

DESCRIPTION

Title of Invention: METHOD FOR PREVENTING FOULING OF HEAT EXCHANGER IN PETROLEUM PROCESS

Technical Field

[0001]

The present disclosure relates to a method for preventing fouling of a heat exchanger in a petroleum process.

Background Art

[0002]

In a distillation process of a petroleum refining plant for refining crude petroleum, after the crude petroleum is heated in a heat exchanger and a heating furnace, the crude petroleum is fed to a distillation tower, and then distillation operation is applied thereto. The crude petroleum undergoes heat hysteresis in the heat exchanger and the heating furnace, so that fouling adheres thereto in a large quantity. One form of components of the fouling is a form in which organic polymeric components called asphaltene are mixed with each other. The fouling adhesion makes the heat exchanger and the heating furnace low in heat exchanger effectiveness to result in an increase in the use amount of a fuel for maintaining the temperature of their outlet. Patent Document 1 discloses a fouling preventing agent that is used for a heat exchanger and a heating furnace and that is to be added in a process fluid positioned before a desalter; and a fouling preventing method.

Citation List

Patent Document

[0003] Patent Document 1: JP 2010-163539 A

Summary of Invention

Technical Problem

[0004] The present disclosure provides, in one or more embodiments therein, a method for preventing fouling of a heat exchanger in a petroleum process.

Solution to Problem

[0005] The present disclosure relates, in one aspect therein, to a method wherein an anticorrosive and a dispersing agent are added to a process fluid passing through a heat exchanger in a petroleum process the heat exchanger is a preheat exchanger, the anticorrosive is a phosphate anticorrosive and/or a polysulfide anticorrosive, and the dispersing agent is selected from the group consisting of a polyolefin ester and a substituted alkylphenol-formaldehyde resin. In another aspect therein, the present disclosure provides a fouling preventing agent to be used for the method for preventing fouling of a heat exchanger as described herein, the fouling preventing agent containing an anticorrosive and a dispersing agent, wherein the anticorrosive is a phosphate anticorrosive and/or a polysulfide anticorrosive, and the dispersing agent is selected from the group consisting of a polyolefin ester and a substituted alkylphenol-formaldehyde resin. In another example described herein, the present disclosure provides an anticorrosive to be used for the method for preventing fouling of a heat exchanger as described herein. In another example described herein, the present disclosure provides a dispersing agent to be used for the method for preventing fouling of a heat exchanger as described herein.

Advantageous Effects of Invention

[0006]

According to the present disclosure, fouling of the heat exchanger can be restrained in the petroleum process. In one or more embodiments, the restraint makes it possible to improve and/or maintain the heat exchanger effectiveness of the heat exchanger, so that fuel costs and cleaning costs can be restrained.

Brief Description of Drawings

[0007]

Fig. 1 is a block diagram illustrating an example of a petroleum refining apparatus equipped with a normal-pressure distillation tower.

Fig. 2 is a sectional view of a heat pipe used in a fouling prevention

test.

Fig. 3 is a sectional view of a state where the heat pipe is inserted into a heat pipe holder.

Description of Embodiments

[0008]

The present disclosure is based on a finding that the adhesion of asphaltene, which is a fouling component in a heat exchanger such as a preheat exchanger, is caused by an intervention of sulfur atoms present in molecules of asphaltene. The disclosure is also based on a finding that when a dispersing agent which has been added for fouling prevention to a process fluid in a petroleum process is combined with an anticorrosive, fouling of a heat exchanger can be remarkably decreased.

[0009]

It has been hitherto considered that fouling of a heat exchanger such as a preheat exchanger is caused by a matter that asphaltene aggregates at a high temperature so that the aggregate adheres onto the heat exchanger. Thus, a dispersing agent is used as a fouling preventing agent. However, it is actually necessary to clean and exchange heat exchangers, such as preheat exchangers, at fixed intervals since the heat exchangers are lowered in heat exchanger effectiveness, or suffer from being blocked up.

[0010]

Accordingly, the present disclosure is, in one aspect therein, a method for preventing fouling of a heat exchanger in a petroleum process, wherein an anticorrosive and a dispersing agent are added to a process fluid passing through the heat exchanger (hereinafter, the method may be

referred to as the “fouling preventing method according to the disclosure”).

[0011]

It is not clear in detail why in the fouling preventing method according to the disclosure, fouling of the heat exchanger, particularly a preheat exchanger, can be restrained. However, a mechanism therefor is presumed as follows. Sulfur atoms of asphaltene form a sulfide on the surface of the heat exchanger so that the sulfide deposits thereon to turn into fouling adhesion. Thus, when an anticorrosive is added thereto, reaction is restrained between asphaltene and the heat exchanger, and consequently, fouling adhesion would be restrained. However, the present disclosure may not be limited by this idea.

[0012]

In the fouling preventing method according to the disclosure, the wording “petroleum process” denotes the whole or a part of any process of producing a petroleum product that may be of various types from a raw material (crude petroleum). In one or more unrestricted embodiments, the petroleum process is a process using at least one apparatus selected from the group consisting of a distillation apparatus, a hydrogenation refining apparatus, a catalytic reforming apparatus, a catalytic decomposition apparatus, a hydrogenation decomposition apparatus, and a thermal decomposition apparatus.

[0013]

In the fouling preventing method according to the disclosure, the “heat exchanger” is a heat exchanger usable in the above-mentioned petroleum process. In one or more unrestricted embodiments, examples

thereof include a preheat exchanger, a preheater, and a reboiler. In these heat exchangers, a region where fouling is especially easily generated to be accumulated is their high-temperature region of about 200°C or higher. The fouling preventing method according to the disclosure is a method for preventing fouling of a heat exchanger having a high-temperature region which turns into a high temperature of about 200°C, for example, 180°C or higher, 190°C or higher, 200°C or higher, 210°C or higher, or 220°C or higher at the time of the processing in the heat exchanger in one or more embodiments. The fouling preventing method according to the disclosure more effectively exhibits the fouling preventing effect at a temperature of about 200°C or higher in one or more embodiments.

[0014]

In the fouling preventing method according to the disclosure, the “process fluid” may be a petroleum raw material to be processed in the above-mentioned petroleum process, and/or an oil flowing in an apparatus for the processing in one or more unrestricted embodiments.

[0015]

In the fouling preventing method according to the disclosure, the wording “fouling” denotes fouling including asphaltene, or fouling including asphaltene adhering and/or accumulating onto the inside of a heat exchanger in one or more unrestricted embodiments. Accordingly, the fouling prevention in the heat exchanger in the disclosure is restraint of the adhesion and/or accumulation of asphaltene onto the inside of a heat exchanger in one or more embodiments.

[0016]

[Anticorrosive]

The anticorrosive usable in the fouling preventing method according to the disclosure may be a high-temperature anticorrosive for use at high temperatures that is used in a petroleum process in one or more embodiments. The anticorrosive for use at high temperatures is an anticorrosive that can exhibit an anticorrosive effect at 200°C or higher in one or more embodiments.

[0017]

One or more embodiments of the anticorrosive are at least one of a phosphate anticorrosive and a polysulfide anticorrosive. More specifically, the anticorrosive is any combination of a phosphate with a polysulfide that is disclosed in Japanese Patent No. 3847837. Examples of the phosphate anticorrosive include, in one or more unrestricted embodiments, methyl phosphate, ethyl phosphate, n-propyl phosphate, isopropyl phosphate, butyl phosphate, pentyl phosphate, hexyl phosphate, cyclohexyl phosphate, heptyl phosphate, nonyl phosphate, decyl phosphate, lauryl phosphate, cetyl phosphate, octadecyl phosphate, heptadecyl phosphate, phenyl phosphate, benzyl phosphate, tolyl phosphate, methylphenyl phosphate, amylphenyl phosphate, and any combination of two or more of these phosphates. Examples of the polysulfide anticorrosive include, in one or more unrestricted embodiments, olefin polysulfides and terpene polysulfides. The molecular weight of the polysulfide is from 200 to 800 or from 300 to 600 in one or more embodiments.

[0018]

The concentration of the anticorrosive in the process fluid to be

supplied to the heat exchanger is from 1.0 to 100.0 ppm, from 2.0 to 80.0 ppm or from 5.0 to 50.0 ppm in one or more embodiments.

[0019]

[Dispersing Agent]

The dispersing agent usable in the fouling preventing method according to the disclosure may be a dispersing agent that has been hitherto used to prevent fouling in a petroleum process, or in a heat exchanger in a petroleum process, or that will be usable hereafter. Examples of the dispersing agent usable in the fouling preventing method according to the disclosure include polyolefin esters and polyalkenyl-substituted succinates in one or more unrestricted embodiments.

[0020]

The concentration of the dispersing agent in the process fluid to be supplied to the heat exchanger is from 1.0 to 100.0 ppm, from 2.0 to 80.0 ppm or from 5.0 to 50.0 ppm in one or more embodiments.

[0021]

In the process fluid to be supplied to the heat exchanger, the ratio of the content proportion (ppm) of the anticorrosive to that of the dispersing agent is from 5/1 to 1/5, from 3/1 to 1/3, or from 2/1 to 1/2 in one or more embodiments.

[0022]

A site where the anticorrosive and the dispersing agent are added to the process fluid is not particularly limited. In one or more embodiments, the site may be a site where the anticorrosive and the dispersing agent, which each have a concentration in the above-mentioned range, can be

introduced into the heat exchanger which is a target in which fouling is to be prevented; or a site positioned before the target heat exchanger. The order of the addition of the anticorrosive and that of the dispersing agent is not particularly limited. In one or more embodiments, the two may be simultaneously or separately added, or may be added in sites different from each other.

[0023]

Fig. 1 is a block diagram illustrating an example of a petroleum refining apparatus equipped with a normal-pressure distillation tower. In this petroleum refining apparatus, crude petroleum supplied through a pump 6 is desalted in a desalter 1, and then heated in a preheat exchanger 2 (heat exchanger 2) to 150 to 180°C. Furthermore, the crude petroleum is further introduced into a preheat exchanger 3 (heat exchanger 3) to be heated to 240 to 280°C, and then heated to 350 to 380°C in a heating furnace 4. The heated petroleum is then introduced into a normal-pressure distillation tower 5. From the tower bottom of the normal-pressure distillation tower 5, a bottom product liquid is fed, through a pump 7, as a heat source to the heat exchangers 3 and 2.

[0024]

When the fouling preventing method according to the disclosure is performed in the heat exchanger 3 in a petroleum process in Fig. 1, a site where an anticorrosive and a dispersing agent are added may be a site positioned before the heat exchanger 3 and represented by an arrow A in one or more unrestricted embodiments, or may be a site represented by an arrow C, which is positioned before the arrow-A-site. When the fouling preventing

method according to the disclosure is performed in the heat exchanger 3 in Fig. 1 and at a heating side thereof, the site where the anticorrosive and the dispersing agent are added may be a site positioned before the heat exchanger 3 and represented by an arrow B in Fig. 1 in one or more unrestricted embodiments.

[0025]

[Fouling Preventing Agent]

The present disclosure relates, in one aspect therein, to a fouling preventing agent to be used for the fouling preventing method according to the disclosure, the fouling preventing agent including an anticorrosive and a dispersing agent. The form of the fouling preventing agent according to the aspect may be a powder or tablet form, or any other solid form in one or more embodiments. The fouling preventing agent may be in a state where the agent is dissolved in a solvent, that is, in a concentrated liquid form.

[0026]

The present disclosure relates, in one aspect therein, to an anticorrosive or dispersing agent to be used for the fouling preventing method according to the disclosure. The anticorrosive or dispersing agent is as described above.

[0027]

[Use]

The present disclosure relates, in one aspect therein, to use of an anticorrosive in the fouling preventing method according to the disclosure. The anticorrosive of this aspect may be the above-mentioned anticorrosive. In one or more embodiments, the use is use of the anticorrosive in a system

to which a dispersing agent is added.

[0028]

The present disclosure relates to the following one or more embodiments:

[1] A method for preventing fouling of a heat exchanger in a petroleum process,

wherein an anticorrosive and a dispersing agent are added to a process fluid passing through the heat exchanger.

[2] The fouling preventing method according to item [1], wherein the anticorrosive is an anticorrosive for use at high temperatures that is usable at 200°C or higher.

[3] The fouling preventing method according to item [1] or [2], wherein the anticorrosive is at least one of a phosphate anticorrosive and a polysulfide anticorrosive.

[4] The fouling preventing method according to any one of items [1] to [3], wherein the content proportion of the anticorrosive in the process fluid supplied to the heat exchanger is from 1.0 to 100.0 ppm.

[5] The fouling preventing method according to any one of items [1] to [4], wherein the content proportion of the dispersing agent in the process fluid supplied to the heat exchanger is from 1.0 to 100.0 ppm.

[6] The fouling preventing method according to any one of items [1] to [5], wherein the ratio of the content proportion (ppm) of the anticorrosive to that of the dispersing agent in the process fluid supplied to the heat exchanger is from 5/1 to 1/5.

[7] The fouling preventing method according to any one of items [1] to

[6], wherein the prevention of the fouling of the heat exchanger is to restrain asphaltene from adhering onto and/or accumulating onto the inside of the heat exchanger.

[8] A fouling preventing agent to be used for the method for preventing fouling of a heat exchanger according to any one of items [1] to [7], the fouling preventing agent containing an anticorrosive and a dispersing agent.

[9] An anticorrosive to be used for the method for preventing fouling of a heat exchanger according to any one of items [1] to [7].

[10] A dispersing agent to be used for the method for preventing fouling of a heat exchanger according to any one of items [1] to [7].

[11] Use of the anticorrosive according to item [9] in a dispersing agent-added system in the method for preventing fouling of a heat exchanger according to any one of items [1] to [7].

[0029]

The present disclosure will be described on the basis of examples, comparative examples, and reference examples described below. However, the disclosure is not limited by these examples.

Examples

[0030]

<Fouling Prevention Test>

The fouling prevention test is a test for examining a fouling preventing effect of a fouling preventing agent for petroleum refining. The test is made by using a heat pipe (heat rod) 21 illustrated in Fig. 2 as a test member to which fouling is to be caused to adhere, bringing the heat pipe into contact with an oil, and measuring a situation that fouling adheres onto

the pipe. This heat pipe 21 is a pipe for a thermal stability tester stipulated in JIS K2276, and is made of soft steel to be in such an hourglass-shaped pipe form that its end regions 21a and 21b each have a large diameter, and its middle region 21c has a small diameter. This heat pipe 21 is inserted into a heat pipe holder 22 illustrated in Fig. 3 and having a pipe shape. An inflow tube 23a and an outflow tube 23b are connected to the upper part and the lower part of the heat pipe holder 22, respectively. A thermocouple 24 is inserted into the center of the heat pipe 21. A temperature adjustor not illustrated makes it possible to cause an electric current from both of the regions 21a and 21b of the heat pipe 21 to flow into the pipe 21 to render the temperature detected by the thermocouple 24 a predetermined temperature. As the tester, the following was used: a hot liquid process simulator tester having the heat pipe 21 and manufactured by a company, Alcor.

[0031]

The tester was used to heat the heat pipe 21 under conditions described below, and then each sample was introduced from the inflow tube 23a thereinto to make a test.

Sample: each of the samples was prepared by dissolving an anticorrosive component and a dispersing agent component shown in Table 1 described below in heavy aromatic naphtha (solvent) to prepare a homogenous solution, and adding this solution in a crude petroleum sample so that each of the components has a predetermined quantity shown in Table 1 for the crude petroleum.

Heat pipe 21 temperature: 360°C (heated to 360°C over 20 minutes);

Tank, line and pump temperatures: 100°C;

Sample volume: 500 mL (the tank was partitioned, so that the sample was not mixed with others when returned thereto);

Sample introducing flow rate: 1 mL/minute;

In-system pressure: 500 psi (pressure adjustment with nitrogen); and

Test period: 5 hours

[0032]

As the anticorrosive component and the dispersing agent component, the following were used, respectively: a phosphate or a polysulfide, which is an anticorrosive for use at high temperatures, or imidazoline, which is an anticorrosive for use at low temperatures; and a polyolefin ester or a polyalkenyl-substituted succinate.

[0033]

<Evaluation Items>

[Sample Outlet-Temperature Variation: Δt]

A measurement was made about the sample temperature which turned to a highest temperature in the outflow tube 23b (heating section outlet) after the start of the test, and the temperature variation (Δt) of the sample temperature after the lapse of 5 hours. As fouling adheres in a larger quantity onto the heat pipe 21, the variation Δt is larger.

[Adhered Matter Quantity: mg]

The tester was cooled and the heat pipe 21 was taken out. The heat pipe 21 was washed with heptane and further washed with acetone, and then dried. The weight of the heat pipe 21 was measured and the weight of the adhered matter (fouling) was calculated.

Respective results of the outlet temperature variation and the

adhered matter quantity are shown in Table 1.

[0034]

Table 1	Anticorrosive component	Concentration mg/L	Dispersing agent component	Concentration mg/L	Δt	Adhered matter (m/g)
Comparative Example 1	Blank	-	-	-	10	6.2
Comparative Example 2	-	-	Polyolefin ester	10	5	3.8
Comparative Example 3	Phosphate	10	-	-	6	1.6
Example 1	Phosphate	10	Polyolefin ester	10	1	0.3
Example 2	Polysulfide	10	Substituted alkylphenol-formaldehyde resin	10	1	0.5
Example 3	Phosphate	10	Polyolefin ester	5	2	0.6
Example 4	Phosphate	5	Polyolefin ester	5	3	1.2
Comparative Example 4	Imidazoline	10	Polyolefin ester	10	5	3.6

[0035]

As shown in Table 1, in Examples 1 to 4, the temperature variation (Δt) thereof was smaller than that in Comparative Examples 1 to 4, and the quantity of the adhered matter which adhered onto their heat pipe was also smaller than that in Comparative Examples 1 to 4.

[0036]

The external appearance of the heat pipe 21 of each of these examples was observed. As a result, as the adhered matter quantity was smaller, metallic luster of the heat pipe 21 was more largely maintained (data not shown).

Reference Signs List

[0037]

- 1: Desalter
- 2: Heat exchanger (preheat exchanger)
- 3: Heat exchanger (preheat exchanger)
- 4: Heating furnace
- 5: Normal-pressure distillation tower
- 6 and 7; pumps

CLAIMS

1. A method for preventing fouling of a heat exchanger in a petroleum process,

wherein an anticorrosive and a dispersing agent are added to a process fluid passing through the heat exchanger,

the heat exchanger is a preheat exchanger,

the anticorrosive is a phosphate anticorrosive and/or a polysulfide anticorrosive, and

the dispersing agent is selected from the group consisting of a polyolefin ester and a substituted alkylphenol-formaldehyde resin.

2. The fouling preventing method according to claim 1, wherein the content proportion of the anticorrosive in the process fluid supplied to the heat exchanger is from 1.0 to 100.0 ppm.

3. The fouling preventing method according to claim 1 or 2, wherein the content proportion of the dispersing agent in the process fluid supplied to the heat exchanger is from 1.0 to 100.0 ppm.

4. The fouling preventing method according to any one of claims 1 to 3, wherein the ratio of the content proportion (ppm) of the anticorrosive to that of the dispersing agent in the process fluid supplied to the heat exchanger is from 5/1 to 1/5.

5. The fouling preventing method according to any one of claims 1 to 4,

wherein the prevention of the fouling of the heat exchanger is to restrain asphaltene from adhering onto and/or accumulating onto the inside of the heat exchanger.

6. A fouling preventing agent to be used for the method for preventing fouling of a heat exchanger according to any one of claims 1 to 5, the fouling preventing agent containing an anticorrosive and a dispersing agent,

wherein the anticorrosive is a phosphate anticorrosive and/or a polysulfide anticorrosive, and

the dispersing agent is selected from the group consisting of a polyolefin ester and a substituted alkylphenol-formaldehyde resin.