



(22) Date de dépôt/Filing Date: 2011/04/27
(41) Mise à la disp. pub./Open to Public Insp.: 2011/10/30
(45) Date de délivrance/Issue Date: 2018/04/03
(30) Priorité/Priority: 2010/04/30 (MXMX/A/2010/004777)

(51) Cl.Int./Int.Cl. *C10L 10/04* (2006.01),
C07D 265/10 (2006.01), *C09K 8/524* (2006.01),
C09K 8/54 (2006.01), *C23F 11/14* (2006.01)

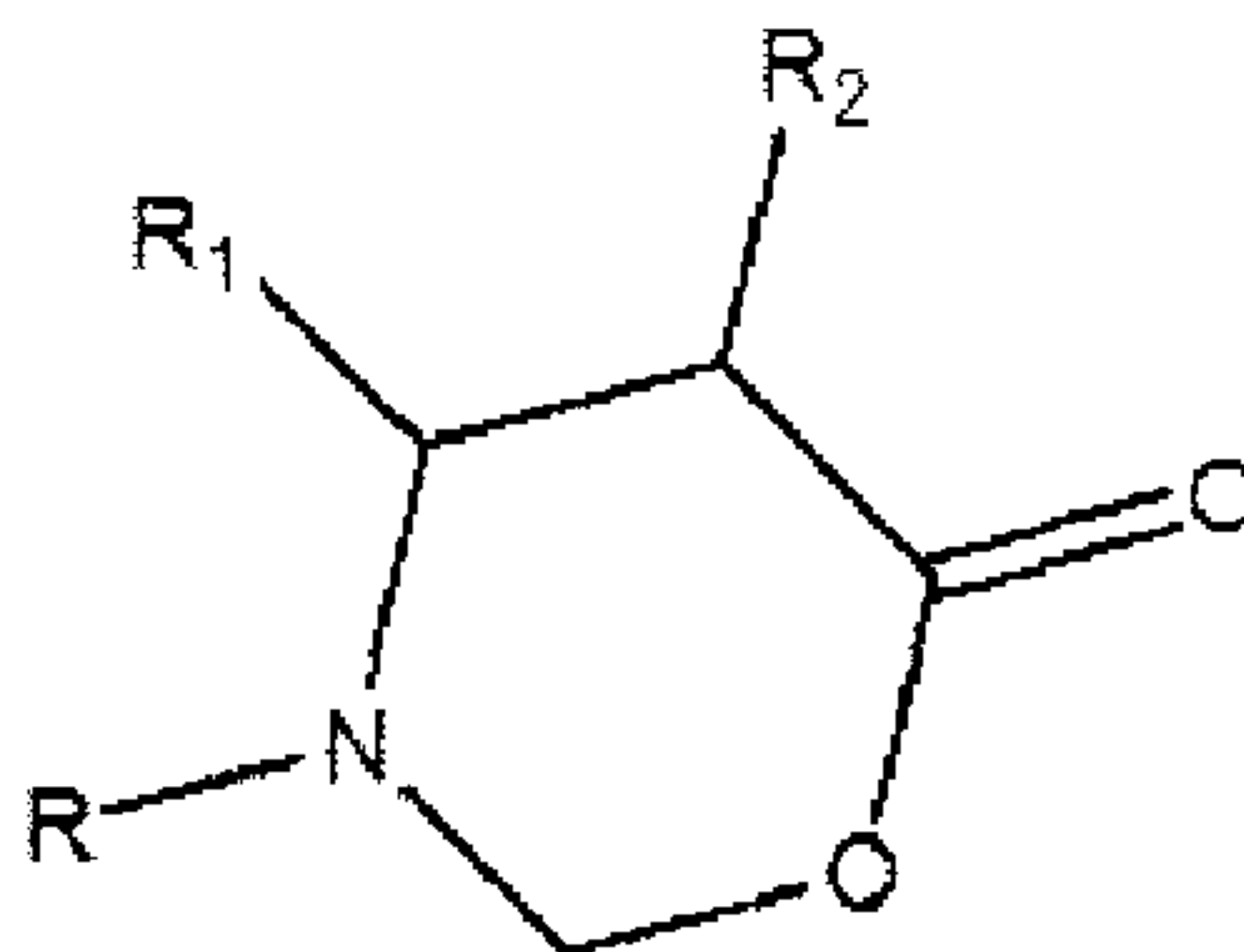
(72) Inventeurs/Inventors:
HERNANDEZ ALTAMIRANO, RAUL, MX;
MENA CERVANTEZ, VIOLETA YASMIN, MX;
ZAMUDIO RIVERA, LUIS SILVESTRE, MX;
BELTRAN CONDE, HIRAM ISAAC, MX;
BUENROSTRO GONZALEZ, EDUARDO, MX

(73) Propriétaire/Owner:
INSTITUTO MEXICANO DEL PETROLEO, MX

(74) Agent: GOWLING WLG (CANADA) LLP

(54) Titre : BASE MULTIFONCTIONNELLE DE 1,3 OXAZINAN-6-ONES COMBINEE A L'INHIBITION DE LA CORROSION ET A L'INHIBITION DE COMPOSES ORGANIQUES LOURDS, DISPERSANTS ET PROCEDES POUR LES OBTENIR

(54) Title: MULTIFUNCTIONAL COMPOSITION BASE 1, 3-OXAZINAN-6-ONES WITH CORROSION INHIBITION AND HEAVY ORGANIC COMPOUNDS INHIBITION AND DISPERSANTS AND OBTAINING PROCESS



(57) Abrégé/Abstract:

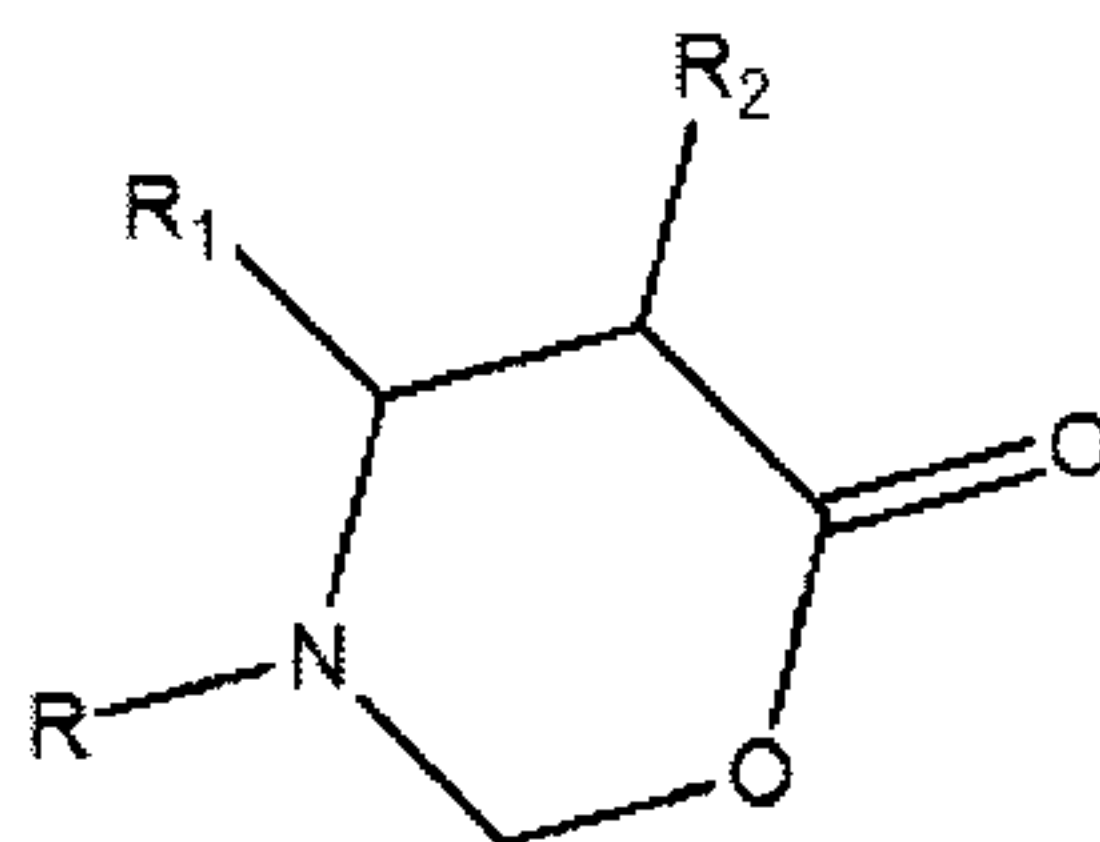
Base compounds including 1,3-oxazinan-6-one having the structure

(see above formula)

where R is a linear or branched alkyl chain of 6 to 18 carbons, a linear or branched chain alkenyl of 8 to 20 carbons or aromatic cycloalkyl having 5 to 12 carbons, R₁ is a radical selected from the group consisting of H and -CH₃ and R₂, is a radical selected from the group consisting of H and CH₃ are disclosed. Compounds are corrosion inhibitors with multifunctional properties serving as inhibitory/dispersants of asphaltene in production processes, transportation, refining and storage of crude oil and derivatives.

ABSTRACT

Base compounds including 1,3-oxazinan-6-one having the structure



where R is a linear or branched alkyl chain of 6 to 18 carbons, a linear or branched chain alkenyl of 8 to 20 carbons or aromatic cycloalkyl having 5 to 12 carbons, R_1 is a radical selected from the group consisting of H and $-\text{CH}_3$ and R_2 , is a radical selected from the group consisting of H and CH_3 are disclosed. Compounds are corrosion inhibitors with multifunctional properties serving as inhibitory/dispersants of asphaltene in production processes, transportation, refining and storage of crude oil and derivatives.

**MULTIFUNCTIONAL COMPOSITION BASE 1, 3-OXAZINAN-6-ONES WITH
CORROSION INHIBITION AND HEAVY ORGANIC COMPOUNDS INHIBITION AND
DISPERSANTS AND OBTAINING PROCESS**

5

DESCRIPTION

TECHNICAL FIELD OF THE INVENTION

10

This invention relates to the development of new base compounds 1, 3-oxazinan-6-ones derivatives of N-alkyl or N-alkenyl or N-cycloalkyl or N-aryl amino propionic acids and paraformaldehyde, and their application as multifunctional corrosion inhibitors of ferrous metals used in production processes, transport and storage of crude oil, which are in contact with a high salt content, where the prevailing hydrogen sulfide, and transport and storage of liquid fuels derived from refining oil, in addition, these compounds possess inhibitory and dispersing of heavy organic compounds in oil production processes and petroleum refining.

15

The compounds object of this invention and their formulations are the property of present low environmental impact.

20

BACKGROUND OF THE INVENTION

In the oil industry there are various problems that cause daily losses of millions dollars caused by falls in crude oil production, as well as failures by wear of pipelines and equipment, predominantly from problems of corrosion and deposition of asphaltenes, which is why a global investigations are aimed at generating solutions through a variety of methods to minimize such problems.

25

Corrosion is a phenomenon that generates millions of dollars in losses in the oil industry because it occurs in virtually all oil production chain from farm to processing it.

- 5 Corrosion is considered the progressive wear of a metallic material due to its interaction with the surrounding environment.

The particular case of the production and exploration operations for oil, the corrosion phenomenon is directly related to the presence of inorganic salts, hydrogen sulfide,
10 organosulfur compounds, organic acids and carbon dioxide

The corrosion phenomenon is also commonly found in transportation and storage of products derived from oil refining as gasoline without desulfurize, gasoline with low sulfur, diesel, alkylated gasoline, jet fuel, kerosene, methyl tertiary butyl ether and
15 others.

Usually in the oil industry, the problems of asphaltene deposition and corrosion have been controlled through the use of chemicals, asphaltene inhibitors and dispersants and corrosion inhibitors, which are composed of two main parts known as the head
20 (hydrophilic part) and tail (hydrophobic part).

The particular case of inhibiting and dispersing asphaltenes, the head (hydrophilic part) is a polar group whose function is to interact with the aromatic rings or polar groups of the asphaltenes, while the tail (hydrophobic part) is an aliphatic chain can
25 be linear or branched and which performs the function of forming a steric barrier that prevents asphaltene molecules interact with each other.

With regard to the phenomenon of corrosion inhibition, corrosion inhibitors widely used in the oil industry are the type of film that is characterized by its molecular
30 structure a head (hydrophilic part) that interacts with the metal surface through two main mechanisms: physisorption, which occurs through an electrostatic attraction and

chemisorption manifested through a coordination bond between metal and an atom capable of transmitting electrons, and a tail (hydrophobic part) that can repel water molecules trying to pass into the metal surface.

5 Because of one of the most economical methods for the prevention and control of these problems is the use of chemical products, the research in this area focuses on the development of chemical compounds that are able to work with more efficient means increasingly aggressive, in addition to complying with environmental regulations that currently govern their use.

10

Oil is a complex mixture of organic compounds which are broadly classified as: 1) Saturated, 2) Aromatic, 3) Resins and 4) Asphaltenes.

15 Of these fractions, asphaltenes play an important role because they are one of the fractions that cause more problems as a result of precipitation originating with this, clogging the pores of reservoir rock, clogging pipes, with a consequent fall in crude oil production and therefore the closure of wells, wear on equipment, high costs of maintenance and repair of equipment, among others.

20 From a chemical structural point, the asphaltene molecular rings are added polyaromatic containing small amounts of heteroatoms (sulfur, nitrogen and oxygen), trace metals (iron, nickel and vanadium), branching linear paraffin and features held together mainly by the type supramolecular interactions π - π . These structural features lead to the asphaltenes are more polar fraction in crude oil and tend to
25 precipitate to changes in temperature, pressure and composition are presented in collection, transport or processing of crude oil.

The phenomenon of precipitation of asphaltenes in crude oil occurs when favorable conditions of temperature, pressure and composition, asphaltene particles small, low
30 molecular weight, are associated, grow and generate larger and heavier aggregates that become insoluble in the medium. The high molecular weight and polar nature of

these asphaltenes generated that they are disseminated to the bottom of the reservoir, piping or equipment and to adhere firmly to the walls themselves. This phenomenon is known by the name of asphaltene deposition.

5 It is noteworthy that in the literature does not exist examples of chemical compounds that are capable of inhibiting corrosion and inhibit and dis asphaltenes dispersed through the same molecular structure.

10 Important examples of corrosion inhibitors used in acid characteristic of the oil industry, we have the following references:

U.S. Patent 3, 623.979, protects the obtaining of compounds base 1-aminoalkyl-2-alkyl imidazolines and their use as corrosion inhibitors for ferrous metals in acidic characteristic of the oil industry. The efficiency of corrosion inhibition of these
15 compounds was evaluated by gravimetric techniques.

U.S. Patent 3, 629, 104, protects the obtaining of organic acid salts of basic compounds derived from 1-aminoalkyl-2-alkyl imidazolines and their use as corrosion inhibitors for ferrous metals in acidic characteristic of the oil industry. The efficiency of
20 corrosion inhibition of these compounds was evaluated by gravimetric techniques.

U.S. Patent 3, 390, 085, protects the mixture of imidazoline salt prepared from the reaction of a fatty acid having 6 to 18 carbons with imidazoline selected from the group consisting of 1-aminoalkyl-2-alkyl hidroxioalquil imidazoline and 1-alkyl-2-
25 imidazolines and their application as corrosion inhibitors in acidic characteristic of the oil industry.

U.S. Patent 4, 388, 214, protects corrosion inhibitors synthesized from the reaction of imidazoline or imidazoline salts with sulfur. These compounds are particularly useful
30 for inhibiting corrosion of metal containers caused by carbon dioxide and hydrogen sulfide during transport and storage of crude oil.

U.S. Patent 5, 062, 992, protects a corrosion inhibiting formulation for oil and water systems, wherein the formulation is resistant to sludge formation and not to stabilize emulsions water/oil. The corrosion inhibitor includes an imidazoline dissolved in an aromatic solvent, a 2-hydroxyalkylcarboxylic acid and glycol. The imidazoline is preferably prepared from the reaction of a long chain fatty acid and a polyamine.

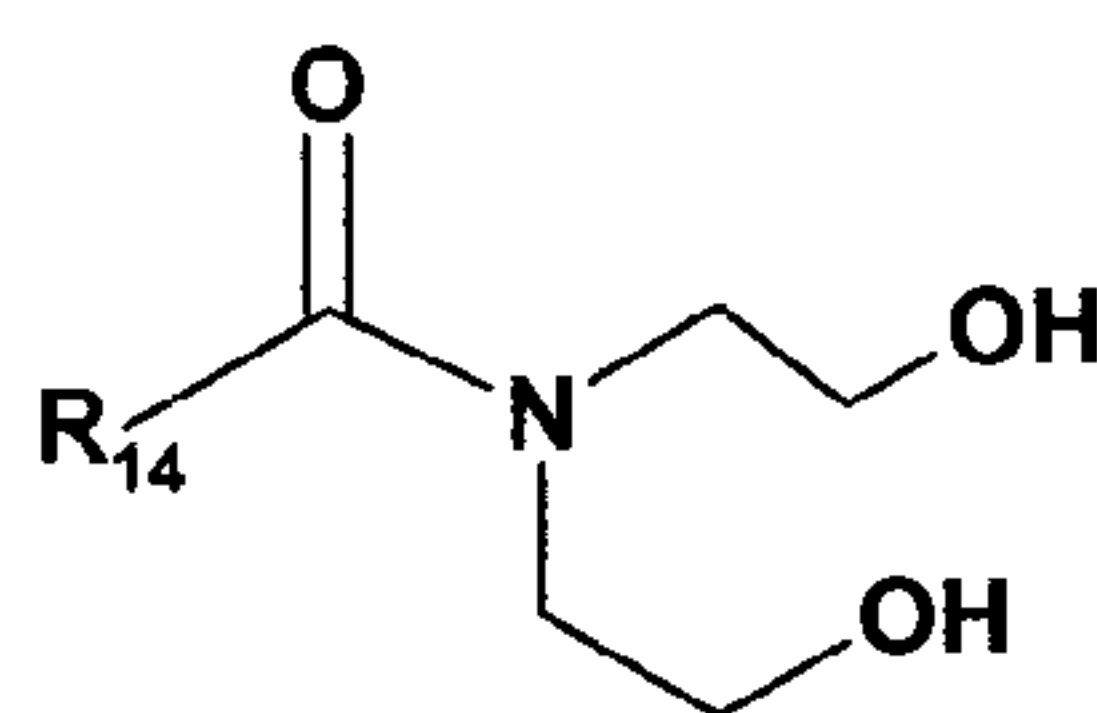
Important examples of corrosion inhibitors used in piping, tanks and other combustible liquid handlers references are presented below:

U.S. Patent 4, 214, 876 (corrosion inhibiting composition) protects the development of a formulation of the corrosion inhibition for ferrous metals exposed to hydrocarbon fuels made from 75 to 95% of an unsaturated aliphatic carboxylic acid of 16 to 18 carbons and 5 to 25% of a monoalkenyl succinic acid with a chain from 8 to 18 carbons, and to use as a solvent hydrocarbon compounds.

U.S. Patent 4, 509, 951 (Corrosion Inhibitor for alcohol-based fuels and gasoline-alcohol mixtures) protects the development of a formulation of the corrosion inhibition for ferrous metals exposed to liquid motor fuels based on alcohol-gasoline blends alcohol consisting of a carboxylic acid poly-unsaturated aliphatic 18-carbon, and the reaction product of a polyamine with a carboxylic acid alkenyl monounsaturated 18-carbon aliphatic or alkenyl succinic anhydride from 8 to 30 carbons.

U.S. Patent 4, 511, 366 (Liquids fuels and concentrates containing corrosion inhibitors) protects the development of a formulation of the corrosion inhibition for ferrous metals exposed to liquid alcohol-based fuel or gasoline-alcohol mixtures composed of an aliphatic carboxylic acid poly-unsaturated 16 to 18 carbons and an alkenyl polyamine.

U.S. Patent 4, 737, 159 (Corrosion inhibitor for liquid fuels) protects the development of a formulation of the corrosion inhibition for ferrous metals exposed to liquid



(2)

Specifically to contain within its structure a carbonyl group, thiocarbonyl, or imine, and its application as a dispersant of asphaltenes in crude oil. Within the structural formula (2), R₁₄ is an alkyl group that may vary from C₁₅ to C₂₁. The patent also indicates that these compounds increases Demulsibility, reduce viscosity, the formation of sediments, surface fouling and corrosion.

U.S. Patent 6,946,524 B2 relates a process for producing polyester-amides, by reacting a polyisobutylene with a first agent selected from the group consisting of monounsaturated fatty having 3 to 21 carbon atoms and derivatives thereof, and a second agent selected group consisting of monoethanolamine and alkylamines of structural formula (3):



(3)

where R represents an alkyl group having from 1 to 4 carbon atoms. The polyester-amides produced are used as stabilizers of asphaltenes in crude oil and crude oil derivatives.

The U.S. patent, 6,313,367 B1, mentioned that several esters and reaction products of ethers are excellent asphaltene dispersants or inhibitors and may be used in hydrocarbons such as crude oil. Asphaltene inhibitor compounds include 1) esters formed from the reaction of polyhydric alcohols with carboxylic acids, 2) ethers formed from the reaction of glycidyl ethers or epoxides with polyhydric alcohols and 3) esters formed from the reaction of glycidyl ethers or epoxides with carboxylic acids.

U.S. Patent 6,204,420 B1, mentions the development of a new formulation where asphaltene dispersing action of carboxylic acids can be greatly improved by the addition of relatively small amounts of esters derived from alkylphosphoric acids. The formulation consists of: A) 5 to 99% by weight of a carboxylic acid having more than 4
5 carbon atoms, an alkyl ethercarboxylic acids with alkyl substituents of C₁₈-C₂₂, C₁₈-C₂₂ substituents of alkenyl or C₆-C₁₈ substituents of alkylaryl, amidecarboxylic acid or a mixture thereof and B) 1 to 95% by weight of a phosphoric acid mono or diester or mixture thereof, which is substituted by an alkyl group of C₁₈-C₂₂, C₁₈-C₂₂ alkenyl, C₆ alkylaryl -C₁₈ or alkoxyated. Where the sum of A and B is 10% by weight.

10

U.S. Patent 6,180,683 B1, mentioned the development of a new formulation with synergistic effect as asphaltene dispersant. The formulation is composed of 5 to 95% of a compound of structural formulas I or II:

15 The present invention overcomes well above the references cited under the new base compounds alkyl or alkenyl cicloalkyl 1, 3 Oxazinan-6-ones derivatives of N-alkyl or N-alkenyl or N-cycloalkyl or N-aryl amino propionic acids and paraformaldehyde have the ability to function as corrosion inhibitors for ferrous metals and as inhibitors/
dispersants of asphaltenes to be applied in crude oil and products derived from them
20 in order to control fouling and blocked problems that are presented in production processes, transportation, refining and storage of the oil industry.

Therefore, one object of this invention is to provide a composition containing an active base compounds derived from 1, 3 oxazinan-6-ones and an aromatic solvent,
25 hydrocarbon, low molecular weight alcohols or a combination thereof, this composition has the multifunctionality of inhibiting corrosion of ferrous metals as well as inhibit and disperse asphaltenes.

Another object of this invention is to provide an active compound such as alkyl,
30 alkenyl or cicloalkyl 1, 3 oxazinan-6-ones and their use as corrosion inhibitors with inhibitory and dispersing asphaltenes in petroleum.

Another object of the present invention is to provide a process for obtaining the active compound alkyl, alkenyl or cicloalkyl 1, 3 oxazinan-6-ones.

BRIEF DESCRIPTION OF THE DRAWINGS OF THE INVENTION

5

It provides the following Figure 1, in order to clearly understand the test of inhibition of corrosion of base compounds 1.3 oxazine-6-ones and their application as multifunctional corrosion inhibitors and inhibitor/dispersants of heavy organic compounds, and serving as a reference in the example application.

10

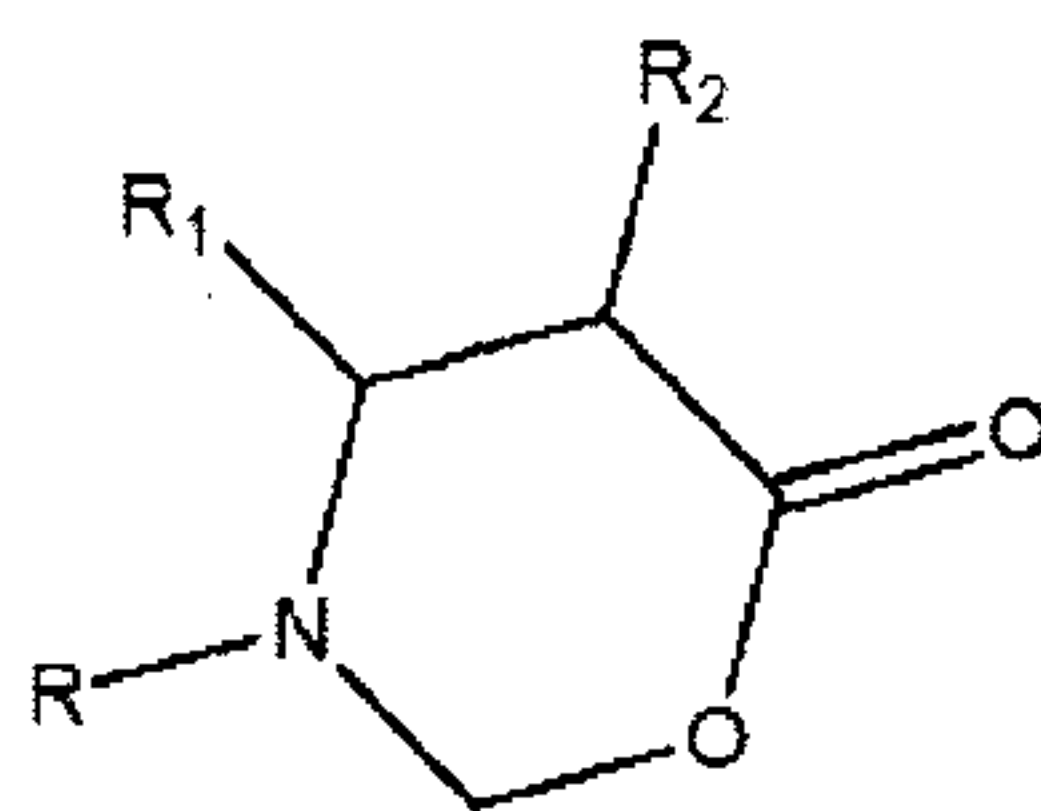
Figure 1 shows the inhibition test device consisting of a test specimen (A), a digitally controlled stirrer (B), a cover of poly (tetrafluoroethylene) (C), a glass (D) hydrocarbon-water mixture (E).

15

DESCRIPTION OF THE INVENTION

New compounds were developed base 1, 3 Oxazinan-6-ones derivatives of N-alkyl or N-alkenyl or N-cycloalkyl or N-aryl amino propionic acids and paraformaldehyde, and their application as multifunctional corrosion inhibitor with inhibitory and dispersant asphaltenes properties in production processes, transportation and oil refining, and transport and storage of hydrocarbons, with the following structural formula (4):

20



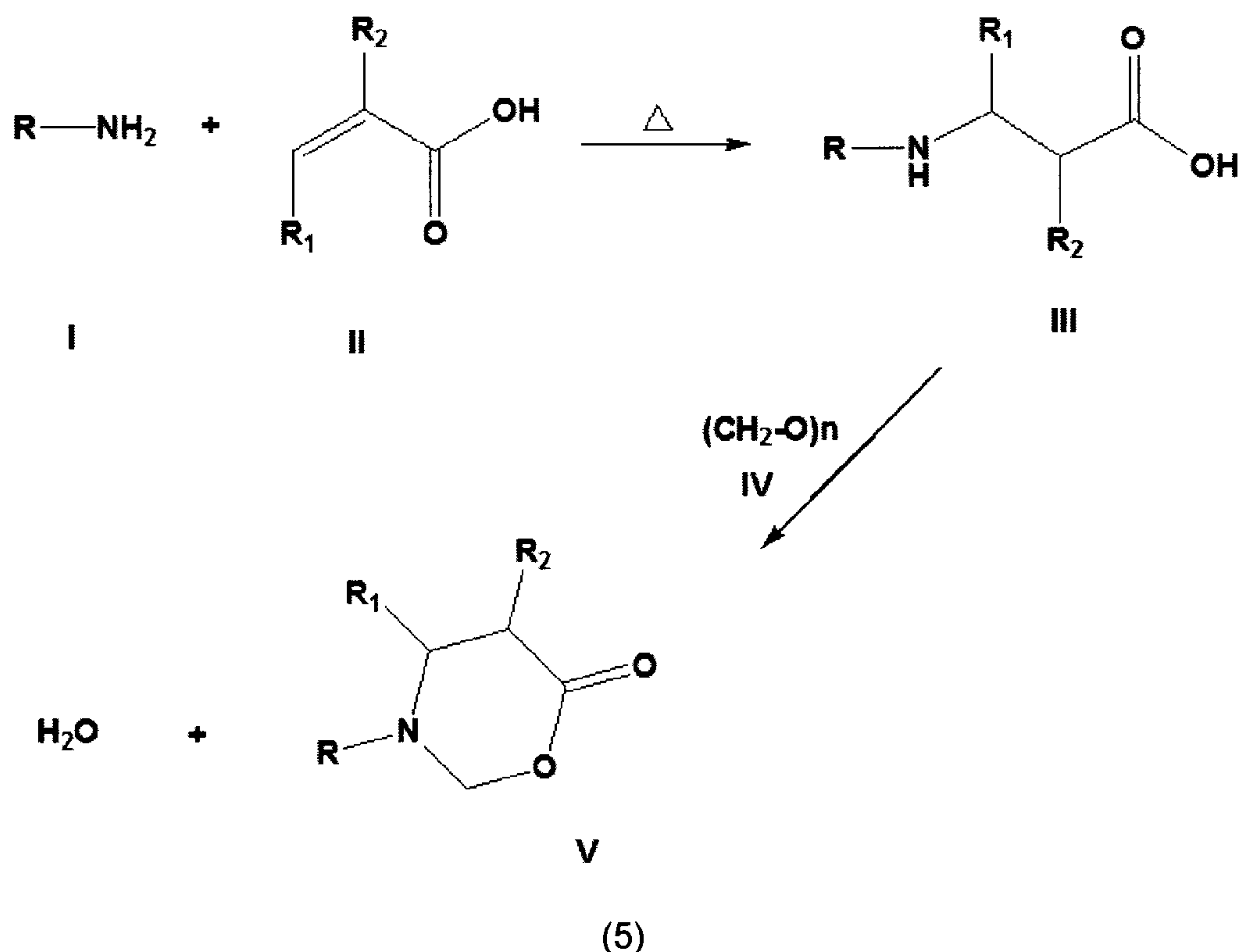
(4)

25

In the structural formula (4), R is a linear or branched alkyl chain of 6 to 18 carbons or a linear or branched chain alkenyl of 8 to 20 carbons or an aromatic or cycloalkyl of 5 to 12

carbons, R_1 is a radical that can be represented by the groups-H, $-CH_3$ and R_2 is a radical that can be H, CH_3 .

The compounds of this invention were prepared according to the following scheme
5 (5).



- 10 The first stage of the obtaining process is the reaction between an alkyl or alkenyl or cycloalkyl or aromatic amine of Formula I with an alpha-beta unsaturated carboxylic acid of formula II to obtain the corresponding N-alkyl or N-alkenyl or N-cycloalkyl or N-aryl propionic acid of structural formula III. The molar ratio of amine alkyl or alkenyl or aromatic carboxylic acid with respect to alpha-beta unsaturated may vary in the
- 15 range of 1:5 to 5:1, preferably in the range of 1:1 to 2:1 and the reaction is carried out in the absence of solvents. The reaction time and temperature depends on the structure of the alkyl or alkenyl or cycloalkyl or aromatic amine and alpha-beta unsaturated carboxylic acid, and the temperature at which the reaction is carried out.

Usually the reaction time varies in the range of 1 to 24 hours and the reaction temperature varies in the range of 80 to 200 ° C.

For alkyl amines can be selected from the following examples: hexylamine, heptylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine or a linear or branched alkenyl amine selected examples: oleylamine, linoleylamine, eurocylamine, behenylamine and taloylamine, or a cycloalkyl or aromatic amine derivative of the examples: cyclohexylamine, benzylamine, aniline, among others.

With respect to acid alpha-beta unsaturated carboxylic preferred for this invention are: acrylic acid, methacrylic acid, crotonic acid and isocrotonic acid.

The second stage of the production process consists of reacting the corresponding N-alkyl or N-alkenyl or N-cycloalkyl or N-aryl propionic acids with paraformaldehyde in the structural formula IV to obtain the corresponding 1, 3 oxazine-6- ones derived of structural formula V. The molar ratio of N-alkyl or N-alkenyl or N-cycloalkyl or N-aryl amino propionic and paraformaldehyde can vary in the range of 1:0.5 to 1:4 preferably in the range of 1:1 to 1:2 and reaction can be carried out in bulk or in the presence of an inert hydrocarbon solvent among which are preferably toluene, xylene mixtures, o-xylene, m-xylene, p-xylene, kerosene and jet fuel. The reaction time depends on the structure of N-alkyl or N-alkenyl or N-cycloalkyl or N-aryl propionic acids, as well as temperature and pressure at which the reaction is carried out. Usually the reaction time varies in the range of 1 to 24 hours, the reaction temperature varies in the range of 60 to 200 °C, preferably in the range of 90 to 180 °C and pressure which holds the reaction varies in the range of 60 to 760 mmHg, preferably in the range of 400 to 585 mm Hg.

The compounds of the present invention and their formulations are useful as:

Additives are added in crude oil and fuel oil as fuel without desulfurize, fuel with low sulfur, diesel, methyl tertbutyl ether, alkylated gasoline, kerosene and jet fuel, to prevent and control corrosion in wells, pipelines and tanks storage. The additive concentration needed to control corrosion of ferrous metals depends on the type of oil or fuel oil derivative thereof, and the presence of other additives.

Additives are added in crude oil and products derived from them to prevent and control the deposition of asphaltenes in wells, pipelines and refining plants. The additive concentration needed to control the deposition of asphaltenes depends on the type of crude oil or derivative thereof, and the presence of other fuel additives.

In general, the concentration of the compounds of this invention varies in crude oil in the range 1 to 2000 parts per million (ppm), preferably from 1 to 1000 ppm.

When another class of additives that control the deposition of organic compounds is present, a smaller amount of additive may be used, and in the case of fuel varies in the range of 1 to 50 parts per million (ppm), preferably from 1 to 20 ppm.

The 1, 3 oxazine-6-ones of the present invention can be formulated as a concentrate using inert organic solvent whose boiling point is between 75 and 300 °C, preferably hydrocarbon solvents such as benzene, toluene, mixed xylenes, o-xylene, m-xylene and p-xylene, diesel, kerosene, jet fuel, alcohols, aliphatic branched and unbranched containing in its structure from 3 to 10 carbon atoms, such as isopropanol, butanol and pentanol, and mixtures of hydrocarbon solvents with aliphatic branched and unbranched. The amount of active in the formulation ranges from 10 to 90 wt%, preferably from 25 to 75 wt%.

The 1, 3 oxazine-6-ones of the present invention can be dosed from 5 to 2000 ppm, depending on conditions of operation of the well or the pipe containing the crude oil or liquid fuel.

EXAMPLES

Here are some practical examples for better understanding of the present invention, without limiting its scope.

5

Example 1. Process for obtaining 3-(octadec-9-enyl)-1, 3-oxazine-6-one (Product 1). In a flask ball three-necked 500 ml equipped with a magnetic stirrer, a dropping funnel, a thermometer and a condenser were added 50 g (0.187 mol) of oleylamine at a temperature of 40 ° C with vigorous stirring was slowly added to 13.48 g (0.187 mol) acrylic acid. The reaction is exothermic and the temperature under these conditions rises gradually to 90 ° C. The reaction mixture was stirred under these conditions for 2 hours and then increased to 100 ° C, thus obtaining a very viscous pale yellow, then to a temperature of 30 ° C were added 2.8 g (0.094 mol) of paraformaldehyde, and temperature was increased to 93 ° C at a pressure of 465 mmHg to remove water of reaction and finally obtained 65 g of product 1, the spectroscopic features are:

15 FTIR (cm⁻¹): 3004.9, 2921.6, 2852.1, 1656.1, 1463.5, 1376.9, 1305.4, 1106.1, 956.9, 721.2. ¹H NMR (CDCl₃), 200 MHz, δ (ppm): 5.28, 3.91, 3.24, 2.84, 2.36, 1.94, 1.21, 0.82. ¹³C NMR (CDCl₃), 50 MHz, δ (ppm): 167.3, 129.7, 129.6, 68.4, 52.4, 48.1, 44.7, 20 32.5, 31.8, 29.4, 29.2, 27.0, 22.5 y 13.9.

Example 2. Process for obtaining the 3-octadecyl-1, 3-oxazine-6-one (Product 2). In a flask ball three-necked 500 ml equipped with a magnetic stirrer, a dropping funnel, a thermometer and a condenser were added 50 g of octadecylamine and a temperature of 40 ° C with vigorous stirring was slowly added to 13.4 g of acrylic acid . The reaction is exothermic and the temperature under these conditions rises gradually to 90 ° C. The reaction mixture was stirred under these conditions for 2 hours and then increased to 100 ° C, thus obtaining a very viscous pale yellow, then to a temperature of 30 ° C were added 2.8 g of paraformaldehyde, and increase temperature at 93 ° C at a pressure of 465 mmHg to remove water of reaction and finally obtained 64 g of product 2, the spectroscopic features are:

FTIR (cm^{-1}): 2922.1, 2852.1, 1655.3, 1461.5, 1375.8, 1302.6, 1105.7, 956.5, 721.3.
 ^1H NMR (CDCl_3), 200 MHz, δ (ppm): 3.93, 3.25, 2.86, 2.38, 1.20, 0.83. ^{13}C NMR
(CDCl_3), 50 MHz, δ (ppm): 167.4, 68.4, 52.5, 48.2, 44.8, 31.8, 29.6, 29.5, 22.6, 22.5 y
14.0.

5

Example 3. Process for obtaining the 3-tetradecyl-1,3-oxazine-6-one (product 3). In a flask ball three-necked 500 ml equipped with a magnetic stirrer, a dropping funnel, a thermometer and a condenser were added 50 g of tetradecylamine and a temperature of 40 ° C with vigorous stirring was slowly added to 16.7 g of acrylic acid.

10 The reaction is exothermic and the temperature under these conditions rises gradually to 90 ° C. The reaction mixture was stirred under these conditions for 2 hours and then increased to 100 ° C, thus obtaining a very viscous pale yellow, then to a temperature of 30 ° C were added 3.5 g of paraformaldehyde, and increase temperature at 93 ° C at a pressure of 465mmHg to remove water of reaction and
15 finally obtained 69 g of product 3, the spectroscopic features are:

FTIR (cm^{-1}): 2921.4, 2853.4, 1657.1, 1462.3, 1375.3, 1304.5, 1108.2, 955.8, 722.4.
 ^1H NMR (CDCl_3), 200 MHz, δ (ppm): 3.95, 3.21, 2.85, 2.33, 1.23, 0.86. ^{13}C NMR
(CDCl_3), 50 MHz, δ (ppm): 167.1, 68.6, 52.7, 48.1, 44.6, 31.9, 29.7, 29.6, 22.7, 22.5 y
14.0.

20

Example 4. Process for obtaining the 3-dodecyl-1,3-oxazine-6-one (Product 4). In a flask ball three-necked 500 ml equipped with a magnetic stirrer, a dropping funnel, a thermometer and a condenser were added 50 g (0.187mol) of dodecylamine and a temperature of 40 ° C with vigorous stirring was slowly added to 19.4 g of acrylic acid.

25 The reaction is exothermic and the temperature under these conditions rises gradually to 90 ° C. The reaction mixture was stirred under these conditions for 2 hours and then increased to 100 ° C, thus obtaining a very viscous pale yellow, then to a temperature of 30 ° C were added 4.1 g of paraformaldehyde, and increase temperature at 93 ° C at a pressure of 465 mmHg to remove water of reaction and
30 finally obtained 72 g of product 4, the spectroscopic features are:

FTIR (cm^{-1}): 2921.6, 2852.4, 1654.1, 1461.9, 1373.4, 1303.6, 1109.5, 951.5, 723.2.
 ^1H NMR (CDCl_3), 200 MHz, δ (ppm): 3.97, 3.26, 2.83, 2.37, 1.15, 0.79. ^{13}C NMR
(CDCl_3), 50 MHz, δ (ppm): 167.2, 68.4, 52.2, 48.2, 44.4, 31.7, 29.5, 29.4, 22.5 y 13.9.

5

Performance testing

To evaluate the efficiency of corrosion inhibition in an environment characteristic of pipes and tanks that transport and store crude oil, used the gravimetric technique known as dynamic testing of wheel and electrochemical technique known as linear polarization. The following describes each test procedures and results.

Determination of the corrosion inhibition efficiency through NACE 1D-182 method.

15 Gravimetric test is commonly called dynamic wheel (Wheel test) that simulates the corrosive environment characteristic of oil production, is a dynamic procedure developed for fluids (oil, water and inhibitor).

For this test using a specimen of 1010 carbon steel with dimensions 2,540 x 1,270 cm
20 x 0,025 cm, which is weighed and placed inside a bottle containing 180 ml of an emulsion or brine aggressive environments simulating acids characteristic of the oil industry, and a certain amount of corrosion inhibitor can vary from 0 to 500 ppm. The bottle is sealed and placed in a hole of a wheel of 58.4 cm in diameter that is within a range, then the oven temperature is increased to 70 ° C, while the wheel rotates at 30
25 rpm for about 46 hours. At the end of the test, specimen is removed from the bottle, washed consecutively with chloroform, acetone, water, a solution of diluted hydrochloric acid, a potassium bicarbonate solution with 5 in weight and water, clean with wire brushing, rinse with soap and water, dried in an oven at 60 °C and
30 reweighed. Depending on weight loss and with reference to a target is calculated efficiency of corrosion inhibition, while for the evaluation of the corrosion rate reported

in thousandths of an inch per year (mpy) are taken into account the following parameters the specimen: a) weight loss, b) area, c) density d) test time.

5 Gravimetric test is commonly called dynamic wheel (Wheel test) that simulates the corrosive environment characteristic of oil production, is a dynamic procedure developed for fluids (oil, water and inhibitor).

Testing equipment and reagents:

- 10 a) Evaluating dynamic for corrosión inhibitors with temperature controller, stirrer speed of 30 rpm and capacity for 52 bottles of 180ml.
- b) Bottles of 200 ml capacity.
- c) Coupon SAE 1010 carbon steel, dimensión 2,540 x 1,270 x 0.025 cm (1" x 0.5" x 0.010").
- 15 d) Glassware for the preparation of a corrosive environment. This consist of a glass reactor of 2 liter, equipped with a cooling bath, mechanical stirrer, bubbler for gas (nitrogen and hydrogen sulfide), has an outlet connected to two traps in serie (the first with sodium hydroxide in pellet form and the second with another sodium hydroxide solution 20% in weight), so that hydrogen sulfide does not contaminate the environment.
- 20 e) Potentiometer for measuring pH.

The test conditions are shown in table 1, while the composition of the brine used is shown in table 2.

25

30

Table 1. Test Conditions,
NACE 1D-182 method

Temperature	70 °C
Aqueous medium	Synthetic brine with 600 ± 50 ppm de H₂S
Test time	46 hours
Organic medium	Kerosene
Volume ratio Synthetic brine/organic medium	90/10
Test volume	180 ml
pH	4
Metals coupons	Steel SAE 1010

5

Table 2. Brine composition used,
1D-182 NACE method.

Salts	Amount (g/l)
NaCl	60.0
CaCl₂.H₂O	6.0
MgCl₂.6H₂O	10.48
Na₂SO₄	3.5

Results:

- 10 The difference in weight of the coupons before and after being exposed to corrosive liquid for 46 hours, is a direct indication of metal lost due to corrosion.

The efficiency of corrosion inhibition is obtained by comparing the reference coupon wear with the wear of the coupons with corrosion inhibitor at different concentrations,

- 15 using the following formula:

$$\% E = (V_0 - V) / V \times 100$$

Where:

V_0 = Corrosion velocity of reference coupon

V = Corrosion velocity of coupon with corrosion inhibitor

- 5 Table 3 shows the results of the products 1 to 6 at different concentrations.

Table 3.

Example	Concentration (ppm)	Corrosion velocity, (mpy's)*	Efficiency, (%)
Reference	0	41.6	0
Product 1	10	2.2	94.9
	25	3.5	91.9
	50	2.4	94.5
	75	2.0	95.2
Product 2	10	5.8	86.4
	25	4.2	90.1
	50	2.8	91.4
	75	0.6	98.5
Product 3	10	4.6	89.3
	25	1.4	96.7
	50	1.4	96.7
	75	1.6	95.9
Product 4	10	32.4	24.3
	25	26.4	38.2
	50	5.2	87.9
	75	2.9	93.0

* mpy's: thousandths of an inch per year

Determination of the efficiency of corrosion inhibition by the methos NACE TM-0172.

Test description:

5 Test Method NACE TM-0172 is to determine the corrosive properties of gasoline, jet fuel and distillate fuels that found in pipelines and storage tanks. Also includes information on metal specimen preparations, equipment and a system for ranking the test samples with corrosion inhibitor.

10 **Testing equipment and aparatous:**

The apparatus consists of:

- A temperature measuring device, and
- 15 • One bathroom. Should be used a thermally controlled bath of mineral oil capable of maintaining a temperature in the test sample 38 ± 1 °C. The bathroom must have a cover with holes to accommodate the test glass and the temperature measuring device.

20 The test device used by the NACE TM-0172 method to determine the efficiency of corrosion inhibition posed by gemini surfactants of the present invention, illustrated by Figure 1, consists of a test specimen (A), a digitally controlled stirrer (B), a cover of poly (tetrafluoroethylene) (C), a glass (D), and hydrocarbon-water mixture (E).

25 The sample must be a steel yarn 81.0 x 12.7 mm, the steel shall conform to UNS* G10150 (Grade 1015), UNS G10180 (1018), UNS G10200 (1020) or UNS G10250 (1025) ASTM A108, used with a plastic handle of poly(tetrafluoroethylene) (PTFE). (* Unified Numbering System).

30 **Test Procedure:** Add 300 ml of fuel to the test vessel and dispensed corrosion inhibitor to the desired concentration, the glass is placed in an oil bath at a

temperature of 38 ± 1 ° C after 30 minutes of continuous stirring add 30 ml of distilled water, and agitation continued for three hours. Subsequently the sample is removed, and left to drain and washed with toluene or xylene followed by acetone.

- 5 **Sample Qualification:** The rating should be based solely on the portion of the sample that remained in the test fluid. The corrosion products formed during the test have had limited opportunity to darken, and all deposits of solids not removed by washing of toluene and acetone should be considered as products of corrosion. Marks on the circle can occur during polishing and should not be interpreted as
- 10 corrosion, classification is based according to Table 4.

Table 4. Samples qualification
NACE TM-0172 method.

Qualification	Percentage of corroded surface
A	0
B++	Less than 0.1 (2 or 3 spots of no more than 1 mm in diameter).
B+	Less than 5
B	5 a 25
C	25 a 50
D	50 a 75
E	75 a 100

- 15 Table 5 shows the results of product 1 with a variety of liquid fuels.

Table 6 shows the results of the products 2 to 6 on gasoline with low sulfur content at different concentrations.

Table 5.

Product	Concentration, (ppm)	Test medium, (fuel)	Qualification, (NACE TM-0172)
Reference	0	All fuels	E
1	10	Primary gasoline (sin desulfurar)	B++
	10	Magna gasoline	A
	10	Premium gasoline	A
	10	Diesel	B++
	10	MTBE	A
	10	Alkylated gasoline	A
	10	Magna gasoline/Ethanol (50:50)	A

Table 6

Product	Concentration, (ppm)	Qualification, (NACE TM-0172)
Reference	0	E
2	10	B++
	25	A
3	10	B+
	25	A
4	10	B+
	25	B++

5 Determination of the efficiency of corrosion inhibition by electrochemical techniques.

Equipment used:

It used a glass electrochemical cell, reference electrode, working electrode, counter
 10 electrode, ph meter, multimeter, potentiostat/galvanostat Autolab PGSTAT 30 71410.

Was also held for the preparation of the bitter brine of pH 4, and the dissolution of chemicals in isopropanol in order to prepare a solution of 1,000 ppm in 100mL.

Test procedure:

5 A specimen of carbon steel 1010 with area of 0.5 cm² is grinding with # 600 sandpaper. The bitter brine is the same as was used for the gravimetric technique. Polarization curves were generated linear open-circuit potential \pm 25 mV. When the test is obtained polarization curve, which is analyzed to determine the corresponding corrosion rate. To make a new experiment is necessary to perform the roughing
10 electrode is placed in the cell and generate another curve. This procedure is repeated until there is a coincidence of at least two curves. The experiments were performed at room temperature with magnetic stirring and bitter brine adjusted to pH 4.0 \pm 1. The corrosion rate (mpy) is determined through manipulation of the curve using the program of the potentiostat.

15

Table 7 shows the results for products 1 to 4 at different concentrations:

Table 7

Product	Concentration, (ppm)	Corrosion velocity, (mpy's)	Efficiency, (%) 20
Reference	0	72	0
1	25	18	75
	50	12	83
2	25	21	71
	50	18	73

Performance evaluation as inhibitors of precipitation or deposition of asphaltenes and asphaltene aggregates as dispersing the compounds of the present invention is
30 carried out through two different tests:

I) Test measuring the mass deposited on metal surface through an electrostatic field and,

5 II) Measurement test asphaltenes dispersed in heptane-crude oil through UV-Visible spectroscopy. Measuring the dispersion of asphaltenes in crude oil-heptane mixtures.

I) Test measuring the mass deposited on metal surface through an electrostatic field.

10

This test consists in inducing the deposition of organic material on a metallic surface by means of applying an electrostatic field. The asphaltenic aggregates suspended in crude oil, in spite of not possessing a net electrical charge, due to their electronic density, are sensitive to electrostatic fields having certain intensity, which generates
 15 an electrostatic charge in them that induces their deposition on the plate connected to the positive pole of the potentiometer. A Teflon array, having two parallel metallic stainless steel plates separated by 5 mm, is introduced to each cell; the system is balanced at the test temperature, and the electric field is applied during 24 h, by the end of which, the plates (previously weighted) are removed from the cells and left to
 20 drain for 8 h, to afterwards be weighted and the quantity of deposited material to be determined. The efficiency of the compound is determined relative to the difference between the mass deposited on the plate from the sample without inhibitor, the reference, and the mass deposited from a crude sample with inhibitor.

25
$$\text{Efficiency} = \frac{\text{Reference mass deposition} - \text{Inhibitor mass deposition}}{\text{Reference mass deposition}}$$

Test conditions:

- Temperature: 50 °C
- Pressure: 0.0774 MPa (ambient)
- 30 • Crude petroleum sample volume: 500 cm³
- Voltage: 800 V

- Amperage: 3000 mA
- Inhibitor dosage: 1000 ppm (mg/L)
- Oil (sample A)

5 Below are shown in Table 8, the characteristics of the oil (Sample A) used in the tests I and II.

Table 8. Characteristics of the oil (Sample A) used in performance tests I and II.

Properties	A
Density to 25 °C and 585 mm Hg	0.852
Composition (% w)	
Crystallizable paraffins	6.13
Saturated hydrocarbon fraction	54.80
Aromatic hydrocarbon fraction	23.57
Polar hydrocarbon fraction (resins)	21.21
Asphaltenes	0.41

10 The test results are shown in table 9

Table 9. Test results

Product	Mass deposited (mg)	Efficiency, (%)
Oil crude	758.2	0
1	10.3	98.6
Comercial 1 (Polyalkenyl succinimides)	68.2	95.0

II) Measurement test asphaltenes dispersed in heptane-crude oil through UV-Visible spectroscopy. Measuring the dispersion of asphaltenes in crude oil-heptane mixtures.

5 The test is based in the fact that asphaltenes are soluble in aromatic hydrocarbons, but insoluble in aliphatic hydrocarbons such as n-heptane. The dispersing capacity of a compound can be evaluated dissolving a small amount of crude oil in aromatic solvent and then adding the aliphatic hydrocarbon to provoke asphaltene precipitation. Given that asphaltenes absorb energy at UV-Visible region of
10 electromagnetic spectrum, it is possible to have a proportional estimation of the amount of precipitated asphaltene by measuring the absorbance of an aliquot of the resulting supernatant liquid at a suitable wavelength within the UV-Visible region. Variants of this methodology have been used to determine the remnant concentration of asphaltene in solution, as a measure of the dispersing efficiency of chemical
15 additives. Among the more representative documents are US 6,313,367 B1 y US 2004/0039125 A1 patents.

During the development of the present invention it was determine that the optimum wavelength to quantify de asphaltene dispersion is 510 nm.

20

The procedure that has been design for this test consists in:

Preparing a concentrate solution of 10, 000 ppm of additive in toluene. Then 9.5 ml of n-heptane and 0.5 ml of concentrated additive to reach additive concentration of 100, 250, 1000 and 500 (mg/L) were added to a test tube, and then the mixture was
25 vigorously agitated for 30 seconds and leave in repose for 24 hours. Afterwards a heptane reference was prepare, 9.5 ml of n-heptane and 0.5 ml of toluene were added to a test tube, immediately afterwards 0.1 ml of light crude oil or 0.1 ml of a 15% solution of heavy crude oil in toluene were also added, then the test tube was vigorously agitated for 30 seconds and leave in repose for 24 hours.

After rest time, take 3 mL of the supernatant of the dispersion, taking care not to disturb the sediment, filter through a 0.45 mm syringe and transfer to the cell of UV-Visible spectrophotometer.

- 5 Measuring the maximum absorbance wavelength of 510 nm selected.

Calculate the scattering efficiency using the following equation to establish the efficiency percentage of dispersant:

$$\%Efficiency = \frac{Test\ tube\ absorbance - Reference\ absorbance}{Reference\ absorbance} \times 100$$

10

The test results are shown in Table 10.

Table No. 10. Test Results of dispersant efficiency determination through UV-Visible spectroscopy, samples of crude oil A.

Product	Dosage (ppm)	Absorbance (U.A.)	Efficiency, (%)
Blanco	-	0.4025	-
1	100	0.7745	92
	250	0.7824	94
	500	0.7964	98
2	500	0.6528	62
Comercial 1 (Polyalkenyl succinimides)	500	0.7256	91

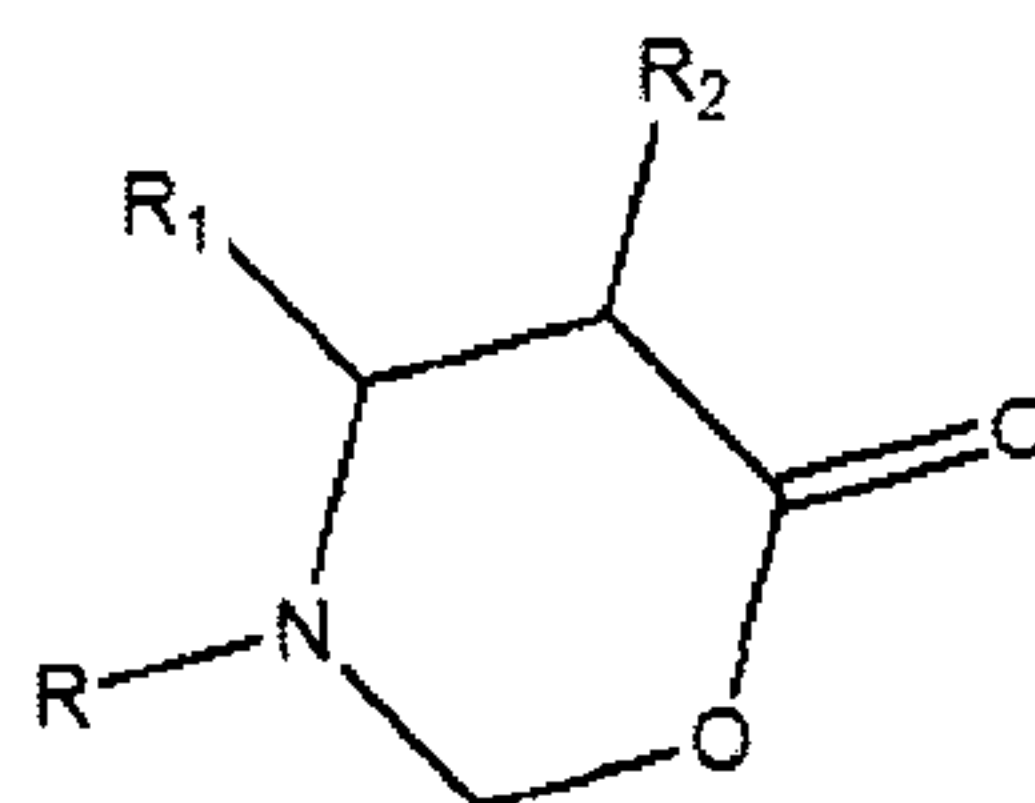
15

Table 10 shows the comparison between the efficiencies for product 1 and the commercial product 1 (derived from polyalkenyl succinimide), it is important to mention that the product 1, the object of this invention, and present a good efficiency (98.6%). On the electrodeposition test and 98% in testing the dispersion of organic

compounds by UV oil has the technical advantage of running as well as a corrosion inhibitor, which was confirmed in the evaluation tests-1D-182 NACE, NACE TM -0172 and linearly polarized electrochemical technique earlier in the present invention.

What is claimed is:

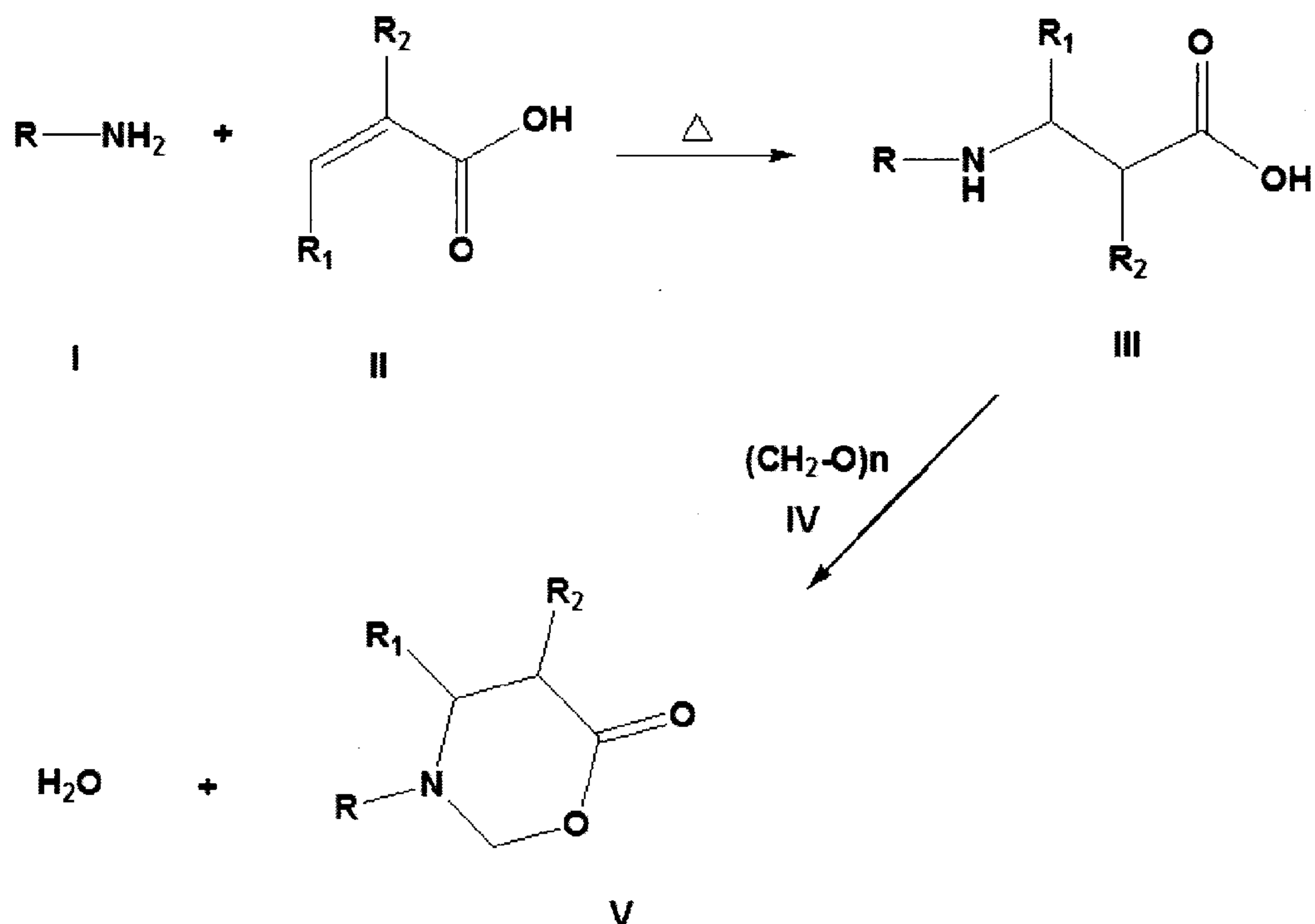
1. A multifunctional corrosion inhibiting composition comprising a 1,3-oxazinan-6-one with corrosion inhibitory properties and capable of dispersing heavy organic compounds in crude oil, said 1,3-oxazinan-6-one present in an amount of 10 to 90% by weight, and a hydrocarbon solvent in an amount of 10 to 90% by weight, where said amounts are based on the total weight of said composition; wherein the 1,3-oxazinan-6-one has the following molecular structure:



where R is a linear or branched alkyl chain of 6 to 18 carbons, a linear or branched chain alkenyl of 8 to 20 carbons, or an aromatic or cycloalkyl having 5 to 12 carbons, R₁ is a radical selected from the group consisting of H and —CH₃ and R₂ is a radical selected from the group consisting of H and CH₃.

2. The multifunctional composition according to claim 1 wherein the 1,3-oxazinan-6-one is present in an amount of from 25 to 75% by weight.
3. The multifunctional composition according to claim 1 wherein the hydrocarbon solvent is present in an amount of from 10 to 50% by weight.
4. The multifunctional composition, according to any one of claims 1 to 3, wherein the hydrocarbon solvents are: benzene, toluene, mixed xylenes, o-xylene, m-xylene, p-xylene, diesel, kerosene, jet fuel, branched or unbranched alcohols containing in its structure from 3 to 10 carbon atoms, and mixtures of branched and unbranched aliphatic hydrocarbon.
5. The multifunctional composition according to claim 4 wherein the branched or unbranched alcohols is selected from the group consisting of isopropanol, butanol and pentanol.

6. A process for obtaining 1, 3-oxazinan-6-one in accordance with claim 1 represented by the following synthesis route:



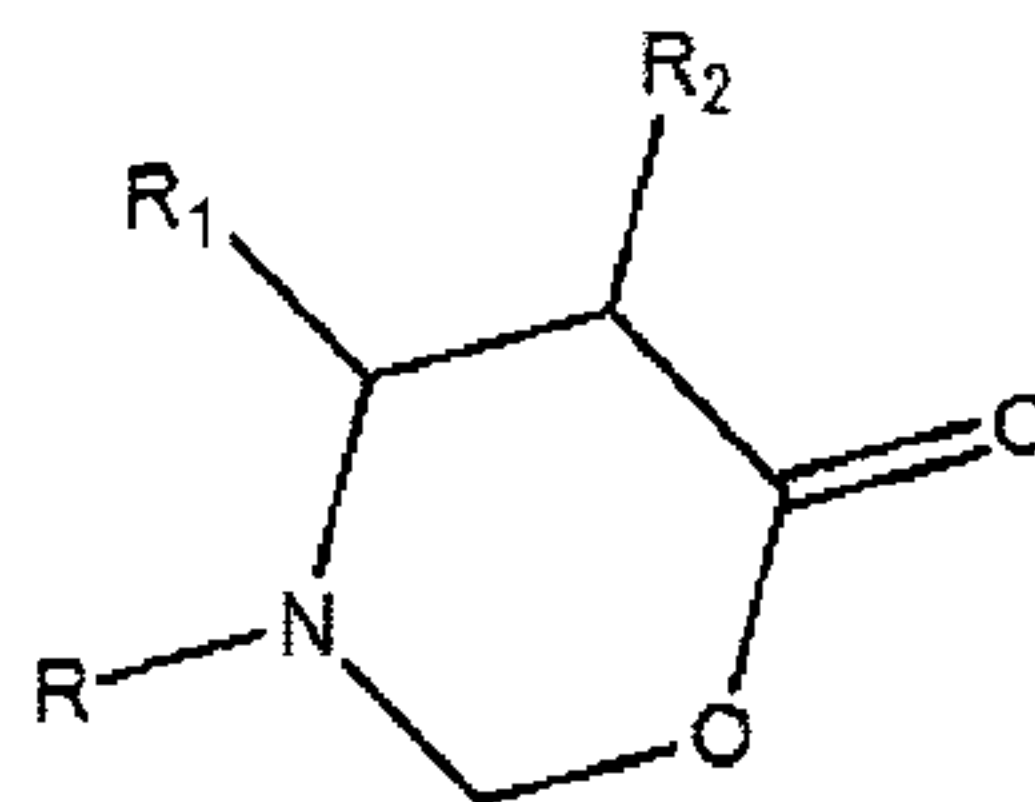
and consists of two stages of reaction:

- I) the first stage consists of reacting an alkyl or alkenyl or cycloalkyl or aromatic amine of Formula I with an α - β unsaturated carboxylic acid of Formula II to obtain the corresponding N-alkyl or N-alkenyl or N-cycloalkyl or N-aryl propionic acid of structural Formula III, and
 - II) the second stage consists of reacting the corresponding N-alkyl or N-alkenyl or N-cycloalkyl or N-aryl propionic acids with paraformaldehyde structural Formula IV to obtain the corresponding 1, 3 oxazinan-6-ones derived from the structural Formula V.
7. The synthesis process in accordance with claim 6, wherein the molar ratio of the alkyl or alkenyl or aromatic amine of Formula I with respect to said α - β unsaturated carboxylic acid of Formula II may vary in the range of 1:5 to 5:1 in the absence of solvents.

8. The synthesis process in accordance with claim 7 wherein the molar ratio may vary in the range of 1:1 to 2:1.
9. The synthesis process in accordance with claims 6 or claim 7, wherein the reaction time varies in the range of 1 to 24 hours.
10. The synthesis process in accordance with any one of claims 6 to 9, wherein the reaction temperature of the first stage varies in the range of 80 to 200 °C.
11. The synthesis process in accordance with any one of claims 6 to 10, wherein the compound I is an alkyl or alkenyl or aromatic or cycloalkyl amine selected from the group consisting of hexylamine, heptylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, oleylamine, linoleylamine, eurocylamine, behenylamine, taloylamine, cyclohexylamine, aniline and benzylamine.
12. The synthesis process in accordance with any one of claims 6 to 11, wherein the compound II is an alpha-beta unsaturated carboxylic acid compound selected from the group consisting of acrylic acid, methacrylic acid, crotonic acid and isocrotonic acid.
13. The synthesis process in accordance with claim 6, wherein the molar ratio of N-alkyl, N-alkenyl, N-cycloalkyl or N-aryl propionic acid and paraformaldehyde varies in the range of 1:0.5 to 1: 4.
14. The synthesis process in accordance with claim 13, wherein the molar ratio varies in the range of 1:1 to 1:2.
15. The synthesis process in accordance with claim 6 or claim 12, wherein the reaction is carried out in bulk or in the presence of an inert hydrocarbon solvent or a solvent selected from the group consisting of toluene, mixed xylene, o-xylene, m-xylene, p-xylene, kerosene and jet fuel.
16. The synthesis process in accordance with any one of claims 6, 12 to 14, wherein the reaction time varies in the range of 1 to 24 hours.

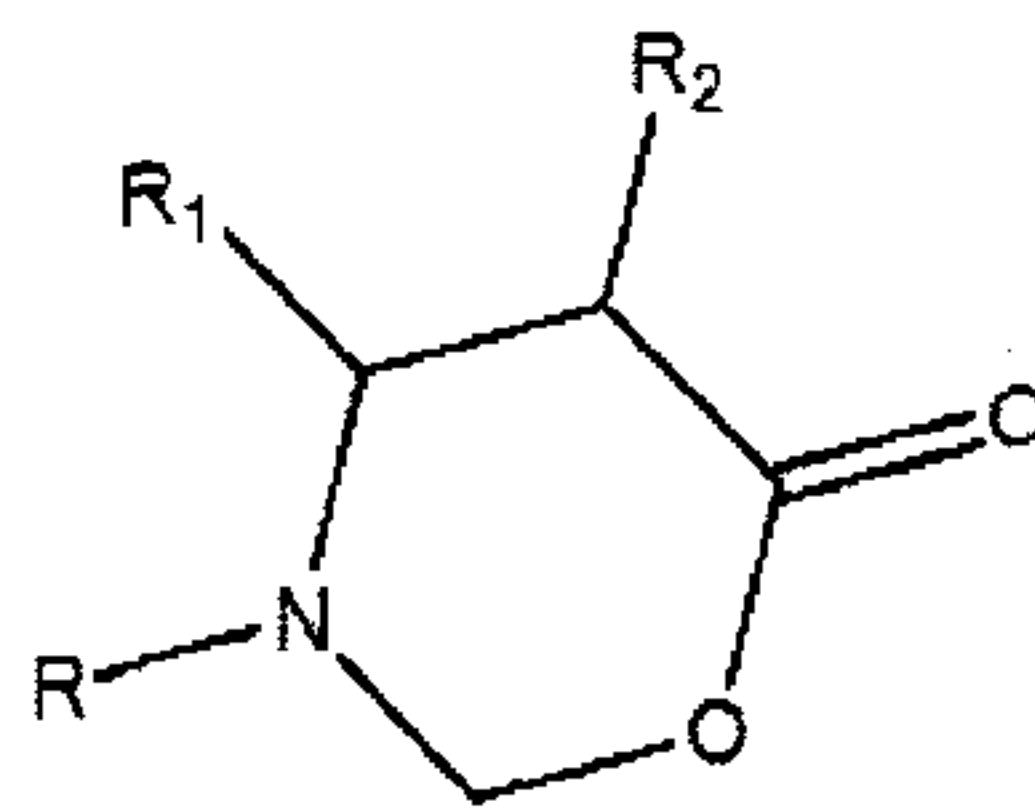
17. The synthesis process in accordance with any one of claims 6, 12 to 14, wherein the reaction temperature of the second stage varies in a range of 60 to 200 ° C, and the pressure varies in a range of 60 to 760 mmHg.
18. The synthesis process in accordance with claim 17 wherein the reaction temperature of the second stage varies in the range of 90 to 180 ° C.
19. The synthesis process in accordance with claim 17 or claim 18 wherein the pressure varies in the range of 400 to 585 mm Hg.
20. The synthesis process in accordance with claim 6 wherein the first stage consists of reacting an alkenyl amine of Formula I with an alpha-beta unsaturated carboxylic acid of Formula II to obtain the corresponding N-alkenyl propionic acid of structural Formula III, and the second stage consists of reacting the corresponding N- alkenyl propionic acids with paraformaldehyde structural Formula IV to obtain the corresponding 1, 3 oxazinan-6-ones derived from the structural Formula V, where R is a linear alkyl chain having 18 carbons, R₁ is H, and R₂ is H.
21. A use of the multifunctional corrosion inhibiting composition comprising a 1,3-oxazinan-6-one according to claim 1 for preventing or controlling corrosion in wells, pipelines and storage tanks containing crude oil or fuel, wherein the composition is added to crude oil or fuels in wells, pipelines and storage tanks.
22. The use according with claim 21 wherein the fuel is selected from the group consisting of gasoline without desulfurizing, alkylated gasoline, low-sulfur diesel, methyl tertiary butyl ether, gasoline, kerosene and jet fuel.
23. The use according to claim 21, wherein the composition is added to crude oil and products derived from crude oil to prevent and control the deposition of asphaltenes in wells, pipelines and refining plants.
24. The use according to claim 21, wherein the 1,3-oxazinan-6-one in crude oil is in a concentration that varies in a range 1 to 2000 parts per million (ppm).
25. The use according to claim 24 where in the concentration varies in a range from 1 to 1000 ppm.

26. The use according to claim 21, wherein the 1,3-oxazinan-6-one in fuel is in a concentration that varies in a range of 1 to 50 parts per million (ppm) when another class additive which controls the deposition of organic compounds is present.
27. The use according to claim 26 wherein the 1,3-oxazinan-6-one in fuel is in a concentration that varies from 1 to 20 ppm when another class additive which controls the deposition of organic compounds is present.
28. The use according to claim 21 wherein the composition comprises a hydrocarbon solvent in an amount of 10% to 90% by weight and the 1,3-oxazinan-6-one in an amount of 10% to 90% by weight based on the weight of the composition.
29. The use according to claim 22 wherein the composition comprises a hydrocarbon solvent in an amount of 10% to 50% by weight and the 1,3-oxazinan-6-one in an amount of 5% to 75% by weight based on the weight of the composition.
30. A stabilized crude oil or fuel comprising crude oil or fuel and an effective amount of a 1,3-oxazinan-6-one to inhibit corrosion of ferrous metals in contact with said stabilized crude oil or fuel; wherein the 1,3-oxazinan-6-one has the following molecular structure:



where R is a linear or branched alkyl chain of 6 to 18 carbons, a linear or branched chain alkenyl of 8 to 20 carbons or aromatic cycloalkyl having 5 to 12 carbons, R₁ is a radical selected from the group consisting of H and —CH₃, and R₂ is a radical selected from the group consisting of H and CH₃.

31. The stabilized crude oil or fuel according to claim 29, wherein said 1,3-oxazinan-6-one of claim 1 is present in an amount of 1 to 2000 ppm.
32. A compound consisting of a 1,3-oxazinan-6-one having the molecular structure:



where R is a linear or branched alkyl chain of 6 to 18 carbons, a linear or branched chain alkenyl of 8 to 20 carbons or aromatic cycloalkyl having 5 to 12 carbons, R₁ is a radical selected from the group consisting of H and —CH₃, and R₂ is a radical selected from the group consisting of H and CH₃.

33. The composition of claim 1, wherein R is a linear or branched alkyl chain having 6 to 18 carbons.
34. The composition of claim 1, wherein R is a linear or branched alkenyl chain having 8 to 20 carbons.
35. The stabilized crude oil or fuel of claim 29, wherein R is a linear or branched alkyl chain having 6 to 18 carbons.
36. The stabilized crude oil or fuel of claim 29, wherein R is a linear or branched alkenyl chain having 8 to 20 carbons.
37. The stabilized crude oil or fuel oil of claim 29, where said 1,3-oxazinan-6-one is selected from the group consisting of 3-(octadec-9-enyl)-1,3-oxazine-6-one, 3-octadecyl-1,3-oxazine-6-one, 3-tetradecyl-1,3-oxazine-6-one, and 3-dodecyl-1,3-oxazine-6-one.
38. The compound of claim 32, wherein R is a linear or branched alkyl chain having 6 to 18 carbon atoms.
39. The compound of claim 32, wherein R is a linear or branched alkenyl chain having 8 to 20 carbon atoms.

FIGURE 1

