HU000031481T2

(19) **HU** (11) Lajstromszám: **E 031 481** (13) **T2**

MAGYARORSZÁG
Szellemi Tulajdon Nemzeti Hivatala

EURÓPAI SZABADALOM
SZÖVEGÉNEK FORDÍTÁSA

(21) Magyar ügyszám: **E 08 850912**
(22) A bejelentés napja: **2008. 09. 12.**

(96) Az európai bejelentés bejelentési száma:
EP 20080850912
(97) Az európai bejelentés közzétételi adatai:
EP 2193179 A2 **2009. 05. 22.**
(97) Az európai szabadalom megadásának meghirdetési adatai:
EP 2193179 B1 **2016. 11. 09.**

(51) Int. Cl.:

C09K 8/60	*(2006.01)*
C10G 75/02	*(2006.01)*
C10L 1/188	*(2006.01)*
C10L 1/26	*(2006.01)*
C10L 10/04	*(2006.01)*
C10M137/14	*(2006.01)*

(86) A nemzetközi (PCT) bejelentési szám:
PCT/IN 08/000586
(87) A nemzetközi közzétételi szám:
WO 09063496

(30) Elsőbbségi adatok:
MU17692007 **2007. 09. 14.** **IN**

(72) Feltaláló(k):
SUBRAMANIYAM, Mahesh, Mumbai 400 064,
Maharashtra (IN)

(73) Jogosult(ak):
Dorf Ketal Chemicals (I) Private Limited,
Mumbai 400 064, MAH (IN)

(74) Képviselő:
SBGK Szabadalmi Ügyvivői Iroda, Budapest

(54) **Új adalékanyag nafténsav korrózió gátlására és eljárás annak alkalmazására**

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

A fordítást a szabadalmas az 1995. évi XXXIII. törvény 84/H. §-a szerint nyújtotta be. A fordítás tartalmi helyességét a Szellemi Tulajdon Nemzeti Hivatala nem vizsgálta.

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 193 179 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
09.11.2016 Bulletin 2016/45

(21) Application number: **08850912.0**

(22) Date of filing: **12.09.2008**

(51) Int Cl.:
C09K 8/60 $^{(2006.01)}$
C10G 75/02 $^{(2006.01)}$
C10L 10/04 $^{(2006.01)}$
C10M 137/14 $^{(2006.01)}$
C10L 1/26 $^{(2006.01)}$
C10L 1/188 $^{(2006.01)}$

(86) International application number:
PCT/IN2008/000586

(87) International publication number:
WO 2009/063496 (22.05.2009 Gazette 2009/21)

(54) A NOVEL ADDITIVE FOR NAPHTHENIC ACID CORROSION INHIBITION AND METHOD OF USING THE SAME

NEUARTIGER ZUSATZ ZUR HEMMUNG DER KORROSION VON NAPHTHENSÄURE SOWIE VERFAHREN ZU SEINER VERWENDUNG

NOUVEL ADDITIF DESTINE A EMPECHER LA CORROSION CAUSEE PAR LES ACIDES NAPHTENIQUES ET PROCEDE D'UTILISATION ASSOCIE

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR

(30) Priority: **14.09.2007 IN MU17692007**

(43) Date of publication of application:
09.06.2010 Bulletin 2010/23

(73) Proprietor: **Dorf Ketal Chemicals (I) Private Limited**
Mumbai 400 064, MAH (IN)

(72) Inventor: **SUBRAMANIYAM, Mahesh**
Mumbai 400 064, Maharashtra (IN)

(74) Representative: **Hirsch & Associés**
137, rue de l'Université
75007 Paris (FR)

(56) References cited:
EP-A1- 0 271 998
US-A- 2 316 078
US-A- 4 906 391
US-A- 5 552 085
US-A1- 2007 119 747
WO-A1-03/093399
US-A- 3 909 447
US-A- 5 552 085
US-A1- 2002 107 150

- **ET AL: 'TPC Group - Polyisobutylene', [Online] 30 October 2014, XP055150108 Retrieved from the Internet: <URL:http://www.tpcgrp.com/tpc-group/products/polyisobutylene-150.html> [retrieved on 2014-10-30]**

EP 2 193 179 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

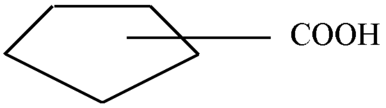
[0001] The present invention discloses the inhibition of metal corrosion in acidic hot hydrocarbons and more particularly to the inhibition of corrosion of iron - containing metals in hot acidic hydrocarbons, especially when the acidity is derived from the presence of naphthenic acid.

DISCUSSION OF PRIOR ART

[0002] It is widely known in the art that the processing of crude oil and its various fractions has led to damage to piping and other associated equipment due to naphthenic acid corrosion. These are corrosive to the equipment used to distill, extract, transport and process the crudes. Generally speaking, naphthenic acid corrosion occurs when the crude being processed has a neutralization number or total acid number (TAN), expressed as the milligrams of potassium hydroxide required to neutralize the acids in a one gram sample, above 0.2. It is also known that naphthenic acid-containing hydrocarbon is at a temperature between about 200 degree C and 400 degree C (approximately 400 degree F-750.degree F), and also when fluid velocities are high or liquid impinges on process surfaces e.g. in transfer lines, return bends and restricted flow areas.

[0003] Corrosion problems in petroleum refining operations associated with naphthenic acid constituents and sulfur compounds in crude oils have been recognized for many years. Such corrosion is particularly severe in atmospheric and vacuum distillation units at temperatures between 400 degree F and 790 degree F. Other factors that contribute to the corrosivity of crudes containing naphthenic acids include the amount of naphthenic acid present, the concentration of sulfur compounds, the velocity and turbulence of the flow stream in the units, and the location in the unit (e.g., liquid/vapor interface).

[0004] As commonly used, naphthenic acid is a collective term for certain organic acids present in various crude oils. Although there may be present minor amounts of other organic acids, it is understood that the majority of the acids in naphthenic based crude are naphthenic in character, i.e., with a saturated ring structure as follows:



[0005] The molecular weight of naphthenic acid can extend over a large range. However, the majority of the naphthenic acid from crude oils is found in gas oil and light lubricating oil. When hydrocarbons containing such naphthenic acid contact iron-containing metals, especially at elevated temperatures, severe corrosion problems arise.

[0006] Naphthenic acid corrosion has plagued the refining industry for many years. This corroding material consists of predominantly monocyclic or bicyclic carboxylic acids with a boiling range between 177 - 443 degree C (350 - 650 degree F). These acids tend to concentrate in the heavier fractions during crude distillation. Thus, locations such as the furnace tubing, transfer lines, fractionating tower internals, feed and reflux sections of columns, heat exchangers, tray bottoms and condensers are primary sites of attack for naphthenic acid. Additionally, when crude stocks high in naphthenic acids are processed, severe corrosion can occur in the carbon steel or ferritic steel furnace tubes and tower bottoms. Recently interest has grown in the control of this type of corrosion in hydrocarbon processing units due to the presence of naphthenic acid in crudes from locations such as China, India, Africa and Europe.

[0007] Crude oils are hydrocarbon mixtures which have a range of molecular structures and consequent range of physical properties. The physical properties of naphthenic acids which may be contained in the hydrocarbon mixtures also vary with the changes in molecular weight, as well as the source of oil containing the acid. Therefore, characterization and behavior of these acids are not well understood. A well known method used to "quantify" the acid concentration in crude oil has been a KOH titration of the oil. The oil is titrated with KOH, a strong base, to an end point which assures that all acids in the sample have been neutralized. The unit of this titration is mg. of KOH/gram of sample and is referred to as the "Total Acid Number" (TAN) or Neutralization Number. Both terms are used interchangeably in the application.

[0008] The unit of TAN is commonly used since it is not possible to calculate the acidity of the oil in terms of moles of acid, or any other of the usual analytical terms for acid content. Refiners have used TAN as a general guideline for predicting naphthenic acid corrosion. For example, many refineries blend their crude to a TAN=0.5 assuming that at these concentrations naphthenic acid corrosion will not occur. However, this measure has been unsuccessful in preventing corrosion by naphthenic acid.

[0009] Naphthenic acid corrosion is very temperature dependent. The generally accepted temperature range for this corrosion is between 205 degree C and 400 degree C (400 degree F and 750 degree F). Corrosion attack by these acids below 205 degree. C. has not yet been reported in the published literature. As to the upper boundary, data suggests that corrosion rates reach a maximum at about 316 - 371 degree C (600 - 700 degree F) and then begin to diminish.

[0010] The concentration and velocity of the acid/oil mixture are also important factors which influence naphthenic acid corrosion. This is evidenced by the appearance of the surfaces affected by naphthenic acid corrosion. The manner of corrosion can be deduced from the patterns and color variations in the corroded surfaces. Under some conditions, the metal surface is uniformly thinned. Thinned areas also occur when condensed acid runs down the wall of a vessel. Alternatively, in the presence of naphthenic acid pitting occurs, often in piping or at welds. Usually the metal outside the pit is covered with a heavy, black sulfide film, while the surface of the pit is bright metal or has only a thin, grey to black film covering it. Moreover, another pattern of corrosion is erosion-corrosion, which has a characteristic pattern of gouges with sharp edges. The surface appears clean, with no visible by-products. The pattern of metal corrosion is indicative of the fluid flow within the system, since increased contact with surfaces allows for a greater amount of corrosion to take place. Therefore, corrosion patterns provide information as to the method of corrosion which has taken place. Also, the more complex the corrosion, i.e., in increasing complexity from uniform to pitting to erosion-corrosion, the lower is the TAN value which triggers the behavior.

[0011] The information provided by corrosion patterns indicates whether naphthenic acid is the corroding agent, or rather if the process of corrosion occurs as a result of attack by sulfur. Most crude contain hydrogen sulfide, and therefore readily form iron sulfide films on carbon steel. In all cases that have been observed in the laboratory or in the field, metal surfaces have been covered with a film of some sort. In the presence of hydrogen sulfide the film formed is invariably iron sulfide, while in the few cases where tests have been run in sulfur free conditions, the metal is covered with iron oxide, as there is always enough water or oxygen present to produce a thin film on the metal coupons. Tests utilized to determine the extent of corrosion may also serve as indicators of the type of corrosion occurring within a particular hydrocarbon treating unit. Metal coupons can be inserted into the system. As they are corroded, they lose material. This weight loss is recorded in units of mg/cm^2 Thereafter, the corrosion rate can be determined from weight loss measurements. Then the ratio of corrosion rate to corrosion product (mpy/mg/cm^2) is calculated. This is a further indicator of the type of corrosion process which has taken place, for if this ratio is less than 10, it has been found that there is little or no contribution of naphthenic acid to the corrosion process. However, if the ratio exceeds 10, then naphthenic acid is a significant contributor to the corrosion process. Distinguishing between sulfidation attack and corrosion caused by naphthenic acid is important, since different remedies are required depending upon the corroding agent. Usually, retardation of corrosion caused by sulfur compounds at elevated temperatures is effected by increasing the amount of chromium in the alloy which is used in the hydrocarbon treating unit. A range of alloys may be employed, from 1.25% Cr to 12% Cr, or perhaps even higher. Unfortunately, these show little to no resistance to naphthenic acid. To compensate for the corroding effects of sulfur and naphthenic acid, an austenitic stainless steel which contains at least 2.5% molybdenum, must be utilized. The corrosive problem is known to be aggravated by the elevated temperatures necessary to refine and crack the oil and by the oil's acidity which is caused primarily by high levels of naphthenic acid indigenous to the crudes.Naphthenic acids is corrosive between the range of about 175 degree C to 420 degree C. At the higher temperatures the naphthenic acids are in the vapor phase and at the lower temperatures the corrosion rate is not serious. The corrosivity of naphthenic acids appears to be exceptionally serious in the presence of sulfide compounds, such as hydrogen sulfide, mercaptans, elemental sulfur, sulfides, disulfides, polysulfides and thiophenols. Corrosion due to sulfur compounds becomes significant at temperatures as low as 232 degree C (450 degree F). The catalytic generation of hydrogen sulfide by thermal decomposition of mercaptans has been identified as a cause of sulfidic corrosion.

[0012] Sulfur in the crudes, which produces hydrogen sulfide at higher temperatures, also aggravates the problem. The temperature range of primary interest for this type of corrosion is in the range of about 175 degree C to about 400 degree C, especially about 205 degree C to about 400 degree C.

[0013] Various approaches to controlling naphthenic acid corrosion have included neutralization and/or removal of naphthenic acids from the crude being processed; blending low acid number oils with corrosive high acid number oils to reduce the overall neutralization number; and the use of relatively expensive corrosion-resistant alloys in the construction of the piping and associated equipment. These attempts are generally disadvantageous in that they require additional processing and/or add substantial costs to treatment of the crude oil. Alternatively, various amine and amide based corrosion inhibitors are commercially available, but these are generally ineffective in the high temperature environment of naphthenic acid corrosion. Naphthenic acid corrosion is readily distinguished from conventional fouling problems such as coking and polymer deposition which can occur in ethylene cracking and other hydrocarbon processing reactions using petroleum based feedstocks. Naphthenic acid corrosion produces a characteristic grooving of the metal in contact with the corrosive stream. In contrast, coke deposits generally have corrosive effects due to carburization, erosion and metal dusting.

[0014] Because these approaches have not been entirely satisfactory, the accepted approach in the industry is to construct the distillation unit, or the portions exposed to naphthenic acid/sulfur corrosion, with the resistant metals such as high quality stainless steel or alloys containing higher amounts of chromium and molybdenum. The installation of corrosion - resistant alloys is capital intensive, as alloys such as 304 and 316 stainless steels are several times the cost of carbon steel. However, in units not so constructed there is a need to provide inhibition treatment against this type of corrosion. The prior art corrosion inhibitors for naphthenic acid environments include nitrogen-based filming corrosion inhibitors. However, these corrosion inhibitors are relatively ineffective in the high temperature environment of naphthenic acid oils.

While various corrosion inhibitors are known in various arts, the efficacy and usefulness of any particular corrosion inhibitor is dependent on the particular circumstances in which it is applied. Thus, efficacy or usefulness under one set of circumstances often does not imply the same for another set of circumstances. As a result, a large number of corrosion inhibitors have been developed and are in use for application to various systems depending on the medium treated, the type of surface that is susceptible to the corrosion, the type of corrosion encountered, and the conditions to which the medium is exposed. For example, U.S. Pat. No. 3,909,447 describes certain corrosion inhibitors as useful against corrosion in relatively low temperature oxygenated aqueous systems such as water floods, cooling towers, drilling muds, air drilling and auto radiator systems. That patent also notes that many corrosion inhibitors capable of performing in non-aqueous systems and/or non-oxygenated systems perform poorly in aqueous and/or oxygenated systems. The reverse is true as well. The mere fact that an inhibitor that has shown efficacy in oxygenated aqueous systems does not suggest that it would show efficacy in a hydrocarbon. Moreover, the mere fact that an inhibitor has been efficacious at relatively low temperatures does not indicate that it would be efficacious at elevated temperatures. In fact, it is common for inhibitors that are very effective at relatively low temperatures to become ineffective at temperatures such as the 175 degree C to 400 degree C encountered in oil refining. At such temperatures, corrosion is notoriously troublesome and difficult to alleviate. Thus, U.S. Pat. No. 3,909,447 contains no teaching or suggestion that it would be effective in non-aqueous systems such as hydrocarbon fluids, especially hot hydrocarbon fluids. Nor is there any indication in U.S. Pat. No. 3,909,447 that the compounds disclosed therein would be effective against naphthenic acid corrosion under such conditions.

[0015] Atmospheric and vacuum distillation systems are subject to naphthenic acid corrosion when processing certain crude oils. Currently used treatments are thermally reactive at use temperatures. In the case of phosphorus-based inhibitors, this is thought to lead to a metal phosphate surface film. The film is more resistant to naphthenic acid corrosion than the base steel. These inhibitors are relatively volatile and exhibit fairly narrow distillation ranges. They are fed into a column above or below the point of corrosion depending on the temperature range. Polysulfide inhibitors decompose into complex mixtures of higher and lower polysulfides and, perhaps, elemental sulfur and mercaptans. Thus, the volatility and protection offered is not predictable.

[0016] The problems caused by naphthenic acid corrosion in refineries and the prior art solutions to that problem have been described at length in the literature, the following of which are representative:

> U.S. Pat. No. 3,531,394 to Koszman described the use of phosphorus and/or bismuth compounds in the cracking zone of petroleum steam furnaces to inhibit coke formation on the furnace tube walls.

[0017] U.S. Pat. No. 4,024,049 to Shell et al discloses compounds substantially as described and claimed herein for use as refinery antifoulants. While effective as antifoulant materials, materials of this type have not heretofore been used as corrosion inhibitors in the manner set forth herein. While this reference teaches the addition of thiophosphate esters such as those used in the subject invention to the incoming feed, due to the non-volatile nature of the ester materials they do not distill into the column to protect the column, the pumparound piping, or further process steps. I have found that by injecting the thiophosphate esters as taught herein, surprising activity is obtained in preventing the occurrence of naphthenic acid corrosion in distillation columns, pumparound piping, and associated equipment.

[0018] U.S. Pat. No. 4,105,540 to Weinland describes phosphorus containing compounds as antifoulant additives in ethylene cracking furnaces. The phosphorus compounds employed are mono- and di-ester phosphate and phosphite compounds having at least one hydrogen moiety complexed with an amine.

[0019] U.S. Pat. No. 4,443,609 discloses certain tetrahydrothiazole phosphonic acids and esters as being useful as acid corrosion inhibitors. Such inhibitors can be prepared by reacting certain 2,5-dihydrothiazoles with a dialkyl phosphite. While these tetrahydrothiazole phosphonic acids or esters have good corrosion and inhibition properties, they tend to break down during high temperature applications thereof with possible emission of obnoxious and toxic substances.

[0020] It is also known that phosphorus-containing compounds impair the function of various catalysts used to treat crude oil, e.g., in fixed-bed hydrotreaters and hydrocracking units. Crude oil processors are often in a quandary since if the phosphite stabilizer is not used, then iron can accumulate in the hydrocarbon up to 10 to 20 ppm and impair the catalyst. Although nonphosphorus-containing inhibitors are commercially available, they are generally less effective than the phosphorus-containing compounds.

[0021] U.S. Pat. No. 4,542,253 to Kaplan et al, described an improved method of reducing fouling and corrosion in ethylene cracking furnaces using petroleum feedstocks including at least 10 ppm of a water soluble mine complexed phosphate, phosphite, thiophosphate or thiophosphite ester compound, wherein the amine has a partition coefficient greater than 1.0 (equal solubility in both aqueous and hydrocarbon solvents).

U.S. Pat. No. 4,842,716 to Kaplan et al describes an improved method for reducing fouling and corrosion at least 10 ppm of a combination of a phosphorus antifoulant compound and a filming inhibitor. The phosphorus compound is a phosphate, phosphite, thiophosphate or thiophosphite ester compound. The filming inhibitor is an imidazoline compound. U.S. Pat. No. 4,941,994 Zetmeisl et al discloses a naphthenic acid corrosion inhibitor comprising a dialkyl or trialkylphosphite in combination with an optional thiazoline.

[0022] A significant advancement in phosphorus-containing naphthenic acid corrosion inhibitors was reported in U.S. Pat. No. 4,941,994, in which the present inventor is identified as a co-inventor. Therein it is disclosed that metal corrosion in hot acidic liquid hydrocarbons is inhibited by the presence of a corrosion inhibiting amount of a dialkyl and/or trialkyl phosphite with an optional thiazoline.

[0023] While the method described in U.S. Pat. No. 4,941,994 provides significant improvements over the prior art techniques, nevertheless, there is always a desire to enhance the ability of corrosion inhibitors while reducing the amount of phosphorus-containing compounds which may impair the function of various catalysts used to treat crude oil, as well as a desire for such inhibitors that may be produced from lower cost or more available starting materials.

[0024] Another approach to the prevention of naphthenic acid corrosion is the use of a chemical agent to form a barrier between the crude and the equipment of the hydrocarbon processing unit. This barrier or film prevents corrosive agents from reaching the metal surface, and is generally a hydrophobic material. Gustavsen et al. NACE Corrosion 89 meeting, paper no. 449, Apr. 17-21, 1989 details the requirements for a good filming agent. U.S. Pat. No. 5,252,254 discloses one such film forming agent, sulfonated alkyl-substituted phenol, and effective against naphthenic acid corrosion.

[0025] U.S. Pat. No. 5,182,013 issued to Petersen et al. on Jan. 26, 1993 describes another method of inhibiting naphthenic acid corrosion of crude oil, comprising introducing into the oil an effective amount of an organic polysulfide. This is another example of a corrosion-inhibiting sulfur species. Sulfidation as a source of corrosion was detailed above. Though the process is not well understood, it has been determined that while sulfur can be an effective anti-corrosive agent in small quantities, at sufficiently high concentrations, it becomes a corrosion agent.

[0026] Phosphorus can form an effective barrier against corrosion without sulfur, but the addition of sulfiding agents to the process stream containing phosphorus yields a film composed of both sulfides and phosphates. This results in improved performance as well as a decreased phosphorus requirement. This invention pertains to the deliberate addition of sulfiding agents to the process stream when phosphorus-based materials are used for corrosion control to accentuate this interaction.

[0027] US Patent No. 5,314,643 to Edmondson et at., describes a process for inhibition of corrosion caused by naphthenic acid and sulphur compounds during the elevated temperature processing of crude oil by use of a corrosion inhihitor consisting of a combination of trialkylphosphate and an alkaline earth metal phosphonate-phenate sulphide, functioning effectively as an inhibitor on the internal metallic surfaces of the equipment used in crude oil refining operations.

[0028] Organic polysulfides (Babaian-Kibala, U.S. Pat. No. 5,552,085), organic phosphites (Zetlmeisl, U.S. Pat. No. 4,941,994), and phosphate/phosphite esters (Babaian-Kibala, U.S. Pat. No. 5,630,964), have been claimed to be effective in hydrocarbon-rich phase against naphthenic acid corrosion. However, their high oil solubility incurs the risk of distillate side stream contamination by phosphorus.

[0029] Phosphoric acid has been used primarily in aqueous phase for the formation of a phosphate/iron complex film on steel surfaces for corrosion inhibition or other applications (Coslett, British patent 8,667, U.S. Pat. Nos. 3,132,975, 3,460,989 and 1,872,091). Phosphoric acid use in high temperature non-aqueous environments (petroleum) has also been reported for purposes of fouling mitigation (U.S. Pat. No. 3,145,886).

[0030] US 2007/0119747 A1 to Bradley et al, Baker Hughes Inc. describes a composition and method of inhibiting corrosion caused by naphthenic acid in fluids includes using a combination of a thiophosphorus compound and a hydrogen sulfide scavenging compound, which is non-acidic imine compound.

[0031] WO 2003/093399 to Eaton discloses a method for reducing naphthenic acid corrosion in a hydrocarbon stream containing a naphthenic acid, wherein the hydrocarbon stream is treated with a treating agent comprising at least one overbase complex of a metal salt and an organic acid complexing agent, wherein a reaction product of phosphorous pentasulphide and polyolefins, such as polyisobutylene is used as the organic acid complexing agent to prepare the treating agent.

[0032] US 2,316,078 A to Loane et al discloses a sulfur-containing reaction product of reacting olefin (polyisobutylene (PIB)) with phosphorus pentasulfide (P_2S_5) in absence of sulfur.

[0033] EP 0271998 to Betz Europ Inc. discloses polyalkenylthiophosphonic acid for reducing corrosion, which is a reaction product of reacting olefin (polyisobutylene (PIB)) with phosphorus pentasulfide (P_2S_5) in a single step of heating and in presence of sulfur, and the resulted reaction product is then steamed followed by drying with nitrogen.

[0034] There remains a continuing need to develop additional options for mitigating the corrosivity of acidic crudes at lower cost. This is especially true at times of low refining margins and a high availability of corrosive crudes from sources such as Europe, China, or Africa, and India. The present invention addresses this need.

OBJECTS AND ADVANTAGES OF PRESENT INVENTION

[0035] Accordingly, the objects and advantages of the present invention are described below.

[0036] Accordingly, the present invention discloses a novel additive chemical composition according to claim 1 which will provide very effective inhibitor for naphthenic acid corrosion inhibition as well as sulphur corrosion inhibition, which is very stable even at high temperature, having very low acid value.

[0037] The present invention also discloses a process for naphthenic acid corrosion inhibition of metallic surfaces of any of hydrocarbon processing units according to claim 9.

SUMMARY OF INVENTION

[0038] The present invention relates to the field of processing hydrocarbons which causes corrosion in the metal surfaces of processing units. The present description addresses the technical problem of high temperature naphthenic acid corrosion and sulphur corrosion and provides a solution to inhibit these types of corrosion. The additive chemical composition is formed by a mixture obtained according to claim 1, including mixing compound A, which is obtained by reacting high reactive polyisobutylene (HRPIB) with phosphorous pentasulphide in presence of catalytic amount of sulphur powder with compound C of Formula 2 which is obtained by reacting compound B with ethylene oxide, wherein each of these two mixtures independently provide high corrosion inhibition efficiency in case of high temperature naphthenic acid corrosion inhibition and sulphur corrosion inhibition. The invention is useful in all hydrocarbon processing units, such as, refineries, distillation columns and other petrochemical industries.

DESCRIPTION OF THE INVENTION

[0039] It has been surprisingly discovered by the inventor of the present invention, that a combination of organophosphorus sulphur compound and other phosphorus compound such as, phosphorous thioacid compound, that is, thiophosphite and / or thiophosphite esters, is very efficiently functioning in controlling naphthenic acid corrosion, providing a synergetic effect of combination of phosphorous compounds. The organophosphorus sulphur compound (A) is made from reaction of polyisobutylene with, phosphorus pentasulphide, in presence of sulphur powder. The chemical compound (B), that is, phosphorous thioacid compound is made by reaction of alcohol and phosphorous pentasulphide. The chemical compound (C) is made by reacting the chemical compound (B) with cyclic oxides, such as ethylene oxide.

[0040] The most effective amount of the corrosion inhibitor to be used in accordance with the present invention can vary depending on the local operating conditions and the particular hydrocarbon being processed. Thus, the temperature and other characteristics of the acid corrosion system can have a bearing on the amount of inhibitor or mixture of inhibitors to be used. Generally, where the operating temperatures and / or the acid concentrations are higher, a proportionately higher amount of the corrosion inhibitor will be required. It has been found that the concentration of the corrosion inhibitors or mixture of inhibitors added to the crude oil may range from about 1 ppm to 5000 ppm. It has also been found that it is preferred to add the inhibitors at a relatively high initial dosage rate of 2000-3000 ppm and to maintain this level for a relatively short period of time until the presence of the inhibitor induces the build-up of a corrosion protective coating on the metal surfaces.

[0041] Once the protective surface is established, the dosage rate needed to maintain the protection may be reduced to a normal operational range of about 100-1500 ppm without substantial sacrifice of protection.

[0042] The inventor of the present invention has carried out extensive experimentation to verify the effectiveness of corrosion - inhibitors in case naphthenic acid corrosion inhibition, by experimenting with combinations of inhibitor - compounds A, B, and C, with different proportions of additive compound (A), that is, polyisobutylene plus phosphorus pentasulphide plus sulphur powder and either of compound (B) and (C) . Experiments were also preformed by using compound (A) alone and compound (B) alone and compound (C) alone separately. The methods used in and results of all these experiments are presented in Examples 1 to 6 and Tables 1 to 5.

[0043] The reacted compound (A) is obtained by reaction of olefins with P_2S_5 (Phosphorus pentasulphide) in presence of sulphur powder. The olefins are high reactive polyisobutylene (HRPIB), such as HRPIB containing greater than 70% of vinyledene double bond.

[0044] The ratio of P_2S_5 to Olefin is 0.05 to 2 mole of P_2S_5 to 1 mole of Olefins. The Sulphur powder is present in catalytic quantity, that is, sulphur powder is 0.5% to 5% of Olefin by weight.

Method of synthesis of additive compound A

[0045] The most preferred embodiment of the present invention is described below:

A weighed quantity of HRPIB (High Reactive Polyisobutylene), phosphorous pentasulphide and sulphur powder are charged into a clean four - necked round bottom flask, equipped with nitrogen inlet, stirrer and thermometer, thereby forming a reaction mixture.

[0046] This reaction mixture is stirred and heated to temperature of 160°C under nitrogen gas purging. At this temperature of 160 °C, the raction leads to evolution of hydrogen sulphide gas (H_2S). The temperature of the reaction mixture is now maintained between 160°C to 180°C, for a period of 1 hour to 2 hours. Then the temperature of the mixture is raised to 220°C. The reaction mixture is then maintained at this temperature of 220 °C for 6 hours.

[0047] The resultant reaction mass is then cooled to temperature of 100 °C, when nitrogen gas is purged into the resultant reaction mass, to drive out the hydrogen sulphide present therein. The resulting polyisobutylene phosphorous sulphur compound, which is the additive compound A of the present invention, is used as a high temperature naphthenic acid corrosion inhibitor. This compound is used neat or diluted in appropriate solvent such as xylene, toluene, and aromatic solvent as any other appropriate solvent to achieve inhibition of high temperature naphthenic acid corrosion.

Method of synthesis of additive compound B

[0048] The present description is not specially concerned with the manner of thiophosphate and thiophosphite ester preparation. Thiophosphate ester compounds are readily prepared as the reaction product, for example, of phosphorous pentasulphide (P_2S_5) and an alcohol and / or thio in a suitable solvent.

[0049] N - octanol is charged into a clean four - necked - flask, which is equipped with stirrer, nitrogen gas inlet and condenser. Appropriate amount of phosphorous pentasulphide is added to the flask in installments. The molar ratio ofN - octanol to P_2S_5 is between 2:1 to 4:1. After raising the temperature to 85°C to 135°C, the H_2S gas is seen to evolve. After one hour the reaction mixture is heated to 115 °C to 165°C and the flask is maintained at that temperature for 1 hour to 3 hours. The sample is cooled and filtered through typically 5 micron filter. The filtered sample is then heated to 65°C to 115°C. The nitrogen gas is now purged for 3 to 7 hours. The resulting compound is the additive compound B2. The additive compound B 2 is tested for its efficiency for naphthenic acid corrosion inhibition. The additive compound (A + B2) is also tested for its efficiency for naphthenic acid corrosion inhibition. The method of synthesis of additive compound B2 is explained in Example 3.

Method of synthesis of additive compound C

[0050] The additive compound B2 is transferred to the autoclave and ethylene oxide is added at 15°C to 50°C till the pressure in the autoclave remains constant, thereby indicating no further absorption of the ethylene oxide by the reactions mixture. The acid value of the final product is 25 mg / KOH. After addition of ethylene oxide, the reaction mixture is maintained at 35°C to 85°C for 3 to 7 hours. The nitrogen gas is then purged for further 3 to 7 hours duration. The resulting sample, that is, additive compound C2 is filtered and tested for its efficiency in naphthenic acid corrosion inhibition. The efficiency of the combination additive compound (A + C2) is also tested. The method of synthesis of additive compound C2 is illustrated in Example 4.

[0051] The present description describes a method for inhibiting corrosion on the metal surfaces of the processing units which process hydrocarbons such as crude oil and its fractions containing naphthenic acid. This is explained in detail in its simplest form wherein the following method steps are carried out, when it is used to process crude oil in process units such as distillation unit. Similar steps can be used in different processing units such as, pumparound piping, heat exchangers and such other processing units.
These method steps are explained below:

a) heating the hydrocarbon containing naphthenic acid to vaporize a portion of the hydrocarbon:
b) allowing the hydrocarbon vapors to rise in a distillation column;
c) condensing a portion of the hydrocarbon vapours passing through the distillation column to produce a distillate;
d) adding to the distillate, from 5 to 2000 ppm of a combination (A) + (C) additive compound of the present invention [(or a comparative combination of (A) + (B)];
e) allowing the distillate containing the invention combination (A) + (C) additive compounds [or a comparative combination of (A) + (B) additive compounds] to contact substantially the entire metal surfaces of the distillation unit to form protective film on such surface, whereby such surface is inhibited against corrosion.

[0052] It is advantageous to treat distillation column, trays, pumparound piping and related equipment to prevent naphthenic acid corrosion, when condensed vapours from distilled hydrocarbon fluids contact metallic equipment at temperatures greater than 200 °C, and preferably greater than 400 °C. The combination (A) + (C) additive compound according to the invention, or the comparative combination (A) + (B) additive compound is generally added to the condensed distillate and the condensed distillate is allowed to contact the metallic surfaces of the distillation column, packing, trays, pump around piping and related equipment as the condensed distillate passes down the column and into the distillation vessel. The distillate may also be collected as product. The corrosion inhibitors remain in the resultant collected product.

[0053] In commercial practice, the additives described may be added to a distillate return to control corrosion in a draw tray and in the column packing while a second injection may be added to a spray oil return immediately below the draw trays to protect the tower packing and trays below the distillate draw tray. It is not so critical where the additive described is added as long as it is added to distillate that is later returned to the distillation vessel, or which contact the metal interior surfaces of the distillation column, trays, pump around piping and related equipments.

[0054] The method of making and using the polyisobutylene phosphorous sulphur compound that is, additive compound A of the present invention for achieving inhibition of high temperature naphthenic acid corrosion is explained below with the help of examples 1 and 5.

Discussion about Unexpected Surprising Synergistic Technical Effects of very High Efficiency in Naphthenic Acid Corrosion Inhibition by use of Additive Compound of present invention.

[0055] The method of using the additive compound described herein, that is, the thiophosphate esters and derivatives thereof, in combination with the polyisobutylene phosphorous sulphur compound of the present invention, for achieving inhibition of high temperature naphthenic acid corrosion is explained below with the help of examples 1 to 6.

[0056] The detailed discussion given below with respect to the results presented in Table 1 to 5 for experiments described in Examples 1 to 6 explains the effectiveness of the additive compound described herein in high temperature, naphthenic acid corrosion inhibition or sulphur corrosion inhibition.

[0057] B2 (not according to the invention) represents a form of additive compound B obtained under particular operating conditions of synthesis.

C1, C2 represents different forms of additive compound C obtained under different operating conditions of synthesis.

[0058] Referring to Table 1 where molar ratio of HRPIB to phosphorous pentasulphide was 1:1, it is observed that, in the static test, as the effective dosage of additive compound A of the present invention was increased from 200 ppm to 400 ppm, the corrosion inhibition efficiency, as calculated by formula given in Example 5, increased from 55.7529 % to 99.6783 %.

[0059] Referring to Table 2, it is observed that, the compound C1 of the present invention, when used in isolation, in two separate total dosages of 150 ppm and 180 ppm (wherein 50% was active dosage), the corrosion inhibition efficiency increased respectively from above 55% to above 76 %. When compound C1 was used in combination with compound A in two separate total dosages of 300 ppm and 360 ppm (with ratio of A : C1 as 1: 1, and when each of dosages of A and C1, was 50% active), the corrosion inhibition efficiency increased from above 90 % to above 99 %.

[0060] Referring to Table 3, it is observed that, the compound C2 of the present invention, when used in isolation, in total dosage of 90 ppm (wherein 50 % was active dosage), the corrosion inhibition efficiency was above 60 %. When the compound C 2 was used in combination with compound A in five separate total dosages ranging between 200 ppm and 400 ppm, (with ratio of A: C2 varying from 1.22: 1 to 3. 44: 1 and when each of dosages of A and C2 was 50 % active), the **corrosion inhibition efficiency which ranged between above 85 % and above 98 %.**

[0061] Referring to Table 4, it is observed that, the compound B2 (not according to the invention), when used in isolation, in two separate total dosages of 90 ppm and 180 ppm (wherein 50 % was active dosage), the corrosion inhibition efficiency was above 49% and above 75 % respectively. When the compound B2 was used in combination with compound A in total dosage of 400 ppm (with ratio of A: B2 as 3.44: 1, and when each of dosages of A and B2 was 50 % active) **the corrosion inhibition efficiency was above 85%.**

[0062] Referring to Table 5, in the High Temperature Naphthenic Acid Corrosion Dynamic Test, it is observed that, the compound A of the present invention, when used in isolation, in total two separate dosages separately of 20 ppm and 50 ppm (wherein 50% was active dosage), the corrosion inhibition efficiency was above 19% and 54% respectively. When the compound C2 was used in combination with compound A, in three separate total dosages from 40 ppm, and 90 ppm, (with ratio of A : C2 varying from 1 : 1 to 1.25 : 1 and when each of dosages of A and C2 was 50 % active) the corrosion inhibition efficiency varied between above 77 % and 100 %.

[0063] Thus it is seen from the earlier discussion that the additive compound comprising the compound A and the compound C of the present invention used for corrosion - inhibition has the following important distinguishing features, as compared to the prior art.

1) The inventor of the present invention, after extensive experimentation, has surprisingly found that the additive compounds used by the inventor, that is, additive compound (A+C) is the POLYMERIC ADDITIVE, which is highly effective in high temperature corrosion inhibition.
The prior - art does not teach or suggest use of a polymeric additive in naphthenic acid corrosion inhibition or sulphur corrosion inhibition or any corrosion inhibition, in general.

2) Another distinguishing feature of the additive compound of present invention is that it has more thermal stability as compared to the additive compounds taught by the prior - art, due to the polymeric nature of the additive compound of present invention. Due to its high thermal stability the additive compound of present invention is very effective in high temperature naphthenic corrosion inhibition or high temperature sulphur corrosion.

3) Yet another distinguishing feature of the additive compound of present invention is that, it has very low acidity as compared to the additive compounds of prior art, for example, the phosphate esters of prior art has very high acidity. The phosphate esters of prior art are known to have a tendency to decompose, even at lower temperatures, to form phosphoric acids, which travel further along the hydrocarbon stream and react with metal surfaces of equipments such as packing of distillation column, to form solid iron phosphate. These solids plug the holes of equipments and thereby lead to fouling of distillation column.

The additive compound of the present invention does not have this deficiency.

4) The distinguishing features between US Patent No. 5552085 and the present invention are described below. Referring to the results of experiments given in Table 1 (examples 5 and 6) of US Patent No 5552085, and comparing the results of NTPE and NNTPE, it is seen that there is no effect of neutralization at dosage of 500 ppm and TAN of 4.5 mg/KOH, as the corrosion inhibition rates are same. Further, comparing results of example 3 and 4, given in the same Table 1, it is seen that corrosion inhibition rate decreases when neutralized or treated thiophosphoric acid compounds are used. These data will teach away from use of neutralizing or treating thiophosphoric acid compounds, when they are used for corrosion inhibition. The present invention teaches that reacting thiophosphoric acid compound with ethylene oxide and using the treated compound for inhibiting corrosion, improves the efficiency of corrosion inhibition, when used singularly or in combination with compound A.

EXAMPLE 1

Synthesis of polymeric organophosphorous sulphur compound - Additive compound A

[0064] The weighed quantities of 68.16 gm of commercially available HRPIB (High Reactive Polyisobutylene with molecular weight 950 approximately), 30.31 gm of Phosphorous Pentasulphide and 1.51 gm of Sulphur Powder are charged into a clean four necked round bottom flask, equipped with N_2 inlet, stirrer and thermometer, thereby forming a reaction mixture. This gives 1: 1 mole ratio of Phosphorous Pentasulphide to Olefin.

[0065] The reaction mixture was stirred and heated to 160°C temperature under nitrogen gas purging. The purging of N_2 gas led to removal of hydrogen sulphide gas, which was generated during the reaction. The temperature of the reaction mixture was maintained between 160°C to 180°C, for a period of 1 hour to 2 hours. Then the temperature of the mixture was raised to 220°C and the mixture was maintained at this temperature for 6 to 10 hours.

[0066] The resultant reaction mass was then cooled to 100°C when nitrogen gas was purged into it, to drive out the hydrogen sulphide gas present therein. The resulting polyisobutylene phosphorous sulphur compound was used as a high temperature naphthenic acid corrosion inhibitor, as well as, sulphur corrosion inhibitor. This compound was used neat or diluted in appropriate solvent such as xylene, toluene, and aromatic solvent as well as any other appropriate solvent to achieve inhibition of high temperature naphthenic acid corrosion as well as sulphur corrosion.

[0067] The above mentioned synthesis is carried out for different mole ratios of HRPIB to Phosphorous Pentasulphide. A similar synthesis was carried out by using normal polyisobutylene instead of HRPIB.

[0068] The resulting polyisobutylene phosphorous sulphur compound was tested for its napthenic acid corrosion inhibition efficiency. The testing method is presented in Example 5. The results are presented in Table 1 at Experiment Numbers 2, 3 and 4.

EXAMPLE 2

Synthesis of additive compound C1 and napthenic acid corrosion inhibition efficiency testing of additive compound (A + C1) using static test method

[0069] The clean four - necked - flask was equipped with stirrer, nitrogen gas inlet and condenser. N - noctanol weighing 400gms was charged in the flask. The phosphorous pentasulphide weighing 187 gms, was then added to the flask in installments. The temperature of the flask was then increased to 110 °C. The H_2S gas was seen to be evolved after addition of P_2S_5. After one hour, the reaction mixture in the flask was heated to 140°C and the flask was maintained at that temperature for one hour. The acid value of the reaction mixture was about 125 mg/KOH. The reaction mixture that is compound B1 was then transferred to the autoclave, and ethylene oxide was added till the pressure remained constant, thereby indicating no further absorption of the ethylene oxide by the reaction mixture. The system was then purged with nitrogen gas to remove the excess of ethylene oxide. The acid value of the final product was about 25 mg/KOH. The resulting compound of example 2 that is compound C1 was tested for its naphthenic acid corrosion efficiency. The efficiency of combination compound (A + C1) was also tested. All of these results are presented in Table 2 at Experiment Numbers 5, 6, 7 and 8.

EXAMPLE 3 (not according to the invention)

Synthesis of additive compound B2 and naphthenic acid corrosion inhibition efficiency testing of additive compound (A + B2) using static test method

[0070] The clean four - necked - flask was equipped with stirrer, nitrogen gas inlet and condenser. N- noctanol weighing 400gms was charged in the flask. Phosphorous pentasulphide weighing 187 gms, was then added to the flask in installments. The temperature of the flask was then increased to 110 °C. The H_2S gas was seen to be evolved after addition of P_2S_5. After one hour, the reaction mixture in the flask was heated to 140 °C and the flask was maintained at that temperature for one hour. The sample was cooled and filtered through 5 micron filter. The sample was heated to 90°C. The nitrogen gas was purged for 5 hours. The resulting sample, that is compound B2 was analvzed for its acid value, which was found to be between 110 to 130 mg /KOH. The compound B2 was tested for its naphthenic acid corrosion efficiency. The efficiency of the combination compound (A + B2) was also tested. The testing method is presented in Example 5. The results are presented in Table 4 at Experiment numbers 15, 16 and 17.

EXAMPLE 4

Synthesis of additive compound C2 and naphthenic acid corrosion inhibition efficiency testing of additive compound (A + C2) using static test method

[0071] This resulting reaction mixture of Example 3, that is, Compound B2, was then transferred to the autoclave, and ethylene oxide was added at 30°C till the pressure remained constant, thereby indicating no further absorption of the ethylene oxide by the reaction mixture. The acid value of the final product was about 25 mg/KOH. After addition of ethylene oxide, the reaction mixture was maintained at 60°C for 5 hours. The nitrogen gas was then purged for further 5hours duration. The sample, that is, compound C2, was filtered and tested for its efficiency in naphthenic acid corrosion inhibition. The efficiency of combination compound (A +C2) was also tested. The testing method is presented in Example 5. The results are presented in Table 3 at Experiment Numbers 9 to 14.

EXAMPLE 5

High Temperature Naphthenic Acid Corrosion Test (STATIC TEST)

[0072] In this example, various amounts of a 50 % formulation of the composition prepared in accordance, with Example 1, and the compounds prepared in accordance with Examples 2 to 4 were tested for corrosion inhibition efficiency on steel coupons in hot oil containing naphthenic acid. A weight loss coupon, immersion test was used to evaluate the compounds described for their effectiveness in inhibition of naphthenic acid corrosion at 290°C temperature. Different dosages of compounds were used, as 50% active solution, as shown in Tables 1 to 4.

[0073] A static test on steel coupon was conducted without using any additive. This test provided a blank test reading.

[0074] The reaction apparatus consisted of a one - litre four necked round bottom flask equipped with water condenser, N_2 purger tube, thermometer pocket with thermometer and stirrer rod. 600 gm (about 750 ml) paraffin hydrocarbon oil (D - 130) was taken in the flask. N_2 gas purging was started with flow rate of 100 cc / minute and the temperature was raised to 100°C, which temperature was maintained for 30 minutes. A compound of example 1 comprising Polyisobutylene and Phosphorous Pentasulphide with sulphur powder was added to the reaction mixture. The reaction mixture was stirred for 15 minutes at 100°C temperature. After removing the stirrer, the temperature of the reaction mixture was raised to 290°C. A pre - weighed weight - loss carbon steel coupon CS 1010 with dimensions 76mm... times 13mm... times 1.6 mm was immersed. After maintaining this condition for 1hour to 1.5 hours, 31 gm of naphthenic acid (commercial grade with acid value of 230 mg /KOH) was added to the reaction mixture. A sample of one gm weight of reaction mixture was collected for determination of acid value, which was found to be approximately 11.7 mg/KOH. This condition was maintained for four hours. After this procedure, the metal coupon was removed, excess oil was rinsed away, the excess corrosion product was removed from the metal surface. Then the metal coupon was weighed and the corrosion rate was calculated in mils per year.

[0075] Similar method was used for testing the efficiency of naphthenic acid corrosion inhibition of other compounds. The results are presented in Table 1 to 4.

Calculation of Corrosion Inhibition Efficiency.

[0076] The method used in calculating Corrosion Inhibition Efficiency is given below. In this calculation, corrosion inhibition efficiency provided by additive compound is calculated by comparing weight loss due to additive with weight loss of blank coupon (without any additive).

$$\text{Corrosion Inhibition Efficiency} = \frac{(\text{Weight loss for blank without additive}) - (\text{weight loss with additive})}{(\text{weight loss for blank without additive})} \text{ X } 100$$

[0077] The corrosion rate in MPY (mils per year) is calculated by the formula,

$$\text{MPY} = \frac{534 \text{ x Weight loss in mg}}{(\text{Density in gm/cc}) \text{ x } (\text{Area in in}^2) \text{ x } (\text{Time of test in hours})}$$

EXAMPLE 6

High Temperature Naphthenic Acid Corrosion Dynamic Test:

[0078] The dynamic testing was carried out by using rotating means provided in the temperature - controlled autoclave and was carried out by using passivated steel coupons. A dynamic test on steel coupon was conducted without using any additive o passivation. This test provided a blank test reading.

[0079] A weight-loss coupon immersion dynamic test was used to evaluate the additive compounds A and (A + C2) for effectiveness in inhibition of naphthenic acid corrosion at 290°C temperature in dynamic condition.

[0080] The following test equipment and materials were used in the Dynamic Corrosion Test:

2. Temperature controlled autoclave
3. Preweighed weight - loss carbon steel coupons CS 1010 with dimensions 76mm...times 13mm... times 1.6 mm.
4. Means to rotate the coupon, to provide a peripheral velocity in excess of 3 m / second.

Material:

[0081]

1. Paraffin hydrocarbon oil (D - 130 - Distilled residue) with naphthenic acid added to provide an acid neutralization number of approximately 2mg /KOH.

2. Nitrogen gas in the vapour space.

[0082] Two pre - weighed weight - loss carbon steel coupons, were clamped to the rotating means of the autoclave. The dynamic test was conducted at 290°C for 4 hours. After the test, the coupons were removed, excess oil was rinsed away, excess corrosion product was removed from the surface of coupons. The coupons were then weighed and the corrosion rate was calculated as mils / year. The results of these dynamic tests are presented in Table 5. The detailed steps of the dynamic test procedure are given below:

1. Take 400 gms of paraffin hydrocarbon oil D - 130 (distilled residue) in the autoclave.
2. Add desired dosage of additive compounds described herein and mix well.
3. Mount the pre - weighed coupons in the autoclave, and set the temperature to 120°C.
4. Start heating and keep the stirring at 500 rpm with continous nitrogen gas purging (bubbling) and after few minutes further increase the rpm of stirrer speed to 1000 rpm.
5. Increase temperature of heating to 160°C and stop nitrogen gas purging,
6. Now raise the temperature to 290°Cand let the autoclave run at temperature 290°C for 2 hours (the passivation time).
7. Lower the temperature to 100°C.
8. Open the reactor and add the naphthenic acid for achieving acid value of TAN 2.0 mg /KOH (the naphthenic acid

is 3.35 gm with acid value of 237 mg/KOH).

9. Stir the sample and collect 2 to 3 ml of naphthenic acid for TAN measurement.
10. Close the autoclave and start heating by raising temperature to 290°C and stir the mixture at 1000 rpm, for 4 hours.
11. Cool the reactor to 100°C.
12. Remove the coupon and clean it initially with toluene / hexane and finally with acetone.
13. Dry the coupon for 5 minutes at 120°C and keep it in the desicator.
14. Weigh the coupon
15. Calculate the naphthenic acid corrosion inhibition efficiency.
16. The results of the dynamic tests are presented at the Experiment Numbers 18 to 22 in Table 5.

TABLE 1

Experiment Sr. No.	Inhibitor	Dosage in ppm	Weight loss in mg	Corrosion Rate MPY	Corrosion Inhibitors Efficiency in %
1	Only metal Blank (No inhibitor Compound)	-	89.5	447.95	-
2	50% active Compound of Example 1, (Polyisobutylene, Phosphorus penta sulphide and sulphur powder) and 50% solvent	200	63.3	316.82	29.27
3	Compound as per experiment No. 2	300	39.6	198.20	55.75
4	Compound as per experiment No. 2	400	15.2	76.08	83.02

TABLE 2

Experiment Sr. No.	Compound (A) dosage in ppm (50% was active)	Compound (C1)dosage in ppm (50 % was active)	Ratio (A) : (C1)	Total Dosage in ppm	Weight loss in mg.	Corrosion Rate MPY	Corrosion Inhibitor Efficiency in %
2	200	-	-	200	63.3	316.82	29.27
3	300	-	-	300	39.6	198.20	55.75
4	400	-	-	400	15.2	76.08	83.02
5	-	150	-	150	39.6	198.20	55.75
6	-	180	-	180	21.1	105.61	76.43
7	150	150	1:1	300	8.1	40.54	90.95
8	180	180	1:1	360	0.2	1.001	99.78

TABLE 3

Experiment Sr. No.	Compound (A) dosage in ppm (50% was active)	Compound (C2)dosage in ppm (50 % was active)	Ratio (A) : (C2)	Total Dosage in ppm	Weight loss in mg.	Corrosion Rate MPY	Corrosion Inhibitor Efficiency in %
2	200	-	-	200	63.3	316.82	29.27
3	300	-	-	300	39.6	198.20	55.75
4	400	-	-	400	15.2	76.08	83.02
9	-	90	-	90	35.0	175.18	60.89
10	310	90	3.44:1	400	1.3	6.51	98.55
11	180	120	1.5:1	300	10.1	50.55	88.72

(continued)

Experiment Sr. No.	Compound (A) dosage in ppm (50% was active)	Compound (C2)dosage in ppm (50 % was active)	Ratio (A) : (C2)	Total Dosage in ppm	Weight loss in mg.	Corrosion Rate MPY	Corrosion Inhibitor Efficiency in %
12	110	90	1.22:1	200	13.2	66.07	85.25
13	230	120	1.92:1	350	6.4	32.03	92.85
14	280	120	2.33:1	400	2.6	13.01	97.10
23	-	150	-	150	24.1	120.63	73.07
24	-	180	-	180	10.0	50.05	88.83

TABLE 4 (not according to the invention)

Experiment Sr. No.	Compound (A) dosage in ppm (50% was active)	Compound (B2)dosage in ppm (50 % was active)	Ratio (A) : (B2)	Total Dosage in ppm	Weight loss in mg.	Corrosion Rate MPY	Corrosion Inhibitor Efficiency in %
2	200	-	-	200	63.3	316.82	29.27
3	300	-	-	300	39.6	198.20	55.75
4	400	-	-	400	15.2	76.08	83.02
15	-	90	-	90	45	225.23	49.72
16	-	180	-	180	22	110.11	75.42
17	310	90	3.44:1	400	12.7	63.56	85.81

TABLE 5

Experiment Sr. No.	Compound (A) dosage in ppm (50% was active)	Compound (C2)dosage in ppm (50 % was active)	Ratio (A) : (C2)	Total Dosage in ppm	Weight loss in mg.	Corrosion Rate MPY	Corrosion Inhibitor Efficiency in %
23	blank	nil	nil	nil	7.5	37.53	-
18	50	-	-	50	6.05	30.28	19.33
19	20	-	-	20	3.45	17.27	54.0
20	50	40	1.25:1	90	0	0	100.0
21	30	30	1:1	60	0.7	3.5	90.67
22	20	20	1:1	40	1.7	8.51	77.33

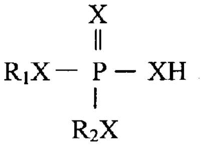
[0083] In view of the details given in foregoing description of the present application, it will be apparent to a person skilled in the art that the present description basically describes the following items:

ITEM 1

[0084] A novel additive for naphthenic acid corrosion inhibition comprising a chemical mixture of corrosion inhibiting amount of an olefin phosphorous sulphur compound A with corrosion inhibiting amount of any one of thiophosphorous sulphur compounds such as compound B and compound C, wherein said olefin phosphorous sulphur compound A is produced by reacting said olefin with phosphorous pentasulphide in presence of catalytic amount of sulphur, capably forming a reaction mixture, with molar ratio of said olefin to said phosphorous pentasulphide being between 1:0.05 to

1:1.5, preferably being 1:1;
and wherein said compound B is a thiophosphorous compound such as phosphorous thioacid ester of the formula 1

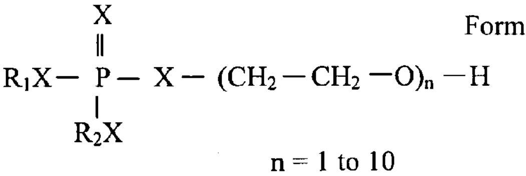
Formula 1



$$R_1X-\overset{\overset{\displaystyle X}{\|}}{\underset{\underset{\displaystyle R_2X}{|}}{P}}-XH$$

wherein X is independently either sulphur or oxygen and at least one X is sulphur and wherein R_1 and R_2 are hydrogen or hydrocarbyl having 5 to 18 carbon atoms and includes mono - , di -, mixtures thereof;
wherein said compound C of the formula 2 is obtained by reacting said compound B with an oxide selected from the group consisting of ethylene oxide, propylene oxide and butylene oxide and wherein the formula 2 comprises resulting compound C obtained after reaction of said compound B with said ethylene oxide, and includes mono - , di -, mixtures thereof;;

Formula 2



$$R_1X-\overset{\overset{\displaystyle X}{\|}}{\underset{\underset{\displaystyle R_2X}{|}}{P}}-X-(CH_2-CH_2-O)_n-H$$

$$n = 1 \text{ to } 10$$

ITEM 2

[0085] A novel additive as described in item 1, wherein said olefin is polyisobutylene, which is either high reactive or normal.

ITEM 3

[0086] A novel additive, as described in item 1 and 2, wherein said olefin Phosphorus sulphur compound is arrived at, by stirring and heating said reaction mixture of item 1, to 160°C under nitrogen gas purging, maintaining said reaction mixture between about 160°C to about 180°C for a period of about 1 hour to about 2 hours, raising temperature of said reaction mixture to from about 185°C to about 250°C, preferably from about 190°C to about 230°C, more preferably from about 210°C to about 225°C and maintaining said reaction mixture with raised temperature for about 1 to about 24 hours, preferably for about 6 to about 10 hours, cooling the reaction mass to 100°C and purging nitrogen gas into reaction vessel to drive out the hydrogen sulphide gas, thereby resulting into said composition.

ITEM 4

[0087] A novel additive according to any one of the preceding items wherein said olefin has between 10 and 1000 carbon atoms.

ITEM 5

[0088] A novel additive according to any one of the preceding items wherein said olefin has a molecular weight of from 200 to 10,000.

ITEM 6

[0089] A novel additive according to any one of the preceding items wherein said olefin has a molecular weight of about 950 to about 1300.

ITEM 7

[0090] A novel additive, as described in item 1, wherein the amount of said mixture of said compound A and said compound B, which should be added to crude oil for high temperature naphthenic acid corrosion inhibition, is from about

1 ppm to about 5000 ppm, preferably from about 1 ppm to about 300 ppm.

ITEM 8

[0091] A novel additive, as described in item 7, wherein the ratio of said compound A to said compound B, by weight, is from about 1:1 to about 4: 1.

ITEM 9

[0092] A novel additive, as described in item 1, wherein the amount of said mixture of said compound A and said compound C, which should be added to crude oil for high temperature naphthenic acid corrosion inhibition, is from about 1 ppm to about 5000 ppm, preferably from about 1 ppm to about 300 ppm.

ITEM 10

[0093] A novel additive, as described in item 9 wherein the ratio of said compound A to said compound C, by weight, is from about 1:1 to about 4: 1.

ITEM 11

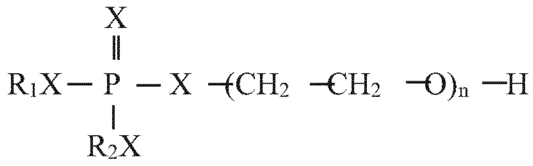
[0094] A process for naphthenic acid corrosion inhibition and / or sulphur corrosion inhibition of metallic surfaces of any of the hydrocarbon, processing units, with said processing units comprising distillation columns, strippers, trays, pump around piping and related equipments, using inhibitor combination compound such as, any mixture from two mixtures, such as, a mixture of two compounds A and B of items 1, 2, 7 and 8, or a mixture of two compounds A and C of items 1, 2, 9 and 10, comprising the steps of:

a. heating the hydrocarbon containing naphthenic acid and / or sulphur compounds, to vapourize a portion of said hydrocarbon;
b. condensing a portion of the hydrocarbon vapours, passing through said hydrocarbon processing unit, to produce a condensed distillate;
c. adding to said distillate, before said condensed distillate is returned to said hydrocarbon processing unit or collected as a product, from about 1 ppm to about 5000 ppm, preferably from about 1ppm to 300 ppm of said inhibitor combination compound such as, any mixture from two mixtures, such as, said mixture of two compounds A and B of items 1, 2, 7 and 8, or said mixture of two compounds A and C of items 1, 2, 9 and 10, wherein ratio by weight of A to B is from about 1 :1 to about 4: 1 and ratio of A to C is from about 1:1 to about 4: 1;
d. allowing said condensed distillate containing said inhibitor combination compound such as, any mixture from two mixtures, such as, said mixture of two compounds A and B of items 1, 2, 7 and 8, or said mixture of two compounds A and C of items 1, 2, 9 and 10, to contact said metallic surfaces of said hydrocarbon processing unit, to form a protective film on said surfaces whereby each surface is inhibited against corrosion; and
e. allowing said condensed distillate to return to said hydrocarbon processing unit, or to be collected as said product.

Claims

1. A additive for high temperature naphthenic acid corrosion inhibition comprising a chemical mixture of:

a) corrosion inhibiting amount of polyisobutylene phosphorous sulphur compound A; and
b) corrosion inhibiting amount of thiophosphorous sulphur compound C,
wherein said polyisobutylene phosphorous sulphur compound A is obtained by reacting an olefin with phosphorous pentasulphide in presence of catalytic amount of sulphur, forming a reaction mixture, wherein molar ratio of said olefin to said phosphorous pentasulphide is between 1:0.05 to 1:2, said olefin is high reactive polyisobutylene (HRPIB), said sulphur is sulphur powder, and wherein said sulphur powder is present in catalytic quantity of 0.5% to 5% of said olefin by weight;
wherein said thiophosphorous sulphur compound C is of the formula 2, is obtained by reacting a thiophosphorous sulphur compound B with ethylene oxide, and wherein the formula 2 comprises resulting compound C obtained after reaction of said compound B with said ethylene oxide,
wherein said thiophosphorous sulphur compound C includes mono-ester, di-ester, mixture thereof;



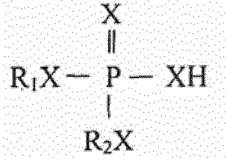
$$R_1X-\overset{\overset{\displaystyle X}{\|}}{\underset{\underset{\displaystyle R_2X}{|}}{P}}-X-(CH_2-CH_2-O)_n-H$$

n = 1 to 10

Formula 2

wherein X is independently either sulphur or oxygen and at least one X is sulphur, and wherein R_1 and R_2 are hydrogen or hydrocarbyl having 5 to 18 carbon atoms; wherein said compound B is a phosphorous thioacid ester of the formula 1

Formula 1



$$R_1X-\overset{\overset{\displaystyle X}{\|}}{\underset{\underset{\displaystyle R_2X}{|}}{P}}-XH$$

wherein X is independently either sulphur or oxygen and at least one X is sulphur and wherein R_1 and R_2 are hydrogen or hydrocarbyl having 5 to 18 carbon atoms,
wherein said phosphorous thioacid ester of the formula 1 includes mono-ester, di-ester, mixture thereof;

wherein weight ratio of the compound A to the compound C varies from 1:1 to 4:1.

2. The additive as claimed in claim 1, wherein said molar ratio of said olefin to said phosphorous pentasulphide is 1:1.

3. The additive as claimed in **claim 1,** wherein said HRPIB contains greater than 70% of vinyledene double bond.

4. The additive as claimed in **claim 1,** wherein said polyisobutylene phosphorus sulphur compound A is obtained by reacting said HRPIB with said phosphorous pentasulphide in the presence of said sulphur powder forming the reaction mixture,

   a) by stirring and heating said reaction mixture of said HRPIB said phosphorous pentasulphide and said sulphur powder to a temperature of 160°C under nitrogen gas purging which led to remove hydrogen sulphide (H_2S) gas generated during the reaction,
   b) maintaining said reaction mixture between 160°C to 180°C for a period of 1 hour to 2 hours,
   c) raising said temperature of said reaction mixture to from 185°C to 250°C,
   d) maintaining said reaction mixture with said raised temperature for 1 to 24 hours,
   e) cooling the reaction mixture to 100°C, and
   f) purging nitrogen gas into reaction vessel to drive out the hydrogen sulphide gas present therein, thereby resulting into said polyisobutylene phosphorus sulphur compound A.

5. The additive as claimed in **claim 4,** wherein said temperature of said reaction mixture of step c) is raised to from 190°C to 230°C.

6. The additive as claimed in **claim 4,** wherein said temperature of said reaction mixture of step c) is raised to from 210°C to 225°C.

7. The additive according to any one of the preceding **claims 1 to 6,** wherein said HRPIB has between 10 and 1000 carbon atoms.

8. The additive according to any one of the preceding **claims 1 to 6,** wherein said HRPIB has a molecular weight of

from 200 to 10,000.

9. A process for naphthenic acid corrosion inhibition of metallic surfaces of any of hydrocarbon processing units, with said processing units comprising distillation columns, strippers, trays, and pump around piping, using an additive comprising a mixture of said compound A and said compound C of **claim 1,** comprising the steps of:

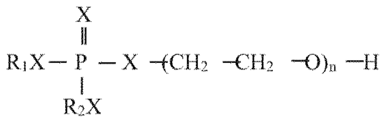
    a. heating hydrocarbon containing naphthenic acid compounds, to vapourize a portion of said hydrocarbon;
    b. condensing a portion of the hydrocarbon vapours, passing through said hydrocarbon processing unit, to produce a condensed distillate;
    c. adding to said distillate, before said condensed distillate is returned to said hydrocarbon processing unit or collected as a product, from 1 ppm to 5000 ppm of said additive, wherein ratio by weight of said compound A to said compound C is from 1:1 to 4:1;
    d. allowing said condensed distillate containing said additive, to contact said metallic surfaces of said hydrocarbon processing unit, to form a protective film on said surfaces whereby each surface is inhibited against corrosion; and
    e. allowing said condensed distillate to return to said hydrocarbon processing unit, or to be collected as said product.

Patentansprüche

1. Zusatzmittel zur Inhibierung von Naphthensäurekorrosion bei hohen Temperaturen, das ein chemisches Gemisch umfasst aus:

    a) einer korrosionsinhibierenden Menge einer phosphorhaltigen Polyisobutylenschwefelverbindung A; und
    b) einer korrosionsinhibierenden Menge einer Thiophosphor-schwefelverbindung C,

    - wobei die phosphorhaltige Polyisobutylenschwefelverbindung A durch Umsetzung eines Olefins mit phosphorhaltigem Pentasulfid in Gegenwart einer katalytischen Menge van Schwefel erhalten wird, wodurch ein Reaktionsgemisch gebildet wird, wobei das Molverhältnis des Olefins zu dem phosphorhaltigen Pentasulfid 1/0,05 bis 1/2 beträgt, wobei es sich bei dem Olefin um hochreaktives Polyisobutylen (HRPIB) handelt, wobei es sich bei dem Schwefel um Schwefelpulver handelt und wobei das Schwefelpulver in einer katalytischen Menge von 0,5 Gew.-% bis 5 Gew.-% bezogen auf das Olefin vorliegt;
    - wobei es sich bei der Thiophosphorschwefelverbindung C um eine Verbindung der Formel 2 handelt, die durch Umsetzung einer Thiophosphorschwefelverbindung B mit Ethylenoxid erhalten wird, und wobei die Formel 2 die erhaltene Verbindung C umfasst, die nach Umsetzung der Verbindung B mit dem Ethylenoxid erhalten wurde;
    - wobei die Thiophosphorschwefelverbindung C Monoester, Diester oder Mischungen davon enthält;



$$R_1X-\overset{\overset{\displaystyle X}{\|}}{\underset{\underset{\displaystyle R_2X}{|}}{P}}-X-(CH_2-CH_2-O)_n-H$$

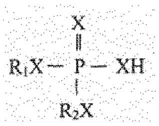
n = 1 bis 10

Formel 2

        -- worin X unabhängig entweder für Schwefel oder für Sauerstoff steht und mindestens ein X für Schwefel steht, und
        -- worin R_1 und R_2 für Wasserstoff oder einen Kohlenwasserstoffrest mit 5 bis 18 Kohlenstoffatomen stehen;

    - wobei es sich bei der Verbindung B um einen phosphorhaltigen Thiosäureester der Formel 1 handelt

Formel 1



$$R_1X-\underset{\underset{R_2X}{|}}{\overset{\overset{X}{\|}}{P}}-XH$$

-- worin X unabhängig entweder für Schwefel oder für Sauerstoff steht und mindestens ein X für Schwefel steht und worin R_1 und R_2 für Wasserstoff oder einen Kohlenwasserstoffrest mit 5 bis 18 Kohlenstoffatomen stehen,

wobei der phosphorhaltige Thiosäureester der Formel 1 Monoester, Diester oder Mischungen davon enthält;
- wobei das Gewichtsverhältnis der Verbindung A zu Verbindung C von 1/1 bis 4/1 variiert.

2. Zusatzstoff nach Anspruch 1, wobei das Molverhältnis des Olefins zum phosphorhaltigen Pentasulfid 1/1 beträgt.

3. Zusatzstoff nach Anspruch 1, wobei das HRPIB mehr als 70% an Vinylidendoppelbindungen enthält.

4. Zusatzstoff nach Anspruch 1, wobei die phosphorhaltige Polyisobutylenschwefelverbindung A durch Umsetzung des HRPIB mit dem phosphorhaltigen Pentasulfid in Gegenwart des Schwefelpulvers erhalten wird, wobei das Reaktionsgemisch folgendermaßen gebildet wird:

a) durch Rühren und Erhitzen des Reaktionsgemischs aus dem HRPIB, dem phosphorhaltigen Pentasulfid und dem Schwefelpulver auf eine Temperatur von 160°C unter Spülen mit Stickstoffgas, was zur Entfernung des während der Reaktion erzeugten Wasserstoffsulfidgases (H_2S) führte,
b) Halten der Reaktionsmischung auf einer Temperatur zwischen 160°C und 180°C während eines Zeitraums von 1 bis 2 Stunden,
c) Anheben der Temperatur des Reaktionsgemischs von 185°C auf 250°C,
d) Halten des Reaktionsgemischs auf der erhöhten Temperatur während 1 bis 24 Stunden,
e) Abkühlen des Reaktionsgemischs auf 100°C, und
f) Einleiten von Stickstoffgas in das Reaktionsgefäß, um das darin vorliegende Wasserstoffsulfidgas auszutreiben, wodurch die phosphorhaltige Polyisobutylenschwefel-verbindung A erhalten wird.

5. Zusatzstoff nach Anspruch 4, wobei die Temperatur des Reaktionsgemischs aus Schritt c) von 190°C auf 230°C angehoben wird.

6. Zusatzstoff nach Anspruch 4, wobei die Temperatur des Reaktionsgemischs aus Schritt c) von 210°C auf 225°C angehoben wird.

7. Zusatzstoff nach einem der vorhergehenden Ansprüche 1 bis 6, wobei das HRPIB zwischen 10 und 1000 Kohlenstoffatome aufweist.

8. Zusatzstoff nach einem der vorhergehenden Ansprüche 1 bis 6, wobei das HRPIB ein Molekulargewicht von 200 bis 10.000 aufweist.

9. Verfahren zum Inhibieren der Naphthensäurekorrosion von metallischen Oberflächen von beliebigen Kohlenwasserstoff verarbeitenden Einheiten, wobei die verarbeitenden Einheiten Destillationssäulen, Abscheider, Blechwannen und Umwälzpumpenleitungen umfassen, unter Verwendung eines Zusatzstoffs, der eine Mischung aus Verbindung A und Verbindung C aus Anspruch 1 umfasst, das die folgenden Schritte umfasst:

a. Erhitzen von Kohlenwasserstoff enthaltenden Naphthen-säureverbindungen, um einen Teil des Kohlenwasserstoffs zu verdampfen;
b. Kondensieren eines Teils der Kohlenwasserstoffdämpfe, die die Kohlenwasserstoff verarbeitende Einheit durch-laufen, um ein kondensiertes Destillat herzustellen;
c. Zugeben, bevor das kondensierte Destillat in die Kohlenwasserstoff verarbeitende Einheit zurückgeführt wird oder als Produkt aufgefangen wird, von 1 ppm bis 5000 ppm des Zusatzstoffs zu dem Destillat, wobei das Gewichtsverhältnis von Verbindung A zu Verbindung C von 1/1 bis 4/1 beträgt;
d. Ermöglichen, dass das kondensierte Destillat, das den Zusatzstoff enthält, mit den metallischen Oberflächen der Kohlenstoff verarbeitenden Einheit in Kontakt kommt, um einen Schutzfilm auf den Oberflächen zu bilden,

wodurch die Korrosion jeder Oberfläche inhibiert wird; und

e. Ermöglichen, dass das kondensierte Destillat in die Kohlenwasserstoff verarbeitende Einheit zurückgeführt wird oder als Produkt aufgefangen wird.

Revendications

1. Additif pour l'inhibition de la corrosion par de l'acide naphténique à haute température comprenant un mélange chimique de :

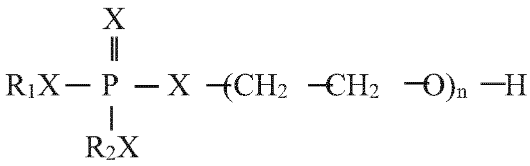
   a) une quantité inhibant la corrosion de composé à base de polyisobutylène phosphore soufre A ; et

   b) une quantité inhibant la corrosion de composé à base de thiophosphore soufre C,

   dans lequel ledit composé à base de polyisobutylène phosphore soufre A est obtenu en faisant réagir une oléfine avec du pentasulfure de phosphore en présence d'une quantité catalytique de soufre, formant un mélange réactionnel, le rapport molaire de ladite oléfine audit pentasulfure de phosphore étant compris dans la plage allant de 1:0,05 à 1:2, ladite oléfine étant un polyisobutylène hautement réactif (HRPIB), ledit soufre étant du soufre en poudre, et ledit soufre en poudre étant présent en une quantité catalytique de 0,5 % à 5 % en poids de ladite oléfine ;

   dans lequel ledit composé à base de thiophosphore soufre C répond à la formule 2, est obtenu en faisant réagir un composé à base de thiophosphore soufre B avec de l'oxyde d'éthylène, et la formule 2 comprenant un composé C résultant obtenu après réaction dudit composé B avec ledit oxyde d'éthylène,

   dans lequel ledit composé à base de thiophosphore soufre C comprend un mono-ester, un di-ester, un mélange de ceux-ci ;



$$\mathrm{R_1X}-\underset{\underset{\mathrm{R_2X}}{|}}{\overset{\overset{\mathrm{X}}{\|}}{\mathrm{P}}}-\mathrm{X}-(\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O})_n-\mathrm{H}$$

n = 1 à 10

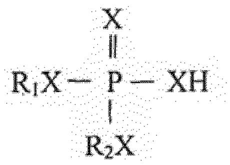
Formule 2

   où X est indépendamment un atome de soufre ou un atome d'oxygène et au moins un X est un atome de soufre, et

   où R_1 et R_2 sont un atome d'hydrogène ou un groupe hydrocarbyle ayant de 5 à 18 atomes de carbone ;

   dans lequel ledit composé B est un ester de thioacide phosphoré de formule 1

Formule 1



$$\mathrm{R_1X}-\underset{\underset{\mathrm{R_2X}}{|}}{\overset{\overset{\mathrm{X}}{\|}}{\mathrm{P}}}-\mathrm{XH}$$

   où X est indépendamment un atome de soufre ou un atome d'oxygène et au moins un X est un atome de soufre et où R_1 et R_2 sont un atome d'hydrogène ou un groupe hydrocarbyle ayant de 5 à 18 atomes de carbone,

   dans lequel ledit ester de thioacide phosphoré de formule 1 comprend un mono-ester, un di-ester, un mélange de ceux-ci ;

   dans lequel le rapport en poids du composé A au composé C varie de 1:1 à 4:1.

2. Additif selon la revendication 1, dans lequel ledit rapport molaire de ladite oléfine audit pentasulfure de phosphore est 1:1.

3. Additif selon la revendication 1, dans lequel ledit HRPIB contient plus de 70 % de double liaison vinylidène.

4. Additif selon la revendication 1, dans lequel ledit composé à base de polyisobutylène phosphore soufre A est obtenu en faisant réagir ledit HRPIB avec ledit pentasulfure de phosphore en présence dudit soufre en poudre formant le mélange réactionnel,

a) en agitant et chauffant ledit mélange réactionnel dudit HRPIB, dudit pentasulfure de phosphore et dudit soufre en poudre à une température à une température de 160 °C sous une purge d'azote gazeux, qui conduit à l'élimination du sulfure d'hydrogène (H_2S) gazeux généré pendant la réaction,
b) en maintenant ledit mélange réactionnel entre 160 °C et 180 °C pendant une période de 1 heure à 2 heures,
c) en augmentant ladite température dudit mélange réactionnel à 185 °C à 250 °C,
d) en maintenant ledit mélange réactionnel à ladite température augmentée pendant 1 à 24 heures,
e) en refroidissant le mélange réactionnel à 100 °C, et
f) en purgeant l'azote gazeux dans le récipient réactionnel pour éliminer le sulfure d'hydrogène gazeux présent à l'intérieur, donnant ainsi ledit composé à base de polyisobutylène phosphore soufre A.

5. Additif selon la revendication 4, dans lequel ladite température dudit mélange réactionnel de l'étape c) est augmentée à 190 °C à 230 °C.

6. Additif selon la revendication 4, dans lequel ladite température dudit mélange réactionnel de l'étape c) est augmentée à 210 °C à 225 °C.

7. Additif selon l'une quelconque des revendications 1 à 6 précédentes, dans lequel ledit HRPIB comprend entre 10 et 1000 atomes de carbone.

8. Additif selon l'une quelconque des revendications 1 à 6 précédentes, dans lequel ledit HRPIB a un poids moléculaire de 200 à 10 000.

9. Procédé d'inhibition de la corrosion par de l'acide naphténique de surfaces métalliques de n'importe quelle unité de traitement d'hydrocarbure, lesdites unités de traitement comprenant des colonnes de distillation, des colonnes de rectification, des plateaux et une pompe autour de la tuyauterie, en utilisant un additif comprenant un mélange dudit composé A et dudit composé C selon la revendication 1, comprenant les étapes consistant à :

a. chauffer un hydrocarbure contenant des composés à base d'acide naphténique, pour vaporiser une partie dudit hydrocarbure ;
b. condenser une partie des vapeurs d'hydrocarbure, passant à travers ladite unité de traitement d'hydrocarbure, pour produire un distillat condensé ;
c. ajouter audit distillat, avant que ledit distillat condensé soit renvoyé vers l'unité de traitement d'hydrocarbure ou collecté en tant que produit, de 1 ppm à 5000 ppm dudit additif, le rapport en poids dudit composé A audit composé C étant de 1:1 à 4:1 ;
d. permettre audit distillat condensé contenant ledit additif d'être mis en contact avec lesdites surfaces métalliques de ladite unité de traitement d'hydrocarbure, pour former un film protecteur sur lesdites surfaces, chaque surface étant ainsi inhibée contre la corrosion ; et
e. permettre audit distillat condensé de retourner dans ladite unité de traitement d'hydrocarbure, ou d'être collecté en tant que ledit produit.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 3909447 A **[0014]**
- US 3531394 A, Koszman **[0016]**
- US 4024049 A, Shell **[0017]**
- US 4105540 A, Weinland **[0018]**
- US 4443609 A **[0019]**
- US 4542253 A, Kaplan **[0021]**
- US 4842716 A, Kaplan **[0021]**
- US 4941994 A, Zetmeisl **[0021] [0022] [0023] [0028]**
- US 5252254 A **[0024]**
- US 5182013 A, Petersen **[0025]**
- US 5314643 A, Edmondson **[0027]**
- US 5552085 A, Babaian-Kibala **[0028] [0063]**
- US 5630964 A, Babaian-Kibala **[0028]**
- GB 8667 A, Coslett **[0029]**
- US 3132975 A **[0029]**
- US 3460989 A **[0029]**
- US 1872091 A **[0029]**
- US 3145886 A **[0029]**
- US 20070119747 A1, Bradley **[0030]**
- WO 2003093399 A, Eaton **[0031]**
- US 2316078 A, Loane **[0032]**
- EP 0271998 A **[0033]**

SBGK
Szabadalmi
Ügyvivői Iroda

716052/ZSO EP2193179

Új adalékanyag nafténsav korrózió gátlására és eljárás annak alkalmazására

Szabadalmi igénypontok

1. Adalékanyag magas hőmérsékletű nafténsav korrózió gátlására, mely:

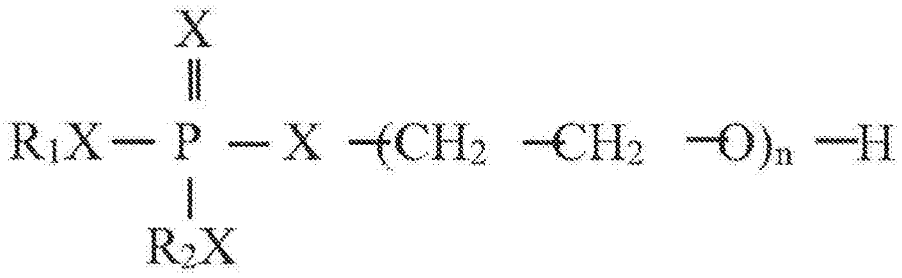
a) korróziógátló mennyiségű A foszfortartalmú poliizobutilén-kénvegyület; és

b) korróziógátló mennyiségű C tiofoszfor-kénvegyület

kémiai keverékét tartalmazza,

ahol az A foszfortartalmú poliizobutilén-kénvegyület egy olefinnek foszforpendaszulfiddal, katalitikus mennyiségű kén jelenlétében végzett reakciójával kerül előállításra, ahol a reakcióelegyben az olefin és foszforpentaszulfid mólaránya 1:0.05 és 1:2 közötti, az olefin erösen reaktív poliizobutilén (HRPIB), a kén kénpor, és ahol a kénpor katalitikus mennyiségben van jelen, az olefinre számítva 0.5-5 tömeg% mennyiségben;

ahol a 2 képletű:



$$R_1X-\underset{\underset{R_2X}{|}}{\overset{\overset{X}{\|}}{P}}-X-(CH_2-CH_2-O)_n-H$$

n = 1-10

(2)

C tiofoszfor-kénvegyület egy B tiofoszfor-kénvegyületnek etilénoxiddal végzett reakciójával kerül előállításra, és ahol a 2 képlet a B vegyület és etilénoxid reakcióját követően keletkezett C vegyületet mutatja,

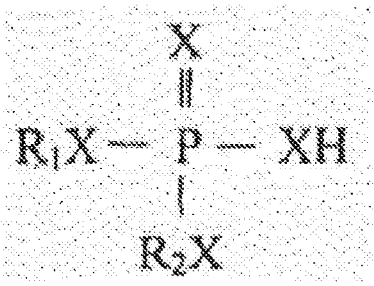
ahol a C tiofoszfor-kénvegyület a monoésztert, diésztert és keverékét foglalja magába;

ahol X egymástól függetlenül kén vagy oxigén és legalább egy X jelentése kén, és

ahol R_1 és R_2 hidrogénatom vagy 5-18 szénatomos szénhidrogéncsoport;

ahol a B vegyület egy 1 képletű:

SZTNH-100001470



$$R_1X-\overset{\overset{\displaystyle X}{\|}}{\underset{\underset{\displaystyle R_2X}{|}}{P}}-XH$$

(1)

foszfortartalmú tiosavészter,

ahol X egymástól függetlenül kén vagy oxigén és legalább egy X jelentése kén, és

ahol R_1 és R_2 hidrogénatom vagy 5-18 szénatomos szénhidrogéncsoport;

ahol az 1 képletű foszfortartalmú tiosavészter a monoésztert, diésztert és keverékét foglalja magába;

ahol az A vegyület és C vegyület tömegaránya 1:1 és 4:1 között változik.

2. Az 1. igénypont szerinti adalékanyag, ahol az olefin és foszforpentaszulfid mólaránya 1:1.

3. Az 1. igénypont szerinti adalékanyag, ahol a HRPIB 70%-nál több vinilénkötést tartalmaz.

4. Az 1. igénypont szerinti adalékanyag, ahol az A foszfortartalmú poliizobutilén-kénvegyület a HRPIB-nek a foszforpentaszulfiddal kénpor jelenlétében végzett reakciójával kerül előállításra, ahol a reakció során

a) a HRPIB, a foszforpentaszulfid és kénpor reakcióelegyét keverjük és 160°C hőmérsékletre melegítjük, nitrogéngázzal történő átöblítés közben, mellyel eltávolítjuk a reakció során keletkezett hidrogénszulfid (H_2S) gázt,

b) a reakcióelegy hőmérsékletét 1-2 órán át 160°C és 180°C közötti hőmérsékleten tartjuk,

c) a reakciókeverék hőmérsékletét 185°C és 250°C közötti hőmérsékletre emeljük,

d) a reakcióelegyet 1-24 órán át ezen az emelt hőmérsékleten tartjuk,

e) a reakcióelegyet 100°C-ra hűtjük, és

f) a reakcióedénybe nitrogéngázt vezetünk be, a jelenlévő hidrogénszulfid gáz kihajtására, ily módon az A foszfortartalmú poliizobutilén-kénvegyületet nyerve.

5. A 4. igénypont szerinti adalékanyag, ahol a c) lépésben a reakcióelegy hőmérsékletét 190°C és 230°C közötti hőmérsékletre emeljük.

6. A 4. igénypont szerinti adalékanyag, ahol a c) lépésben a reakcióelegy hőmérsékletét 210°C és 225°C közötti hőmérsékletre emeljük.

7. Az 1-6. igénypontok bármelyike szerinti adalékanyag, ahol a HRPIB szénatomszáma 10 és 1000 közötti.

8. Az 1-6. igénypontok bármelyike szerinti adalékanyag, ahol a HRPIB molekulatömege 200 és 10,000 közötti.

9. Eljárás bármely szénhidrogén-feldolgozó egység nafténsav által okozott korróziójának gátlására, ahol a feldolgozó egységek desztillációs oszlopok, sztrippelő berendezések, tálcák és cirkulációs csövek, az 1. igénypont szerinti A vegyület és C vegyület keverékét tartalmazó adalékanyag alkalmazásával, melynek során:

a. szénhidrogént tartalmazó nafténsav-vegyületeket melegítünk, a szénhidrogén egy részének elpárologtatására;

b. a szénhidrogén-feldolgozó egységen áthaladó szénhidrogén-gőzök egy részét kondenzáljuk, kondenzált desztillátum előállítására;

c. a desztillátumhoz, mielőtt a kondenzált desztillátumot visszatápláljuk a szénhidrogén-feldolgozó egységbe vagy azt termékként kinyerjük, 1 ppm - 5000 ppm adalékanyagot adunk, ahol az A vegyület és a C vegyület tömegaránya 1:1 és 4:1 közötti;

d. az adalékanyagot tartalmazó kondenzátumot a szénhidrogén-feldolgozó egység fémfelületével érintkeztetjük, a felületeken védőfilm létrehozására, ahol valamennyi felület korrózió ellen gátolt; és

e. a kondenzált desztillátumot visszaengedjük a szénhidrogén-feldolgozó egységbe, vagy a termékként kinyerjük.

Szentp[illegible] Zsolt
szabadalmi ügyvivő
SBGK Sza[illegible]dalmi Ügyvivői Iroda
H-1062 [illegible]pest, Andrássy út 113.
Telefon: [illegible]000 Fax: 461-1099
Email: sz[illegible]peteri_zs@sbgk.hu