

USE OF ORGANIC POLYSULPHIDES AGAINST CORROSION BY ACIDIC CRUDES

5 The present invention pertains to the field of the treatment of acidic crude petroleums in refineries. It relates more especially to a method of combating corrosion in refining units which process acidic crudes, comprising the use of specific polysulphide compounds.

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Petroleum refineries may be confronted with a serious corrosion problem when they are required to process certain crudes known as acidic crudes. These acidic crudes consist essentially of naphthenic acids, which
15 are the origin of this corrosion phenomenon, which is a very particular phenomenon since it takes place in a liquid medium which is a non-conductor of electrical current. These naphthenic acids correspond to saturated cyclic hydrocarbons which carry one or more carboxylic groups. The acidity of a petroleum crude is described
20 by a measurement standardized in accordance with ASTM standard D 664-01. It is expressed in mg of potassium hydroxide required to neutralize 1 g of petroleum and is referred to as TAN (total acid number). It is known
25 in this technical field that a crude petroleum having a TAN of more than 0.2 is qualified as acidic, and may lead to damage within the units of a refinery.

This corrosion reaction depends heavily on local
30 conditions such as, for example, the temperature and the metallic nature of the walls in the unit concerned, the space velocity of the hydrocarbon, and the presence of a gas/liquid interface. Accordingly, even after major studies on the topic, refiners encounter great
35 difficulty in predicting the extent of the corrosion reactions and their location.

One of the industrial solutions to this corrosion problem involves using apparatus made of stainless

steels - that is, alloys of iron with, in particular, chromium and molybdenum. However, this solution remains little used, owing to the high capital investment cost. That choice, moreover, must preferably be considered during the design of the refinery, since stainless steels have mechanical properties inferior to those of the carbon steels normally used, and require an appropriate infrastructure.

10 The existence of these technical difficulties in processing acidic crudes therefore means that, in general, these crudes are sold to refiners at a price level lower than that of the standard crudes.

15 Another solution to the problem of processing an acidic crude petroleum, which is used in practice by refiners, involves diluting it with another, non-acidic petroleum crude, so as to give a low average acidity, lower for example than the 0.2 TAN threshold. In this case the concentration of naphthenic acid becomes low enough to give rise to acceptable corrosion rates. This solution remains limited in scope, however. The reason for this is that certain acidic crudes have TANs of more than 2, which curtails their use to not more than 10% of the total volume of crudes entering the refinery. Moreover, certain blends of crudes sometimes lead to the converse of the desired effect, even after dilution, in other words to an acceleration of the corrosion reactions by naphthenic acids.

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An alternative approach for combating this corrosion problem is to introduce, into the acidic crude petroleum to be processed, chemical additives which inhibit or prevent the attack of the metal walls of the unit in question. This route is often very economic in comparison to that indicated above, involving the use of special steels or alloys.

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Laboratory studies, such as that of Turnbull

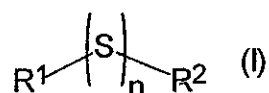
- (Corrosion - November 1998 in Corrosion, volume 54, No. 11, page 922), have envisaged the addition of small amounts (of the order of 0.1%) of hydrogen sulphide to the crude petroleum, for the purpose of reducing the corrosion by naphthenic acids. This solution, however, is not applicable in the refinery, since the hydrogen sulphide, which is gaseous at ambient temperature, is highly toxic, thereby making the consequences of any leak extremely serious, and limiting its use. Moreover, at even higher temperature, the hydrogen sulphide itself becomes highly corrosive and, in other parts of the refinery, will lead to aggravation of the generalized corrosion.
- 15 US Patent 5182013 describes the use, for solving this corrosion problem, of other sulphur compounds, namely polysulphides having alkyl radicals containing from 6 to 30 carbon atoms.
- 20 EP Patent 742277 describes the inhibitory activity of a combination of a trialkyl phosphate and an organic polysulphide. US Patent 5552085 recommends the use of thiophosphorus compounds such as organic thiophosphates or thiophosphites. AU Patent 693975 discloses as
- 25 inhibitor a mixture of trialkyl phosphate and phosphoric esters of sulphurized phenol neutralized with lime.

However, the handling of organophosphorus compounds is very delicate, owing to their high toxicity. In addition, they are poisons for the hydrotreating catalysts which are installed to purify the hydrocarbon cuts obtained from atmospheric and vacuum distillations. For these two reasons at least, their use in the field of refining is undesirable.

Surprisingly it has been found that the use of a specific class of organic polysulphides, namely poly-alkyl sulphides in which the number of carbons in each

alkyl radical is between 2 and 5, allows the corrosion caused by naphthenic acids to be inhibited more effectively than using the organic polysulphides known to date, and without the need to introduce phosphorus inhibitors as well.

The invention accordingly provides a method of combating the corrosion caused by naphthenic acids to the metal walls of a refining unit, characterized in that it comprises the addition to the hydrocarbon stream for processing by the unit of an effective amount of one or more hydrocarbon compounds of formula



in which

- n is an integer between 2 and 15 and
- the symbols R^1 and R^2 , which are identical or different, each represent a linear or branched alkyl radical containing between 2 and 5 carbon atoms, it being possible for these radicals to contain, optionally, one or more heteroatoms such as oxygen or sulphur; or
- R^1 and R^2 , which are identical or different, each represent a cycloalkyl radical containing between 3 and 5 carbon atoms, it being possible for these radicals to contain, optionally, one or more heteroatoms such as oxygen or sulphur.

The polysulphides of formula (I) are prepared according to processes which are known per se, such as those described in patents US 2708199, US 3022351 and US 3038013. Some of them are commercial products.

Preferably R^1 and R^2 are linear or branched alkyl radicals and n is between 2 and 6.

According to another preferred version the radicals R^1 and R^2 are identical, owing to the improved stability

of the corresponding compound of formula (I).

According to a version which is even more preferred,
poly(di-tert-butyl sulphide)s are used as a mixture of
5 compounds of formula (I). These products, industrial in
origin, are obtained for example from the reaction of
sulphur with tert-butyl mercaptan. The reaction
conditions allow industrial products to be prepared
that are composed of a mixture of polysulphides with a
10 number of sulphur atoms varying between 3 and 10, with
a number-average value of between 2 and 6.

The amount of compound(s) of formula (I) to be added to
the hydrocarbon stream for processing by the refining
15 unit corresponds generally to a concentration,
expressed by equivalent weight of sulphur of the said
compound relative to the weight of the hydrocarbon
stream, of between 1 and 5000 ppm, preferably between 5
and 500 ppm. While remaining within this concentration
20 range, it will be possible to set a high content at the
start-up of the method according to the invention, then
to reduce this content subsequently to a maintenance
level.

25 The method according to the invention makes it possible
advantageously to process hydrocarbon streams, and more
particularly crude petroleums, whose TAN is greater
than 0.2 and preferably greater than 1.

30 The temperature at which the method is employed
corresponds to that at which the corrosion reactions by
naphthenic acids take place, and is generally between
200 and 450°C and more particularly between 250 and
350°C.

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The addition of the compound of formula (I) to the
hydrocarbon stream may be carried out in close
proximity to where the corrosion reaction occurs or
else, at a lower temperature, upstream of the process

of the said unit. This addition may be carried out by any means known to the skilled person which ensures control of the injection rate and effective dispersion of the additive in the hydrocarbon: for example, by
5 means of a nozzle or of a mixer.

The metal walls of the refining unit in which the corrosion can be prevented by the method according to the invention are any walls liable to come into contact
10 with the stream of acidic hydrocarbon to be processed. The walls involved may therefore equally be the inner walls proper of units such as the atmospheric and vacuum distillation towers, or the surface of internal elements thereof, such as their plates or packings, or
15 else peripheral elements thereof, such as their offtake and entry lines, pumps, preheating ovens or heat exchangers, in so far as these elements are taken to a local temperature of between 200 and 450°C.

20 Non-limiting examples of hydrocarbon streams to be processed in accordance with the method according to the invention include the petroleum crude, the residue from atmospheric distillation, the gas-oil cuts obtained from atmospheric and vacuum distillations, and
25 the vacuum residue and distillate obtained from vacuum distillation.

The examples which follow are given purely to illustrate the invention and should not be interpreted
30 as limiting its scope.

In these examples a corrosion test is implemented whose conditions are given below.

35 **Description of the corrosion test:**

This test employs an iron powder, which simulates a metal surface, and a mineral oil in which is dissolved a mixture of naphthenic acids, simulating an acidic

crude stream. The characteristics of these reactants are as follows:

- white mineral oil having a density of 0.838
- powder of spherical iron particles having a size
5 of -40+70 mesh (i.e. from approximately 212 to 425 μm)
- mixture of naphthenic acids having from 10 to 18 carbon atoms, a boiling point of between 270 and 324°C and an average molar mass of 244 g/mol.

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The following components are introduced into a 150 ml glass reactor equipped with a dropping funnel and a water condenser and fitted with a stirring system and a temperature-measurement system:

- 15 - 70 ml (or 58.8 g) of the mineral oil,
- 2 g of the iron powder,
- 2.8 g of the naphthenic acid mixture.

The initial TAN of the reaction mixture is 10.

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These reactants are kept in contact at a temperature of 250°C for 2 hours under an atmosphere of dry nitrogen, in order to avoid oxidation reactions.

- 25 At the end of the test the concentration of iron dissolved in the medium is determined by a conventional method employing mineralization of a sample, the taking-up of the residue in acidified water, and an assay using an electron torch.

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This concentration of dissolved iron (expressed in ppm) is directly proportional to the corrosion rate of the iron powder that is generated by the mixture of naphthenic acids present in the mineral oil.

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EXAMPLE 1: Reference test in the absence of inhibitor

The above test is employed without any compound of formula (I) being added, with 2 repetitions.

The results are indicated in Table I below.

Table I

	Iron concentration (ppm)
Test 1	180
Test 2	227
Average	203.5

5 **EXAMPLE 2: Tests in the presence of polyalkyl sulphides**

Example 1 is repeated with the addition of different types of polyalkyl sulphides in mineral oil during the charging of the reactor. The amount of these
10 derivatives added is calculated so as to give a concentration of 500 ppm, expressed in equivalent weight of sulphur, in the mineral oil present in the reactor.

15 The results collated in Table II below are obtained.

Likewise indicated in this table is the degree of inhibition of the corrosion brought about by the naphthenic acid mixture. This degree is expressed in %
20 and is defined by the following formula:

$$\text{inhibition (\%)} = \left(1 - \frac{[\text{iron}] \text{ with inhibitor}}{[\text{iron}] \text{ without inhibitor}} \right) \times 100$$

in which [iron] is the concentration of dissolved iron
25 measured with or without inhibitor, the concentration of iron without inhibitor being equal to 203.5 ppm in accordance with Example 1.

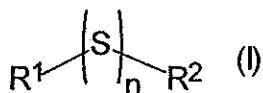
Table II

Compound of formula (I)	Commercial name*	Iron concentration (ppm)	Degree of inhibition (%)
Di-tert-butyl trisulphide	TPS 44	4	98%
Di-tert-butyl tetrasulphide	TPS 54	7	97%

* supplier: ARKEMA

CLAIMS

1. Method of combating the corrosion caused by naphthenic acids to the metal walls of a refining unit, characterized in that it comprises the addition to the hydrocarbon stream for processing by the unit of an effective amount of one or more hydrocarbon compounds of formula



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in which

- n is an integer between 2 and 15 and
- the symbols R^1 and R^2 , which are identical or different, each represent a linear or branched alkyl radical containing between 2 and 5 carbon atoms, it being possible for these radicals to contain, optionally, one or more heteroatoms such as oxygen or sulphur; or
- R^1 and R^2 , which are identical or different, each represent a cycloalkyl radical containing between 3 and 5 carbon atoms, it being possible for these radicals to contain, optionally, one or more heteroatoms such as oxygen or sulphur.

2. Method according to Claim 1, characterized in that a compound of formula (I) is used in which R^1 and R^2 are linear or branched alkyl radicals and n is between 2 and 6.

3. Method according to either of Claims 1 and 2, characterized in that a compound of formula (I) is used in which the radicals R^1 and R^2 are identical.

4. Method according to one of Claims 1 to 3, characterized in that a mixture of poly(di-tert-butyl sulphide)s is used in which the average value of the number of sulphur atoms is between 2 and 6.

5. Method according to one of Claims 1 to 4, characterized in that the amount of compound(s) of formula (I) corresponds to a concentration, expressed by equivalent weight of sulphur relative to the weight of the hydrocarbon stream, of between 1 and 5000 ppm, preferably between 5 and 500 ppm.

6. Method according to one of Claims 1 to 5, characterized in that the stream of hydrocarbons to be processed has a TAN of more than 0.2 and preferably more than 1.

7. Method according to one of Claims 1 to 6, characterized in that it is carried out at a temperature of between 200 and 450°C and more particularly between 250 and 350°C.

8. Method according to one of Claims 1 to 7, characterized in that the hydrocarbon stream to be processed is selected from petroleum crude, the residue from atmospheric distillation, the gas-oil cuts obtained from atmospheric and vacuum distillations, and the vacuum residue and distillate obtained from vacuum distillation.