

[DESCRIPTION]

[TITLE OF INVENTION]

PETROLEUM-BASED AROMATICS-CONTAINING OIL, RUBBER COMPOSITION,
5 TIRE, AND METHOD FOR PRODUCING TIRE

[Technical Field]

[0001]

The present invention relates to a petroleum-based aromatic-containing oil, a
10 rubber composition, a tire, and a method for producing a tire.

Priority is claimed on Japanese Patent Application No. 2019-035837, filed
February 28, 2019, the content of which is incorporated herein by reference.

[Background Art]

15 [0002]

In general, rubber products often contain process oils in order to improve the
processability and softness of rubber compositions. For example, in a synthetic rubber
such as a styrene-butadiene copolymer rubber (SBR), extender oils are blended (rubber
compounding oils) at the time of its synthesis. Further, process oils are blended in
20 rubber processed products such as tires in order to improve the processability and the
quality of the rubber processed products. Here, although the expressions are divided
into extender oils and process oils, these are sometimes collectively referred to as process
oils.

On the other hand, in Europe, a regulation (REACH regulation) that rubber
25 compounding oils containing a specific amount or more of a specific carcinogenic

polycyclic aromatic compound must not be used for producing tires or tire components has been applied since 2010. For this reason, there has been a demand for rubber compounding oils conforming to the REACH regulation.

[0003]

5 The trend of fuel efficiency in the field of automobiles has attracted much attention, and further improvements have also been required for the fuel efficiency of tires. With the start of the tire labeling system in January 2010, tires have been strongly required to improve in terms of “rolling resistance performance” indicating the fuel efficiency and “wet grip performance” indicating the braking performance. However, in
10 general, the rolling resistance performance and the wet grip performance are in a contradictory relationship, and compatibility of these at a high level has been a problem.

[0004]

For improving the rolling resistance performance of tires, in addition to the reduction of air resistance, the refinement of tread patterns, and the like, there is a
15 method for suppressing the hysteresis loss of the rubber composition, that is, the tread compound itself. In recent years, a compound containing silica has become widespread as a reinforcing material, which is one of tire formulations. Since silica particles aggregate with each other in the compound simply by blending, the silica molecules rub against each other when the rubber is deformed, and energy loss is likely to occur. On
20 the other hand, with the aim of improving the rolling resistance performance while maintaining the wet grip performance, a method of controlling the existence form of silica by applying terminally modified silica or a silane coupling agent has been proposed.

According to Patent Document 1, a rubber composition for a tire has been
25 disclosed which is obtained by a production method including a first base kneading step

for kneading a rubber component, hydrous calcium carbonate and a silane coupling agent, and a second base kneading step for kneading a kneaded product obtained by the first base kneading step, and silica. According to this document, it is possible to obtain a rubber composition for tires that is excellent in silica dispersibility and can improve fuel efficiency, wet grip performance and wear resistance in a balanced manner.

[Citation List]

[Patent Document]

[0005]

[Patent Document 1] Japanese Unexamined Patent Application, First Publication No. 2012-153787

[Summary of Invention]

[Technical Problem]

[0006]

However, tires are required to further improve the “rolling resistance performance” and the “wet grip performance” and to enhance the compatibility of these. Various approaches improving rubber members other than silica and silane coupling agents are expected to meet such demands.

[0007]

The present invention has been made in order to solve the above-mentioned problems, with an object of providing a petroleum-based aromatic-containing oil that can produce a rubber composition excellent in rolling resistance performance and wet grip performance, and satisfies the REACH regulation.

Further, the present invention has an object of providing a rubber composition

containing a petroleum-based aromatic-containing oil that satisfies the REACH regulation and having excellent rolling resistance performance and wet grip performance.

Furthermore, the present invention has an object of providing a tire containing the petroleum-based aromatic-containing oil and a method for producing the tire.

5

[Solution to Problem]

[0008]

As a result of intensive studies in order to solve the above problems, the inventors of the present invention have found that it is possible to produce a rubber
10 composition excellent in rolling resistance performance and wet grip performance by adding an oil containing saturated components and, among the aromatic components, especially bicyclic aromatic components, in the following specific amounts, and they were therefore able to complete the present invention.

That is, one aspect of the present invention is the following petroleum-based
15 aromatic-containing oil, rubber composition, tire, and method for producing a tire.

[0009]

(1) A petroleum-based aromatic-containing oil, wherein a ratio of saturated components by a clay-gel method is 45% by mass or less,

a ratio of bicyclic aromatic components fractionated by HPLC is 16% by mass
20 or more and 29% by mass or less with respect to 100% by mass of the aforementioned aromatic components,

a content of benzo(a)pyrene is 1 mass ppm or less, and

a total content of the following specific polycyclic aromatic hydrocarbons 1) to
8) is 10 mass ppm or less:

25 1) benzo(a)pyrene (BaP);

- 2) benzo(e)pyrene (BeP);
- 3) benzo(a)anthracene (BaA);
- 4) chrysene (CHR);
- 5) benzo(b)fluoranthene (BbFA);
- 5 6) benzo(j)fluoranthene (BjFA);
- 7) benzo(k)fluoranthene (BkFA); and
- 8) dibenzo(a,h)anthracene (DBAhA).

(2) The petroleum-based aromatic-containing oil according to (1) above,
wherein the aforementioned ratio of saturated components by the clay-gel method is 22%
10 by mass or more.

(3) The petroleum-based aromatic-containing oil according to (1) or (2) above,
wherein the aforementioned ratio of bicyclic aromatic components fractionated by HPLC
is less than 23% by mass with respect to 100% by mass of the aforementioned aromatic
components.

15 (4) The petroleum-based aromatic-containing oil according to any one of (1) to
(3) above, wherein the aforementioned ratio of saturated components by the clay-gel
method is 36% by mass or less.

(5) The petroleum-based aromatic-containing oil according to any one of (1) to
(4) above, wherein the aforementioned ratio of bicyclic aromatic components
20 fractionated by HPLC is 22% by mass or less with respect to 100% by mass of the
aforementioned aromatic components.

(6) The petroleum-based aromatic-containing oil according to any one of (1) to
(5) above, which is an extender oil or process oil used by mixing with a rubber.

(7) A rubber composition containing the petroleum-based aromatic-containing
25 oil according to any one of (1) to (6) above and a rubber.

(8) A tire containing the petroleum-based aromatic-containing oil according to any one of (1) to (6) above.

(9) A method for producing the tire according to Claim 8, which includes blending and vulcanizing a rubber and the petroleum-based aromatic-containing oil
5 according to any one of (1) to (6) above.

[Advantageous Effects of Invention]

[0010]

According to the present invention, it is possible to provide a petroleum-based
10 aromatic-containing oil that can produce a rubber composition excellent in rolling resistance performance and wet grip performance, and satisfies the REACH regulation.

Further, according to the present invention, it is possible to provide a rubber composition containing a petroleum-based aromatic-containing oil that satisfies the REACH regulation and having excellent rolling resistance performance and wet grip
15 performance.

Furthermore, according to the present invention, it is possible to provide a tire containing the aforementioned petroleum-based aromatic-containing oil and a method for producing the aforementioned tire.

20 [Brief Description of Drawings]

[0011]

FIG. 1 is a process diagram illustrating an example of a method for producing a petroleum-based aromatic-containing oil according to an embodiment of the present invention.

25 FIG. 2A is a process diagram illustrating an example of a process for preparing a

tire composition according to an embodiment of the present invention.

FIG. 2B is a process diagram illustrating an example of a process for preparing a tire composition according to an embodiment of the present invention.

5 [Description of Embodiments]

[0012]

Hereinafter, embodiments of the petroleum-based aromatic-containing oil, rubber composition, tire, and method for producing a tire of the present invention will be described.

10 [0013]

<<Petroleum-based aromatic-containing oil>>

In the petroleum-based aromatic-containing oil of the embodiment, a ratio of saturated components by a clay-gel method, a ratio of bicyclic aromatic components fractionated by HPLC, a content of benzo(a)pyrene, and a content of a specific polycyclic aromatic hydrocarbons satisfy specific numerical ranges. For rubber compositions or tires containing a petroleum-based aromatic-containing oil that satisfies the following numerical values for these items, the values of $\tan\delta$ (50°C) and $\tan\delta$ (0°C) become favorable, and the compatibility of the wet grip performance and the rolling resistance performance improves.

20 [0014]

Here, the term “wet grip performance” refers to the so-called braking performance, and $\tan\delta$ (0°C) obtained by a dynamic viscoelasticity test serves as an indicator thereof. The term “rolling resistance performance” refers to the so-called fuel efficiency performance, and $\tan\delta$ (50°C) obtained by a dynamic viscoelasticity test serves as an indicator thereof.

[0015]

The phrase “petroleum-based” described above means to contain a hydrocarbon oil derived from petroleum. The term “aromatic-containing oil” described above means that the ratio of saturated components by the clay-gel method and the ratio of bicyclic aromatic components fractionated by HPLC satisfy the following numerical ranges.

The petroleum-based aromatic-containing oil of the embodiment is not particularly limited in terms of production method and classification as long as it satisfies the numerical ranges of each of the above items. For example, an atmospheric distillation residue, an atmospheric distillation fraction, a vacuum distillation fraction, a vacuum distillation residue, a deasphalted oil, solvent-extracted raffinate, a hydro-refined oil, a dewaxed oil, an extract obtained by solvent extraction and the like can be mentioned, and it is preferable to contain an oil produced by the method for producing a petroleum-based aromatic-containing oil described later. The content ratio of the petroleum-derived hydrocarbon oil in the petroleum-based aromatic-containing oil may be 50% by mass or more, 80% by mass or more, and 95% by mass or more.

[0016]

Hereinafter, each item related to the properties of the petroleum-based aromatic-containing oil of the embodiment will be described.

[0017]

The components of petroleum-based oil can be classified into saturated components, aromatic components, and polar components (% by mass) by the clay-gel method. The following values of the saturated components, the aromatic components, or the polar components (% by mass) according to the clay-gel method are values with respect to the total amount of 100% by mass of the saturated components, the aromatic components and the polar components.

[0018]

The petroleum-based aromatic-containing oil of the embodiment has a ratio of saturated components by the clay-gel method of 45% by mass or less, preferably 36% by mass or less, and more preferably 30% by mass or less. The petroleum-based aromatic-
5 containing oil of the embodiment preferably has a ratio of saturated components by the clay-gel method of 5% by mass or more, more preferably 20% by mass or more, and still more preferably 22% by mass or more. As an example of the numerical ranges for the above numerical values, the petroleum-based aromatic-containing oil of the embodiment may have a ratio of saturated components by the clay-gel method of 5% by mass or more
10 and 45% by mass or less, 20% by mass or more and 36% by mass or less, or 22% by mass or more and 30% by mass or less.

When the above ratio of saturated components satisfies the above numerical values, the values of $\tan\delta$ (50°C) and $\tan\delta$ (0°C) of the rubber composition or tire containing the above oil become favorable, and the compatibility of the wet grip
15 performance and the rolling resistance performance improves.

It is considered that this is because, since the saturated components have an appropriate balance in terms of the polarity of the hydrocarbon and exhibit a certain affinity for rubber and also a certain affinity for a rubber compounding agent, when the above ratio of saturated components is within the above range, the physical properties of
20 the produced rubber composition or tire become suitable.

[0019]

The petroleum-based aromatic-containing oil of the embodiment preferably has a ratio of aromatic components by the clay-gel method of 50% by mass or more, more preferably 51% by mass or more, and still more preferably 58% by mass or more. The
25 petroleum-based aromatic-containing oil of the embodiment preferably has a ratio of

aromatic components by the clay-gel method of 74% by mass or less, more preferably 70% by mass or less, and still more preferably 69% by mass or less. As an example of the numerical ranges for the above numerical values, the petroleum-based aromatic-containing oil of the embodiment may have a ratio of aromatic components by the clay-gel method of 50% by mass or more and 74% by mass or less, 51% by mass or more and 70% by mass or less, or 58% by mass or more and 69% by mass or less.

When the above ratio of aromatic components satisfies the above numerical values, the values of $\tan\delta$ (50°C) and $\tan\delta$ (0°C) of the rubber composition or tire containing the above oil become favorable, and the compatibility of the wet grip performance and the rolling resistance performance improves.

It is considered that this is because, since the aromatic components exhibit a high affinity for rubber, when the above ratio of aromatic components is within the above range, the physical properties of the produced rubber composition or tire become suitable.

[0020]

The petroleum-based aromatic-containing oil of the embodiment preferably has a ratio of polar components by the clay-gel method of 1% by mass or more, more preferably 2% by mass or more, and still more preferably 3% by mass or more. The petroleum-based aromatic-containing oil of the embodiment preferably has a ratio of polar components by the clay-gel method of 11% by mass or less, more preferably 10% by mass or less, and still more preferably 9% by mass or less. As an example of the numerical ranges for the above numerical values, the petroleum-based aromatic-containing oil of the embodiment may have a ratio of polar components by the clay-gel method of 1% by mass or more and 11% by mass or less, 2% by mass or more and 10% by mass or less, or 3% by mass or more and 9% by mass or less.

The above ratio of polar components is in a contradictory relationship with the above ratios of saturated components and aromatic components, and when the above ratio of polar components satisfies the above numerical values, the values of $\tan\delta$ (50°C) and $\tan\delta$ (0°C) of the rubber composition or tire containing the above oil become
5 favorable, and the compatibility of the wet grip performance and the rolling resistance performance improves.

[0021]

The ratios of saturated components, aromatic components and polar components (% by mass) by the clay-gel method can be obtained in accordance with the requirements
10 of ASTM D2007-11 Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay-Gel Absorption Chromatographic Method.

[0022]

The petroleum-based aromatic-containing oil of the embodiment has a ratio of
15 bicyclic aromatic components fractionated by HPLC of 16% by mass or more, preferably 17% by mass or more, more preferably 19% by mass or more, and still more preferably 20% by mass or more with respect to 100% by mass of the aforementioned aromatic components. The petroleum-based aromatic-containing oil of the embodiment has a ratio of bicyclic aromatic components fractionated by HPLC of 29% by mass or less,
20 preferably less than 23% by mass, and more preferably 22% by mass or less with respect to 100% by mass of the aforementioned aromatic components. As an example of the numerical ranges for the above numerical values, the petroleum-based aromatic-containing oil of the embodiment may have a ratio of bicyclic aromatic components fractionated by HPLC of 16% by mass or more and 29% by mass or less, 17% by mass or
25 more and less than 23% by mass, 19% by mass or more and 22% by mass or less, or 20%

by mass or more and 22% by mass or less, with respect to 100% by mass of the
aforementioned aromatic components. Here, when the above ratio of bicyclic aromatic
components satisfies the above numerical values, the values of $\tan\delta$ (50°C) and $\tan\delta$
(0°C) of the rubber composition or tire containing the above oil become favorable, and
5 the compatibility of the wet grip performance and the rolling resistance performance
improves.

It is considered that this is because the ratio of aromatic components having two
or more rings among the aromatic components greatly contributes to the compatibility of
the wet grip performance and the rolling resistance performance, as examined from the
10 data shown in Examples described later. Among them, the bicyclic aromatic
components have favorable properties also from the viewpoint of satisfying the REACH
regulation in addition to the improvement of wet grip performance and rolling resistance
performance.

[0023]

15 The petroleum-based aromatic-containing oil of the embodiment preferably has
a ratio of monocyclic aromatic components fractionated by HPLC of 48% by mass or
more, more preferably more than 60% by mass, and still more preferably more than 62%
by mass with respect to 100% by mass of the aforementioned aromatic components.
The petroleum-based aromatic-containing oil of the embodiment preferably has a ratio of
20 monocyclic aromatic components fractionated by HPLC of 80% by mass or less, more
preferably 78% by mass or less, and still more preferably 76% by mass or less with
respect to 100% by mass of the aforementioned aromatic components. As an example
of the numerical ranges for the above numerical values, the petroleum-based aromatic-
containing oil of the embodiment may have a ratio of monocyclic aromatic components
25 fractionated by HPLC of 48% by mass or more and 80% by mass or less, more than 60%

by mass and 78% by mass or less, or more than 62% by mass and 76% by mass or less, with respect to 100% by mass of the aforementioned aromatic components.

The above ratio of monocyclic aromatic components is in a contradictory relationship with the above ratio of aromatic components having two or more rings, and when the above ratio of monocyclic aromatic components satisfies the above numerical values, the values of $\tan\delta$ (50°C) and $\tan\delta$ (0°C) of the rubber composition or tire containing the above oil become favorable, and the compatibility of the wet grip performance and the rolling resistance performance improves.

[0024]

The petroleum-based aromatic-containing oil of the embodiment preferably has a ratio of aromatic components having three or more rings fractionated by HPLC of 4% by mass or more, more preferably 5% by mass or more, and still more preferably 6% by mass or more with respect to 100% by mass of the aforementioned aromatic components. The petroleum-based aromatic-containing oil of the embodiment preferably has a ratio of aromatic components having three or more rings fractionated by HPLC of 20% by mass or less, more preferably 18% by mass or less, and still more preferably less than 16% by mass with respect to 100% by mass of the aforementioned aromatic components. As an example of the numerical ranges for the above numerical values, the petroleum-based aromatic-containing oil of the embodiment may have a ratio of aromatic components having three or more rings fractionated by HPLC of 4% by mass or more and 20% by mass or less, 5% by mass or more and 18% by mass or less, or 6% by mass or more and less than 16% by mass, with respect to 100% by mass of the aforementioned aromatic components.

When the above ratio of aromatic components having three or more rings satisfies the above numerical values, the values of $\tan\delta$ (50°C) and $\tan\delta$ (0°C) of the

rubber composition or tire containing the above oil become favorable, and the compatibility of the wet grip performance and the rolling resistance performance improves, which is also favorable from the viewpoint of satisfying the REACH regulation.

5 [0025]

Fractionation of aromatic components by HPLC can be carried out by the measurement conditions described in Examples described later.

[0026]

In the petroleum-based aromatic-containing oil of the embodiment,
10 the content of benzo(a)pyrene is 1 mass ppm or less, and
the total content of the following specific specific polycyclic aromatic hydrocarbons (PAHs) 1) to 8) is 10 mass ppm or less:

1) benzo(a)pyrene (BaP);

2) benzo(e)pyrene (BeP);

15 3) benzo(a)anthracene (BaA);

4) chrysene (CHR);

5) benzo(b)fluoranthene (BbFA);

6) benzo(j)fluoranthene (BjFA);

7) benzo(k)fluoranthene (BkFA); and

20 8) dibenzo(a,h)anthracene (DBAhA).

[0027]

When the contents of these benzo(a)pyrene and the above specific polycyclic aromatic hydrocarbons (PAHs) are within the above range, it is possible to obtain a safer rubber compounding oil that complies with the regulation on the content in extender oil
25 in the REACH regulation.

[0028]

The contents of these compounds can be obtained by separating and concentrating the target components, and then preparing a sample to which an internal standard material is added, followed by quantitative analysis by GC-MS analysis.

5 The contents of benzo(a)pyrene and specific polycyclic aromatic hydrocarbons (PAHs) can be obtained in accordance with the requirements of European standard EN 16143: 2013 Petroleum products - Determination of content of Benzo(a)pyrene (BaP) and selected polycyclic aromatic hydrocarbons (PAH) in extender oils - Procedure using double LC cleaning and GC/MS analysis.

10 [0029]

The petroleum-based aromatic-containing oil of the embodiment preferably has a kinematic viscosity at 100°C of 8 mm²/s or more, more preferably 10 mm²/s or more, and still more preferably 14 mm²/s or more. The petroleum-based aromatic-containing oil of the embodiment preferably has a kinematic viscosity at 100°C of less than 25 mm²/s, more preferably 23 mm²/s or less, and still more preferably 22 mm²/s or less.

As an example of the numerical ranges for the above numerical values, the petroleum-based aromatic-containing oil of the embodiment may have a kinematic viscosity at 100°C within a range of 8 mm²/s or more and less than 25 mm²/s, 10 mm²/s or more and 23 mm²/s or less, or 14 mm²/s or more and 22 mm²/s or less. When the above kinematic viscosity value satisfies the above numerical value, since the viscosity of the rubber composition or tire containing the petroleum-based aromatic-containing oil becomes even more favorable, the values of tanδ (50°C) and tanδ (0°C) become favorable, and the compatibility of the wet grip performance and the rolling resistance performance further improves. Furthermore, when the above kinematic viscosity value is equal to or less than the above upper limit value, the transfer and workability for

blending the petroleum-based aromatic-containing oil into the rubber are improved.

[0030]

The kinematic viscosity at 100°C can be determined in accordance with the requirements of JIS K2283: 2000.

5 [0031]

The petroleum-based aromatic-containing oil of the embodiment preferably has an aniline point of 52°C or higher, more preferably 56°C or higher, and still more preferably 60°C or higher. The petroleum-based aromatic-containing oil of the embodiment preferably has an aniline point of 95°C or lower, more preferably 92°C or
10 lower, still more preferably 88°C or lower, and particularly preferably 84°C or lower.

As an example of the numerical ranges for the above numerical values, the petroleum-based aromatic-containing oil of the embodiment may have an aniline point within a range of 52°C or higher and 95°C or lower, 52°C or higher and 92°C or lower, or 56°C or higher and 88°C or lower, or 60°C or higher and 84°C or lower. An aniline point refers
15 to a temperature at which equal amounts of aniline and oil are miscible, and serves as an indicator of rubber compatibility. When the aniline point is equal to or less than the above upper limit value, since the oil mixes with aniline without excessive heating, the rubber compatibility is enhanced, which is preferable. In other words, when the aniline point value satisfies the above numerical values, the affinity of the petroleum-based
20 aromatic-containing oil for rubber improves, and the physical properties of the produced rubber composition or tire become even more favorable.

[0032]

Aniline points can be obtained in accordance with the requirements of ASTM D611-12 Standard Test Methods for Aniline Point and Mixed Aniline Point of Petroleum
25 Products and Hydrocarbon Solvents.

[0033]

The petroleum-based aromatic-containing oil of the embodiment preferably has a glass transition point (T_g) of -60°C or higher, more preferably -56°C or higher, and still more preferably -54°C or higher. The petroleum-based aromatic-containing oil of the
5 embodiment preferably has a glass transition point (T_g) of -34°C or lower, more preferably -36°C or lower, and still more preferably -38°C or lower. As an example of the numerical ranges for the above numerical values, the petroleum-based aromatic-containing oil of the embodiment may have a glass transition point (T_g) within a range of
10 -60°C or higher and -34°C or lower, -56°C or higher and -36°C or lower, or -54°C or higher and -38°C or lower. When the glass transition point satisfies the above numerical values, the physical properties of the produced rubber composition or tire become even more favorable, which is important for improving the wet grip performance and the rolling resistance performance.

[0034]

15 The glass transition point can be determined by the measurement conditions described in Examples described later.

[0035]

The petroleum-based aromatic-containing oil of the embodiment preferably has a viscosity specific gravity constant (VGC) of 0.85 or more, more preferably 0.86 or
20 more, and still more preferably 0.87 or more. The petroleum-based aromatic-containing oil of the embodiment preferably has a viscosity specific gravity constant (VGC) of 0.92 or less, more preferably 0.91 or less, and still more preferably 0.90 or less. As an example of the numerical ranges for the above numerical values, the petroleum-based aromatic-containing oil of the embodiment may have a viscosity specific gravity constant
25 (VGC) of 0.85 or more and 0.92 or less, 0.86 or more and 0.91 or less, or 0.87 or more

and 0.90 or less. The viscosity specific gravity constant is an index representing the composition of oil, and in general, the value tends to decrease as the paraffinicity increases, and the value tends to increase as the aromaticity increases. When the above viscosity specific gravity constant value satisfies the above numerical value, since the physical properties of the rubber composition or tire containing the petroleum-based aromatic-containing oil become favorable, the values of $\tan\delta$ (50°C) and $\tan\delta$ (0°C) become even more favorable, and the compatibility of the wet grip performance and the rolling resistance performance further improves.

[0036]

The viscosity specific gravity constant (VGC) can be obtained in accordance with the requirements of ASTM D2140-08 Standard Practice for Calculating Carbon-Type Composition of Insulating Oils of Petroleum Origin.

[0037]

The petroleum-based aromatic-containing oil of the embodiment preferably has a %CA value by ring analysis of 8 or more, more preferably 9 or more, and still more preferably 10 or more. The petroleum-based aromatic-containing oil of the embodiment preferably has a %CA value by ring analysis of 28 or less, more preferably 26 or less, and still more preferably 24 or less. As an example of the numerical ranges for the above numerical values, the petroleum-based aromatic-containing oil of the embodiment may have a %CA value by ring analysis of 8 or more and 28 or less, 9 or more and 26 or less, or 10 or more and 24 or less.

When the above %CA value satisfies the above numerical value, the amount of highly carcinogenic polycyclic aromatics is suppressed, while aromaticity that improves the compatibility with rubber tends to develop at the same time, the values of $\tan\delta$ (50°C) and $\tan\delta$ (0°C) of the rubber composition or tire containing the above oil become

favorable, and the compatibility of the wet grip performance and the rolling resistance performance further improves.

[0038]

The %CA value can be obtained in accordance with the requirements of ASTM
5 D2140-08 Standard Practice for Calculating Carbon-Type Composition of Insulating Oils
of Petroleum Origin.

[0039]

The petroleum-based aromatic-containing oil of the embodiment is suitably used
as an extender oil or process oil mixed with rubber.

10 [0040]

[Method for producing petroleum-based aromatic-containing oil]

Hereinafter, a method for producing the petroleum-based aromatic-containing
oil of the embodiment will be described. According to the above method, the
petroleum-based aromatic-containing oil of the present invention can be produced. The
15 petroleum-based aromatic-containing oil of the present invention is not limited to those
produced by the method for producing a petroleum-based aromatic-containing oil
according to the following embodiment.

[0041]

The method for producing the petroleum-based aromatic-containing oil of the
20 embodiment includes:

a step of obtaining an extract obtained by subjecting raffinate obtained by
solvent extraction to further solvent extraction, or

a step of obtaining raffinate obtained by subjecting an extract obtained by
solvent extraction to further solvent extraction, or

25 a step of mixing an extract obtained by subjecting raffinate obtained by solvent

extraction to further solvent extraction, and raffinate obtained by subjecting raffinate obtained by solvent extraction to further solvent extraction or a base oil obtained by refining the raffinate.

Examples of an object to be extracted with a solvent include a vacuum
5 distillation fraction obtained by vacuum distillation of a residue obtained by atmospheric distillation of crude oil. In solvent extraction, an extract can be obtained by extracting the object of solvent extraction with a solvent having an affinity for aromatic hydrocarbons, and separating and recovering the solvent and the extract. For the crude oil serving as a starting material, although various crude oils such as paraffinic crude oil
10 and naphthenic crude oil can be used alone or in combination, it is particularly preferable to use paraffinic crude oil.

[0042]

Hereinafter, the step of mixing an extract obtained by subjecting raffinate obtained by solvent extraction to further solvent extraction, and raffinate obtained by
15 subjecting raffinate obtained by solvent extraction to further solvent extraction or a base oil obtained by refining the raffinate will be described.

FIG. 1 is a process diagram illustrating an example of a method for producing a petroleum-based aromatic-containing oil according to the embodiment. Crude oil is first treated by an atmospheric distillation apparatus (not shown) to obtain an
20 atmospheric distillation residue. The atmospheric distillation residue is sent to a vacuum distillation apparatus 10 and distilled under reduced pressure to obtain a vacuum distillation fraction 11. The vacuum distillation fraction 11 is sent to a first solvent extraction apparatus 30a. In the first solvent extraction apparatus 30a, the vacuum distillation fraction 11 is separated into raffinate 31a and an extract 33a. The separated
25 raffinate 31a is sent to a second solvent extraction apparatus 30b. In the second solvent

extraction apparatus 30b, the raffinate 31a is separated into raffinate 31b and an extract 33b. The raffinate 31b is hydro-refined by a hydro-refining apparatus 40 to become a hydro-refined oil 41, and further dewaxed by a dewaxing apparatus 50 to obtain a dewaxed oil 51. A petroleum-based aromatic-containing oil 62 can be obtained by
5 mixing the obtained dewaxed oil 51 and the extract 33b.

[0043]

Here, although a case where the dewaxed oil 51 and the extract 33b are mixed to obtain the petroleum-based aromatic-containing oil 62 has been described, instead of the dewaxed oil 51, the raffinate 31b or the hydro-refined oil 41 may be mixed with the
10 extract 33b.

[0044]

Further, the extract 33b may be used as the petroleum-based aromatic-containing oil 62.

[0045]

15 Moreover, although not shown, raffinate obtained by subjecting the extract 33a to further solvent extraction may be used as a petroleum-based aromatic-containing oil.

[0046]

The vacuum distillation is preferably carried out under a condition in which the end point of the distillate oil is 580°C or higher when converted to the normal pressure
20 condition, or a condition in which the initial boiling point of the residue is 450°C or higher, because the content of aromatics in the obtained extract can be easily adjusted within a predetermined range.

In solvent extraction, in order to obtain the extracts 33a and 33b, it is preferable to carry out an extraction treatment with a solvent having a selective affinity for aromatic
25 hydrocarbons. The solvent having a selective affinity for aromatic hydrocarbons may

be a polar solvent, and one or more members selected from the group consisting of furfural, phenol and N-methyl-2-pyrrolidone can be used. Although a specific extraction condition for setting the extract yield within the above range cannot be uniquely determined because it also depends on the composition of deasphalted oil, it can be determined by appropriately selecting the solvent ratio, pressure, temperature and the like. In general, it is preferable to be brought into contact with the solvent at a tower top temperature of 100 to 155°C, more preferably 100 to 140°C; a tower bottom temperature of 40 to 120°C, more preferably 50 to 110°C; and a solvent ratio with respect to oil of 1 to 5, more preferably 1.5 to 4.5.

On the other hand, in the solvent extraction, in order to obtain the raffinates 31a and 31b, it is preferable to carry out a solvent refining treatment for extraction with a solvent having an affinity for aromatic hydrocarbons. As the solvent having a selective affinity for aromatic hydrocarbons, one or more members of furfural, phenol and N-methyl-2-pyrrolidone can be selected and used. In this solvent refining step, under a condition in which an ordinary lubricant base oil is refined, for example, when furfural is used as an extraction solvent, it is preferable to be brought into contact with the solvent at a tower top temperature of 60 to 150°C, more preferably 70 to 140°C; a tower bottom temperature of 40 to 90°C, more preferably 50 to 80°C; and a solvent ratio with respect to oil of 0.5 to 4, more preferably 1 to 3.

In addition, if desired, a more preferable base oil can be obtained by dewaxing raffinate through hydro-refining and/or solvent dewaxing or a hydro-dewaxing treatment. The above hydro-refining process is preferably carried out under the conditions of a hydrogen pressure of 5 to 15 MPa, a temperature of 250 to 400°C and a liquid hourly space velocity (LHSV) of 1 to 5 h⁻¹ in the presence of a catalyst in which one or more active metals such as nickel, cobalt and molybdenum are supported on a carrier such as

alumina and silica-alumina. Further, the above solvent dewaxing process is preferably carried out, for example, in the presence of a mixed solvent of methyl ethyl ketone / toluene at a solvent / oil ratio (volume ratio) = 1/1 to 5/1 and a temperature of -10 to -40°C; and the hydrodewaxing process is preferably carried out under the conditions of a hydrogen pressure of 5 to 15 MPa, a temperature of 300 to 400°C, and LHSV of 1 to 5 Hr⁻¹ in the presence of a zeolite catalyst.

In the hydro-refining process, in the presence of a catalyst, impurities such as sulfur and nitrogen contents that adversely affect the use and storage of process oil can be removed as light hydrogenation reaction products by bringing hydrogen at high temperature and high pressure into contact with raw oil. As a result, stability, hue and the like can be improved. In the solvent dewaxing process, the low temperature fluidity can be improved by mixing with the raw oil using one or more solvents selected from the group consisting of acetone, methyl ethyl ketone, benzene and toluene; and then precipitating wax fractions such as normal paraffin through a cooling step, followed by filtration with a filter for separation and removal of the wax fractions.

The petroleum-based aromatic-containing oil of the embodiment can be produced by using an extract obtained by subjecting the raffinate obtained as described above to further solvent extraction.

Alternatively, the petroleum-based aromatic-containing oil of the embodiment can be produced by using a raffinate obtained by subjecting the extract obtained as described above to further solvent extraction.

Alternatively, the petroleum-based aromatic-containing oil of the embodiment can be produced by mixing the extract obtained as described above and the base oil at a mass ratio of 95/5 to 5/95, particularly preferably 80/20 to 20/80.

<<Rubber composition>>

Hereinafter, a rubber composition of the embodiment will be described. The rubber composition of the present invention is not limited to the following rubber composition.

5 FIGS. 2A and 2B are process diagrams illustrating an example of a process for preparing a tire composition from a raw rubber. A tire composition serving as a raw material for a tire contains a raw rubber and various compounding agents. An extender oil may be blended in a synthetic rubber at the time of its synthesis, and a rubber composition (also referred to as oil extended rubber) containing an extender oil in
10 advance may be used as the raw rubber (see FIG. 2A). Alternatively, a raw rubber containing no extender oil (also referred to as non-oil extended rubber) may be used (see FIG. 2B). A process oil and various compounding agents are added to the raw rubber (see FIGS. 2A and 2B).

 The raw rubber (rubber composition) which is an oil extended rubber can be
15 obtained by subjecting a monomer to a polymerization reaction, and can be produced by adding an extender oil in the process. For example, the oil extended rubber can be produced by a method in which a reaction solution containing a monomer which is a rubber raw material of a raw rubber and an extender oil is subjected to a polymerization reaction; or a method in which a reaction solution containing a monomer which is a
20 rubber raw material of a raw rubber is subjected to a polymerization reaction, and then an extender oil is added to the polymer solution (FIG. 2A).

 The tire composition (rubber composition) can be produced by mixing and kneading the above raw rubber, the petroleum-based aromatic-containing oil according to the present invention and the compounding agent using, for example, a known rubber
25 kneading machine such as a roller, a mixer and a kneader. The tire composition can be

vulcanized in an arbitrary condition.

In the present specification, those containing a raw rubber and the petroleum-based aromatic-containing oil of the embodiment (extender oil or process oil) is referred to as a rubber composition.

5 The rubber composition of the embodiment is suitable as a rubber composition for a tire used in the production of a tire. As one embodiment, the present invention provides a tire composition containing a raw rubber, the petroleum-based aromatic-containing oil according to the present invention and a compounding agent. The tire composition is a concept included in the rubber composition of the embodiment. The
10 tire composition (rubber composition) may be vulcanized or unvulcanized.

Here, although the expressions are divided into extender oils and process oils, these are sometimes collectively referred to as process oils.

[0048]

Hereinafter, the compositions of the rubber composition and the tire
15 composition will be described.

[0049]

As the raw rubber, an elastomeric polymer can be used, and examples thereof include diene-based rubbers such as natural rubbers, isoprene rubbers, butadiene rubbers, 1,2-butadiene rubbers, styrene-butadiene rubbers, isoprene-butadiene rubbers, styrene-
20 isoprene-butadiene rubbers, ethylene-propylene-diene rubbers, halogenated butyl rubbers, halogenated isoprene rubbers, halogenated isobutylene copolymers, chloroprene rubbers, butyl rubbers and halogenated isobutylene-p-methylstyrene rubbers, nitrile rubbers and chloroprene rubbers; olefin-based rubbers such as butyl rubbers, ethylene-propylene-based rubbers (EPDM, EPM), ethylene-butene rubbers (BBM),
25 chlorosulfonated polyethylenes, acrylic rubbers and fluororubbers; epichlorohydrin

rubbers; polysulfide rubbers; silicone rubbers and urethane rubbers. Further, thermoplastic elastomers such as polystyrene-based elastomeric polymers (SBS, SIS, SEBS) which may be hydrogenated, polyolefin-based elastomeric polymers, polyvinyl chloride-based elastomeric polymers, polyurethane-based elastomeric polymers, polyester-based elastomeric polymers or polyamide-based elastomeric polymers may be used. These can be used alone or in any combination thereof.

From the viewpoint of compatibility with petroleum-based aromatic-containing oil, the elastomeric polymer is preferably at least one selected from the group consisting of natural rubbers, isoprene rubbers, styrene-butadiene rubbers, butadiene rubbers, butyl rubbers, chloroprene rubbers, and acrylic nitrile rubbers. Furthermore, from the viewpoint that it can be suitably used for a tread portion that exhibits the rolling resistance performance and the wet grip performance as the tire performance, the elastomeric polymer is preferably at least one selected from the group consisting of natural rubbers, isoprene rubbers, styrene butadiene rubbers, and butadiene rubbers.

[0050]

As the extender oil or the process oil, the petroleum-based aromatic-containing oil according to the embodiment can be used.

[0051]

Examples of the compounding agent include fillers, anti-aging agents, antioxidants, crosslinking agents (vulcanizing agents), crosslinking accelerators, resins, plastics, vulcanization accelerators, and vulcanization acceleration aids (vulcanization aids).

[0052]

Examples of the filler include carbon black, silica and silane compounds (silane coupling agents), and silica and/or silane coupling agents are preferable.

Carbon black is classified into hard carbon and soft carbon based on the particle size. Soft carbon has low reinforcing properties for rubber, and hard carbon has strong reinforcing properties for rubber. When the rubber composition of the embodiment contains carbon black, it is preferable to use hard carbon having particularly strong reinforcing properties. Carbon black is preferably blended in an amount of 10 to 250 parts by mass, more preferably 20 to 200 parts by mass, and still more preferably 30 to 50 parts by mass with respect to 100 parts by mass of the elastomeric polymer.

Silica is not particularly limited, and examples thereof include dry white carbon, wet white carbon, colloidal silica, and precipitated silica. Among these, wet white carbon containing hydrous silicic acid as a main component is preferable. Each of these silica materials can be used alone, or two or more types thereof can be used in combination. The specific surface area of these silica materials is not particularly limited, but is suitable from the viewpoint of improving reinforcing properties, wear resistance, heat generating properties and the like, when it is usually in the range, in terms of a nitrogen adsorption specific surface area (BET method), of 10 to 400 m²/g, preferably 20 to 300 m²/g, and more preferably 120 to 190 m²/g. Here, the nitrogen adsorption specific surface area is a value measured by the BET method in accordance with ASTM D3037-81.

Although the silane compound is not particularly limited, a sulfur-containing silane coupling agent is preferable, and bis(3-triethoxysilylpropyl)disulfide is more preferable.

[0053]

Examples of the crosslinking agent (vulcanizing agent) include powdered sulfur, precipitated sulfur, highly dispersible sulfur, surface-treated sulfur, and insoluble sulfur.

25 [0054]

Examples of the vulcanization accelerator include thiuram-based agents such as tetramethylthiuram disulfide (TMTD) and tetraethylthiuram disulfide (TETD), aldehyde/ammonia-based agents such as hexamethylenetetramine, guanidine-based agents such as diphenylguanidine, thiazole-based agents such as dibenzothiazyl disulfide (DM), and cyclohexylbenzothiazyl sulfenamide-based agents such as N-cyclohexyl-2-benzothiazolyl sulfenamide.

[0055]

Examples of the vulcanization acceleration aid include fatty acids such as acetyl acid, propionic acid, butanoic acid, stearic acid, acrylic acid and maleic acid; fatty acid zinc salts such as zinc acetylate, zinc propionate, zinc butanoate, zinc stearate, zinc acrylate and zinc maleate; and zinc oxide.

[0056]

The blended amounts of these raw rubbers, the petroleum-based aromatic-containing oil according to the present invention and the compounding agent can be set to general blended amounts as long as they are not contrary to the object of the present invention.

[0057]

As an example, with respect to 100 parts by mass of the elastomeric polymer, 30 to 100 parts by mass of a filler, 80 parts by mass or less of a petroleum-based aromatic-containing oil, 0.5 to 5 parts by mass of an anti-aging agent, 1 to 10 parts by mass of a crosslinking agent, 0 to 20 parts by mass of a resin, 0.5 to 5 parts by mass of a vulcanization accelerator, and 1 to 10 parts by mass of a vulcanization acceleration aid may be blended.

When silica and/or a silane coupling agent is used as the filler, silica and/or the silane coupling agent is preferably blended in an amount of 10 to 300 parts by mass,

more preferably 50 to 150 parts by mass, and still more preferably 70 to 100 parts by mass with respect to 100 parts by mass of the elastomeric polymer. The content of the silane compound (silane coupling agent) is preferably 0.1 to 30 parts by mass, and more preferably 1 to 20 parts by mass with respect to 100 parts by mass of the elastomeric polymer.

The petroleum-based aromatic-containing oil is preferably blended in an amount of 0.5 to 80 parts by mass, more preferably 10 to 50 parts by mass, and still more preferably 20 to 40 parts by mass with respect to 100 parts by mass of the elastomeric polymer.

10 [0058]

According to the rubber composition of the embodiment, it is possible to provide a rubber composition excellent in rolling resistance performance and wet grip performance.

[0059]

15 <<Tire / Tire production method>>

A tire of the embodiment contains the petroleum-based aromatic-containing oil according to the above embodiment.

The tire of the embodiment can be produced by blending and vulcanizing a rubber and the petroleum-based aromatic-containing oil of the embodiment.

20 In other words, the tire of the embodiment may include the above tire composition (rubber composition), and can be produced by vulcanizing the tire composition. Specifically, for example, the tire can be produced by vulcanizing and molding the above tire composition. More specifically, for example, the tire can be produced by heating and melting the above tire composition, extruding the heated and melted tire composition, then molding the resulting composition using a tire molding

25

machine, followed by heating and pressurization using a vulcanizer.

[0060]

As an example, a tire is composed of each tire portion such as a tread, a carcass, a sidewall, an inner liner, an under tread, and a belt portion. The tire of the embodiment preferably contains the petroleum-based aromatic-containing oil according to the above embodiment in a tread portion. The tire of the embodiment preferably has a tire tread composed of the tire composition of the embodiment. By containing the petroleum-based aromatic-containing oil in the tread portion serving as the ground contact surface, the rolling resistance performance and the wet grip performance are suitably exhibited.

[0061]

According to the tire and the method for producing a tire of the embodiment, it is possible to provide a tire excellent in rolling resistance performance and wet grip performance.

[0062]

The reason why the petroleum-based aromatic-containing oil of the embodiment is effective in improving the compatibility of the wet grip performance and the rolling resistance performance of the tire composition (rubber composition) is assumed to be as follows.

Since both performances are in contradiction with each other, if one can be improved without impairing the other, the compatibility of the two can be improved as a result. Normally, those known as fuel efficient tires achieve the compatibility of performances by blending silica, and are particularly aimed at improving the fuel efficient performance. However, since silica has many hydrophilic groups on the surface and is difficult to blend with rubber polymers, silica particles tend to aggregate with each other. In that case, when the tire is deformed during traveling, the silica

particles rub against each other and generate heat, resulting in unnecessary energy loss.

Therefore, the point is how to disperse silica in the rubber polymer. It is thought that the petroleum-based aromatic-containing oil containing the above-mentioned specific component in a specific amount acts on the dispersion and dissolution of various

5 compounding agents including silica, and their behaviors in the rubber polymer have favorable effects on each physical property, which leads to the improvement of compatibility between the two contradictory performances as a result.

[Examples]

10 [0063]

Next, the present invention will be described in more detail with reference to Examples, but the present invention is not limited to the following Examples.

[0064]

1. Production of process oil

15 [0065]

<Example 1-1>

Naphthenic crude oil was subjected to an atmospheric distillation apparatus, the obtained atmospheric distillation residue was subjected to a vacuum distillation apparatus, the obtained vacuum distillation fraction equivalent to 500N was subjected to
20 a first furfural extraction apparatus (operating conditions: adjusted within ranges of a tower top temperature of 70 to 100°C; a tower bottom temperature of 40 to 70°C; and a solvent ratio of 1.0 to 2.0), the obtained raffinate fraction was subjected to a second furfural extraction apparatus (operating conditions: adjusted within ranges of a tower top temperature of 100 to 130°C; a tower bottom temperature of 70 to 90°C; and a solvent
25 ratio of 2.0 to 3.0, so that the kinematic viscosity of the extracted fraction at 100°C was

close to 20 mm²/s), and the obtained extracted fraction was used as a process oil of

Example 1.

[0066]

<Example 2-1>

5 Middle East crude oil was subjected to an atmospheric distillation apparatus, the
obtained atmospheric distillation residue was subjected to a vacuum distillation
apparatus, the obtained vacuum distillation fraction equivalent to 500N was subjected to
a first furfural extraction apparatus (operating conditions: adjusted within ranges of a
tower top temperature of 100 to 130°C; a tower bottom temperature of 70 to 100°C; and
10 a solvent ratio of 1.6 to 3.0), the obtained extracted fraction was subjected to a second
furfural extraction apparatus (operating conditions: adjusted within ranges of a tower top
temperature of 70 to 100°C; a tower bottom temperature of 40 to 70°C; and a solvent
ratio of 1.0 to 2.0, so that the kinematic viscosity of the raffinate fraction at 100°C was
close to 20 mm²/s), and the obtained raffinate fraction was used as a process oil of

15 Example 2.

[0067]

<Example 3-1>

Middle East crude oil was subjected to an atmospheric distillation apparatus, the
obtained atmospheric distillation residue was subjected to a vacuum distillation
20 apparatus, the obtained vacuum distillation fraction equivalent to 350N was subjected to
a first furfural extraction apparatus (operating conditions: adjusted within ranges of a
tower top temperature of 80 to 100°C; a tower bottom temperature of 50 to 70°C; and a
solvent ratio of 1.0 to 1.5), the obtained raffinate fraction was subjected to a second
furfural extraction apparatus (operating conditions: adjusted within ranges of a tower top
25 temperature of 105 to 125°C; a tower bottom temperature of 75 to 95°C; and a solvent

ratio of 2.0 to 3.0), and the obtained extracted fraction was used as an extract (M).

Middle East crude oil was subjected to an atmospheric distillation apparatus, the obtained atmospheric distillation residue was subjected to a vacuum distillation apparatus, the obtained vacuum distillation fraction equivalent to 900N was subjected to a first furfural extraction apparatus (operating conditions: adjusted within ranges of a tower top temperature of 80 to 100°C; a tower bottom temperature of 50 to 70°C; and a solvent ratio of 0.8 to 1.4), the obtained raffinate fraction was subjected to a second furfural extraction apparatus (operating conditions: adjusted within ranges of a tower top temperature of 110 to 130°C; a tower bottom temperature of 80 to 100°C; and a solvent ratio of 2.0 to 3.0), and the obtained extracted fraction was used as an extract (N).

Middle East crude oil was subjected to an atmospheric distillation apparatus, the obtained atmospheric distillation residue was subjected to a vacuum distillation apparatus, the obtained vacuum distillation fraction equivalent to 900N was subjected to a furfural extraction apparatus (operating conditions: adjusted within ranges of a tower top temperature of 105 to 125°C; a tower bottom temperature of 65 to 85°C; and a solvent ratio of 1.0 to 3.0), the obtained raffinate fraction was subjected to a hydro-refining apparatus (operating conditions: adjusted, using a noble metal-based catalyst, within ranges of a liquid hourly space velocity of 1.0 to 2.0 h⁻¹; a reaction temperature of 270 to 330°C; a hydrogen oil ratio of 1,400 to 2,800 NL/L; and a hydrogen partial pressure of 4.0 to 6.0 MPa), the obtained hydro-refined oil was subjected to a solvent dewaxing apparatus (operating conditions: adjusted, using a mixed solvent of methyl ethyl ketone and toluene, within ranges of a primary solvent ratio of 0.7 to 2.0, a secondary solvent ratio of 0.7 to 2.0, and a dewaxing temperature of -15 to -25°C), and the obtained dewaxed oil was used as a dewaxed oil (O).

The extract (M), the extract (N) and the dewaxed oil (O) were mixed at a weight

ratio of 25/50/25 to obtain a process oil of Example 3.

[0068]

<Example 4-1>

Middle East crude oil was subjected to an atmospheric distillation apparatus, the
5 obtained atmospheric distillation residue was subjected to a vacuum distillation
apparatus, the obtained vacuum distillation residue was subjected to a deasphalting
extraction apparatus (operating conditions: adjusted within ranges of a tower top
temperature of 55 to 85°C; a tower bottom temperature of 45 to 75°C; and a solvent ratio
of 1.0 to 4.0) with compressed liquefied propane, the obtained deasphalted oil was
10 subjected to a furfural extraction apparatus (operating conditions: adjusted within ranges
of a tower top temperature of 110 to 130°C; a tower bottom temperature of 60 to 80°C;
and a solvent ratio of 3.0 to 4.0), and the obtained extracted fraction was used as an
extract (E).

The above extract (E) and the dewaxed oil (F) described later were mixed at a
15 weight ratio of 40/60 to obtain a process oil of Example 4.

[0069]

<Comparative Example 1-1>

Middle East crude oil was subjected to an atmospheric distillation apparatus, the
obtained atmospheric distillation residue was subjected to a vacuum distillation
20 apparatus, the obtained vacuum distillation fraction equivalent to 500N was subjected to
a furfural extraction apparatus (operating conditions: adjusted within ranges of a tower
top temperature of 100 to 130°C; a tower bottom temperature of 50 to 80°C; and a
solvent ratio of 1.0 to 3.0), the obtained raffinate fraction was subjected to a hydro-
refining apparatus (operating conditions: adjusted, using a noble metal-based catalyst,
25 within ranges of a liquid hourly space velocity of 1.0 to 3.0 h⁻¹; a reaction temperature of

280 to 340°C; a hydrogen oil ratio of 1,500 to 2,500 NL/L; and a hydrogen partial pressure of 6.0 to 10.0 MPa), the obtained hydro-refined oil was subjected to a solvent dewaxing apparatus (operating conditions: adjusted, using a mixed solvent of methyl ethyl ketone and toluene, within ranges of a primary solvent ratio of 1.0 to 2.0, a
5 secondary solvent ratio of 0.5 to 1.4, and a dewaxing temperature of -15 to -25°C), and the obtained dewaxed oil was used as a dewaxed oil (G).

Middle East crude oil was subjected to an atmospheric distillation apparatus, the obtained atmospheric distillation residue was subjected to a vacuum distillation apparatus, and the obtained vacuum distillation residue was used as a vacuum distillation
10 residue (H).

Naphthenic crude oil was subjected to an atmospheric distillation apparatus, the obtained atmospheric distillation residue was subjected to a vacuum distillation apparatus, the obtained vacuum distillation fraction equivalent to 1,000N was subjected to a hydro-refining apparatus (operating conditions: adjusted, using a noble metal-based
15 catalyst, within ranges of a liquid hourly space velocity of 1.0 to 3.0 h⁻¹; a reaction temperature of 270 to 340°C; a hydrogen oil ratio of 1,400 to 2,800 NL/L; and a hydrogen partial pressure of 3.0 to 9.0 MPa), and the obtained hydro-refined oil was used as a hydro-refined oil (I).

Naphthenic crude oil was subjected to an atmospheric distillation apparatus, the
20 obtained atmospheric distillation residue was subjected to a vacuum distillation apparatus, and the obtained vacuum distillation residue was used as a vacuum distillation residue (J).

The dewaxed oil (G) and the vacuum distillation residue (H) were mixed at a weight ratio of 50/50, and the hydro-refined oil (I) and the vacuum distillation residue (J)
25 were mixed at a weight ratio of 50/50, and both mixtures were mixed so that the

kinematic viscosity at 100°C was close to 30 mm²/s to obtain a process oil of

Comparative Example 1.

[0070]

<Comparative Example 2-1>

5 Naphthenic crude oil was subjected to an atmospheric distillation apparatus, the
obtained atmospheric distillation residue was subjected to a vacuum distillation
apparatus, the obtained vacuum distillation fraction equivalent to 2,000N was subjected
to a hydro-refining apparatus (operating conditions: adjusted, using a noble metal-based
catalyst, within ranges of a liquid hourly space velocity of 1.0 to 3.0 h⁻¹; a reaction
10 temperature of 270 to 340°C; a hydrogen oil ratio of 1,400 to 2,800 NL/L; and a
hydrogen partial pressure of 3.0 to 9.0 MPa), and the obtained hydro-refined oil was used
as a process oil of Comparative Example 2.

[0071]

<Comparative Example 3-1>

15 Middle East crude oil was subjected to an atmospheric distillation apparatus, the
obtained atmospheric distillation residue was subjected to a vacuum distillation
apparatus, the obtained vacuum distillation fraction equivalent to 500N was subjected to
a furfural extraction apparatus (operating conditions: adjusted within ranges of a tower
top temperature of 105 to 125°C; a tower bottom temperature of 55 to 75°C; and a
20 solvent ratio of 1.2 to 2.8), the obtained raffinate fraction was subjected to a hydro-
refining apparatus (operating conditions: adjusted, using a noble metal-based catalyst,
within ranges of a liquid hourly space velocity of 2.0 to 3.0 h⁻¹; a reaction temperature of
310 to 360°C; a hydrogen oil ratio of 1,500 to 2,500 NL/L; and a hydrogen partial
pressure of 8.5 to 12.0 MPa), the obtained hydro-refined oil was subjected to a solvent
25 dewaxing apparatus (operating conditions: adjusted, using a mixed solvent of methyl

ethyl ketone and toluene, within ranges of a primary solvent ratio of 1.0 to 2.0, a secondary solvent ratio of 0.5 to 1.4, and a dewaxing temperature of -15 to -25°C), and the obtained dewaxed oil was used as a dewaxed oil (F). The above dewaxed oil (F) was used as a process oil of Comparative Example 3.

5 [0072]

<Comparative Example 4-1>

The above extract (E) and the dewaxed oil (F) were mixed at a weight ratio of 80/20 to obtain a process oil of Comparative Example 4.

[0073]

10 2. Measurement of process oil properties

Using the process oils obtained in the above Examples and Comparative Examples as samples, the following items were measured.

[0074]

[Clay-gel method]

15 Aromatic components, saturated components and polar components (% by mass) were determined by a clay-gel method (clay gel column chromatography): ASTM D2007-11 Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay-Gel Absorption Chromatographic Method.

20 [0075]

[Fractionation of aromatic components by HPLC]

Fractionation of aromatic components by high performance liquid chromatography (HPLC) was carried out by the following procedure with reference to the previous report "Separation of aromatic and polar compounds in fossil fuel liquids by liquid chromatography" published in (Analytical Chemistry, 1983, 55, p.1375-1379).

25

Pretreatment was performed by diluting the sample five-fold with hexane. A Spherisorb A5Y column (250 × 4.6 mm, manufactured by Waters Corporation) was used, the flow rate was set to 2.5 mL/min, a UV detector was used as a detector, and the measurement was carried out at a wavelength of 270 nm. Hexane was used as an eluent for a period from 0 to 10.0 minutes after sample introduction. During a period from 10.0 to 30.0 minutes, the content of dichloromethane was linearly increased so as to change from hexane (100% by mass) to a mixed solution of dichloromethane (40% by mass) and hexane (60% by mass). The mixed solution of 40% by mass of dichloromethane and 60% by mass of hexane was changed to 100% by mass of dichloromethane during a period from 30.0 to 30.1 minutes after sample introduction, and 100% by mass of dichloromethane was used after 30.1 minutes.

From the obtained peak areas, the contents (% by mass) of aromatic hydrocarbons having different aromatic rings were determined by the following formula. Here, an area of monocyclic aromatic components (aromatic components having one ring) is the total peak area from the peak of benzene to a peak immediately before naphthalene, an area of bicyclic aromatic components (aromatic components having two rings) is the total peak area from the peak of naphthalene to a peak immediately before anthracene, and an area of tricyclic or higher aromatic components (aromatic components having three or more rings) is the total peak area after the peak of anthracene.

Monocyclic aromatic components (% by mass) = ((area of monocyclic aromatic components) / ((area of monocyclic aromatic components) + 0.1 × (area of bicyclic aromatic components) + 0.025 × (area of tricyclic or higher aromatic components))) × 100;

Bicyclic aromatic components (% by mass) = (0.1 × (area of bicyclic aromatic components)) / ((area of monocyclic aromatic components) + 0.1 × (area of bicyclic

aromatic components) + 0.025 × (area of tricyclic or higher aromatic components))) × 100;

Tricyclic or higher aromatic components (% by mass) = (0.025 × (area of tricyclic aromatic components) / ((area of monocyclic aromatic components) + 0.1 × (area of bicyclic aromatic components) + 0.025 × (area of tricyclic or higher aromatic components))) × 100

[0076]

[Kinematic viscosity (100°C)]

It was measured in accordance with the requirements of JIS K2283: 2000.

10 [0077]

[Aniline point]

It was measured in accordance with the requirements of ASTM D611-12 Standard Test Methods for Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents.

15 [0078]

[Glass transition point (T_g)]

A glass transition point was obtained from a heat capacity change peak in a glass transition region, which was measured when the temperature was raised at a constant rate of temperature increase by a differential scanning calorimeter (DSC). The initial temperature was usually set to a temperature about 30°C to 50°C lower than the expected glass transition point, and after holding at the initial temperature for a certain period of time, the temperature started to increase. More specifically, the measurement was performed under the following conditions.

Apparatus: DSC7020 manufactured by Hitachi High-Tech Science Corporation

25 Initial temperature: -90°C, held for 10 minutes

Rate of temperature increase: 10°C/min

End temperature: 30°C, held for 5 minutes

[0079]

[Viscosity specific gravity constant (VGC)]

5 It was measured in accordance with the requirements of ASTM D2140-08
Standard Practice for Calculating Carbon-Type Composition of Insulating Oils of
Petroleum Origin.

[0080]

[%CA]

10 It was measured in accordance with the requirements of ASTM D2140-08
Standard Practice for Calculating Carbon-Type Composition of Insulating Oils of
Petroleum Origin.

[0081]

[Contents of benzo(a)pyrene and specific polycyclic aromatic hydrocarbons (PAHs)]

15 They were measured in accordance with the requirements of European standard
EN 16143: 2013 Petroleum products - Determination of content of Benzo(a)pyrene (BaP)
and selected polycyclic aromatic hydrocarbons (PAH) in extender oils - Procedure using
double LC cleaning and GC/MS analysis.

PAHs refer to the following:

- 20 1) benzo(a)pyrene (BaP);
 2) benzo(e)pyrene (BeP);
 3) benzo(a)anthracene (BaA);
 4) chrysene (CHR);
 5) benzo(b)fluoranthene (BbFA);
25 6) benzo(j)fluoranthene (BjFA);

7) benzo(k)fluoranthene (BkFA); and

8) dibenzo(a,h)anthracene (DBAhA).

[0082]

3. Production of rubber composition

5 <Example 1-2 to Example 4-2>

A rubber polymer, the above process oil produced in Examples 1-1 to 4-1, and other compounding agents (silica, a silane coupling agent, an anti-aging agent, a vulcanization aid, zinc oxide, sulfur and a vulcanization accelerator) were prepared with the following composition, and then mixed and kneaded to obtain an unvulcanized rubber composition, which was then subjected to a press-vulcanizing and molding process at 160°C.

[0083]

<Comparative Example 1-2 to Comparative Example 4-2>

15 A rubber polymer, the above process oil produced in Comparative Examples 1-1 to 4-1, and other compounding agents (same as above) were prepared with the following composition, and then mixed and kneaded to obtain an unvulcanized rubber composition, which was then subjected to a press-vulcanizing and molding process at 160°C.

[0084]

20 The composition of a tire composition is shown in Table 1 below. The abbreviation phr in the table represents parts by mass of various compounding agents with respect to 100 parts by mass of the rubber polymer.

[0085]

[Table 1]

	Blended amounts (phr)
Rubber polymer (SBR)	100
Silica	80

Silane coupling agent	6.4
Anti-aging agent	2
Vulcanization aid	1
Zinc oxide	3
Process oil	37.5
Sulfur	2.2
Vulcanization accelerator A	1.7
Vulcanization accelerator B	2.0

[0086]

- Rubber polymer (SBR): BunaVSL4526 manufactured by Lanxess AG

- Silica: ULTRASIL7000GR manufactured by Evonik Industries AG

5 - Silane coupling agent: Si75 manufactured by Evonik Industries AG

- Anti-aging agent: Nocrac 6C manufactured by Ouchi Shinko Chemical

Industrial Co., Ltd.

- Vulcanization aid: stearic acid manufactured by NOF Corporation

- Zinc oxide: Zinc oxide No. 3 manufactured by Toho Zinc Co., Ltd.

10 - Process oil: each process oil produced in Examples and Comparative Examples

- Sulfur: commercially available sulfur for vulcanization

- Vulcanization accelerator A: Nocceler cz manufactured by Ouchi Shinko

Chemical Industrial Co., Ltd.

- Vulcanization accelerator B: Nocceler d manufactured by Ouchi Shinko

15 Chemical Industrial Co., Ltd.

[0087]

Rubber mixing and kneading method: a two-stage kneading process shown below was used.

(First stage)

20 - Testing machine: Labo Plastomill B-600 manufactured by Toyo Seiki Seisakusho, Ltd.

- Testing machine volume: 600cc
 - Filling rate: 70% (mass ratio)
 - Rotational frequency: 100 rpm
 - Temperature: started at 100°C with an upper limit of 155°C
- 5 - Kneading time: approximately 9 minutes

(Second stage)

- Testing machine: Electric heating type high temperature roll machine
manufactured by Ikeda Kikai Kogyo Co., Ltd.

- Size: 6 inches ϕ $\times$ 16 inches
- 10 - Rotational frequency: Front roll 25 rpm
- Rotational ratio: ratio of the front and rear rolls (front: rear) 1: 1.22
 - Temperature: 23 $\pm$ 10°C

[0088]

4. Measurement of physical properties of rubber composition

- 15 Test pieces of 8 mm ϕ $\times$ 10 mm were produced from the rubber kneaded pieces after press vulcanization and molding of the above Examples and Comparative Examples, and the following items were measured with respect to the test pieces.

[0089]

[Tan δ (0°C)]

- 20 Using a viscoelasticity measuring device ARES manufactured by TA Instruments, measurement was performed in a twist mode at a frequency of 10 Hz, a measurement temperature range of -50°C to 100°C, a rate of temperature increase of 2 °C/min, and a dynamic strain of 0.1%. From the obtained variable temperature tan δ , the value at 0°C was extracted.

- 25 Tan δ (0°C) is an indicator of wet grip performance, and the larger the value, the

better the wet grip performance.

[0090]

[Tan δ (50°C)]

Using a viscoelasticity measuring device ARES manufactured by TA

- 5 Instruments, measurement was performed in a twist mode at a frequency of 10 Hz, a measurement temperature range of -50°C to 100°C, a rate of temperature increase of 2 °C/min, and a dynamic strain of 0.1%. From the obtained variable temperature tan δ , the value at 50°C was extracted.

- 10 Tan δ (50°C) is an indicator of rolling resistance performance, and the smaller the value, the better the rolling resistance performance.

[0091]

5. Results

- The above measurement results are shown below. The above-mentioned Example 1-1 and Example 1-2 are abbreviated as Example 1. The other Examples and
15 Comparative Examples will be abbreviated in the same manner.

[0092]

The measurement results of each item are shown in Table 2 below. The values of tan δ (0°C) and tan δ (50°C) are expressed as relative values with the actual values of Example 4 (0.594 and 0.105, respectively) being regarded as 1.

- 20 [0093]

[Table 2]

			Examples				Comparative Examples				
			1	2	3	4	1	2	3	4	
Process oil	Fractionation of aromatic components by HPLC	Monocyclic aromatic components	% by mass	73.6	68.8	64.4	58.9	67.0	71.5	87.9	46.8
		Bicyclic aromatic components	% by mass	17.9	20.6	21.8	22.8	18.5	18.8	9.1	30.8
		Tricyclic or higher aromatic components	% by mass	8.5	10.6	13.8	18.3	14.5	9.7	3.0	22.4
	Clay gel column chromatography	Aromatic components	% by mass	62.0	67.4	71.9	50.5	39.5	41.2	34.6	70.8
		Saturated components	% by mass	34.2	24.5	22.6	44.6	45.4	55.3	64.9	21.4
		Polar components	% by mass	3.8	8.1	5.5	4.9	15.1	3.5	0.5	7.8
	Ring analysis (ASTM D2140)	Kinematic viscosity (100°C)	mm ² /s	19.24	18.17	21.35	19.81	29.40	20.01	10.91	43.54
		Aniline point	°C	80.3	64.4	74.0	93.8	90.4	97.6	110.0	76.4
		Glass transition point	°C	-39.3	-47.3	-51.7	-58.5	-54.1	-53.6	-69.1	-44.1
		VGC		0.879	0.891	0.890	0.854	0.861	0.849	0.815	0.896
Rubber composition	Benzofalpyrene	%CA	12.1	22.4	22.7	16.7	22.4	13.2	5.7	25.8	
		Total of 8 PAHs	ppm	○	○	○	○	○	○	○	○
	tan δ (0°C) wet grip performance		ppm	○	○	○	○	○	○	○	○
			ppm	○	○	○	○	○	○	○	○
tan δ (50°C) rolling resistance performance		1.29	1.10	1.04	1.00	1.09	0.93	0.70	1.32		
		0.91	0.95	0.97	1.00	1.02	0.99	0.93	1.08		

Each item of process oil: an underline indicates that the numerical value is outside the specific range in the embodiment.
Benzofalpyrene: "○" indicates that the content is less than 1 ppm (within the standard value in the REACH Regulation).
Total of 8 PAHs: "○" indicates that the content is less than 10 ppm (within the standard value in the REACH Regulation).
tanδ (0°C): an underline indicates that the numerical value is less than 1 (inferior in wet grip performance).
tanδ (50°C): an underline indicates that the numerical value is more than 1 (inferior in rolling resistance performance).

[0094]

The process oils of Examples 1 to 4 satisfy the ranges of “ratio of saturated components by the clay-gel method” and “ratio of bicyclic aromatic components

fractionated by HPLC” specified in the embodiment. The rubber compositions of Examples 1 to 4 obtained by blending the above process oils exhibited satisfactory wet grip performance and rolling resistance performance in a compatible manner, and were extremely excellent.

5 In particular, it can be seen that the rubber compositions of Examples 1 to 3 obtained by blending a process oil of which the “ratio of aromatic components by the clay-gel method” satisfies the specified range in the embodiment exhibited satisfactory wet grip performance and rolling resistance performance in a compatible manner with favorable numerical values.

10 Further, it was confirmed that the contents of benzo(a)pyrene and specific polycyclic aromatic hydrocarbons (PAHs) in all the process oils of Examples and Comparative Examples satisfied the REACH regulation.

[0095]

15 As described above, each configuration and a combination thereof in each embodiment are merely examples, and additions, omissions and substitutions of configurations as well as other modifications can be made without departing from the spirit or scope of the present invention. Moreover, the present invention is not limited by each embodiment, but is limited only by the scope of the claims.

20 [Industrial Applicability]

[0096]

It is possible to provide a petroleum-based aromatic-containing oil that can produce a rubber composition excellent in rolling resistance performance and wet grip performance, and satisfies the REACH regulation.

25

[Reference Signs List]

[0097]

10: Vacuum distillation apparatus;

11: Vacuum distillation fraction;

5 30a, 30b: Solvent extraction apparatus;

31a, 31b: Raffinate;

33a, 33b: Extract;

40: Hydro-refining apparatus;

41: Hydro-refined oil;

10 50: Dewaxing apparatus;

51: Dewaxed oil;

62: Petroleum-based aromatic-containing oil

[CLAIMS]

[Claim 1]

A petroleum-based aromatic-containing oil,

5 wherein a ratio of saturated components by a clay-gel method is 45% by mass or less,

a ratio of bicyclic aromatic components fractionated by HPLC is 16% by mass or more and 29% by mass or less with respect to 100% by mass of aromatic components by the clay-gel method,

10 a content of benzo(a)pyrene is 1 mass ppm or less, and

a total content of the following specific polycyclic aromatic hydrocarbons 1) to 8) is 10 mass ppm or less:

1) benzo(a)pyrene;

2) benzo(e)pyrene;

15 3) benzo(a)anthracene;

4) chrysene;

5) benzo(b)fluoranthene;

6) benzo(j)fluoranthene;

7) benzo(k)fluoranthene; and

20 8) dibenzo(a,h)anthracene.

[Claim 2]

The petroleum-based aromatic-containing oil according to Claim 1, wherein said ratio of saturated components by the clay-gel method is 22% by mass or more.

[Claim 3]

The petroleum-based aromatic-containing oil according to Claim 1 or 2, wherein said ratio of bicyclic aromatic components fractionated by HPLC is less than 23% by mass with respect to 100% by mass of said aromatic components.

5

[Claim 4]

The petroleum-based aromatic-containing oil according to any one of Claims 1 to 3, wherein said ratio of saturated components by the clay-gel method is 36% by mass or less.

10

[Claim 5]

The petroleum-based aromatic-containing oil according to any one of Claims 1 to 4, wherein said ratio of bicyclic aromatic components fractionated by HPLC is 22% by mass or less with respect to 100% by mass of said aromatic components.

15

[Claim 6]

The petroleum-based aromatic-containing oil according to any one of Claims 1 to 5, which is an extender oil or process oil used by mixing with a rubber.

20

[Claim 7]

A rubber composition comprising the petroleum-based aromatic-containing oil according to any one of Claims 1 to 6 and a rubber.

[Claim 8]

25

A tire comprising the petroleum-based aromatic-containing oil according to any

one of Claims 1 to 6.

[Claim 9]

A method for producing the tire according to Claim 8, which comprises blending
5 and vulcanizing a rubber and the petroleum-based aromatic-containing oil according to
any one of Claims 1 to 6.