

DESCRIPTION

Title of Invention

RUBBER COMPOUNDING OIL AND METHOD FOR MANUFACTURING THE
5 SAME

Technical Field

[0001]

The present invention relates to a rubber compounding oil used in a 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) , and method for manufacturing the
same.

Priority is claimed on Japanese Patent Application No. 2012-089331, filed in
Japan, the content of which is incorporated herein by reference.

15

Background Art

[0002]

When manufacturing a rubber product, such as a tire, a 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 respect to 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, a so-called "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 hydrocarbon as necessary. The EXTRACT contains a relatively large amount of a heavy aromatic compound.

[0004]

Meanwhile, in Europe, a strict environmental regulation stipulating that "regarding the content of polycyclic aromatic hydrocarbon (PAH) in oil used for tires, the 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 been in effect since 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 aromatic hydrocarbon.

[0005]

Meanwhile, 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 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 a 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°C to 650°C, which has been distilled under reduced pressure, using furfural or the like.

In addition, PTL 2 discloses a 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 hydrotreated 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 replaces the above related arts, and an object of the invention is to provide a manufacturing method in which a 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 manufactured using simple steps.

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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, and completed the

20 invention by succeeding in the manufacturing a rubber compounding oil using the ethylene bottom oil as a raw material through simple steps and simple operations.

That is, the invention relates to the following [1] to [15].

[1] A method for manufacturing a rubber compounding oil, including the steps

of:

25 preparing ethylene bottom oil obtained by thermally decomposing a

naphtha-containing raw material,

supplying the ethylene bottom oil as a component (C_v) when the 100°C kinetic viscosity of the ethylene bottom oil is 10 mm²/s or more, or separating the component (C_v) having a 100°C kinetic viscosity of 10 mm²/s or more from the ethylene bottom oil

5 when the 100°C kinetic viscosity is less than 10 mm²/s, and

hydrogenating the component (C_v).

[2] The method for manufacturing a rubber compounding oil according to the above [1], in which the component (C_v) is a distillation residual liquid of the ethylene bottom oil.

10 [3] The method for manufacturing a rubber compounding oil according to the above [1] or [2], in which the component (C_v) has a content ratio of aromatic carbon of 55% or more and 100% or less.

[4] The method for manufacturing a rubber compounding oil according to any one of the above [1] to [3], in which the component (C_v) has a total content of a PAH8
15 substance of 0 wtppm or more and 3000 wtppm or less.

[5] The method for manufacturing a rubber compounding oil according to any one of the above [1] to [4], in which the component (C_v) has a total sulfur concentration of 0 mass% or more and 1 mass% or less.

[6] The method for manufacturing a rubber compounding oil according to any
20 one of the above [1] to [5], in which the naphtha-containing raw material contains 1 mass% to 99 mass% of one or more selected from the group consisting of kerosene, light oil and NGL.

[7] The method for manufacturing a rubber compounding oil according to any one of the above [1] to [6], in which a pressure of the hydrogenating step is 1.0 MPaG to

20.0 MPaG.

[8] The method for manufacturing a rubber compounding oil according to any one of the above [1] to [7] in which a temperature of the hydrogenating step is 100°C to 400°C.

5 [9] The method for manufacturing a rubber compounding oil according to any one of the above [1] to [8], in which, in the hydrogenating step, a catalyst, in which one of alumina, silica, titania, zirconia, boria, magnesia, Y-type zeolite, X-type zeolite, L-type zeolite, beta-type zeolite, chebazite, erionite, mordenite, ZSM-type zeolite and MFI-type zeolite or a composite oxide or oxide mixture made of two or more thereof is used as a
10 carrier, and a metal of at least one element of Groups 6, 8, 9 and 10 in the periodic table is supported on the carrier, is used.

[10] The method for manufacturing a rubber compounding oil according to any one of the above [1] to [9], in which the component (C_v) is diluted using one or more solvent selected from the group consisting of saturated hydrocarbon, saturated ether and
15 the rubber compounding oil, and is used in the hydrogenating step.

[11] The method for manufacturing a rubber compounding oil according to any one of the above [1] to [10], in which the hydrogenating step is carried out in a trickle-bed type reactor.

[12] A rubber compounding oil obtained using the manufacturing method
20 according to any one of the above [1] to [11].

[13] The rubber compounding oil according to the above [12], in which a total content of a PAH8 substance 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.

[14] The rubber compounding oil according to the above [12] or [13], in which a
25 content ratio of aromatic carbon is 5% to 50%.

[15] The rubber compounding oil according to any one of the above [12] to [14], in which a 100°C kinetic viscosity is 10 mm²/s to 100 mm²/s.

Advantageous Effects of Invention

5 [0010]

According to the invention, it is possible to manufacture a rubber compounding oil, in which benzo[a]pyrene or other polycyclic aromatic hydrocarbon is reduced so as to satisfy the above regulation in Europe using simple steps. 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.

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Description of Embodiments

[0011]

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

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However, 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.

20 The invention provides a method for manufacturing a rubber compounding oil including a hydrogenating step in which, of ethylene bottom oil obtained by thermally decomposing a naphtha-containing raw material, a component (C_v) having a 100°C kinetic viscosity of 10 mm²/s or more is hydrogenated. That is,

the method for manufacturing a rubber compounding oil of the invention includes a hydrogenating step in which, of ethylene bottom oil obtained by thermally

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decomposing a naphtha-containing raw material, a component (C_v) having a 100°C kinetic viscosity (kinetic viscosity at 100°C) of 10 mm²/s or more is used as a raw material, and is hydrogenated.

Using the above method, a rubber compounding oil, in which benzo[a]pyrene or
5 other polycyclic aromatic hydrocarbon is reduced so as to satisfy the above regulation in Europe, can be manufactured as described below in detail.

[0012]

The term hydrogenation refers to a reaction in which a hydrogen atom is added to the carbon-carbon double bond of a raw material. In addition, in the present
10 specification, the value of the kinetic viscosity is a value measured according to JIS K2283.

[0013]

<Method for manufacturing rubber compounding oil>

[Ethylene bottom oil]

15 In the petrochemical industry, in general, naphtha is thermally decomposed at a high temperature, the obtained thermally decomposed 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), decomposed kerosene and decomposed gasoline, and made into a product. Among the above
20 distillates, 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 decomposition 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 decomposition plant of naphtha is also called a naphtha
25 cracker. Meanwhile, the boiling point of the ethylene bottom oil varies depending on

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

[0014]

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

The term 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
10 is separated and collected from natural gas produced from underground through a 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, light oil and NGL depending on
cases is referred to as the naphtha-containing raw material.

15 [0015]

In a case in which a raw material including naphtha and at least one of kerosene,
light oil and NGL is used as the naphtha-containing raw material, the total content of
kerosene, light oil and NGL can be arbitrarily selected. For example, the total content
of kerosene, light oil and NGL can be set to 1 mass% to 99 mass% in 100 mass% of the
20 naphtha-containing raw material. Since the naphtha-containing raw material having a
high content of kerosene, light oil and NGL includes a large amount of kerosene, light oil
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, light oil
and NGL in terms of economic efficiency as a naphtha cracker. On the other hand, from
25 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.

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, light oil and NGL can be used as a raw material for thermal decomposition with no problem.

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

[0016]

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

[0017]

Meanwhile, 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 ppm to 150 ppm (corresponding 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 can be arbitrarily selected, but is generally less than 10 mm²/s, preferably 1 mm²/s to 10 mm²/s, and more preferably 3 mm²/s 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 substance in the ethylene bottom oil is generally 500 wtppm to 10000 wtppm, preferably 0 wtppm to 7000 wtppm, and more preferably 0 wtppm to 3000 wtppm.

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

The total sulfur concentration in the ethylene bottom oil can be arbitrarily selected, but is generally 0 mass% to 0.2 mass%, preferably 0 mass% to 0.18 mass%, and more preferably 0 mass% to 0.15 mass%.

The concentration of asphaltene in the ethylene bottom oil is generally 0% to 5%,
5 preferably 0.1% to 3%, and more preferably 0.2 % to 1.5 %.

[0018]

[Component (C_v)]

In the hydrogenating step of the embodiment, the ethylene bottom oil obtained
10 by thermally decomposing the naphtha-containing raw material or the component (C_v),
which is included in the ethylene bottom oil and has a 100°C kinetic viscosity of 10
mm²/s or more, is used as a raw material, and this raw material is hydrogenated. Here,
in a case in which a component having a 100°C kinetic viscosity of less than 10 mm²/s is
hydrogenated, since the viscosity of the obtained rubber compounding oil is too low,
15 when the rubber compounding oil is kneaded with rubber at a high temperature, oil vapor
is violently generated or the rubber compounding oil becomes liable to bleed out from
vulcanized rubber into which the rubber compounding oil has been compounded. The
100°C kinetic viscosity of the component (C_v) can be arbitrarily selected as long as the
viscosity is 10 mm²/s or more, but is preferably 20 mm²/s or more. In addition, the
20 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 viewpoint of handling of the
component (C_v) in the manufacturing steps.

[0019]

In a case in which the 100°C kinetic viscosity of the ethylene bottom oil obtained by thermally decomposing the naphtha-containing raw material is 10 mm²/s or more, the ethylene bottom oil can be supplied to the hydrogenating 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, components having a low boiling point, which are included in the ethylene bottom oil, are removed using a distillation step or the like 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 is supplied to the hydrogenating 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.

[0020]

In the component (C_v) supplied to the hydrogenating step, the content ratio of aromatic carbon is preferably 55% or more and 100% or less. The content ratio of aromatic carbon is more preferably 60% to 90%, and still more preferably 65% to 80%. When the content ratio of aromatic carbon is less than 55%, the content ratio of aromatic carbon in the finally obtained rubber compounding oil becomes lower than the desired value, and the compatibility of the rubber compounding oil with rubber degrades. As a result, there is a possibility that the rubber compounding oil may become liable to bleed out from vulcanized rubber 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 rubber

into which the rubber compounding oil has been compounded.

[0021]

In addition, the total content of PAH8 in the component (C_v) is preferably 0 wtpm or more and 3000 wtpm or less with respect to the component (C_v). The total content of PAH8 is more preferably 0 wtpm to 2000 wtpm, and still more preferably 0 wtpm to 1000 wtpm. When the total content exceeds 3000 wtpm, 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 mass% or more and 1 mass% or less with respect to the component (C_v). The total sulfur concentration is more preferably 0 mass% to 0.3 mass%, and still more preferably 0 mass% to 0.2 mass%.

The concentration of asphaltene in the component (C_v) is preferably 0% or more 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.

The content of the benzo[a]pyrene in the component (C_v) can be arbitrarily selected but is generally 0 wtpm to 500 wtpm, preferably 0 wtpm to 300 wtpm, and more preferably 0 wtpm to 250 wtpm.

[0022]

[Hydrogenating step]

In the hydrogenating step, hydrogenation, in which the component (C_v) having a

100°C kinetic viscosity of 10 mm²/s or more is reacted with hydrogen gas, is carried out, the PAH8 substance included in the component (C_v) is reduced, and the content ratio of aromatic carbon and the like are controlled, thereby obtaining a rubber compounding oil.

Here, as described above, when the 100°C kinetic viscosity of the ethylene bottom oil
5 obtained by thermally decomposing 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, whereby the obtained distillation residual liquid having a 100°C kinetic viscosity of 10
10 mm²/s or more 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 hydrogenation.

[0023]

15 The hydrogenating step is carried out using a continuous reaction method or a batch reaction method in the presence of a solid catalyst. The continuous reaction method is preferable in terms of productivity.

The reaction pattern is preferably a gas-liquid reaction. A trickle-bed method using a trickle-bed type reactor, in which the component (C_v) is made to flow
20 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 pattern 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. Meanwhile, when the reaction pattern 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 hydrogenating treatment becomes difficult.

[0024]

In a case in which hydrogenation is carried out using the continuous reaction method, 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 in a range of 100 Nm^3 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 hydrogenated, and when the flow amount of the hydrogen gas exceeds 1000 Nm^3 , economic disadvantages are caused.

[0025]

Any catalysts that can act as a catalyst of a hydrogenation reaction can be used as the solid catalyst. Among the above, a catalyst, in which one of alumina, silica, titania, zirconia, boria, magnesia, Y-type zeolite, X-type zeolite, L-type zeolite, beta-type zeolite, chebazite, erionite, mordenite, ZSM-type zeolite and MFI-type zeolite 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, is preferably used. Examples of the metal of Group 6 in the periodic table include Cr, 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. Preferable examples of the supported metal include combinations, such as Ni-Mo, Co-Mo and Ni-W.

Meanwhile, in a case in which zeolite is used, in addition to the above zeolites, for example, faujasite and the like can be used as well; however, among the above, Y-type zeolite is preferable.

[0026]

The liquid hourly space velocity (LHSV) in an industrial plant may be appropriately adjusted in a range of generally 0.1 hr^{-1} to 10 hr^{-1} , preferably 0.2 hr^{-1} to 9 hr^{-1} , and more preferably 0.3 hr^{-1} 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 be not sufficiently hydrogenated.

[0027]

The temperature for hydrogenation can be arbitrarily selected, but is generally set to 100°C to 400°C , preferably in a range of 170°C to 370°C , and more preferably in a range of 250°C to 350°C . When the reaction temperature is lower than 100°C , there are cases in which the component (C_v) is not sufficiently hydrogenated, and, when the reaction temperature exceeds 400°C , there is a possibility that the original unit of the raw material may deteriorate due to the hydrogenation decomposition of the component (C_v).

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

[0028]

In addition, during hydrogenation, in order to remove reaction heat being generated, the reaction may be performed after diluting the component (C_v) using a

solvent. For example, in a case in which aromatic ring hydrogenation is actively made to proceed in order to control the polarity of the obtained rubber compounding oil, the reaction heat becomes higher, and when the reaction heat is not removed, there are cases in which the control of the reaction temperature becomes difficult. In addition, even
5 from the viewpoint of preventing the fouling of the catalyst, it becomes effective means for diluting the component (C_v), which is a substrate, using a solvent.

The solvent used for dilution needs to be inert in the hydrogenating step of the embodiment; to sufficiently dissolve the component (C_v); to have a lower boiling temperature than the obtained rubber compounding oil so that the solvent can be easily
10 separated from the rubber compounding oil through distillation or 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.

15 In addition, a rubber compounding oil manufactured by undergoing the hydrogenating step of the embodiment can also be used as the solvent. In a case in which a 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, and some of the mixture of the solvent and the product may be circulated and reused as the
20 solvent. Therefore, a process, in which a rubber compounding oil is used as the solvent, is economically effective.

[0029]

In a case of the batch reaction method, an autoclave or the like is used as a reactor. At this time, the reaction time is preferably 1 hour to 5 hours. A variety of
25 conditions, such as the solid catalyst being used, the ratio between the component (C_v)

and the hydrogen gas, the temperature and pressure for hydrogenation, are the same as in the case of the continuous reaction method. In addition, even in the case of the batch reaction method, hydrogenation may be carried out after the component (C_v) is diluted using the solvent.

5 [0030]

After the completion of the hydrogenation reaction, the reaction liquid is separated into gas and liquid, and hydrogen sulfide generated as a byproduct due to hydrogenation is purged outside the system, thereby obtaining a condensate liquid. In addition, purification, such as distillation, is carried out on the condensate liquid as
10 necessary, whereby the target rubber compounding oil can be obtained.

Meanwhile, when hydrogen sulfide is purged outside the system, the 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 from an economic aspect, it is preferable to circulate the hydrogen gas to the reactor for
15 hydrogenation and reuse the hydrogen gas after the hydrogen sulfide is selectively removed using an absorbing liquid, such as amine or caustic soda.

[0031]

<Rubber compounding oil>

According to the manufacturing method described above, it is possible to
20 manufacture a rubber compounding oil, in which benzo[a]pyrene or other polycyclic aromatic hydrocarbon is reduced using the ethylene bottom oil, which is used in a limited range, using simple steps. 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 wtppm or more and 10 wtppm or less, and the content of benzo[a]pyrene is 0
25 wtppm or more and 1 wtppm or less with respect to the rubber compounding oil.

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

[0032]

5 In addition, the kinetic viscosity of the rubber compounding oil at 100°C is preferably in a range of 10 mm²/s to 100 mm²/s, more preferably in a range of 30 mm²/s to 70 mm²/s, and still more preferably in a range of 20 mm²/s to 40 mm²/s. When the kinetic viscosity is too low, there are cases in which the ordinary state properties of vulcanized rubber into which the rubber compounding oil has been compounded become
10 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, since the fluidity is low, there is a tendency for handling properties to degrade.

[0033]

In addition, the content ratio of aromatic carbon in the manufactured rubber
15 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 become liable to bleed out from vulcanized rubber into which the rubber compounding oil has been compounded, or, furthermore, the addition of the rubber compounding oil adversely influences the
20 ordinary state properties and heat aging properties of the vulcanized rubber 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. Meanwhile, the content ratio of aromatic carbon is a value obtained using ¹³C-NMR as described above.

25 [0034]

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 burning point, safety and handling property, and from the viewpoint of improving the low gas mileage property, grip property and heat aging resistance in a case in which a rubber composition for tires, into which the rubber compounding oil has been compounded, is prepared, and a tire is manufactured using the composition.

[0035]

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

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

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

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

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

15 Glass transition point (T_g): generally -60°C to -10°C, and preferably -55°C to -30°C.

Here, the glass transition point (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).

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

[0036]

As described above, according to the manufacturing method of the embodiment,
5 it is possible to manufacture a rubber compounding oil, in which benzo[a]pyrene or other polycyclic aromatic hydrocarbon is reduced using the ethylene bottom oil, which is used in a limited range, using simple steps.

[Examples]

[0037]

10 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.

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

15 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.

Column length: 30 m

20 Injection: 280°C

Initial temperature: 80°C

Temperature increase rate: 10°C/min

Final temperature: 300°C

[0038]

(2) The content ratio of aromatic carbon

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

(i) Preparation of an NMR sample

5 0.18 g to 0.20 g of a specimen and 0.60 g 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 higher from the bottom of the tube.

(ii) Measurement method

10 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) were carried out (generally, automatic setting) on the obtained FID signals using
15 Excalibur for Windows (registered trade mark) version 4.5 (manufactured by Nihon Denshi Co., Ltd.).

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

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

[0039]

(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) and the following measurement method.

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 potassium nitrate

Oxygen introduction pressure: 0.4 MPaG

Argon introduction pressure: 0.4 MPaG

Temperature at the specimen introducer: 850°C to 950°C

Specimen: injected using a micro syringe to as much as 30 µL

[0040]

(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

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 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
5 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
10 area of the asphaltene portion with respect to the total peak area was used as the concentration of asphaltene (asphaltene rate) (%).

[0041]

[Example 1]

Naphtha was prepared, and ethylene bottom oil was obtained by thermally
15 decomposing the naphtha. The thermal decomposition at this time was carried out under conditions of 825°C. The 100°C kinetic viscosity of the ethylene bottom oil obtained by thermally decomposing the naphtha was measured, and was 3.8 mm²/s. Then, the following distillation step was carried out on the ethylene bottom oil. Meanwhile, the properties of the ethylene bottom oil are described in Table 1.

20 (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
25 bottom oil was prepared in an oven, the reflux ratio was set to 5 under a vacuum

condition of several Torr, the oven 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
5 described in Table 1.

[0042]

(Hydrogenating step)

5.0 g of the residual oil (distillation residual liquid), 50 cc of
decahydronaphthalene and 3.0 g of hydrogen reducing agent NiSAT 310RS
10 manufactured by Sud-Chemie Inc. were prepared in an autoclave having a capacity of
100 cc at 300°C, gas-phase portions were purged using nitrogen gas, and then the
pressure was increased up to 3 MPaG using hydrogen gas. After that, the inside of the
vessel was stirred at 200 rpm, and was heated up to 150°C. After that, the state was
maintained over 2.0 hours.

15 After the completion of the reaction, the liquid in the vessel was
pressure-filtered so as to separate the catalyst. After that, the decahydronaphthalene
was distilled using an evaporator, thereby obtaining a rubber compounding oil.

The properties of the obtained rubber compounding oil are described in Table 1.

Meanwhile, the above-used catalyst had nickel supported by a carrier mainly
20 including silica and alumina.

[0043]

[Example 2]

100 g of the residual oil (distillation residual liquid) obtained in Example 1 was
dissolved in decahydronaphthalene, thereby obtaining 2000 g of solution (α).

Meanwhile, 20 g of NiSAT 310RS manufactured by Sud-Chemie Inc. was loaded into a reaction tube (an inner diameter of 19.4 mm and an effective catalyst-loaded length of 420 mm), hydrogen gas was circulated at 300°C under atmospheric pressure, and the catalyst was subjected to a hydrogen reducing treatment.

- 5 After that, the solution (α) (solution with 5 mass% of the residual oil) and hydrogen gas were supplied at flow amounts of 25 g/h and 10 NL/h respectively to the reaction tube at a reaction pressure of 3 MPaG and a catalyst layer temperature of 250°C. The trickle-bed reaction method, in which the solution (α) and hydrogen gas were supplied in parallel and downstream to the reaction tube, was used. Meanwhile, the LHSV in terms
10 of the component (C_v) is 0.044 hr^{-1} .

The fluid at the exit of the reactor was separated into gas and liquid under atmospheric pressure, thereby obtaining a reaction liquid including the rubber compounding oil. For the reaction liquid obtained after 4 hours from the beginning of the reaction, the total content of PAH8 and the content of benzo[a]pyrene were analyzed.

- 15 The respective contents are converted in terms of the rubber compounding oil, and the values are described in Table 1.

Meanwhile, the decahydronaphthalene was distilled from the above reaction liquid using an evaporator, and the content ratio of aromatic carbon and the 100°C kinetic viscosity were measured for the obtained rubber compounding oil. The results are

- 20 described in Table 1.

[0044]

[Table 1]

		Example 1	Example 2
Ethylene bottom oil	100°C kinetic viscosity (mm ² /s)	3.8	3.8
	Content ratio of aromatic carbon (%)	82	82
	Total content of PAH8 (wtppm)	1484	1484
	Content of benzo[a]pyrene (wtppm)	110	110
	Total sulfur concentration (wtppm)	1080	1080
	Concentration of asphaltene (%)	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
	Content ratio of aromatic carbon (%)	77	77
	Total content of PAH8 (wtppm)	2110	2110
	Content of benzo[a]pyrene (wtppm)	134	134
	Total sulfur concentration (wtppm)	1430	1430
Rubber compounding oil	100°C kinetic viscosity (mm ² /s)	36.3	43.5
	Content ratio of aromatic carbon (%)	32	38
	Total content of PAH8 (wtppm)	1.0	9.6
	Content of benzo[a]pyrene (wtppm)	Not detected (detection limit or lower)	0.1

5

According to the respective examples, it was possible to manufacture a rubber compounding oil, in which the content of benzo[a]pyrene and the total content of PAH8 were reduced using simple steps so as to satisfy the above regulation in Europe.

10 Industrial Applicability

[0045]

According to the invention, it is possible to obtain a raw material source of a rubber compounding oil, which was obtained in the past only from the fraction of distillation under reduced pressure and the residue of distillation under reduced pressure of crude oil, from the bottom component of a thermal decomposition process of naphtha

15

fraction, which is obtained through 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 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 light oil, as well as naphtha are jointly used, as a thermal decomposition raw material, and therefore the production amount of the ethylene bottom oil also increases. Therefore, the invention has an extremely large industrial merit.

CLAIMS

1. A method for manufacturing a rubber compounding oil, comprising the steps of:

5 preparing ethylene bottom oil obtained by thermally decomposing a naphtha-containing raw material;

supplying the ethylene bottom oil as a component (C_v) when the 100°C kinetic viscosity of the ethylene bottom oil is 10 mm²/s or more, or separating the component (C_v) having a 100°C kinetic viscosity of 10 mm²/s or more from the ethylene bottom oil

10 when the 100°C kinetic viscosity is less than 10 mm²/s; and

hydrogenating the component (C_v).

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

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

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

20 wherein the component (C_v) has a content ratio of aromatic carbon of 55% or more and 100% or less.

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

wherein the component (C_v) has a total content of a PAH8 substance of 0 wtppm or more to 3000 wtppm or less.

5. The method for manufacturing a rubber compounding oil according to

5 Claim 1,

wherein the component (C_v) has a total sulfur concentration of 0 mass% or more to 1 mass% or less.

6. The method for manufacturing a rubber compounding oil according to

10 Claim 1,

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

7. The method for manufacturing a rubber compounding oil according to

15 Claim 1,

wherein a pressure of the hydrogenating step is 1.0 MPaG to 20.0 MPaG.

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

Claim 1,

20 wherein a temperature of the hydrogenating step is 100°C to 400°C.

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

Claim 1,

25 wherein, in the hydrogenating step, a catalyst, in which one of alumina, silica, titania, zirconia, boria, magnesia, Y-type zeolite, X-type zeolite, L-type zeolite, beta-type

zeolite, chebazite, erionite, mordenite, ZSM-type zeolite and MFI-type zeolite or a composite oxide or oxide mixture made of two or more thereof is used as a carrier, and a metal of at least one element of Groups 6, 8, 9 and 10 in the periodic table is supported on the carrier, is used.

5

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

wherein the component (C_v) is diluted using one or more solvents selected from the group consisting of saturated hydrocarbon, saturated ether and the rubber

10 compounding oil, and is used in the hydrogenating step.

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

wherein the hydrogenating step is carried out in a trickle-bed type reactor.

15

12. A rubber compounding oil obtained using the manufacturing method according to any one of Claims 1 to 11.

13. The rubber compounding oil according to Claim 12,

20 wherein a total content of a PAH8 substance 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.

14. The rubber compounding oil according to Claim 12,

wherein a content ratio of aromatic carbon is 5% to 50%.

25

15. The rubber compounding oil according to Claim 12,
wherein a 100°C kinetic viscosity is 10 mm²/s to 100 mm²/s.