

DESCRIPTION



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PROCESS FOR REMOVING MERCURY FROM LIQUID HYDROCARBON

5 Technical Field

The present invention relates to a process for removing mercury from a liquid hydrocarbon, and more particularly to an industrially useful process for removing an ionic mercury from an ionic mercury-containing liquid hydrocarbon placed in a container in a simple and efficient manner.

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Background Art

As known in the art, natural gas liquid (NGL) recovered by removing liquefied petroleum gas from natural gases obtained from gas field contains mercury in an amount of from several tens to several hundreds ppb although it varies depending upon the production area. When such a liquid hydrocarbon containing mercury is used as a raw material for producing ethylene, etc., the activity of hydrogenation catalysts are reduced or the apparatus is corroded or it mechanical strength is reduced, because the mercury forms amalgams with platinum, palladium, copper or aluminum. For this reason, it has been strongly demanded to develop a technique for removing mercury from the liquid hydrocarbon.

Japanese Patent Application Laid-Open No. 10-251667 proposes to remove mercury by using an apparatus comprising a hydrogenation zone having a packed bed of hydrogenation catalyst and an adsorption zone having a packed bed of porous carbonaceous material. In this method, after the hydrogenation process at 100 to 400°C, mercury is adsorbed onto activated carbon having strictly controlled properties such as a specific surface area and a pore size. Therefore, the proposed method is complicated in its operation and has drawbacks of requiring a complicated adsorbent preparation and strictly controlled operation conditions because of involving the adsorption



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process.

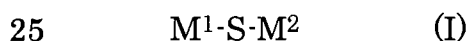
The inventors made various studies on a simple method of removing mercury from a mercury-containing liquid hydrocarbon, and found that the mercury is effectively removed by ionizing the mercury in the liquid hydrocarbon and then contacting the ionized mercury with a specific sulfur compound.

Disclosure of Invention

It is an object of the present invention to provide an industrially useful process for removing ionized mercury from an ionized mercury-containing liquid hydrocarbon using a specific sulfur compound in simple and effective manner.

As a result of extensive research in view of the above object, the inventors have found that the ionic mercury is effectively contacted with the specific sulfur compound and effectively removed from the ionic mercury-containing hydrocarbon by circulating the ionic mercury-containing hydrocarbon into a container through a circulating means while introducing the specific sulfur compound into a suction side and/or discharge side of the circulating means with optional mechanical stirring of the liquid hydrocarbon in the container. The present invention has been accomplished on the basis of this finding.

Thus, the present invention provides a process for removing mercury from a liquid hydrocarbon, which comprises a step of contacting an ionic mercury-containing liquid hydrocarbon placed in a container with a sulfur compound represented by the general formula (I):



wherein M^1 and M^2 may be the same or different and are each independently a hydrogen atom, an alkali metal or an ammonium group, thereby removing the ionic mercury, wherein the container is equipped with a circulating means for circulating the ionic mercury-containing liquid hydrocarbon into the container, and wherein the sulfur compound is introduced into a suction side and/or a

discharge side of the circulating means while circulating the ionic mercury-containing liquid hydrocarbon through the circulating means. The ionic mercury-containing liquid hydrocarbon in the container may be mechanically stirred, if desired.

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Best Mode for Carrying Out the Invention

The ionized mercury-containing liquid hydrocarbons to be treated by the process of the present invention are not particularly restricted, and may include any hydrocarbons which are liquid at ordinary temperature.

10 Examples of the liquid hydrocarbons include crude oil, straight run naphtha, kerosene, gas oil, vacuum distillates, topped crude, and natural gas condensate (NGL). Of these liquid hydrocarbons, preferred is the natural gas condensate.

15 The mercury contained in the liquid hydrocarbon may be in either of elementary form or ionic form. The elementary mercury is converted into the ionic form by the ionization treatment described later. The concentration of mercury of the liquid hydrocarbon to be treated is not particularly restricted, and is usually 2 to 1,000 µg/L, preferably 5 to 100 µg/L.

20 The crude oil to be treated in the present invention is not particularly restricted. Examples of the crude oil are those produced in Saudi Arabia, United Arab Emirates, Nigeria, Canada, Mexico, Iran, Iraq, China, Kuwait, Malaysia, Venezuela, America, Australia, Russia, Libya, Philippines, Indonesia, Norway, Thai Land, Qatar, Argentina, England, and Japan. These crude oils may be used in combination of two or more.

25 The straight run naphtha, kerosene, gas oil, vacuum distillate and topped crude are obtained by processing the crude oil by known methods.

30 In the process of the present invention, the mercury contained in the liquid hydrocarbon must be ionized before its removal from the liquid hydrocarbon. Although the ionization method is not particularly restricted, the elementary mercury may be ionized by contacting the liquid hydrocarbon

with a substance capable of converting elementary mercury into ionic mercury. Examples of the mercury-ionizing substance include an iron compound such as iron sulfate, iron chloride, iron sulfide, iron oxide and iron nitrate; a copper compound such as copper sulfate, copper chloride, copper oxide, copper nitrate and copper sulfide; a vanadium compound such as vanadium oxide, vanadium sulfide and vanadium sulfate; a manganese compound such as manganese oxide, manganese sulfide and manganese sulfate; a nickel compound such as nickel oxide, nickel sulfide and nickel sulfate; an inorganic peroxide such as hydrogen peroxide; an organic peroxide such as peracetic acid; atmospheric oxygen; and a crude oil tank sludge. These mercury-ionizing substances may be used alone or in combination of two or more. The crude oil tank sludge is a settled sludge at the bottom of a crude oil tank, and contains elements such as Fe, Si, Na, Al, P, Zn, Cu, Ca, Mg, V, K, Cr, Mn, Ni, C, H, N, O and S.

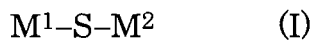
The manganese compounds such as manganese oxide may be of any shape such as powdery form, pulverized form, columnar form, spherical form, fibrous form and honeycomb form. In addition, the manganese compounds may be supported on a carrier such as silica, alumina, silica-alumina, zeolite, ceramic, glass, resin and activated carbon. The supporting amount is not particularly restricted, and is preferably 0.1 to 30% by weight based on the weight of the carrier.

The conditions for ionizing the elementary mercury by contacting the liquid hydrocarbon with the mercury-ionizing substance are not particularly restricted. The ionization temperature is usually -50 to 100°C, preferably 0 to 60°C. The ionization pressure may be not specifically limited as far as the liquid hydrocarbon is maintained in a liquid state at the ionization temperature being used. The mercury-ionizing substance is used preferably in an amount of 1 to 10,000 mol per one mole of the elementary mercury in the liquid hydrocarbon.

In the process of the present invention, the ionized mercury-containing liquid hydrocarbon is received in a container and subjected to a treatment for

removing the ionized mercury. Examples of the container include a crude oil tank, a naphtha tank, a condensate tank, etc., although not limited thereto. Also, water may be present in these containers.

The sulfur compound used for removing the ionic mercury from the liquid hydrocarbon is represented by the general formula (I):



wherein M^1 and M^2 may be the same or different and are each independently a hydrogen atom, an alkali metal or an ammonium group.

Examples of the alkali metal for M^1 and M^2 of the formula (I) include sodium, potassium, lithium and cesium. Examples of the sulfur compounds represented by the formula (I) include hydrogen sulfide, sodium sulfide, sodium hydrosulfide, potassium sulfide, potassium hydrosulfide, ammonium sulfide, and ammonium hydrosulfide. These sulfur compounds may be used alone or in combination of two or more. Of these sulfur compounds, preferred are hydrogen sulfide, sodium sulfide and sodium hydrosulfide.

In the process of the present invention, the ionic mercury-containing liquid hydrocarbon fed into the container is contacted with the sulfur compound of the formula (I) to convert the ionic mercury to a solid mercury compound insoluble to the liquid hydrocarbon. Then, the solid mercury compound is removed from the liquid hydrocarbon by filtration, sedimentation, etc. To efficiently contact the sulfur compound with the ionic mercury, the ionic mercury-containing liquid hydrocarbon in the container is circulated through a circulating means, while introducing the sulfur compound to a suction side and/or a discharge side of the circulating means. The circulating means comprises a pump which pumps up the liquid hydrocarbon by suction from the container and discharges the pumped-up liquid hydrocarbon into the container, and a conduit for passing through the liquid hydrocarbon. Generally, a suction inlet is disposed around the vicinity of the container bottom, and a discharge outlet is disposed around the vicinity of the container top. The circulating rate is preferably 1 to 5,000 m³/h.

A part of an existing conduit for feeding the liquid hydrocarbon into the container or a part of an existing conduit for discharging the liquid hydrocarbon from the container may be used as the circulation conduit. Also, a circulation line usually used for separating water from a crude oil in the crude oil receiving
5 for storage may be used as the circulation conduit.

The form of the sulfur compound being introduced is not particularly restricted. For example, when hydrogen sulfide is used as the sulfur compound, it may be directly introduced in an inherent gaseous state or in the form of solution in water or a liquid organic substance such as naphtha,
10 kerosene, light oil and heavy oil. When a sulfur compound, such as sodium sulfide, which is solid at room temperature is used, the solid sulfur compound may be introduced in the form of an aqueous solution.

The supplied amount of the sulfur compound of the formula (I) is 1 to 10,000 mol, preferably 100 to 5,000 mol per one mole of the mercury contained
15 in the liquid hydrocarbon. The total amount of the sulfur compound is supplied over 1 to 300 h while circulating the liquid hydrocarbon. After supplying the total amount, the circulation of the liquid hydrocarbon is preferably continued for 1 to 300 h.

The conditions for the contact between the sulfur compound and the ionic
20 mercury are not particularly restricted. The contact temperature is usually -50 to 100°C, preferably 0 to 60°C. Any suitable pressure is usable as long as the liquid hydrocarbon is maintained in a liquid state at the contact temperature being used.

In the process of the present invention, the contact between the ionic
25 mercury with the sulfur compound is further enhanced by mechanically stirring the liquid hydrocarbon in the container.

The present invention will be described in more detail by reference to the following examples. However, it should be noted that the following examples are illustrative and not intended to limit the invention thereto.

30 EXAMPLE 1

Into a tank equipped with a circulation conduit, was fed 38,000 m³ of a liquid hydrocarbon (density: 0.7363 g/cm³ at 15°C) containing 15.3 µg/L of ionic mercury. A pump with a capacity of 15 m³/h was disposed between the inlet and the outlet of the circulation conduit. Hydrogen sulfide was introduced at a feeding rate of 4.8 kg/h into a suction side of the pump while operating the pump. After introducing hydrogen sulfide over 21.4 h, the liquid hydrocarbon was further circulated for additional 24 h. During the circulation, the temperature and pressure were controlled to 20°C and ordinary pressure, respectively. Simultaneously with the circulation of the liquid hydrocarbon, the liquid hydrocarbon in the tank was stirred by a stirrer.

The surface of the liquid hydrocarbon in the tank was 12 m high from the bottom of the tank. Immediately after stopping the stirring and circulation of the liquid hydrocarbon, a portion of the liquid hydrocarbon was sampled from a position of 1 m high from the bottom. The sampled liquid hydrocarbon was filtered through a filter of 0.5 µm pore size. The concentration of mercury of the resultant filtrate was 1 µg/L.

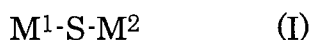
After 10 days from stopping the stirrer and the pump for circulation, a portion of the liquid hydrocarbon was sampled at the position of 1 m high from the bottom. The concentration of mercury of the sampled liquid hydrocarbon was 1 µg/L without filtration.

Industrial Applicability

In accordance with the present invention, ionic mercury is effectively removed from an ionic mercury-containing liquid hydrocarbon placed in a container in extremely simple and industrially useful manner.

CLAIMS

1. A process for removing mercury from a liquid hydrocarbon, which comprises a step of contacting an ionic mercury-containing liquid hydrocarbon
5 placed in a container with a sulfur compound represented by the general formula (I):



wherein M^1 and M^2 may be the same or different and are each independently a hydrogen atom, an alkali metal or an ammonium group, thereby removing the
10 ionic mercury,

wherein the container is equipped with a circulating means for circulating the ionic mercury-containing liquid hydrocarbon into the container, and

wherein the sulfur compound is introduced into a suction side and/or a discharge side of the circulating means while circulating the ionic mercury-
15 containing liquid hydrocarbon through the circulating means.

2. The process according to claim 1, wherein the ionic mercury-containing liquid hydrocarbon in the container is mechanically stirred.

3. The process according to claim 1 or 2, wherein the sulfur compound is at least one compound selected from the group consisting of hydrogen sulfide,
20 sodium sulfide, sodium hydrosulfide, potassium sulfide, potassium hydrosulfide, ammonium sulfide, and ammonium hydrosulfide.

4. The process according to any one of claims 1 to 3, wherein the liquid hydrocarbon is circulated at a rate of 1 to 5000 m³/h.

5. The process according to any one of claims 1 to 4, wherein the sulfur
25 compound is introduced in an amount of 1 to 10,000 mol per one mole of mercury contained in the liquid hydrocarbon.

6. The process according to any one of claims 1 to 5, wherein 1 to 10,000 mol of the sulfur compound per one mole of mercury contained in the liquid hydrocarbon is introduced over 1 to 300 h.

30 7. The process according to any one of claims 1 to 6, wherein the liquid

hydrocarbon is further circulated for additional 1 to 300 h after introducing the sulfur compound.