

METHOD FOR REMOVING SULFUR-CONTAINING COMPOUND

TECHNICAL FIELD

[0001]

5 The present invention relates to a sulfur-containing compound removal method, more specifically, a sulfur-containing compound removal method in which carbon disulfide and mercaptanes contained in hydrocarbons are removed, and in a subsequent step, which can contribute to a quality improvement of products obtained by a distillation purifying.

10

BACKGROUND ART

[0002]

 In recent years, various hydrocarbon fractions, which are by-products of manufacturing ethylene and the like by cracking naphtha and the like, accompany larger amount of sulfur-containing compounds derived components contained in a raw material than conventional ones. Among all, C5 fractions, composed mainly of hydrocarbons having a carbon number of 5, accompany carbon disulfide, mercaptanes, dimethylsulfide, etc., which have boiling points close to that of the C5 fractions; especially, carbon disulfide and mercaptanes are contained in a large amount. In case when content of the sulfur-containing compounds is large in amount, said sulfur-containing compounds are mixed in isoprene, piperylene, dicyclopentadiene, etc. which are obtained by purifying C5 fractions; and when manufacturing rubbers and resins with raw materials of said isoprene, piperylene, dicyclopentadiene, etc., polymerization reactions may be suppressed and odorization of the obtained products may occur. Thus, removing the sulfur-containing compounds is required.

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25

[0003]

Patent article 1: Japanese Patent Application Laid-Open No.

2005-281602 teaches a method of bringing hydrocarbons, including carbon disulfide, into contact with polyamine and alkaline water to remove the carbon disulfide.

PRIOR ART DOCUMENT

5 [0004]

Patent document 1: Japanese Patent Application Laid-Open No. 2005-281602

SUMMARY OF THE INVENTION

Technical Problems

10 [0005]

With the method described in the Patent document 1, an equipment cost for waste water treatment becomes large when considering an application to industrial process; and thus, further improvement is demanded. In addition, it was insufficient to remove mercaptanes contained in hydrocarbons.

15 [0006]

The object of the present invention, in consideration of conventional techniques such as those described above, is to provide a method to easily and efficiently remove the sulfur-containing compounds, especially carbon disulfide and mercaptanes, from the sulfur-containing compound contained

20 hydrocarbons.

Solution to Problem

[0007]

By keen examination for solving said problem, the inventors have found that an object of the present invention can be achieved by the following:

25 carbon disulfide and mercaptanes are easily removed by bringing hydrocarbons, containing carbon disulfide and mercaptanes, into contact with amide compounds and nitrites.

[0008]

Summary of the invention is as follows:

(A) A sulfur-containing compound removal method involving a step of bringing crude hydrocarbons, including at least one sulfur-containing compound selected from the group consisting of carbon disulfide and mercaptans, into contact with amide compounds and nitrites.

5 (B) A manufacturing method of purified hydrocarbons involving the sulfur-containing compound removal method as described in above (A).

EFFECTS OF THE INVENTION

[0009]

10 According to the sulfur-containing compound removal method of the invention, the sulfur-containing compounds, especially carbon disulfide and mercaptanes, included in hydrocarbons is easily and efficiently removed; and in a subsequent step, which can contribute to a quality improvement of products obtained by the distillation purifying.

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BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

[0010]

[FIG. 1] Fig. 1 is a schematic configuration of an apparatus used in the invention. BEST MODE FOR WORKING THE INVENTION

20 [0011]

Hereinafter, the invention will be described in detail. The method of removing the sulfur-containing compounds of the invention includes a method of bringing crude hydrocarbons, including at least one sulfur-containing compound selected from a group consisting of carbon disulfide and mercaptans, into contact with amide compounds and nitrites.

25

[0012]

The crude hydrocarbons are generally a hydrocarbon including various sulfur-containing compounds. Among those sulfur-containing compounds,

removal objects are carbon disulfide and mercaptanes according to the present invention.

[0013]

The crude hydrocarbons are not particularly limited; however, C4
5 fractions composed mainly of hydrocarbons having a carbon number of 4 or
C5 fractions composed mainly of hydrocarbons having a carbon number of 5
are preferable. Said crude hydrocarbons are fractions which are by-products
of manufacturing ethylene and the like by cracking naphtha and the like.

[0014]

10 Among those, the present invention is particularly effective for crude
hydrocarbons composed mainly of C5 fractions; carbon disulfide and
mercaptanes have boiling points close to that of C5 fractions and that
separation of carbon disulfide and mercaptanes is difficult.

[0015]

15 Examples of hydrocarbons having a carbon number of 4 included in C4
fractions may include 1,3-butadiene, n-butane, isobutane, 1-butene, 2-butene,
isobutene, and vinylacetylene and the like. Examples of hydrocarbons having
a carbon number of 5 included in C5 fractions may include isoprene,
isoamylene, amylene, n-pentane, isopentane, piperylene, cyclopentane,
20 cyclopentene, and cyclopentadiene and the like.

[0016]

Examples of mercaptanes, a kind of sulfur-containing compounds, may
include chain mercaptanes, cyclic mercaptanes, etc. The carbon number of
mercaptanes is preferably 20 or less, more preferably 1 to 15, and the most
25 preferably 1 to 10.

[0017]

Examples of the chain mercaptanes may include methyl mercaptan, ethyl
mercaptan, normal propyl mercaptan, isopropyl mercaptan, etc. Examples of
the cyclic mercaptanes may include cyclopentyl mercaptan, cyclohexyl

mercaptan, 2-methyl-cyclopentyl mercaptan, 3-methyl-cyclopentyl mercaptan, etc. Among all, ethyl mercaptan is preferable for the sulfur-containing compounds, which is a processing object of the removal method of the invention; the boiling point of ethyl mercaptan is particularly close to that of isoprene which is one of the targets for distillation purifying. One or more kinds of mercaptans may be included in the crude hydrocarbons.

[0018]

Though the crude hydrocarbons, a processing objects of the invention, are not particularly limited as long as they contains carbon disulfide and/or mercaptanes, the crude hydrocarbons contain carbon disulfide and mercaptanes preferably 10,000 ppm or less, more preferably 1,000 ppm or less, and the most preferably 500 ppm or less in total. Further, the crude hydrocarbons contain carbon disulfide and mercaptanes preferably 1 ppm or more in total. In case when a total amount of the carbon disulfide and mercaptanes is within the above range, the sulfur-containing compounds are possible to be removed efficiently.

[0019]

Examples of the amide compounds used in the invention may include chain amide compounds, cyclic amide compounds, etc. The carbon number of the amide compounds are preferably 20 or less, more preferably 3 to 15, and the most preferably 3 to 10.

[0020]

Examples of the chain amide compounds may include
N,N-dimethylformamide, N-methyl-N-phenylformamide,
N,N-diphenylformamide, N,N-dimethylacetamide,
N-methyl-N-phenylacetamide, N,N-diphenylacetamide,
N,N-diethylformamide, N-ethyl-N-phenylformamide, N,N-diethyl-acetamide,
N-ethyl-N-phenylacetamide, etc. Examples of the cyclic amide compounds may include N-methylpyrrolidone, N-ethylpyrrolidone, N-methylpiperidinone,

N-ethylpiperidinone, etc. Among all, the chain amide compounds are preferable, the chain amide compounds which are liquid at 50 °C under 1 atm are more preferable in view of operability, and N,N-dimethylformamide is the most preferable. The amide compounds may be used alone or 2 or more kinds
5 may be used in combination.

[0021]

Examples of the nitrites used in the invention may include an alkali metal nitrites, alkaline earth metal nitrites, etc. Concrete examples of the alkali metal nitrites include sodium nitrites and potassium nitrites, etc. Concrete
10 examples of the alkaline earth metal nitrites include magnesium nitrites, calcium nitrites, etc. Among all, in view of solubility, alkali metal nitrites are preferable, sodium nitrite and potassium nitrite are more preferable, and sodium nitrite is the most preferable.

[0022]

15 Nitrites may be used in a form of salt; nitrites may be used in a form of aqueous solution by dissolving in water when mixed with the amide compounds in view of solubility. Dissolution of nitrites in water before mixing with amide compounds may help to easily dissolve the nitrites in the amide compounds. In case of using the aqueous solution, nitrite concentration
20 is not limited as long as it is dissolved in water; it is preferably 50 wt.% or less, and more preferably 20 wt.% or less.

[0023]

In the invention, the method to bring the crude hydrocarbons, including carbon disulfide and mercaptans, into contact with the amide compounds and
25 the nitrites is not particularly limited; there are (a) a method wherein the crude hydrocarbons, including carbon disulfide and mercaptans, the amide compounds and nitrites are made to mix and contact simultaneously and (b) a method wherein the amide compounds and nitrites are mixed, and then the crude hydrocarbons, including carbon disulfide and mercaptans, is brought

into contact with said mixture; the above (b) method is preferable in view of removing carbon disulfide and mercaptans. Further, both methods (a) and (b) may be batch type or continuous type.

[0024]

5 Though a quantitative ratio of amide compounds and crude hydrocarbons during a process of the contact (hereinafter, merely referred to as "a contact process") is not particularly limited, in a weight ratio of amide compounds/crude hydrocarbons, it is preferably 0.1/1 to 100/1, more preferably 0.5/1 to 50/1, and the most preferably 1/1 to 10/1. In case when the
10 ratio of amide compounds and crude hydrocarbons is within the above range, the sulfur-containing compounds can be sufficiently removed.

[0025]

 Though an amount of nitrites used in the contact process is not particularly limited, in the amide compounds, it is preferably 0.01 to 1,000
15 ppm, preferably 0.1 to 100 ppm, and the most preferably 0.5 to 50 ppm. In case when additional amount of nitrites is within the above arrange, the nitrites can be sufficiently dissolved in the amide compounds, and the sulfur-containing compounds can be efficiently removed.

[0026]

20 Though a quantitative ratio of nitrites and carbon disulfide is not particularly limited, with a mole ratio of nitrites/carbon disulfide, it is preferably 0.01/1 to 100/1, more preferably 0.02/1 to 50/1, and the most preferably 0.03/1 to 30/1. Though quantitative ratio of nitrites and mercaptans is not particularly limited, with a mole ratio of nitrites/mercaptans,
25 it is preferably 0.1/1 to 100/1, more preferably 0.2/1 to 50/1, and the most preferably 0.3/1 to 30/1. In case when an additional amount of nitrites is within the above range, the sulfur-containing compounds can be efficiently removed.

[0027]

Though a temperature during the contact process is not particularly limited, it is preferably 0 to 250 °C, and more preferably 10 to 200 °C. In case when the temperature during the contact is too low, there are cases that the sulfur-containing compounds are not efficiently removed, while when too high, unsaturated hydrocarbons in crude hydrocarbons may cause polymerization reaction and it may lead to a production of polymer compound and a decline in productivity. For instance, in case when isoprene is included in crude hydrocarbons and when a temperature during the contact is too high, a dimer of isoprene and the like may be produced decreasing isoprene yield.

10 [0028]

The contact process may be performed under an atmospheric pressure or under a pressure of around 0 to 3 MPa. Though the contact time is not particularly limited, it is preferably 1sec. to 30 minutes, and more preferably 1 minute to 180 minutes.

15 [0029]

Though the reason carbon disulfide and mercaptanes in crude hydrocarbons are removed by the contact with amide compounds and nitrites are not theoretically restricted, it is thought as following. Namely, carbon disulfide and mercaptanes react with amide compounds and nitrites by the contact process above, and subsequently, converted to sulfur-containing compounds of high boiling point or to sulfur-containing compounds of low boiling point. As a result, during or after the contact process, the sulfur-containing compounds of low boiling point volatilize through the distillation operation and the like, preferably through the distillation process; the sulfur-containing compounds of high boiling point become liquids or salts and separated as a residue. Consequently, carbon disulfide and mercaptanes in crude hydrocarbons are thought to be removed.

[0030]

Fig. 1 is a preferable embodiment of carbon disulfide and mercaptanes

removal method of the invention, however, the invention is not limited thereto. In an embodiment of Fig. 1, a mixture of amide compounds and a nitrite water solution are introduced from pipe 1 on a side surface upper side of contact vessel 3, and crude hydrocarbons including carbon disulfide and mercaptans are introduced from pipe 2 on a side surface lower side; they are brought into contact in vessel 3. Subsequently, hydrocarbon fractions are separated from amide compounds and nitrites, and purified hydrocarbons in which the sulfur-containing compounds are reduced is obtained from top pipe 4 of contact vessel 3. Though a separation condition is not particularly limited, in case when separating C5 fractions, executing the distillation process with keeping a liquid temperature to 120 to 160 °C after the contact process leads to obtain purified hydrocarbons from top pipe 4.

[0031]

A pressure-proof vessel equipped with an agitator or a circulator is preferably used as the contact vessel. After the above contact process in the pressure-proof vessel, purified hydrocarbons in which contents of carbon disulfide and mercaptanes are reduced is obtained from top pipe 4 by releasing pressure.

[0032]

An outflow from bottom pipe 5 of contact vessel 3 includes unreacted amide compounds, nitrites, and various additives, and the outflow may be collected for reuse.

[0033]

In an embodiment of Fig. 1, in case of removing carbon disulfide and mercaptans, in order to suppress a contamination of the contact vessel 3, heterocyclic polar compounds such as furfural, methyl furfural, hydroxymethyl furfural, thiophenecarboxyaldehyde, nicotinic aldehyde, pyridoxal and the like; aromatic nitro compounds such as nitrobenzene, nitrotoluene, nitroxylenes, nitrobenzyl, dinitrobenzene, trinitroxylenes and

the like; and aromatic aldehydes such as benzaldehyde, tolualdehyde, cuminaldehyde, phenylacetaldehyde, cinnamaldehyde, phthalaldehyde, isophthalaldehyde, terephthalaldehyde may be added to amide compounds as additives. Among all, furfural, nitrobenzene and benzaldehyde are preferable; 5 furfural is the most preferable.

[0034]

An additional amount of those additives are preferably 0.01 to 30 pts.wt. and more preferably 0.05 to 15 pts.wt., with respect to 100 pts.wt. of amide compounds.

10 [0035]

By bringing crude hydrocarbons into contact with amide compounds and nitrites, and then performing the distillation process, in which said hydrocarbons are separated from amide compounds and nitrites and collected thereof, a total content of carbon disulfide and mercaptanes included in the 15 obtained purified hydrocarbons is decreased; the total content is decreased to preferably 300 ppm or less, and more preferably 100 ppm or less, and the most preferably 50 ppm or less; the total content is decreased to a value lower than the total content of carbon disulfide and mercaptanes in crude hydrocarbons.

[0036]

20 As described above, in the sulfur-containing compound removal method of the invention, the crude hydrocarbons are preferably C4 fractions composed mainly of hydrocarbons having a carbon number of 4 or C5 fractions composed mainly of hydrocarbons having a carbon number of 5.

[0037]

25 In addition, the sulfur-containing compound removal method of the invention preferably further includes, after bringing crude hydrocarbons into contact with amide compounds and nitrites, a distillation process, in which said amide compounds and said nitrites are separated from the crude hydrocarbons and then purified hydrocarbons, in which content of the

sulfur-containing compounds are decreased, are collected.

[0038]

In addition, according to the sulfur-containing compound removal method of the invention, the sulfur-containing compounds in the crude hydrocarbons is preferably 1 ppm or more and 10,000 ppm or less; the sulfur-containing compounds in the purified hydrocarbons is preferably 300 ppm or less, and less than the sulfur-containing compounds in the crude hydrocarbons.

[0039]

Further, a manufacturing method of purified hydrocarbons of the invention preferably includes said sulfur-containing compound removal method.

EXAMPLES

[0040]

Hereinafter, the present invention will be described based on the examples and comparative examples, but the present invention is not limited to these examples. Note that “parts”, “%” and “ppm” in the examples and comparative examples are based on the mass unless mentioned otherwise. Measurements of the contents of the sulfur-containing compounds in the crude hydrocarbons and in the purified hydrocarbons are performed with the following equipment under the following conditions.

[0041]

Equipment: GC7890, manufactured by Agilent

Column: DB-1 (length: 30m, inner diameter: 0.32mm, film thickness: 0.25μm)

Column Temp: held at 40 °C for 10 minutes, subsequently raised by 10 °C per minute, held at 250 °C for 3 minutes

Inlet temperature: 140 °C

Carrier gas: helium (a flow amount per minute: 1.17 ml)

Detector: 355 sulfur chemiluminescence detector (SCD), manufactured by

Agilent

[0042]

<Example 1>

A stainless made pressure-proof vessel with agitator was charged with
5 69.0 parts of a crude C5 fraction solution (Composition: 2.1% C4
(hydrocarbons having a carbon number of 4), 22. 0% normal pentane, 20.1%
isopentane, 6.9% amylene, 7.4% isoamylene, 1.5% 1,4-pentadiene, 15.6%
isoprene, 10.6% piperylene, 1.1% cyclopentane, 2.5% cyclopentene, 6.6%
cyclopentadiene and 3.6% C6 (hydrocarbons having a carbon number of 6)),
10 including 13.3 ppm carbon disulfide and 2.0 ppm ethyl mercaptan, and 323.6
parts of a solution including 97.4 % dimethyl formamide, 2.6% furfural and
0.07 ppm sodium nitrite. The temperature was raised to 120°C while stirring
the mixed solution of said two solutions, held for 1 hour, and subsequently a
gaseous C5 fraction was extracted from the top of the vessel while keeping the
15 temperature of the solution at 120°C to 160°C. And then, 67.6 parts of purified
C5 fraction, including 9.8 ppm carbon disulfide and 1.3 ppm ethyl mercaptan,
was obtained. Also, 309.3 parts of a solution, not including both carbon
disulfide and ethyl mercaptan, was remained in the vessel. As a result, 27.8%
of carbon disulfide and 36.3% of ethyl mercaptan included in the crude C5
20 fraction solution were removed.

[0043]

<Comparative Example 1>

A stainless made pressure-proof vessel with agitator was charged with
64.4 parts of a crude C5 fraction solution (Composition: 2.1% C4
25 (hydrocarbons having a carbon number of 4), 22. 0% normal pentane, 20.1%
isopentane, 6.9% amylene, 7.4% isoamylene, 1.5% 1,4-pentadiene, 15.6%
isoprene, 10.6% piperylene, 1.1% cyclopentane, 2.5% cyclopentene, 6.6%
cyclopentadiene and 3.6% C6 (hydrocarbons having a carbon number of 6)),
including 26.9 ppm carbon disulfide and 1.8 ppm ethyl mercaptan, and 303.3

parts of a solution, including 97.4 % dimethyl formamide and 2.6% furfural and not including sodium nitrite. The temperature was raised to 120°C while stirring the mixed solution of said two solutions, held for 1 hour, and subsequently gaseous C5 fractions were extracted from the top of the vessel while keeping the temperature of the solution at 120°C to 160°C. And then, 63.9 parts of C5 fraction, including 27.1 ppm carbon disulfide and 1.8 ppm ethyl mercaptan, was obtained. Also, 288.6 parts of a solution, not including both carbon disulfide and ethyl mercaptan, was remained in the vessel. As a result, carbon disulfide included in the crude C5 fraction was not removed and only 0.8% of ethyl mercaptan was removed.

[0044]

<Example 2>

A stainless made pressure-proof vessel with agitator was charged with 8.6 parts of a crude C5 fraction solution (Composition: 94.1% isoprene and 2.8% 2-butyne), including 149.6 ppm carbon disulfide and 13.4 ppm ethyl mercaptan, and 46.4 parts of a solution including 96.1% dimethyl formamide, 3.9% furfural and 8.9 ppm sodium nitrite. The temperature was raised to 120°C while stirring the mixed solution, held for 1 hour, and subsequently a gaseous C5 fraction was extracted from the top of the vessel while keeping the temperature of the solution at 120°C to 160°C. And then, 8.6 parts of a purified C5 fraction, including 19.2 ppm carbon disulfide and 9.1 ppm ethyl mercaptan, was obtained. Also, 42.1 parts of a solution not including both carbon disulfide and ethyl mercaptan was remained in the vessel. As a result, 87.2% of carbon disulfide and 32.1% of ethyl mercaptan included in the crude C5 fraction solution were removed.

[0045]

<Example 3>

A stainless made pressure-proof vessel with agitator was charged with 9.6 parts of a crude C5 fraction solution (Composition: 94.1% isoprene and

2.8% 2-butyne), including 34.0 ppm carbon disulfide and 9.0 ppm ethyl mercaptan, and 51.8 parts of a solution including 96.1 % dimethyl formamide, 3.9% furfural and 3.3 ppm sodium nitrite. The temperature was raised to 120°C while stirring the mixed solution of said two solutions, held for 1 hour, and subsequently a gaseous C5 fraction was extracted from the top of the vessel while keeping the temperature of the solution at 120°C to 160°C. And then, 9.6 parts of a purified C5 fraction, including 8.3 ppm carbon disulfide and 5.7 ppm ethyl mercaptan, were obtained. Also, 45.2 parts of a solution not including both carbon disulfide and ethyl mercaptan was remained in the vessel. As a result, 75.6% of carbon disulfide and 36.7% of ethyl mercaptan included in the crude C5 fraction solution were removed.

The above results are shown in the following table.

[0046]

[Table 1]

	A crude C5 fraction			A purified C5 fraction			Removal rate (%)	
	Charged Amount (mass parts)	CS ₂ (ppm)	CH ₃ CH ₂ SH (ppm)	Collected Amount (mass parts)	CS ₂ (ppm)	CH ₃ CH ₂ SH (ppm)	CS ₂	CH ₃ CH ₂ SH
Ex. 1	69.0	13.3	2.0	67.6	9.8	1.3	27.8	36.3
Comp. Ex. 1	64.4	26.9	1.8	63.9	27.1	1.8	0	0.8
Ex. 2	8.6	149.6	13.4	8.6	19.2	9.1	87.2	32.1
Ex. 3	9.6	34.0	9.0	9.6	8.3	5.7	75.6	36.7

CS₂: carbon disulfide

5 CH₃CH₂SH: ethyl mercaptan

[0047]

Reference Signs List

- 1: pipe on the side surface upper side
- 10 2: pipe on the side surface lower side
- 3: contact vessel (pressure-proof vessel)
- 4: top pipe
- 5: bottom pipe

CLAIMS

1. A sulfur-containing compound removal method comprising
a step of bringing a crude hydrocarbon, comprising at least one sulfur-containing
5 compound selected from the group consisting of carbon disulfide and mercaptans, into
contact with an amide compound and a nitrite.
2. The sulfur-containing compound removal method as set forth in claim
1, wherein
10 the crude hydrocarbon is C4 fraction composed mainly of a hydrocarbon having
a carbon number of 4 or C5 fraction composed mainly of a hydrocarbon having a
carbon number of 5.
3. The sulfur-containing compound removal method as set forth in claim 1,
15 subsequent to the step of bringing the crude hydrocarbon into contact with the amide
compound and the nitrite, further comprising a distillation step, wherein
the amide compound and the nitrite are separated from the crude hydrocarbon
and then a purified hydrocarbon, in which a content of the sulfur-containing compound
is decreased, is collected.
20
4. The sulfur-containing compound removal method as set forth in claim 2,
subsequent to the step of bringing the crude hydrocarbon into contact with the amide
compound and the nitrite, further comprising a distillation step, wherein
the amide compound and the nitrite are separated from the crude hydrocarbon
25 and then a purified hydrocarbon, in which a content of the sulfur-containing compound
is decreased, is collected.
5. The sulfur-containing compound removal method as set forth in claim 3,
wherein

the content of sulfur-containing compound in the crude hydrocarbon is 1 ppm or more and 10,000 ppm or less, and

the content of the sulfur-containing compound in the purified hydrocarbon is 300 ppm or less and less than the content of the sulfur-containing compound in the crude
5 hydrocarbon.

6. The sulfur-containing compound removal method as set forth in claim 4, wherein

the content of sulfur-containing compound in the crude hydrocarbon is 1 ppm or
10 more and 10,000 ppm or less, and

the content of the sulfur-containing compound in the purified hydrocarbon is 300 ppm or less and less than the content of the sulfur-containing compound in the crude hydrocarbon.

15 7. A manufacturing method of the purified hydrocarbon including the sulfur-containing compound removal method as set forth in any one of claims 3 to 6.