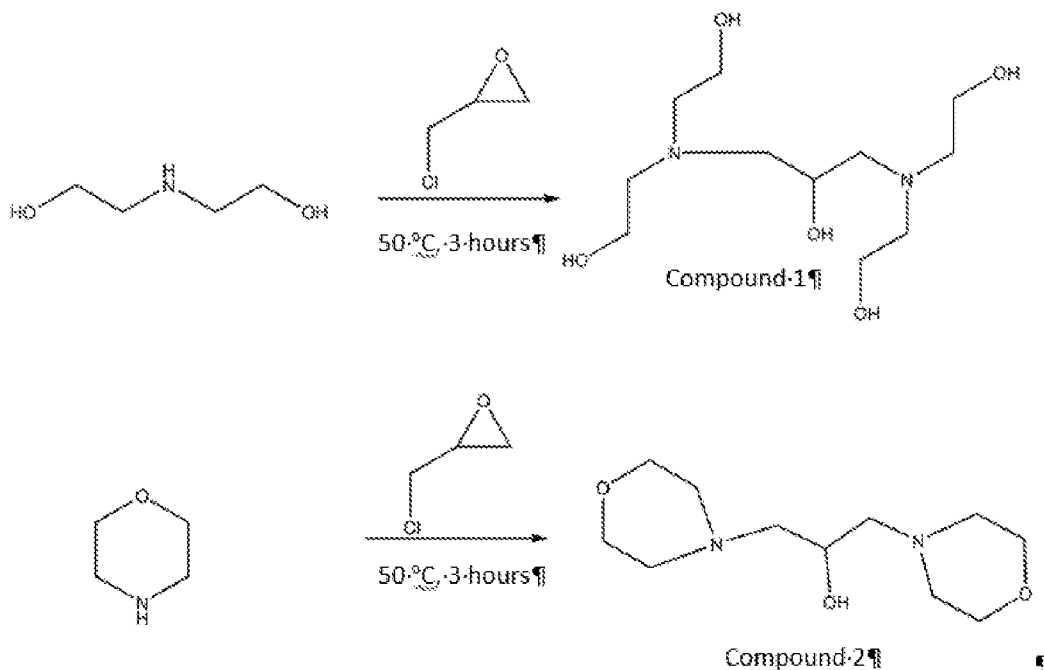
Example 1

Process for preparing second amine (Compound 1):

[0081] The general outline of the process disclosed in the present disclosure has been depicted as Scheme-1 in the following section. Epichlorohydrin (1 mole) was mixed with

2 moles of diethanolamine (at least one amine) at a temperature of 50 °C. The mixture was stirred for a period of 3 hours to obtain the Compound 1. LC-MS peak at 267 confirmed the formation of compound.

[0082]



5

Scheme 1

Example 2

Process for preparing second amine (Compound 2):

[0083] Epichlorohydrin (1 mole) was mixed with 2 moles of morpholine at a temperature of 50 °C stirred for a period of 3 hours to obtain the Compound 2. LC-MS peak at 231 confirmed the formation of compound.

[0084] The amines (at least one amine) used in the Example 1 and Example 2 can be replaced by the following amines alone or in combination to obtain the at least one second amine of the present disclosure.

- 15 (a) monoethanolamine, (b) triethanolamine, (c) cyclohexylamine, (d) piperazine, (e) diethylaminoethanol, (f) methyldiethanolamine, (g) ethyl ethanolamine, (h) aminoethyl piperazine.

A person skilled in the art would be able to modify the provided process to obtain alternate combinations. For instance, the Compound 3 (refer Table 1) was prepared in a manner similar to the process employed to obtain Compound 1, by conveniently replacing diethanolamine with monoethanolamine.

5 **Example 3**

Process of preparing the Formulation of the present disclosure:

[0085] The formulation of the present disclosure was prepared as follows: 90 % (w/w) of the first amine and 10 % (w/w) of the second amine were mixed together at a temperature in the range of 25 °C - 60 °C for a period in the range of 10 minutes – 120
10 minutes to obtain the formulation of the present disclosure.

Example 4

Process of preparing the Formulation with the additive:

[0086] The formulation with the additive was prepared in a similar manner as described in Example 3, wherein the weight percentages of the components were kept as below:
15 90 % (w/w) of the first amine; 8 % (w/w) of the second amine; and 2 % (w/w) of at least one additive. For instance, said additive is 1-decyl-3-methylimidazolium chloride (ionic liquid). The solution of morpholine, compound 2 and 1-decyl-3-methylimidazolium chloride were heated at 40-60 °C for 20 min to obtain the neutralizing amine formulation.

20 **Example 5**

Neutralizing capacity of the Formulation of the present disclosure:

[0087] The studies were performed by using high temperature (70 °C) pH measurements in a closed system. The inhibitory efficiency was calculated based on amine required to obtain the pH in the range of 8 to 9. From the data given in Table 1 below it is clear that
25 the Formulations 2, 4 and 6 comprising 10 % concentration of Compound 1, Compound 2, and Compound 3, respectively, significantly improved the neutralizing activity in a synergetic manner in comparison with the base amine. Similarly, the Formulation 7 comprising 8% of compound 1 and 2% of 1-decyl-3-methylimidazolium chloride (IL). The lower dosage to achieve said pH range was considered particularly useful.

30 **Table 1**

Formula tion	Dietha nol amine (base amine; w/w)	Comp ound 1 (w/w)	Morpho line (base amine; w/w)	Compo und 2 (w/w)	Monoet hanola mine (base amine; w/w)	Compound 3 (w/w)	ionic liquid (1- decyl-3- methylimi dazolium chloride)	Relative dosage required to reach pH 8 to 9 (in percentage)
Formula tion 1	100 %	0 %	0 %	0 %				
Formula tion 2	90 %	10 %	0 %	0 %				50 % of formulation 1
Formula tion 3	0 %	0 %	100 %	0 %				-
Formula tion 4	0 %	0 %	90	10				37 % of formulation 3
Formula tion 5	0%	0%	0%	0%	100%	0%		
Formula tion 6	0%	0%	0%	0%	90%	10%		60 % of formulation 5

Formula tion 7	90%	8%	0%	0%	0%	0%	2%	52 % of formulation 1
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[0088] Thus, it can be summarized that the obtained thermic fluid composition is only acceptable when certain specific base fluids are used during the preparation. In other words, the inventive Formulations 2, 4, 6 and 7 comprising a combination of at least one first amine and at least one second amine in a weight ratio range 8:1 to 10:1, required lower dose to achieve the required pH range.

Example 6

Corrosion inhibition by the Formulation of the present disclosure:

[0089] The corrosion rate experiments are performed with HCl solution. The HCl was neutralized with suitable amount of amine from the Formulations of Table 2. The corrosion rate experiments were performed on Carbon steel coupon at 120 °C in a closed system by using high temperature and high pressure reactor. Said system simulates the water system in an oil refinery overhead system.

[0090] The summary of the corrosion rates is given below in Table 2. As can be seen, the amine blend (formulation) has superior activity in comparison with pure amine.

Table 2

SNo	SAMPLE NAME	COUPON METALLURGY	AVERAGE WEIGHT LOSS (in gm)	METAL LOSS (in mils)	Normalized corrosion rate
1	Formulation 1	CS	0.1889	0.2296	100
2	Formulation 2	CS	0.1631	0.1859	82
3	Formulation 7	CS	0.1489	0.1748	76.6

CS- carbon steel

[0091] The Formulations 1 and 2 depicted in the Table 2 above, correspond to the Formulations 1 and 2 of the Table 1. The numbering has hence been retained to ensure

clarity. Further, the Formulation 7 comprises 90 % by weight diethanol amine, 8% by weight compound 1 and 2% by weight ionic liquid (1-decyl-3-methylimidazolium chloride).

[0092] The results depicted in the Table 2 indicate the surprising enhancement in corrosion inhibition observable upon involvement of Formulation of the instant Application (refer Formulations 2 and 7). In particular, the inventive Formulation 2 was found to slow down the corrosion rate in carbon steel dramatically (a reduction in rate by 18%), whereas the inventive Formulation 7 revealed a reduction in rate by ~24% in comparison to the base amine (diethanolamine). Thus, the enhancement suggested by Formulation 7, clearly indicates the beneficial role of the ionic liquid additive.

[0093] Although the subject matter has been described in considerable detail with reference to certain examples and implementations thereof, other implementations are possible.

Advantages of the present disclosure:

[0094] The present disclosure provides a formulation comprising at least one first amine and at least one second amine, wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1. The formulation is capable of neutralizing acidic components, i.e., the neutralizing formulation effectively neutralizes the acidic species, such as hydrochloric acid (HCl) or acidic sulfur species, and as a result combat the primary corrosion problem encountered in crude distillation unit overhead systems, thus minimizing the deposition of resulting amine salt to on overhead condensing equipment surfaces. Fouling of overhead condensing in crude distillation unit is minimized by the usage of formulation of the present disclosure, thereby reducing the productivity loss due to cleaning and/or replacing fouled equipment. The process of preparation of the formulation, as well as a method for reducing fouling of petroleum refinery are also disclosed herein.

I/We Claim:

1. A formulation comprising:
 - a) at least one first amine; and
 - b) at least one second amine,
- 5 wherein the at least one first amine to the at least one second amine weight ratio is in the range of 8: 1 – 10: 1.
2. The formulation as claimed in claim 1, wherein the at least one first amine to the at least one second amine weight ratio is 9: 1.
3. The formulation as claimed in claim 1, wherein the at least one first amine has a
- 10 weight percentage in the range of 50 to 95 % with respect to the formulation.
4. The formulation as claimed in claim 1, wherein the at least one first amine is selected from the group consisting of diethanolamine, morpholine, monoethanolamine, diethylaminoethanol, triethanolamine, cyclohexylamine, piperazine, methyldiethanolamine, ethyl ethanolamine, aminoethyl piperazine,
- 15 and combinations thereof.
5. The formulation as claimed in claim 1, wherein the at least one second amine has a weight percentage in the range of 5 to 15 % with respect to the formulation.
6. The formulation as claimed in claim 1, wherein the at least one second amine is a product of epichlorohydrin and the at least one first amine.
- 20 7. The formulation as claimed in claim 1, wherein the formulation optionally comprises at least one additive having a weight percentage in the range of 0 to 5 % with respect to the formulation and selected from the group consisting of surfactant amines, ionic liquids, and combinations thereof.
8. A process for preparing the formulation as claimed in any one of the claims 1 -
- 25 7, the process comprising:
 - a. obtaining the at least one first amine;
 - b. obtaining the at least one second amine;
 - c. contacting the at least one first amine, the at least one second amine, and optionally the at least one additive to obtain the formulation.

9. The process as claimed in claim 8, wherein the at least one second amine is a reaction product obtained by contacting epichlorohydrin, and at least one first amine at a temperature in the range of 40 – 60 °C for a period in the range of 2 – 4 hours.
- 5 10. The process as claimed in claim 8, wherein contacting the at least one first amine, the at least one second amine, and optionally the at least one additive to obtain the formulation is carried out at a temperature in the range of 25 °C - 60 °C for a period in the range of 10 minutes – 120 minutes.
- 10 11. A method of reducing fouling in a petroleum refinery comprising, adding the formulation as claimed in claim 1 to a water system.
12. The method as claimed in claim 11, wherein the water system is in an oil refinery overhead system.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2019/050494

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G7/10 C10G75/04
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

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

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X	US 2005/183325 A1 (SUTKOWSKI ANDREW C [GB]) 25 August 2005 (2005-08-25) paragraphs [0008], [0044] - paragraph [0045]; claim 1 -----	1-10
X	US 5 176 847 A (KREMER LAWRENCE N [US]) 5 January 1993 (1993-01-05) figure 1; example 2 ----- -/-	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2019/050494

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International application No

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