

DESCRIPTION

Title of Invention

RUBBER COMPOUNDING OIL AND METHOD FOR MANUFACTURING THE
5 SAME

Technical Field

[0001]

The present invention relates to rubber compounding oil used in the form of a
10 mixture with rubber when manufacturing a rubber product, such as a tire, (also referred
to as process oil for rubber and plasticizer for rubber), a method for manufacturing the
same, and a method for manufacturing a tire rubber composition.

Priority is claimed on Japanese Patent Application No. 2012-115574, filed May
21, 2012, the content of which is incorporated herein by reference.

15

Background Art

[0002]

When manufacturing a rubber product, such as a tire, rubber compounding oil is
compounded with rubber, and permeate a polymer structure of the rubber, thereby
20 facilitating manufacturing or processing of the rubber product, such as kneading,
extrusion and molding, and improving properties of the rubber product. The rubber
compounding oil needs to have favorable compatibility with rubber.

Rubber can be classified into natural rubber and synthetic rubber, and there are a
variety of kinds of synthetic rubber. Among the above, natural rubber and
25 styrene-butadiene rubber are particularly widely used as tire rubber. In addition, rubber

compounding oil including a large amount of aromatic hydrocarbon and having a high affinity to rubber is generally used as the rubber compounding oil compounded with the rubber.

[0003]

5 As the rubber compounding oil, an EXTRACT is used. The EXTRACT is obtained by carrying out deasphalting on a lubricating oil distillate or a depressurized residue, which is obtained by distilling crude oil under reduced pressure, and then carrying out an extraction treatment on oil, which is obtained through a dewaxing treatment or a hydrotreating treatment, using a solvent having an affinity to aromatic
10 hydrocarbon as necessary. The EXTRACT contains a relatively large amount of a heavy aromatic compound.

[0004]

In addition, in Europe, a strict environmental regulation stipulating that “regarding the content of polycyclic aromatic hydrocarbon (PAH) in oil used for tires, the
15 content of benzo[a]pyrene shall be 1 wtppm or less with respect to the oil, and the total content of PAH in eight subject substances shall be 10 wtppm or less with respect to the oil” has taken effect on 2010.

As such, for oil used as the rubber compounding oil or the like, there is a desire for a decrease in the concentration of aromatic hydrocarbon including polycyclic
20 aromatic hydrocarbon.

[0005]

In addition, the above eight subject substances are called “PAH 8 substances”, and refer to the following eight substances of PAH, which are the subjects of regulation in Europe. Hereinafter, there are cases in which the following substances will be
25 referred to simply as PAH8.

- (1) Benzo[a]anthracene
- (2) Chrysene
- (3) Benzo[b]fluoranthene
- (4) Benzo[j]fluoranthene
- 5 (5) Benzo[k]fluoranthene
- (6) Benzo[e]pyrene
- (7) Benzo[a]pyrene
- (8) Dibenzo[a,h]anthracene
- [0006]

10 For example, PTL 1 discloses process oil in which the content of a polycyclic aromatic compound is reduced by carrying out an extraction step on a lubricating oil distillate having a boiling point of 260 to 650°C, which has been distilled under reduced pressure, using furfural or the like.

In addition, PTL 2 discloses rubber compounding oil in which the content of a
15 specific carcinogenic polycyclic aromatic compound is reduced using a specific EXTRACT and a specific lubricant base oil while a high viscosity, a high burning point and a high aromaticity are maintained.

Furthermore, PTL 3 discloses a rubber plasticizer manufactured by mixing naphthene base oil and naphthene-based asphalt, which have been hydrorefined at a high
20 pressure and a high temperature at a regulated ratio.

Citation List

Patent Literature

[0007]

25 [PTL 1] Japanese Patent No. 3658155

[PTL 2] Japanese Unexamined Patent Application, First Publication No.

2010-229314

[PTL 3] Japanese Patent No. 3473842

5 Summary of Invention

Technical Problem

[0008]

However, in the related arts described in PTL 1 to 3, there are problems in that steps of obtaining a target substance are complicated, and the manufacturing costs are

10 high.

The invention is to replace the above related arts, and an object of the invention is to provide a manufacturing method in which rubber compounding oil, in which benzo[a]pyrene or other polycyclic aromatic hydrocarbon is reduced so as to satisfy the above regulation in Europe, can be stably manufactured for a long period of time.

15

Solution to Problem

[0009]

As a result of thorough studies on the above problems, the present inventors paid attention to ethylene bottom oil obtained from a petrochemical plant, succeeded the long-term stable manufacturing of rubber compounding oil, in which a decrease in the activity of a catalyst over time is suppressed so as to reduce benzo[a]pyrene or other polycyclic aromatic hydrocarbon, by carrying out specific two steps of hydrogenation using the ethylene bottom oil as a raw material, and completed the invention.

20

That is, the invention relates to the following [1] to [17].

25

[1] A method for manufacturing rubber compounding oil, including a step in

which ethylene bottom oil obtained by thermal cracking of a naphtha-containing raw material is prepared, a hydrodesulfurization step in which at least part of the ethylene bottom oil is hydrodesulfurized as a raw material of desulfurized oil, thereby obtaining the desulfurized oil, and a hydrogenation step in which an aromatic ring of the

5 desulfurized oil is aromatic hydrogenated.

[2] The method for manufacturing rubber compounding oil according to the above [1], in which, in the hydrodesulfurization step, the raw material is reacted with hydrogen gas at 250 to 400°C using a hydrodesulfurization catalyst having at least one element selected from molybdenum and tungsten as a catalyst element and at least one

10 element selected from cobalt and nickel as a promoter metal supported on a carrier including any of alumina, silica, titania, zirconia, silica alumina and zeolite as a main component.

[3] The method for manufacturing rubber compounding oil according to the above [1] or [2], in which, in the hydrodesulfurization step, the raw material is reacted

15 with the hydrogen gas at a pressure of 1.0 to 20.0 MPaG.

[4] The method for manufacturing rubber compounding oil according to any of the above [1] to [3], in which, in the hydrogenation step, the desulfurized oil is reacted with the hydrogen gas at 100 to 300°C using a hydrogenation catalyst having at least one element selected from the group consisting of iron, cobalt, nickel, ruthenium, rhodium,

20 palladium, iridium and platinum supported on a carrier made of an inorganic compound.

[5] The method for manufacturing rubber compounding oil according to any of the above [1] to [4], in which, in the hydrogenation step, the desulfurized oil is reacted with the hydrogen gas at a pressure of 1.0 to 20.0 MPaG.

[6] The method for manufacturing rubber compounding oil according to any of

25 the above [1] to [5], in which, in a case in which the hydrodesulfurization step is carried

out in a flow reactor using a hydrogenation catalyst, a cumulative amount of sulfur in the desulfurized oil supplied in the hydrogenation step for one year is 0.01 ton or less per ton of the hydrogenation catalyst.

[7] The method for manufacturing rubber compounding oil according to any one
5 of the above [1] to [6], in which the hydrodesulfurization step includes a reaction step in which the raw material is reacted with the hydrogen gas so as to convert a sulfur compound in the raw material into hydrogen sulfide and a gas-liquid separating step in which a reaction liquid obtained in the reaction step is separated into gas and liquid and the hydrogen sulfide is removed from the reaction liquid as gas, thereby obtaining the
10 desulfurized oil, and, in the gas-liquid separating step, the reaction liquid is depressurized, thereby removing the hydrogen sulfide.

[8] The method for manufacturing rubber compounding oil according to any one of the above [1] to [7], in which the raw material is a component (C_v) having a 100°C kinetic viscosity of 10 mm²/s or more in the ethylene bottom oil.

15 [9] The method for manufacturing rubber compounding oil according to the above [8], in which the component (C_v) is a distillation residual liquid of the ethylene bottom oil.

[10] The method for manufacturing rubber compounding oil according to any one of the above [1] to [9], in which the naphtha-containing raw material contains 1 to 99
20 mass% of one or more selected from the group consisting of kerosene, gas oil and NGL.

[11] The method for manufacturing rubber compounding oil according to any one of the above [1] to [10], in which, in the hydrodesulfurization step, the raw material diluted using one or more solvent selected from the group consisting of saturated hydrocarbon, saturated ether and the rubber compounding oil is reacted with the
25 hydrogen gas.

[12] The method for manufacturing rubber compounding oil according to any one of the above [1] to [11], in which, in the hydrodesulfurization step and the hydrogenation step, the respective reaction is carried out using a trickle-bed type reactor.

[13] Rubber compounding oil obtained using the manufacturing method
5 according to any one of the above [1] to [12].

[14] The rubber compounding oil according to the above [13], in which a total content of PAH8 substances is 0 wtppm or more and 10 wtppm or less, and a content of benzo[a]pyrene is 0 wtppm or more and 1 wtppm or less.

[15] The rubber compounding oil according to the above [13] or [14], in which a
10 content ratio of aromatic carbon is 5 to 50%.

[16] The rubber compounding oil according to any one of the above [13] to [15], in which a 100°C kinetic viscosity is 10 to 100 mm²/s.

[17] A method for manufacturing a tire rubber composition, in which the rubber compounding oil according to any one of the above [13] to [16] is mixed with at least one
15 kind of rubber selected from the group consisting of natural rubber, styrene butadiene rubber, polybutadien rubber, butyl rubber, isoprene rubber and nitrile rubber.

Advantageous Effects of Invention

[0010]

20 According to the invention, it is possible to stably manufacture for a long period of time rubber compounding oil, in which benzo[a]pyrene or other polycyclic aromatic hydrocarbon is reduced so as to satisfy the above regulation in Europe. In addition, according to the method, it is also possible to effectively use ethylene bottom oil which was used in a limited range of use in the past.

Brief Description of Drawings

[0011]

FIG. 1 is a graph in which a total sulfur concentration and a total content of PAH8 of rubber compounding oil obtained in Example 1 are plotted with respect to a reaction time.

FIG. 2 is a graph in which a total content of PAH of rubber compounding oil obtained in Comparative example 1 are plotted with respect to a reaction time.

Description of Embodiments

10 [0012]

Hereinafter, the invention will be described in detail using an example of an embodiment.

In addition, the invention is not limited by the following description, and is limited only by the scope of the claims. The addition, removal, substitution and other alternation of the location, amount, number, shape and the like are allowed within the scope of the purport of the invention.

The invention provides a method for manufacturing rubber compounding oil including a hydrodesulfurization step in which at least part of ethylene bottom oil obtained by thermal cracking of a naphtha-containing raw material is hydrogenated and desulfurized as a raw material, thereby obtaining desulfurized oil and a hydrogenation step in which an aromatic ring of the desulfurized oil is aromatic hydrogenated. That is, the method for manufacturing rubber compounding oil of the invention includes a hydrodesulfurization step in which at least part of ethylene bottom oil obtained by thermal cracking of a naphtha-containing raw material, that is, part or all of the ethylene bottom oil (for example, a component separated from the ethylene bottom oil through

distillation or the like) is used as a raw material, the ethylene bottom oil is hydrodesulfurized, thereby obtaining desulfurized oil, and a hydrogenation step in which an aromatic ring of the obtained desulfurized oil is aromatic hydrogenated .

When part or all of ethylene bottom oil is used as a raw material, and
5 hydrogenation is carried out on the raw material through two steps as above, it is possible to stably manufacture for a long period of time rubber compounding oil, in which benzo[a]pyrene or other polycyclic aromatic hydrocarbon is reduced so as to satisfy the above regulation in Europe.

[0013]

10 In addition, aromatic hydrogenation refers to a reaction in which a hydrogen atom is added to the aromatic carbon-carbon double bond of a raw material.

[0014]

<Method for manufacturing rubber compounding oil>

(Ethylene bottom oil)

15 In the petrochemical industry, in general, naphtha is thermally cracked at a high temperature, the obtained thermally cracked substance is distilled, separated into different distillates, such as olefins (for example, ethylene, propylene and the like), aromatic compounds (for example, benzene, toluene, xylene and the like), cracked kerosene and cracked gasoline, and made into a product. Among the above distillates,
20 the heavy distillate having a highest boiling point is referred to as "ethylene bottom oil", and is used in, for example, a raw material of carbon black and the like and a fuel.
Since the thermal cracking plant of naphtha is often referred to as an ethylene plant, the heavy distillate is called ethylene bottom oil. In addition, there are cases in which the thermal cracking plant of naphtha is also called a naphtha cracker. In addition, the
25 boiling point of the ethylene bottom oil varies depending on conditions; however,

generally, the 50% distillate temperature is approximately 200 to 280°C.

[0015]

In the present embodiment, ethylene bottom oil obtained through the thermal cracking of naphtha; and ethylene bottom oil obtained by thermal cracking of naphtha
5 and, furthermore, a raw material including at least one of kerosene, gas oil and natural gas liquid (NGL) can be used as the ethylene bottom oil.

The NGL refers to a liquid component having a high boiling point when extracting natural gas, and is, specifically, a collective term of liquid hydrocarbon which is separated and collected from natural gas produced from the underground through a
10 winze (for example, refer to the homepage of Japan Oil, Gas and Metals National Corporation (JOGMEC)). In the present specification, a raw material which contains at least naphtha, and further includes at least one of kerosene, gas oil and NGL depending on cases is referred to as the naphtha-containing raw material.

[0016]

15 In a case in which a raw material including naphtha and at least one of kerosene, gas oil and NGL is used as the naphtha-containing raw material, the total content of kerosene, gas oil and NGL can be set to 1 to 99 mass% in 100 mass% of the naphtha-containing raw material. Since the naphtha-containing raw material having a high content of kerosene, gas oil and NGL includes a large amount of kerosene, gas oil
20 and NGL, which are cheaper than naphtha, the naphtha-containing raw material is superior to a naphtha-containing raw material having a low content of kerosene, gas oil and NGL in terms of economic efficiency as a naphtha cracker. On the other hand, from the naphtha-containing raw material having a large content, a large amount of the ethylene bottom oil, which is a heavy oil and is used in a limited range, is obtained.
25 Therefore, in the past, there were cases in which there was a problem with a method for

using the naphtha-containing raw material having a large content. In contrast to the above, since the ethylene bottom oil is effectively used in the manufacturing method of the embodiment, even the naphtha-containing raw material having a large total content of kerosene, gas oil and NGL can be used as a raw material for thermal cracking with no
5 problem.

In addition, there are cases in which the total proportion of kerosene, gas oil and NGL in 100 mass% of the naphtha-containing raw material is called non-naphtha feedstock ratio.

[0017]

10 The properties of the ethylene bottom oil obtained by thermal cracking of the naphtha-containing raw material vary depending on the kind of the naphtha-containing raw material, the conditions of thermal cracking, the operation conditions of a purification distillation tower, and the like. Examples of the ordinary properties include a total content of PAH8 of 1000 to 3000 wtpm with respect to the ethylene bottom oil, a
15 content of benzo[a]pyrene of 50 to 200 wtpm with respect to the ethylene bottom oil, a 100°C kinetic viscosity (kinetic viscosity at 100°C) of less than 10 mm²/s, and a content ratio of aromatic carbon of 50% or more with respect to the ethylene bottom oil.

[0018]

In addition, in the specification, the values of the kinetic viscosity are measured
20 based on JIS K2283.

In addition, PAH8 including benzo[a]pyrene can be quantified using a gas chromatograph mass spectrometer (GC-MS) or the like.

In addition, in the specification, the content ratio of aromatic carbon refers to a ratio (percentage) of the area integrated value of peaks of 110 to 150 ppm (corresponding
25 to the number of aromatic carbon atoms) to the area integrated value of all peaks

(corresponding to the total number of carbon atoms) in the nuclear magnetic resonance spectrum (^{13}C -NMR) measurement. The ethylene bottom oil or the rubber compounding oil obtained from the ethylene bottom oil using the manufacturing method of the embodiment includes many compounds having an aromatic ring or a condensed ring thereof as aromatic compounds. However, it is difficult to identify and quantify the above compounds one by one. Therefore, in a case in which the amount of the aromatic compounds included in the above subject substances is determined, generally, it is common to use the content of aromatic carbon (Ca%), which is measured using ASTM D2140, as an index. However, in recent years, it has become possible to directly obtain the amount of the aromatic compounds from the measurement using NMR. Therefore, in the specification, the ratio of the aromatic carbon, which is obtained using ^{13}C -NMR as described above, will be used as the content ratio of aromatic carbon.

In addition, the ethylene bottom oil used in the invention generally has the following characteristics.

The 100°C kinetic viscosity of the ethylene bottom oil is generally less than 10 mm²/s, preferably 1 to 10 mm²/s, and more preferably 3 to 7 mm²/s.

The content ratio of aromatic carbon in the ethylene bottom oil is generally 50% or more, preferably 55 to 80%, and more preferably 60 to 75%.

The amount of the PAH8 substances in the ethylene bottom oil is generally 500 to 10000 wtppm, preferably 0 to 7000 wtppm, and more preferably 0 to 3000 wtppm.

The content of the benzo[a]pyrene in the ethylene bottom oil is generally 30 to 1000 wtppm, preferably 0 to 600 wtppm, and more preferably 0 to 200 wtppm.

The total sulfur concentration in the ethylene bottom oil is generally 0 to 0.2 mass%, preferably 0.02 to 0.18 mass%, and more preferably 0.05 to 0.15 mass%.

The concentration of asphaltene in the ethylene bottom oil is generally 0 to 5%,

preferably 0.1 to 3%, and more preferably 0.2 to 1.5 mass%.

[0019]

(Component (C_v))

In the hydrodesulfurization step of the embodiment, part or all of the ethylene
5 bottom oil obtained by thermal cracking of the naphtha-containing raw material is used
as a raw material, and the ethylene bottom oil is hydrodesulfurized. In addition, part of
the ethylene bottom oil may be considered as oil included in the ethylene bottom oil. It
is preferable that the component (C_v) having a 100°C kinetic viscosity of 10 mm²/s or
more in the ethylene bottom oil be used as the raw material, and the component is
10 hydrodesulfurized. When the component (C_v) having a 100°C kinetic viscosity of 10
mm²/s or more is hydrodesulfurized, the viscosity of the obtained rubber compounding
oil does not become to be low. Therefore, a problem, such as the oil vaporization
during the kneading rubber at high temperature or bleeding out of the rubber
compounding oil from a vulcanized substance of a rubber composition, is not easily
15 caused.

The 100°C kinetic viscosity of the component (C_v) is preferably 20 mm²/s or
more. In addition, the preferable upper limit value of the 100°C kinetic viscosity of the
component (C_v) can be arbitrarily selected, but is preferably 10000 mm²/s or less, more
preferably 1000 mm²/s or less, and more preferably 500 mm²/s or less from the
20 viewpoint of handling of the component (C_v) in the manufacturing steps.

[0020]

In a case in which the 100°C kinetic viscosity of the ethylene bottom oil
obtained by thermal cracking of the naphtha-containing raw material is 10 mm²/s or more,
the ethylene bottom oil can be supplied to the hydrodesulfurization step as the component

(C_v) as it is. In contrast to the above, in a case in which the 100°C kinetic viscosity of the ethylene bottom oil is less than 10 mm²/s, the ethylene bottom oil may be supplied to the hydrodesulfurization step as it is, but it is more preferable that components having a low boiling point, which are included in the ethylene bottom oil, be removed using a distillation step so that the distillation residual liquid (residual oil), from which the above components have been removed, is adjusted so as to obtain a 100°C kinetic viscosity of 10 mm²/s or more, and the distillation residual liquid be supplied to the hydrodesulfurization step as the component (C_v). The distillation step may be any of atmospheric distillation; distillation under reduced pressure (vacuum distillation); and a combination of atmospheric distillation and distillation under reduced pressure; and can be appropriately selected.

[0021]

In the component (C_v) supplied to the hydrodesulfurization step, the content ratio of aromatic carbon is preferably 55 to 100%. When the content ratio of aromatic carbon is less than 55%, there is a tendency of the content ratio of aromatic carbon in the finally obtained rubber compounding oil to become lower than the desired value. The content ratio of aromatic carbon in the component (C_v) is more preferably 60 to 95%, and still more preferably 70 to 90%.

[0022]

In addition, the total content of PAH8 in the component (C_v) is preferably 0 to 3000 wtppm with respect to the component (C_v). The total content of PAH8 is more preferably 0 to 2000 wtppm, and still more preferably 0 to 1000 wtppm. When the total content exceeds 3000 wtppm, there are cases in which it becomes difficult to sufficiently reduce the total content of PAH8 in the finally obtained rubber compounding oil.

In addition, the total sulfur concentration in the component (C_v) is preferably 0 to 1 mass% with respect to the component (C_v). The total sulfur concentration is more preferably 0 to 0.3 mass%, and still more preferably 0 to 0.2 mass%.

The concentration of asphaltene in the component (C_v) is preferably 0% or more
5 and 3% or less with respect to the component (C_v). The concentration of asphaltene is more preferably 0.1 to 2.5%, and still more preferably 0.2 to 2%. When the total sulfur concentration exceeds 1 mass%, there are cases in which it becomes difficult to sufficiently reduce the total content of PAH8 in the finally obtained rubber compounding oil.

10 The content of the benzo[a]pyrene in the component (C_v) is generally 0 to 500 wtppm, preferably 0 to 300 wtppm, and more preferably 0 to 250 wtppm.

[0023]

(Hydrodesulfurization step)

Hereinafter, the hydrodesulfurization step will be described using a case in
15 which the hydrodesulfurization step is carried out using the above component (C_v) as a raw material as a preferable example.

The hydrodesulfurization step includes a reaction step in which the component (C_v) is reacted with hydrogen gas so as to convert a sulfur compound included in the component (C_v) into hydrogen sulfide (H_2S), and a gas-liquid separating step in which
20 the reaction liquid obtained in the reaction step is separated into gas and liquid, and the hydrogen sulfide is removed from the reaction liquid as gas, thereby obtaining desulfurized oil. In addition, the reaction step and the gas-liquid separating step may be carried out in the same step. When the hydrodesulfurization step is carried out, and the sulfur compound in the raw material is reduced, in the hydrogenation step described

below, a decrease in the activity of a catalyst, which is caused by the accumulation of sulfur in a hydrogenation catalyst, can be suppressed, and it becomes possible to stably manufacture for a long period of time rubber compounding oil.

Here, as described above, when the 100°C kinetic viscosity of the ethylene
5 bottom oil obtained by thermal cracking of the naphtha-containing raw material is 10
mm²/s or more, the ethylene bottom oil can be used as the component (C_v) as it is. On
the other hand, when the 100°C kinetic viscosity is less than 10 mm²/s, the ethylene
bottom oil is subjected to the distillation step so as to remove components having a low
boiling point, and the distillation residual liquid having a 100°C kinetic viscosity of 10
10 mm²/s or more, which has been obtained by the above removal, is used as the component
(C_v). That is, in a case in which the kinetic viscosity of the ethylene bottom oil is low, it
is possible to obtain a component having a 100°C kinetic viscosity of 10 mm²/s or more
through the distillation step, and to use the component as a raw material for
hydrodesulfurization.

15 [0024]

In the hydrodesulfurization step, a reaction step is carried out using a flow
reactor or a batch reactor in the presence of a solid catalyst. The flow reactor is
preferable in terms of productivity.

The reaction is preferably conducted in a gas-liquid phase. A trickle-bed
20 method using a trickle-bed type reactor, in which the component (C_v) is made to flow
downstream to a layer filled with the solid catalyst, and hydrogen gas, which is brought
into contact with the component (C_v), is also made to flow downstream, is more
preferable. When the reaction phase is a gas-phase reaction, the amount of energy
necessary to evaporate the component (C_v) or the solvent becomes excessive, which

causes economic disadvantages. In addition, when the reaction phase is a liquid-phase reaction, since there is a limitation on the amount of hydrogen dissolved in the component (C_v) or the solvent, a desired hydrogenation treatment becomes difficult.

[0025]

5 In a case in which the reaction step is carried out using the flow reactor, the flow amount of hydrogen gas is preferably adjusted so that the ratio of the hydrogen gas being supplied to 1 ton of the supply amount of the component (C_v) becomes 100 to 1000 Nm^3 . When the flow amount of the hydrogen gas is less than 100 Nm^3 , there are cases in which the component (C_v) is not sufficiently hydrodesulfurized, and when the flow amount of
10 the hydrogen gas exceeds 1000 Nm^3 , economic disadvantages are caused.

[0026]

Any catalysts that can act as a catalyst of a hydrodesulfurization reaction can be used as the solid catalyst being used.

For example, a catalyst, in which one of alumina, silica, titania, zirconia, boria,
15 magnesia, zeolites (Y-type zeolite, X-type zeolite, L-type zeolite, beta-type zeolite, ZSM zeolite, such as ZSM-5, MFI-type zeolite, chebazite, mordenite, erionate) or a composite oxide or oxide mixture made of two or more thereof is used as a carrier, and the metal of at least one element of Groups 6, 8, 9 and 10 in the periodic table is supported on the carrier, can be used. Examples of the metal of Group 6 in the periodic table include Cr,
20 Mo and W. Examples of the metals of Groups 8, 9 and 10 in the periodic table include Co, Ni, Rh, Ru, Pd, Pt and the like.

In a case in which two or more supported metals are used, preferable examples thereof include combinations, such as Ni-Mo, Co-Mo and Ni-W. In addition, in a case in which a composite oxide or an oxide mixture is used as a carrier, for example, a carrier
25 molded using zeolite, alumina, silica alumina and the like as the matrix is preferably used.

In a case in which zeolite is used, Y-type zeolite is preferable.

[0027]

Among the above, from the viewpoint of high sulfur resistance or desulfurization ability, a hydrodesulfurization catalyst having at least one element selected from Mo and W as a catalyst element and at least one element selected from Co and Ni as a promoter metal supported on a carrier including any of alumina, silica, titania, zirconia, silica alumina and zeolite as a main component is preferably used.

[0028]

The liquid space velocity (LHSV) in an industrial plant may be appropriately adjusted in a range of generally 0.1 to 10 hr^{-1} , preferably 0.2 to 9 hr^{-1} , and more preferably 0.3 to 8 hr^{-1} by the component (C_v) standard. When the LHSV is less than 0.1 hr^{-1} , the amount of the solid catalyst becomes excessive, which is not advantageous in terms of economic efficiency, and, on the other hand, when the LHSV exceeds 10 hr^{-1} , there is a possibility that the component (C_v) may not be sufficiently hydrodesulfurized.

15 [0029]

The temperature for the reaction step can be arbitrarily selected, but is generally set to 100 to 450°C , preferably 170 to 430°C , more preferably 250 to 400°C , and still more preferably 270°C to 350°C . When the reaction temperature is lower than the lower limit value of the above range, there are cases in which the component (C_v) is not sufficiently hydrodesulfurized, and, when the reaction temperature exceeds the upper limit value of the above range, there is a possibility that the raw material unit consumption may deteriorate due to the hydrocracking of the component (C_v).

20 The pressure is generally set to 1.0 to 20.0 MPaG , preferably 1.5 to 13 MPaG , and more preferably in a range of 2.0 to 5.0 MPaG as a gauge pressure. When the

pressure is below the above range, there are cases in which desired hydrodesulfurization do not sufficiently proceed.

[0030]

In addition, during the hydrodesulfurization step, in order to remove reaction
5 heat being generated, the component (C_v) diluted using a solvent may be reacted with
hydrogen gas. In the reaction step of the hydrodesulfurization step, there are cases in
which aromatic ring hydrogenation as well as hydrodesulfurization proceeds at the same
time, and, in this case, there is a tendency for the reaction heat to become significant. In
addition, for example, there are cases in which the aromatic ring hydrogenation is
10 actively made to proceed in order to control the polarity of the obtained rubber
compounding oil, and, at this time, the reaction heat is large, and, when the reaction heat
is not removed, there is a possibility that the control of the reaction temperature becomes
difficult. In addition, even from the viewpoint of preventing the fouling of the catalyst,
it becomes effective means for diluting the component (C_v), which is a base material,
15 using a solvent.

The solvent used for dilution needs to be inert in the reaction step of the
hydrodesulfurization step of the embodiment; to sufficiently dissolve the component
(C_v); to have a lower boiling point than the obtained rubber compounding oil so that the
solvent can be easily separated from the rubber compounding oil through distillation or
20 the like afterwards; and the like. A solvent that satisfies the above conditions can be
appropriately selected from saturated hydrocarbon, saturated ethers and the like, and, for
example, decahydronaphthalene, tetralin, tetrahydrofuran, 1,4-dioxane and the like can
be preferably exemplified.

In addition, rubber compounding oil manufactured in the embodiment can also
25 be used as the solvent. In a case in which rubber compounding oil is selected as a

solvent, since the solvent and the product (rubber compounding oil) are the same, it is not necessary to separate both from each other, and some of the mixture of the solvent and the product may be circulated and reused as the solvent. Therefore, a process, in which rubber compounding oil is used as the solvent, is economically effective.

5 [0031]

In the case of the batch reactor, an autoclave or the like is used as a reactor. At this time, the reaction time is preferably 1 to 5 hours. A variety of conditions, such as the solid catalyst being used, the ratio between the component (C_v) and the hydrogen gas, the temperature and pressure for hydrodesulfurization, are the same as in the case of the
10 flow reactor. In addition, even in the case of the batch reactor, reaction may be carried out after the component (C_v) is diluted using the solvent.

[0032]

After the completion of the reaction step in the hydrodesulfurization step, the gas-liquid separating step, in which the reaction liquid obtained in the reaction step is
15 separated into gas and liquid, hydrogen sulfide is removed from the reaction liquid as gas, and purged outside the system, is carried out. Due to the degassing, a residual oil (desulfurized oil) having a reduced sulfur concentration or a liquid component containing a residual oil and a solvent in a case in which a dilution solvent is used can be obtained. The desulfurized oil or liquid component is supplied to the following hydrogenation step.

20 When hydrogen sulfide is purged outside the system as described above, unreacted hydrogen gas accompanies the hydrogen sulfide. In a case in which a large amount of the hydrogen gas accompanies the hydrogen sulfide, and has a large adverse influence in an economic aspect, after selecting and removing the hydrogen sulfide using an absorbing liquid such as amine or caustic soda, it is preferable to circulate the
25 hydrogen gas to the reactor in the hydrodesulfurization step or to send the hydrogen gas

to a reactor in the subsequent hydrogenation step, thereby reusing the hydrogen gas.

In addition, the hydrogen sulfide is removed using gas-liquid separation more effectively under reduced pressure. Therefore, it is preferable to depressurize the reaction liquid obtained in the reaction step, and to remove the hydrogen sulfide.

5 However, when the operation pressure is too low, the degassing efficiently proceeds, but there is a possibility that the subsequent absorption operation, in which an absorbing liquid, such as amine or caustic soda, is used, may be influenced. In addition, the power cost during the circulation of the hydrogen gas also increases. Therefore, the operation pressure during the separation of gas and liquid is appropriately set in consideration of
10 the optimal process value.

[0033]

(Hydrogenation step)

In the hydrogenation step, the aromatic ring of the desulfurized oil obtained through the hydrodesulfurization step is aromatic hydrogenated. Thereby, it is possible
15 to remove the PAH8 substances included in the desulfurized oil, to control the concentration of the aromatic compound included, and to manufacture rubber compounding oil in which benzo[a]pyrene or other polycyclic aromatic hydrocarbon is reduced so as to satisfy the above regulation in Europe.

[0034]

20 The hydrogenation step is carried out in the presence of a solid catalyst using a flow reactor or a batch reactor. From the viewpoint of the productivity, the flow reactor is preferable.

As the reaction form, a gas-liquid reaction is preferable. The gas-liquid reaction is preferably a trickle-bed method in which a trickle bed type reactor, in which
25 the desulfurized oil is made to flow downstream into a solid catalyst-filled layer and the

hydrogen gas that is brought into contact with the desulfurized oil is also made to flow downstream, is used. When the reaction form is a gas-phase reaction, the amount of energy necessary to evaporate the desulfurized oil or the solvent becomes excessive, and the reaction becomes economically disadvantageous. On the other hand, when the
5 reaction form is a liquid-phase reaction, since only a limited amount of hydrogen is dissolved in the desulfurized oil or the solvent, a desired aromatic-hydrogenation treatment becomes difficult.

In addition, in order to remove the reaction heat caused by the aromatic hydrogenation, dilution using a solvent may be carried out in the same manner as in the
10 hydrodesulfurization step. The solvents described in the description of the hydrodesulfurization step can be used as a preferable solvent.

In addition, in a case in which a dilution solvent is used in the hydrodesulfurization step, the desulfurized oil is supplied to the hydrogenation step as a raw material in a state in which the desulfurized oil is mixed with the solvent. Thereby,
15 even in the hydrogenation step, aromatic hydrogenation proceeds in a state in which the raw material is diluted using the solvent, and the reaction heat can be removed.

[0035]

In a case in which hydrogenation is carried out using the flow reactor, the flow rate of the hydrogen gas is preferably adjusted so that the fraction of the hydrogen gas
20 being supplied becomes in a range of 100 to 1000 Nm³ per ton of the supply amount of the desulfurized oil. When the flow rate of the hydrogen gas is less than 100 Nm³, there are cases in which the aromatic hydrogenation becomes insufficient, and, when the flow rate of the hydrogen gas exceeds 1000 Nm³, the aromatic hydrogenation becomes economically disadvantageous.

25 [0036]

As the solid catalyst used in the hydrogenation step, solid catalysts that can serve as a catalyst of the hydrogenation reaction can be used. For example, it is also possible to use the same catalyst as for the reaction step of the hydrodesulfurization step described above. However, since the object of the hydrogenation step is the aromatic hydrogenation of the desulfurized oil, a catalyst having a high aromatic hydrogenation performance in spite of a low sulfur resistance is preferably used.

As the catalyst, a catalyst, in which one of alumina, silica, titania, zirconia, boria, magnesia and zeolite; a composite oxide or an oxide mixture made of two or more thereof; or activated charcoals, is used as an inorganic compound carrier, and at least one of metals belonging to Groups 8 to 10 in the periodic table is supported on the carrier, is preferably used.

Specific example thereof include a hydrogenation catalyst having at least one selected from the group consisting of iron, cobalt, nickel, ruthenium, rhodium, palladium, iridium and platinum as a catalyst element supported on a carrier made of an inorganic compound, such as alumina, silica, zeolite or activated charcoal. Among the catalyst elements, at least one of nickel, palladium and platinum is more preferable.

[0037]

The liquid space velocity (LHSV) in an industrial plant may be appropriately adjusted in a range of generally 0.1 to 10 hr^{-1} , preferably 0.2 to 9 hr^{-1} , and more preferably 0.3 to 8 hr^{-1} by the desulfurized oil standard. When the LHSV is less than 0.1 hr^{-1} , the amount of the solid catalyst becomes excessive, which is not advantageous in terms of economic efficiency, and, on the other hand, when the LHSV exceeds 10 hr^{-1} , there is a possibility that the hydrogenation becomes insufficient.

[0038]

In addition, in a case in which the hydrogenation step is carried out using a flow

reactor, the cumulative amount of sulfur included in the desulfurized oil supplied to the hydrogenation step for one year is preferably 0.01 ton or less per ton of the hydrogenation catalyst. The reason for setting the cumulative amount as above is as follows. That is, in the hydrogenation catalyst used in the hydrogenation step, the sulfur included in the desulfurized oil is gradually accumulated, and the activity of the catalyst degrades. Particularly, since a high aromatic hydrogenation capability matters more for the hydrogenation catalyst used in the hydrogenation step, there are cases in which the hydrogenation catalyst is poor in terms of sulfur resistance. This decrease in the activity of the catalyst may become a cause impairing the stable operation of a plant. Therefore, the amount of sulfur in the desulfurized oil is preferably controlled to be low in terms of operation management. Specifically, the cumulative amount of sulfur included in the desulfurized oil supplied to the hydrogenation step is preferably managed in consideration of the necessary service life of the catalyst. From the above viewpoint, as described above, the cumulative amount of sulfur included in the desulfurized oil supplied to the reactor of the hydrogenation step is preferably 0.01 ton or less per ton of the hydrogenation catalyst (including the weight of the carrier) in the actual one-year (8760 hours) operation of a plant. The cumulative amount is more preferably 0.005 ton or less per ton of the catalyst, and still more preferably 0.001 ton or less per ton of the catalyst.

[0039]

The temperature of the hydrogenation step is generally 50 to 400°C, preferably in a range of 70 to 350°C, and more preferably in a range of 100 to 300°C. When the reaction temperature is below the above range, there are cases in which the PAH8 substances are insufficiently reduced, and, when the reaction temperature is above the range, there is a possibility that the raw material unit consumption degrades due to the

hydrocracking of the desulfurized oil.

The pressure of the hydrogenation step is generally set to 1.0 to 20.0 MPaG, preferably 1.5 to 13 MPaG, and more preferably in a range of 2.0 to 5.0 MPaG as a gauge pressure. When the pressure is below the above range, there are cases in which desired aromatic hydrogenation does not sufficiently proceed, and there are cases in which the total content of PAH8 in the finally obtained rubber compounding oil exceeds 10 wtppm or it becomes difficult to control the content ratio of the aromatic carbon in the rubber compounding oil.

[0040]

In the case of the batch reactor, an autoclave or the like is used as a reactor. At this time, the reaction time is preferably 1 to 5 hours. A variety of conditions, such as the solid catalyst being used, the ratio between the desulfurized oil and the hydrogen gas, the temperature and pressure for aromatic hydrogenation, are the same as in the case of the flow reactor.

[0041]

After the completion of the hydrogenation step, the reaction liquid is separated into gas and liquid, which are a liquid component (condense liquid) and a gas component (unreacted hydrogen gas or the like), using a well-known method. In addition, the target rubber compounding oil can be obtained by distilling or the like the liquid component as necessary so as to remove the solvent or carry out purification or the like.

The hydrogenation step is carried out after the hydrodesulfurization step has been carried out in advance. Therefore, the amount of sulfur accumulated in the hydrogenation catalyst, which is used in the hydrogenation step, is small, and a decrease in the activity of the catalyst is suppressed. Therefore, long-term stable operation becomes possible.

[0042]

<Rubber compounding oil>

According to the manufacturing method described above, it is possible to stably manufacture for a long period of time rubber compounding oil, in which benzo[a]pyrene or other polycyclic aromatic hydrocarbon is reduced using the ethylene bottom oil that has been used in a limited range. The rubber compounding oil obtained in the above manner satisfies the above regulation in Europe, that is, the condition that the total content of PAH8 is 0 to 10 wtpm, and the content of benzo[a]pyrene is 0 to 1 wtpm with respect to the rubber compounding oil.

10 In addition, the total content of PAH8 is more preferably 0 to 5 wtpm, and still more preferably 0 to 3 wtpm. The content of the benzo[a]pyrene is more preferably 0 to 0.5 wtpm, and still more preferably 0 to 0.2 wtpm.

[0043]

In addition, the kinetic viscosity of the rubber compounding oil at 100°C is preferably in a range of 10 to 100 mm²/s, more preferably in a range of 30 to 70 mm²/s, and still more preferably in a range of 20 to 40 mm²/s. When the kinetic viscosity is too low, there are cases in which the ordinary state properties of the vulcanized substance of a rubber composition, into which the rubber compounding oil has been compounded, become insufficient, or the heat aging properties deteriorate due to the evaporation of the oil component during heat aging. On the other hand, when the kinetic viscosity is too high, the fluidity is low, and there is a tendency for handling properties to degrade.

[0044]

In addition, the content ratio of aromatic carbon in the manufactured rubber compounding oil is preferably 5 to 50%, and more preferably 10 to 40%. When the content ratio is less than 5%, the compatibility with rubber degrades. As a result, there

is a possibility that the rubber compounding oil may bleed out from the vulcanized substance of a rubber composition into which the rubber compounding oil has been compounded, or, furthermore, the addition of the rubber compounding oil adversely influences the ordinary state properties and heat aging properties of the vulcanized substance of a rubber composition into which the rubber compounding oil has been compounded. On the other hand, when the content ratio exceeds 50%, there is a tendency for the total content of PAH8 in the rubber compounding oil to exceed 10 wtppm. In addition, the content ratio of aromatic carbon is a value obtained using ^{13}C -NMR as described above.

10 [0045]

In addition, the rubber compounding oil preferably further has a variety of the following properties from the viewpoint of affinity to rubber, softening property, high flash point, safety and handling property, and from the viewpoint of improving the low gas mileage property, grip performance and heat aging resistance in a case in which the rubber compounding oil is compounded so as to prepare a rubber composition for tires, and a tire is manufactured using the composition.

[0046]

Density at 15°C: generally 0.90 to 1.10 g/cm³, and preferably 0.95 to 1.05 g/cm³

Flash point: generally 200°C or higher, and preferably 250°C or higher.

20 Kinetic viscosity at 40°C: generally 20 to 2000 mm²/s, and preferably 100 to 1000 mm²/s.

Aniline point: generally 20 to 110°C, and preferably 30 to 80°C.

Pour point: generally -40 to 30°C, and preferably -30 to 20°C.

Glass transition temperature (T_g): generally -60 to -10°C, and preferably -55 to

-30°C.

Here, the glass transition temperature (T_g) refers to a temperature computed from a peak of heat amount change in a glass transition area, which is observed when the temperature is increased at a constant temperature increase rate (10°C/minute) using a differential scanning calorimeter (DSC).

The total sulfur concentration in the rubber compounding oil can be arbitrarily selected, but is generally 0 to 1 mass%, preferably 0 to 0.1 mass%, and more preferably 0 to 0.01 mass%.

The concentration of asphaltene in the rubber compounding oil can be arbitrarily selected, but is generally 0 to 2%, preferably 0 to 0.5%, and more preferably 0 to 0.3%.

[0047]

<Rubber composition>

When the rubber compounding oil described above is kneaded with rubber, such as natural rubber, styrene butadiene rubber, poly butadiene rubber, butyl rubber, isoprene rubber or nitrile rubber, using a well-known apparatus, for example, a rubber composition for tires can be obtained. Examples of the kneading apparatus of rubber include a kneader, a Banbury mixer (registered trademark), a biaxial extruder, a twin roll, a calendar roll, and the like. In addition to the rubber compounding oil, a crosslinking agent; a sulfur compound; a filler; a reinforcing agent, such as carbon black; a fiber; an antioxidant and the like are blended with the rubber composition as necessary, and then a vulcanizing (crosslinking) reaction is caused, whereby a rubber product can be produced. Examples of the rubber product include tires and the like.

[0048]

As described above, according to the manufacturing method of the embodiment, it is possible to stably manufacture for a long period of time rubber compounding oil, in

which the activity of a hydrogenation catalyst decreases only slightly, and benzo[a]pyrene or other polycyclic aromatic hydrocarbon is reduced using the ethylene bottom oil, which has been used in a limited range.

[Examples]

5 [0049]

Hereinafter, the invention will be specifically described based on examples, but the invention is not limited to the examples.

In the respective examples, a variety of measurements were carried out using the following methods.

10 (1) The total content of PAH8 and the content of benzo[a]pyrene

The contents were measured using the SIM analyses of GC-MS. The conditions were set as follows.

Internal standard substance: perylene d-12

Column: HP-5MS 5% Phenyl Methyl Siloxane was used.

15 Column length: 30 m

Injection: 280°C

Initial temperature: 80°C

Temperature increase rate: 10°C/min

Final temperature: 300°C

20 [0050]

(2) The content ratio of aromatic carbon

The content ratio was measured through ¹³C-NMR measurement (measurement device: JEOL EX-400 (manufactured by Nihon Denshi Co., Ltd.))

(i) Preparation of an NMR sample

0.18 g to 0.20 g of a specimen and 0.60 to 0.65 g of chloroform-D (Wako Chloroform-D (D, 99.8%) + 0.05 v/v% TMS, 536-74263) were mixed, and the mixture was added to an NMR specimen tube (inner diameter ϕ of 4.2 mm) to be 4 cm high from the bottom of the tube.

5 (ii) Measurement method

The pulse delay was set to 20 seconds, and the content ratio was measured using non-NOE mode gated decoupling at a cumulated number of 2000 times.

(iii) Analysis method

Phase correction, base line correction and reference peak setting (TMS, CHCl_3)
10 are carried out (generally, automatic setting) on the obtained FID signals using Excalibur for Windows (registered trademark) version 4.5 (manufactured by Nihon Denshi Co., Ltd.).

The content ratio of aromatic carbon (%): $D_{Ar} = 100 \times S_{Ar} / (S_{Ar} + S_{Al})$ was
computed from the peak area S_{Al} between the chemical shifts δ 10 to 50 ppm and the
15 peak area S_{Ar} between the chemical shifts δ 110 to 150 ppm.

In addition, in ordinary ethylene bottom oil and hydrides thereof, carbon peaks
appear only between the chemical shifts δ 10 to 50 ppm and between 110 to 150 ppm,
and carbon peaks do not appear in other areas. The above fact shall apply to ethylene
bottom oils, components (C_v), rubber compounding oils and the like, which will be
20 measured in the following examples.

[0051]

(3) Total sulfur concentration

The total sulfur concentration was measured using a sulfur chlorine analyzer
(manufactured by Mitsubishi Chemical Industries Ltd., Model No. TSX-10).

Electrolytic solution: an aqueous solution of 25 mg of sodium azide; 50 mL + glacial acetic acid; 0.3 mL + potassium iodide; 0.24 g

Dehydration liquid: phosphoric acid; 7.5 mL + pure water; 1.5 mL

Counter electrode solution: aqueous solution of 10 mass% of special-grade

5 potassium nitrate

Oxygen introduction pressure: 0.4 MPaG

Argon introduction pressure: 0.4 MPaG

Temperature at the specimen introducer: 850 to 950°C

Specimen: injected using a micro syringe as much as 30 μ L

10 [0052]

(4) The concentration of asphaltene

The concentration was measured using an IATROSCAN MK-6 (manufactured by Mitsubishi Chemical Medience Corporation) and the following measurement method.

(i) Preparation of a sample

15 A specimen was dissolved in THF so as to produce 1 wt% of a solution. The specimen was spotted at approximately 1 mm from the original point of a sintered thin layer rod for iatroscan CHROMA ROD-SIII (manufactured by Mitsubishi Chemical Medience Corporation) using a spotting guide and a micro dispenser attached to the IATROSCAN MK-6. The sintered thin layer rod was sequentially developed in
20 n-hexane, toluene and a solvent mixture of dichloromethane/0.1 vol% methanol using a developing layer DT-150 (developing solvent, 70 ml). When switching the developing solvent, the solvent was removed at 120°C using a rod dryer TK-8.

(ii) Measurement method

The concentration was measured using a hydrogen flame ionization detector at a
25 scanning speed of 30 seconds/scanning.

(iii) Analysis method

The asphaltene portion, resin portion, aromatic portion and saturated portion were classified respectively using a SIC 480II for IATROSCAN (manufactured by System Instruments Co., Ltd.) from peaks adjacent to the original point, and the peak
5 area of the asphaltene portion with respect to the total peak area was used as the concentration of asphaltene (asphaltene rate) (%).

[0053]

<Example 1>

Naphtha was prepared, and ethylene bottom oil was obtained by thermal
10 cracking of the naphtha. The thermal cracking was carried out under conditions of 825°C. The 100°C kinetic viscosity of the ethylene bottom oil obtained by thermal cracking of the naphtha was measured, and was 3.8 mm²/s. Then, the following distillation step was carried out on the ethylene bottom oil. In addition, the properties of the ethylene bottom oil are described in Table 1.

15 (Distillation step)

The ethylene bottom oil was distilled under reduced pressure so as to remove components having a low boiling point, thereby obtaining a residual oil (distillation residual liquid) having a 100°C kinetic viscosity of 373 mm²/s.

Specifically, in a tray-type Oldershaw (10 theoretical plates), 1 L of the ethylene
20 bottom oil was prepared in a flask, the reflux ratio was set to five under a vacuum condition of several Torr, the flask was heated to a temperature of 220°C, and distilled components were removed, thereby obtaining the residual oil (distillation residual liquid).

The properties of the obtained residual oil (distillation residual liquid) are
25 described in Table 1.

[0054]

(Hydrodesulfurization step and hydrogenation step)

The residual oil (distillation residual liquid) was dissolved in decahydronaphthalene, thereby obtaining a 5wt% residual oil solution (1). In addition,
5 the following reactions were carried out using a reaction apparatus having a reaction tube-1 and a reaction tube-2.

The reaction tube-1 (hydrodesulfurization reaction tube; inner diameter 20 mm) was filled with 20 g of HDMAX300 manufactured by Sud-Chemie Inc. In addition, the present catalyst was a hydrodesulfurization catalyst including molybdenum oxide (15 to
10 20 wt%), nickel oxide (3.0 to 6.0 wt%) and aluminum oxide (balance) as the main components, and having molybdenum as a catalyst element and nickel as a promoter metal supported on an alumina carrier.

In addition, the reaction tube-2 (aromatic hydrogenation reaction tube; inner diameter 20 mm) was filled with 10 g of NiSAT310RS manufactured by Sud-Chemie Inc.
15 The present catalyst was a hydrogenation catalyst containing nickel (52 ± 4.0 wt%), silica (28.0 ± 3.0 wt%) and alumina (10.0 ± 1.0 wt%), and having nickel supported on a carrier made of an inorganic compound.

A sulfurization treatment was carried out on the catalyst filling the reaction tube-1 at 340°C and a hydrogen pressure of 2.1 MPaG using a dimethyl
20 disulfide-containing decahydronaphthalene solution.

After that, the temperature of the catalyst layer in the reaction tube-1 was set to 300°C, hydrogen gas and the residual oil solution (1) were continuously supplied to the reaction tube-1 in gas-liquid co-current at a hydrogen pressure of 3.0 MPaG and a hydrogen flow rate of 10 NL/h=8000 Nm³/t (the supply amount of hydrogen gas per tone

of the raw material residual oil) and at 25 g/h (the residual oil solution (1)) respectively, thereby carrying out the reaction step of the hydrodesulfurization step. The fluid at the exit of the reactor was separated into gas and liquid in the atmospheric pressure, thereby obtaining a liquid component (2) (desulfurized oil/decahydronaphthalene). In addition, at this time, the liquid space velocity (LHSV) was 0.035 hr^{-1} .

The total sulfur concentration of the liquid component 24 hours after the beginning of the reaction was 16 wtppm in terms of the base material (a state in which the decahydronaphthalene was removed).

A hydrogen reducing treatment was carried out on the catalyst filling the reaction tube-2 at 300°C in the atmospheric pressure. Next, the temperature of the catalyst layer in the reaction tube-2 was set to 150°C , hydrogen gas and the liquid component (2) were continuously supplied to the reaction tube-2 in gas-liquid co-current at a hydrogen pressure of 3.0 MPaG and a hydrogen flow rate of $10 \text{ NL/h}=8000 \text{ Nm}^3/\text{t}$ (the supply amount of hydrogen gas per tone of the raw material desulfurized oil) and at 25 g/h (the liquid component (2)) respectively, thereby causing an aromatic hydrogenation reaction. The fluid at the exit of the reactor was separated into gas and liquid in the atmospheric pressure, thereby obtaining a liquid component (3) which is a mixture of aromatic hydrogenated oil (rubber compounding oil) and decahydronaphthalene. In addition, at this time, the liquid space velocity (LHSV) was 0.075 hr^{-1} .

The total content of PAH8 in the liquid component (3) 24 hours after the beginning of the reaction was 3.1 wtppm in terms of the base material, and the concentration of benzo[a]pyrene was 0 wtppm. Other properties are described in Table 1.

The above respective reactions were continued for 4000 hours, and the aging data of the total sulfur concentration and the concentration of PAH8 substances in the

condense liquid (the liquid components (2) and (3)), which was obtained after the gas-liquid separation of the fluid at the exit of the reaction tube-1 and the reaction tube-2, in terms of the base material are shown in FIG. 1. It is found from the data of the reaction tube-2 in FIG. 1 that the total content of PAH8 was maintained at 10 wtppm or less even after 4000 hours had elapsed.

[0055]

In addition, it is found from FIG. 1 that the average value of the total sulfur concentration of the condense liquid (liquid component (2)) of the fluid at the exit of the reaction tube-1 at a reaction time of 0 hr to 4000 hr in terms of the base material is approximately 7 wtppm. The reaction tube-2 is supplied with the liquid component (2) at 25 g/h. Since the supplied liquid contains 5 mass% (the remainder is decahydronaphthalene) of desulfurized oil, the reaction tube-2 is supplied with desulfurized oil at 1.25 g/h. Since the sulfur component (total sulfur concentration) is 7 wtppm, the sulfur component is supplied to the reaction tube-2 at 8.75×10^{-6} g/h. When this flow rate is multiplied by 8760 hr (one year), the cumulative sulfur amount over one year becomes 0.077 g. Since the amount of the catalyst in the reaction tube-2 is 10 g, the cumulative amount of sulfur in the desulfurized oil, which is supplied to the hydrogenation step for one year, becomes 0.0077 ton per ton of the hydrogenation catalyst.

[0056]

<Comparative example 1>

The 5 wt% residual oil solution (1) was supplied, and a reaction was caused in the same manner as in Example 1 except that a reaction apparatus having only the reaction tube-2 was used instead of the reaction apparatus having the reaction tube-1 and the reaction tube-2, the amount of the catalyst filling the reaction tube-2 at that time was

set to 20 g, and the temperature of the catalyst layer in the reaction tube-2 was set to 250°C.

That is, a hydrogen reducing treatment was carried out on the catalyst (the filling amount was 20 g) filling the reaction tube-2 at 300°C in the atmospheric pressure. Next, the temperature of the catalyst layer in the reaction tube-2 was set to 250°C, hydrogen gas and the residual oil solution (1) were continuously supplied to the reaction tube-2 in gas-liquid co-current 1 at a hydrogen pressure of 3.0 MPaG and a hydrogen flow rate of 10 NL/h=8000 Nm³/t (the supply amount of hydrogen gas per tone of the raw material oil) and at 25 g/h (the residual oil solution (1)) respectively, thereby causing a hydrogenation reaction. The fluid at the exit of the reactor was separated into gas and liquid in the atmospheric pressure, thereby obtaining a liquid component (4). The total content of PAH8 in the liquid component (4) four hours after the beginning of the reaction was 9.6 wtppm in terms of the base material, and the concentration of benzo[a]pyrene was 0.1 wtppm.

The aging data of the total content of PAH8 in the condense liquid (the liquid component (4)), which was obtained after the gas-liquid separation of the fluid at the exit of the reaction tube-2, in terms of the base material when the above reactions were continued for 96 hours are shown in FIG. 2. In addition, a variety of properties are described in Table 1. It is found from the data in FIG. 2 that, in Comparative example 1, the concentration of the PAH8 substances satisfies the regulation in Europe, which is 10 wtppm or less, for four hours from the beginning of the reaction. However, it is found that, after 4 hours, the concentration immediately exceeds the regulation value, and the activity of the catalyst rapidly decreases.

[0057]

<Comparative example 2>

The 5 wt% residual oil solution (1) was supplied, and a reaction was caused in the same manner as in Example 1 except that a reaction apparatus having only the reaction tube-1 was used instead of the reaction apparatus having the reaction tube-1 and the reaction tube-2.

5 That is, a sulfurization treatment was carried out on the catalyst filling the reaction tube-1 at 340°C and a hydrogen pressure of 2.1 MPaG using a dimethyl disulfide-containing decahydronaphthalene.

After that, the temperature of the catalyst layer in the reaction tube-1 was set to 300°C, hydrogen gas and the residual oil solution (1) were continuously supplied to the
10 reaction tube-1 in gas-liquid co-current at a hydrogen pressure of 3.0 MPaG and a hydrogen flow rate of 10 NL/h=8000 Nm³/t (the supply amount of hydrogen gas per tone of the raw material residual oil) and at 25 g/h (the residual oil solution (1)) respectively, thereby causing a hydrogenation reaction. The fluid at the exit of the reactor was separated into gas and liquid in the atmospheric pressure, thereby obtaining a liquid
15 component (5).

The total content of PAH8 in the liquid component (5) four hours after the beginning of the reaction was 138 wtppm in terms of the base material, and the concentration of benzo[a]pyrene was 1.6 wtppm.

[0058]

20 <Comparative example 3>

The 5 wt% residual oil solution (1) was supplied, and a reaction was caused in the same manner as in Comparative example 2 except that the hydrogen pressure was set to 5.0 MPaG instead of 3.0 MPaG, thereby obtaining a liquid component (6). The total content of PAH8 in the liquid component (6) four hours after the beginning of the
25 reaction was 27 wtppm in terms of the base material, and the concentration of

benzo[a]pyrene was 0.3 wtppm.

[0059]

[Table 1]

		Example 1	Comparative example 1	Comparative example 2	Comparative example 3
Ethylene bottom oil	100°C kinetic viscosity (mm ² /s)	3.8	3.8	3.8	3.8
	Content ratio of aromatic carbon (%)	82	82	82	82
	Total content of PAH8 (wtppm)	1484	1484	1484	1484
	Content of benzo[a]pyrene (wtppm)	110	110	110	110
	Total sulfur concentration (wtppm)	1080	1080	1080	1080
	Concentration of asphaltene (%)	1.3	1.3	1.3	1.3
Component (C _v) (distillation residual liquid (residual oil) of distillation under reduced pressure)	100°C kinetic viscosity (mm ² /s)	373	373	373	373
	Content ratio of aromatic carbon (%)	77	77	77	77
	Total content of PAH8 (wtppm)	2110	2110	2110	2110
	Content of benzo[a]pyrene (wtppm)	134	134	134	134
	Total sulfur concentration (wtppm)	1430	1430	1430	1430
Rubber compounding oil	100°C kinetic viscosity (mm ² /s)	42	-	-	-
	Content ratio of aromatic carbon (%)	31	-	-	-
	Total content of PAH8 (wtppm)	3.1	255	138	27
	Content of benzo[a]pyrene (wtppm)	0	15	1.6	0.3
	Total sulfur concentration (wtppm)	0	320	-	-
	Reaction time (hr)	4000	96	4	4

[0060]

According to the examples, it was possible to stably manufacture for a long period of time rubber compounding oil, in which the content of benzo[a]pyrene and the total content of PAH8 were reduced so as to satisfy the above regulation in Europe.

5

Industrial Applicability

[0061]

According to the invention, it is possible to stably obtain for a long period of time a raw material source of rubber compounding oil, which was limited to the distillate
10 of distillation under reduced pressure and the residue of distillation under reduced pressure of crude oil in the past, from the bottom component of a thermal cracking process of naphtha distillate obtained through the atmospheric distillation of crude oil, that is, ethylene bottom oil. In the past, since the use of the ethylene bottom oil was limited to low-priced products, such as a raw material of carbon black or fuel, the
15 manufacturing method of the invention is advantageous from the viewpoint of the effective use of the ethylene bottom oil. Particularly, in recent years, there has been a tendency to use a raw material, for which cheap heavy components, such as kerosene and gas oil, as well as naphtha are jointly used, as a raw material of thermal cracking, and therefore the production amount of the ethylene bottom oil also increases. Therefore,
20 the invention has an extremely large industrial merit. In the invention, it is possible to stably manufacture rubber compounding oil for a long period of time by suppressing a decrease in the activity of a catalyst over time.

CLAIMS

1. A method for manufacturing rubber compounding oil comprising:

a step in which ethylene bottom oil obtained by thermal cracking of a

5 naphtha-containing raw material is prepared;

a hydrodesulfurization step in which at least part of the ethylene bottom oil is hydrodesulfurized as a raw material of desulfurized oil, thereby obtaining the desulfurized oil; and

a hydrogenation step in which an aromatic ring of the desulfurized oil is
10 aromatic hydrogenated.

2. The method for manufacturing rubber compounding oil according to Claim

1,

wherein, in the hydrodesulfurization step, the raw material is reacted with
15 hydrogen gas at 250 to 400°C using a hydrodesulfurization catalyst having at least one element selected from molybdenum and tungsten as a catalyst element and at least one element selected from cobalt and nickel as a promoter metal supported on a carrier including any of alumina, silica, titania, zirconia, silica alumina and zeolite as a main component.

20

3. The method for manufacturing rubber compounding oil according to Claim

1,

wherein, in the hydrodesulfurization step, the raw material is reacted with the hydrogen gas at a pressure of 1.0 to 20.0 MPaG.

25

4. The method for manufacturing rubber compounding oil according to Claim 1,

wherein, in the hydrogenation step, the desulfurized oil is reacted with the hydrogen gas at 100 to 300°C using a hydrogenation catalyst having at least one element selected from the group consisting of iron, cobalt, nickel, ruthenium, rhodium, palladium, 5 iridium and platinum supported on a carrier made of an inorganic compound.

5. The method for manufacturing rubber compounding oil according to Claim 1,

10 wherein, in the hydrogenation step, the desulfurized oil is reacted with the hydrogen gas at a pressure of 1.0 to 20.0 MPaG.

6. The method for manufacturing rubber compounding oil according to Claim 1,

15 wherein, in a case in which the hydrogenation step is carried out in a flow reactor using a hydrogenation catalyst, a cumulative amount of sulfur in the desulfurized oil supplied in the hydrogenation step for one year is 0.01 ton or less per ton of the hydrogenation catalyst.

20 7. The method for manufacturing rubber compounding oil according to Claim 1,

wherein the hydrodesulfurization step includes a reaction step in which the raw material is reacted with the hydrogen gas so as to convert a sulfur compound in the raw material into hydrogen sulfide,

25 a gas-liquid separating step in which a reaction liquid obtained in the reaction

step is separated into gas and liquid and the hydrogen sulfide is removed from the reaction liquid as gas, thereby obtaining the desulfurized oil, and

in the gas-liquid separating step, the reaction liquid is depressurized, thereby removing the hydrogen sulfide.

5

8. The method for manufacturing rubber compounding oil according to Claim

1,

wherein the raw material is a component (C_v) having a 100°C kinetic viscosity of 10 mm²/s or more in the ethylene bottom oil.

10

9. The method for manufacturing rubber compounding oil according to Claim

8, wherein the component (C_v) is a distillation residual liquid of the ethylene bottom oil.

10. The method for manufacturing rubber compounding oil according to Claim

15 1,

wherein the naphtha-containing raw material contains 1 to 99 mass% of one or more selected from the group consisting of kerosene, gas oil and NGL.

11. The method for manufacturing rubber compounding oil according to Claim

20 1,

wherein, in the hydrodesulfurization step, the raw material diluted using one or more solvent selected from the group consisting of saturated hydrocarbon, saturated ether and the rubber compounding oil is reacted with the hydrogen gas.

25

12. The method for manufacturing rubber compounding oil according to Claim

1,

wherein, in the hydrodesulfurization step and the hydrogenation step, the respective reaction is carried out using a trickle-bed type reactor.

5 13. Rubber compounding oil obtained using the manufacturing method according to any one of Claims 1 to 12.

14. The rubber compounding oil according to Claim 13,
wherein a total content of PAH8 substances is 0 wtppm or more and 10 wtppm
10 or less, and a content of benzo[a]pyrene is 0 wtppm or more and 1 wtppm or less.

15. The rubber compounding oil according to Claim 13,
wherein a content ratio of aromatic carbon is 5 to 50%.

15 16. The rubber compounding oil according to Claim 13,
wherein a 100°C kinetic viscosity is 10 to 100 mm²/s.

17. A method for manufacturing a tire rubber composition,
wherein the rubber compounding oil according to Claim 13 is mixed with at
20 least one kind of rubber selected from the group consisting of natural rubber, styrene butadiene rubber, polybutadiene rubber, butyl rubber, isoprene rubber and nitrile rubber.