

METHOD AND APPARATUS FOR HANDLING UNSATURATED HYDROCARBON

TECHNICAL FIELD

5 **[0001]** The present disclosure relates to a method for handling an unsaturated hydrocarbon and an apparatus for handling an unsaturated hydrocarbon.

BACKGROUND

10 **[0002]** Unsaturated hydrocarbons such as 1,3-butadiene and isoprene are used as monomers in raw materials of polymers in various fields such as synthetic rubbers and paints. In one example of a method that is conventionally used to obtain such an unsaturated hydrocarbon in high purity, a hydrocarbon mixture such as a C₄ fraction or a C₅ fraction obtained in production of ethylene through cracking of naphtha is distilled to separate and recover the desired
15 unsaturated hydrocarbon. Distillation of the hydrocarbon mixture is performed using a distillation column such as a tray column or a packed column.

20 **[0003]** One issue with unsaturated hydrocarbons such as mentioned above is that produced polymerized product may adhere to components of various pieces of equipment used in handling of the unsaturated hydrocarbon. For example, when an unsaturated hydrocarbon is separated and recovered using a distillation column such as described above, unintended polymerization of the unsaturated hydrocarbon may occur in the distillation column. Polymerized product that is deposited as a result of this polymerization reaction strongly
25 adheres to components inside the distillation column and causes various problems such as hindering liquid and gas flow, and reducing separation performance of the distillation column. Consequently, it is necessary to periodically suspend operation of a separation and recovery apparatus including the distillation column in order to remove the polymerized product
30 though cleaning by physical external force or the like.

[0004] PTL 1 proposes a technique of setting the amount of a sulfur-containing compound in raw material, in terms of the amount of sulfur, within a specific range with the aim of inhibiting deposition of polymerized product such as described above and limiting the reduction in efficiency

caused by periodically suspending operation of a separation and recovery apparatus.

CITATION LIST

5 Patent Literature

[0005] PTL 1: JP 2003-128595 A

SUMMARY

(Technical Problem)

10 [0006] On the other hand, there has been demand for a new technique that can resolve problems caused by polymerized products such as described above in a simpler manner. Accordingly, an objective of the present disclosure is to provide a method and an apparatus for handling an unsaturated hydrocarbon that enable efficient handling of the unsaturated hydrocarbon over a long
15 period.

(Solution to Problem)

[0007] The inventors conducted diligent investigation with the aim of solving the problem set forth above. Through this investigation, the inventors discovered that by coating the surface of a component included in equipment
20 such as a distillation column with a metal oxide and/or a metalloid oxide, adhesion of a polymerized product such as described above to the surface of the component can be inhibited, liquid and gas flow can be stabilized, and a desired process or operation can be performed efficiently over a long period. In this manner, the inventors completed the present disclosure.

25 [0008] Specifically, the present disclosure aims to advantageously solve the problem set forth above by disclosing a method for handling an unsaturated hydrocarbon comprising a step of handling a composition containing the unsaturated hydrocarbon using at least one piece of equipment selected from the group consisting of a distillation column, a heat exchanger, a reactor, a
30 pump, a pipe, and a valve, wherein at least one component of the equipment that comes into contact with the composition is a component including a coating containing at least one of a metal oxide and a metalloid oxide. It is difficult for polymerized product deposited through polymerization of an unsaturated hydrocarbon to adhere to a component that is coated by a metal

oxide and/or metalloid oxide coating in this manner. Therefore, equipment including this component can be used to efficiently handle an unsaturated hydrocarbon over a long period.

5 [0009] In the presently disclosed method for handling an unsaturated hydrocarbon, the unsaturated hydrocarbon may be an unsaturated hydrocarbon having a carbon number of at least 4 and not more than 10.

[0010] Moreover, in the presently disclosed method for handling an unsaturated hydrocarbon, the composition may be a hydrocarbon mixture having a 1,3-butadiene concentration of at least 0.1 mass% and not more than 10 99.9 mass% or a hydrocarbon mixture having an isoprene concentration of at least 0.1 mass% and not more than 99.9 mass%.

[0011] Furthermore, in the presently disclosed method for handling an unsaturated hydrocarbon, the coating preferably has an average thickness of at least 0.5 μm and not more than 100 μm . When the average thickness of the 15 coating is within the range set forth above, adhesion of polymerized product to the component can be further inhibited, and handling of the unsaturated hydrocarbon can be performed efficiently over a longer period.

Note that the average thickness of a coating on the surface of a component referred to in the present disclosure can be measured by radio 20 frequency glow discharge optical emission spectroscopy (rf-GD-OES).

[0012] In the presently disclosed method for handling an unsaturated hydrocarbon, the metal oxide is preferably at least one selected from the group consisting of chromium oxide, aluminum oxide, tin oxide, zirconium oxide, and yttrium oxide, and the metalloid oxide is preferably at least one 25 selected from the group consisting of boron oxide, silicon oxide, germanium oxide, arsenic oxide, tellurium oxide, and polonium oxide. When any one of the metal oxides and metalloid oxides listed above is used as the coating on the surface of the component, adhesion of polymerized product to the component can be further inhibited, and handling of the unsaturated 30 hydrocarbon can be performed efficiently over a longer period.

[0013] In the presently disclosed method for handling an unsaturated hydrocarbon, the component including a coating containing at least one of a metal oxide and a metalloid oxide may be a component that includes a base material and the coating on a surface of the base material, and in which the

base material contains at least one of iron and titanium.

Moreover, in the presently disclosed method for handling an unsaturated hydrocarbon, the component including a coating containing at least one of a metal oxide and a metalloid oxide preferably has a contact angle with water of 70° or less. When the contact angle of the surface of the component with water is 70° or less, adhesion of polymerized product to the component can be further inhibited, and handling of the unsaturated hydrocarbon can be performed efficiently over a longer period.

The contact angle of the surface of a component with water referred to in the present disclosure can be measured by a drop method. Specifically, the contact angle of the surface of a component with water can be obtained by performing measurements at 10 arbitrary points on the surface of the component under conditions of a measurement temperature of $23^{\circ}\text{C} \pm 3^{\circ}\text{C}$, a humidity of $50\% \text{ RH} \pm 20\% \text{ RH}$, a drop volume of $1 \mu\text{L}$, and a wait time from landing to measurement of 5 s, and then calculating an average value of the measurements as the contact angle.

[0014] In the presently disclosed method for handling an unsaturated hydrocarbon, the composition preferably further contains an alkali metal salt. When the composition contains an alkali metal salt, adhesion of polymerized product to the component can be further inhibited, and handling of the unsaturated hydrocarbon can be performed efficiently over a longer period.

Although it is not clear why adhesion of polymerized product to the component can be further inhibited through inclusion of an alkali metal salt in the composition, the reason is presumed to be as follows. When the composition contains an alkali metal salt, alkali metal ions (for example, sodium ions or potassium ions) originating from the alkali metal salt are adsorbed by the coating at the surface of the component through electrostatic interactions, and hydrophilicity of the surface of the component increases dramatically. By noticeably improving hydrophilicity of the surface of the component in this manner, affinity with a polymerized product of the unsaturated hydrocarbon, which is hydrophobic, is significantly reduced, and this can further inhibit adhesion of the polymerized product.

[0015] In the presently disclosed method for handling an unsaturated hydrocarbon, the alkali metal salt is preferably at least one selected from the

group consisting of NaNO_3 , NaNO_2 , Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4 , Na_2SO_4 , KNO_3 , KNO_2 , K_3PO_4 , K_2HPO_4 , KH_2PO_4 , and K_2SO_4 . When the composition contains any one of the alkali metal salts listed above, adhesion of polymerized product to the component can be further inhibited, and handling
5 of the unsaturated hydrocarbon can be performed efficiently over a longer period.

[0016] The presently disclosed method for handling an unsaturated hydrocarbon may, for example, be a method for separating and recovering an unsaturated hydrocarbon that is a target from a starting material, and the step
10 of handling the composition may, for example, be a step of performing distillation of a mixture containing the unsaturated hydrocarbon. In other words, the presently disclosed method for handling an unsaturated hydrocarbon may be a method for separating and recovering an unsaturated hydrocarbon that is a target from a starting material, comprising a step of
15 performing distillation of a mixture containing the unsaturated hydrocarbon using a distillation column, wherein at least one component of the distillation column that comes into contact with the mixture is a component including a coating containing at least one of a metal oxide and a metalloid oxide. The method set forth above enables efficient separation and recovery of the
20 unsaturated hydrocarbon over a long period.

[0017] In the presently disclosed method for handling an unsaturated hydrocarbon, the starting material used in separation and recovery of the unsaturated hydrocarbon that is a target therefrom may be a C_4 fraction or a C_5 fraction.

25 [0018] Moreover, in the presently disclosed method for handling an unsaturated hydrocarbon, the step of performing distillation of the mixture in separation and recovery of the unsaturated hydrocarbon that is a target from the starting material may be a step of performing extractive distillation.

[0019] Furthermore, the present disclosure aims to advantageously solve the
30 problem set forth above by disclosing an apparatus for handling an unsaturated hydrocarbon comprising equipment that handles a composition containing the unsaturated hydrocarbon, wherein the equipment is at least one selected from the group consisting of a distillation column, a heat exchanger, a reactor, a pump, a pipe, and a valve, and at least one component of the

equipment that comes into contact with the composition is a component including a coating containing at least one of a metal oxide and a metalloid oxide. An unsaturated hydrocarbon can be efficiently handled over a long period using equipment that includes a component coated by a metal oxide and/or metalloid oxide coating in this manner.

[0020] In the presently disclosed apparatus for handling an unsaturated hydrocarbon, the coating preferably has an average thickness of at least 0.5 μm and not more than 100 μm . When the average thickness of the coating is within the range set forth above, adhesion of polymerized product to the component can be further inhibited, and handling of the unsaturated hydrocarbon can be performed efficiently over a longer period.

[0021] In the presently disclosed apparatus for handling an unsaturated hydrocarbon, the metal oxide is preferably at least one selected from the group consisting of chromium oxide, aluminum oxide, tin oxide, zirconium oxide, and yttrium oxide, and the metalloid oxide is preferably at least one selected from the group consisting of boron oxide, silicon oxide, germanium oxide, arsenic oxide, tellurium oxide, and polonium oxide. When any one of the metal oxides and metalloid oxides listed above is used as the coating at the surface of the component, adhesion of polymerized product to the component can be further inhibited, and handling of the unsaturated hydrocarbon can be performed efficiently over a longer period.

[0022] In the presently disclosed apparatus for handling an unsaturated hydrocarbon, the component including a coating containing at least one of a metal oxide and a metalloid oxide may be a component that includes a base material and the coating on a surface of the base material, and in which the base material contains at least one of iron and titanium.

Moreover, in the presently disclosed apparatus for handling an unsaturated hydrocarbon, the component including a coating containing at least one of a metal oxide and a metalloid oxide preferably has a contact angle with water of 70° or less. When the contact angle of the surface of the component with water is 70° or less, adhesion of polymerized product to the component can be further inhibited, and handling of the unsaturated hydrocarbon can be performed efficiently over a longer period.

[0023] The presently disclosed apparatus for handling an unsaturated

hydrocarbon may, for example, be an apparatus for separating and recovering an unsaturated hydrocarbon, the equipment may, for example, be a distillation column, and the distillation column may, for example, perform distillation of a mixture containing the unsaturated hydrocarbon. In other words, the
5 presently disclosed apparatus for handling an unsaturated hydrocarbon may be a separation and recovery apparatus for an unsaturated hydrocarbon comprising a distillation column that performs distillation of a mixture containing the unsaturated hydrocarbon, wherein at least one component of the distillation column that comes into contact with the mixture is a
10 component including a coating containing at least one of a metal oxide and a metalloid oxide. The apparatus set forth above enables efficient separation and recovery of the unsaturated hydrocarbon over a long period.

[0024] In a case in which the presently disclosed apparatus for handling an unsaturated hydrocarbon is a separation and recovery apparatus for an
15 unsaturated hydrocarbon, the distillation column may be an extractive distillation column.

(Advantageous Effect)

[0025] According to the present disclosure, it is possible to provide a method and an apparatus for handling an unsaturated hydrocarbon that enable efficient
20 handling of the unsaturated hydrocarbon over a long period.

Moreover, according to the present disclosure, it is possible to provide a separation and recovery method and a separation and recovery apparatus for an unsaturated hydrocarbon that enable efficient separation and recovery of the unsaturated hydrocarbon over a long period.

25

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] In the accompanying drawings:

FIG. 1 illustrates schematic configuration of one example of a distillation column used in a presently disclosed separation and recovery
30 method and a presently disclosed separation and recovery apparatus; and

FIG. 2 illustrates schematic configuration of one example of a presently disclosed separation and recovery apparatus for an unsaturated hydrocarbon.

DETAILED DESCRIPTION

[0027] The following provides a detailed description of embodiments of the present disclosure.

5 The presently disclosed method is a method for handling an unsaturated hydrocarbon. Moreover, the presently disclosed apparatus is an apparatus for handling an unsaturated hydrocarbon that can, for example, be used to handle an unsaturated hydrocarbon using the presently disclosed method.

10 [0028] The presently disclosed method for handling an unsaturated hydrocarbon includes a step of handling a composition containing the unsaturated hydrocarbon using specific equipment. Moreover, the presently disclosed apparatus for handling an unsaturated hydrocarbon includes specific equipment for implementing a step of handling the composition.

15 No specific limitations are placed on the step of handling the composition containing the unsaturated hydrocarbon using the specific equipment other than being a process or operation in which the specific equipment comes into contact with the composition (for example, inside of the equipment). Examples of the step of handling the composition using the specific equipment include a step of distilling the composition inside a distillation column; a step of heating or cooling the composition by passing
20 the composition through a heat exchanger; a step of subjecting the composition to a chemical reaction (for example, a polymerization reaction of the unsaturated hydrocarbon) inside a reactor; a step of transferring the composition using a pump (for example, a compressor); a step of transferring the composition inside a pipe; and a step of controlling the transfer direction, pressure, and/or flow rate of the composition using a valve.
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No specific limitations are placed on the composition containing the unsaturated hydrocarbon so long as it contains the unsaturated hydrocarbon. For example, the composition may be a composition that is composed solely
30 of one or more unsaturated hydrocarbons or may be a composition that contains one or more unsaturated hydrocarbons and one or more substances other than unsaturated hydrocarbons. The composition containing the unsaturated hydrocarbon may, for example, be a starting material such as a C₄ fraction or a C₅ fraction subsequently described in the "Separation and

recovery method for unsaturated hydrocarbon” section.

[0029] The specific equipment includes a component having a surface that is partially or fully covered by a coating containing at least one of a metal oxide and a metalloid oxide at a location that comes into contact with the composition containing the unsaturated hydrocarbon (hereinafter, also referred to as an “oxide-coated component”). The coating at the surface of the oxide-coated component is stably present without readily detaching from the surface of the component or contributing to superfluous chemical reactions. This coating can inhibit adhesion of polymerized product to the surface of the component when the polymerized product is deposited inside the specific equipment during handling of the unsaturated hydrocarbon.

In the step of handling the composition containing the unsaturated hydrocarbon using the specific equipment, the temperature of the composition may be set as 30°C or higher, or as 40°C or higher, or may be set as 200°C or lower, or as 180°C or lower. When the presently disclosed method and/or apparatus is used, adhesion of polymerized product to the surface of the component can be sufficiently inhibited even when the temperature of the composition is within a range such as set forth above in which deposition of polymerized product tends to occur.

[0030] The following describes a method for separating and recovering an unsaturated hydrocarbon that is a target from a starting material (separation and recovery method for an unsaturated hydrocarbon) as one example of the presently disclosed method, and also describes an apparatus for separating and recovering an unsaturated hydrocarbon that is a target from a starting material (separation and recovery apparatus for an unsaturated hydrocarbon) as one example of the presently disclosed apparatus. However, the presently disclosed method and apparatus are not limited to the following examples.

[0031] A separation and recovery method for an unsaturated hydrocarbon that is one aspect of the presently disclosed method (hereinafter, also referred to simply as the “presently disclosed separation and recovery method for an unsaturated hydrocarbon”) can be used in separation and recovery of an unsaturated hydrocarbon that is a target from a starting material that contains the unsaturated hydrocarbon. A separation and recovery apparatus for an unsaturated hydrocarbon that is one aspect of the presently disclosed

apparatus (hereinafter, also referred to simply as the “presently disclosed separation and recovery apparatus for an unsaturated hydrocarbon”) can suitably be used in separation and recovery of an unsaturated hydrocarbon using the aforementioned separation and recovery method for an unsaturated
5 hydrocarbon.

[0032] (Separation and recovery method for unsaturated hydrocarbon)

In the presently disclosed separation and recovery method for an unsaturated hydrocarbon, an operation of distillation using a distillation column is performed once or a plurality of times with respect to a mixture
10 containing an unsaturated hydrocarbon in separation and recovery of the unsaturated hydrocarbon from a starting material. A feature of the method is that at least one performance of the distillation is performed using a distillation column including the previous described oxide-coated component at a location that comes into contact with the mixture containing the
15 unsaturated hydrocarbon.

The coating at the surface of the oxide-coated component is stably present without readily detaching from the surface of the component or contributing to superfluous chemical reactions even under harsh conditions inside the distillation column. Moreover, the coating can inhibit polymerized
20 product adhering to the surface of the component when the polymerized product is deposited inside the distillation column during separation and recovery of the unsaturated hydrocarbon. Consequently, destabilization of liquid and gas flow tends not to occur when the presently disclosed separation and recovery method for an unsaturated hydrocarbon is used even in a
25 situation in which separation and recovery are performed continuously over a long period. This can reduce the frequency with which it is necessary to perform large-scale cleaning that is accompanied by suspension of operation of a separation and recovery apparatus.

[0033] <Starting material>

30 No specific limitations are placed on the starting material so long as it contains an unsaturated hydrocarbon and examples thereof include any C₄ hydrocarbon mixture that contains an unsaturated hydrocarbon having a carbon number of 4, such as a C₄ fraction obtained in production of ethylene through cracking of naphtha; any C₅ hydrocarbon mixture containing an

unsaturated hydrocarbon having a carbon number of 5, such as a C₅ fraction obtained in production of ethylene in the same manner as the C₄ fraction; and a crude mixture containing unreacted unsaturated hydrocarbon that is recovered after any polymerization reaction.

5 Of these examples, a C₄ fraction and a C₅ fraction can suitably be used as the starting material.

[0034] <Unsaturated hydrocarbon and mixture containing the same>

Examples of the unsaturated hydrocarbon that is contained in the starting material and is a target for separation and recovery include, but are
10 not specifically limited to, unsaturated hydrocarbons having a carbon number of at least 4 and not more than 10 such as isoprene, piperylene, dicyclopentadiene, and 1,3-butadiene.

Note that the mixture containing the unsaturated hydrocarbon that is a target for distillation may be the previously described starting material or a
15 fraction obtained through distillation of the starting material. More specifically, the mixture may, for example, be a hydrocarbon mixture containing 1,3-butadiene in a concentration of at least 0.1 mass% and not more than 99.9 mass% or a hydrocarbon mixture containing isoprene in a concentration of at least 0.1 mass% and not more than 99.9 mass%.

20 The mixture containing the unsaturated hydrocarbon preferably further contains an alkali metal salt. When the mixture contains an alkali metal salt, adhesion of polymerized product to the component can be further inhibited, and separation and recovery of the unsaturated hydrocarbon can be performed efficiently over a longer period.

25 The alkali metal salt is preferably NaNO₃, NaNO₂, Na₃PO₄, Na₂HPO₄, NaH₂PO₄, Na₂SO₄, KNO₃, KNO₂, K₃PO₄, K₂HPO₄, KH₂PO₄, or K₂SO₄, and more preferably NaNO₂ from a viewpoint of further inhibiting adhesion of polymerized product to the component, but is not specifically limited to these examples.

30 One of these alkali metal salts may be used individually, or two or more of these alkali metal salts may be used in combination.

[0035] <Distillation using distillation column>

In order to obtain the target unsaturated hydrocarbon from the starting material set forth above, it is preferable that a distillation operation is

performed a plurality of times to separate a plurality of components having different boiling points. In the presently disclosed separation and recovery method for an unsaturated hydrocarbon, at least one of these distillation operations is performed using a distillation column including an oxide-coated component.

The component having a coating at the surface thereof in the distillation column may be any component that comes into contact with the mixture containing the unsaturated hydrocarbon during distillation. For example, the component may be a tray, a distillation column main shell, a nozzle, a seal pan, a tray weir, a distributor, a collector, or a chimney tray.

[0036] The presently disclosed separation and recovery method for an unsaturated hydrocarbon includes, for example, an extractive distillation step of performing extractive distillation of a starting material to obtain a fraction containing a target unsaturated hydrocarbon and an impurity removal step of removing an impurity other than the target unsaturated hydrocarbon from the fraction obtained through the extractive distillation step. In the presently disclosed separation and recovery method for an unsaturated hydrocarbon, the distillation column including an oxide-coated component may be used in extractive distillation in the aforementioned extractive distillation step or may be used in impurity removal in the aforementioned impurity removal step.

[0037] [Distillation column]

One example of a distillation column that can be used in the presently disclosed separation and recovery method for an unsaturated hydrocarbon is an extractive distillation column such as illustrated in FIG. 1, for example.

Note that although the following describes a case in which the extractive distillation column in FIG. 1 includes an "oxide-coated tray" (tray having a surface that is partially or fully covered by a coating including at least one of a metal oxide and a metalloid oxide) as an oxide-coated component, the present disclosure is not limited to this case.

[0038] -Example of configuration of distillation column-

A distillation column 1 illustrated in FIG. 1 includes a column main body 2, a condenser 3 that cools and liquifies gas (vapor) discharged from the top of the column main body 2, a reflux drum 4 that stores a fraction liquified by the condenser 3, a reflux line 5 that resupplies a portion of the fraction

stored in the reflux drum 4 at a position near the top of the column main body, a reboiler 6 located at the bottom of the column main body 2, and trays 7 that divide an internal space of the column main body 2. Note that each of the trays 7 includes a plurality of holes. Although the number of trays 7 is schematically illustrated as being 7 stages, the number of trays 7 is not specifically limited. For example, the number of trays 7 may be set as 50 stages to 300 stages in consideration of the energy cost necessary for distillation.

When the distillation column 1 is used to perform distillation of a mixture containing an unsaturated hydrocarbon, the mixture containing the unsaturated hydrocarbon may be gasified as necessary and then supplied into the column main body 2. Note that any solvent may also be supplied into the column main body 2 as necessary. The solvent may be any of the solvents subsequently described in the "Separation and recovery apparatus for unsaturated hydrocarbon" section. Moreover, the previously described alkali metal salt or a polymerization inhibitor such as subsequently described in the "Separation and recovery apparatus for unsaturated hydrocarbon" section may be included in the solvent so as to enable addition thereof to the mixture containing the unsaturated hydrocarbon. The mixture containing the unsaturated hydrocarbon and the solvent that is supplied as necessary are heated and converted to gas by the reboiler 6, and rise inside the column main body 2 by passing mainly through the holes in the trays 7. In the distillation column used in the presently disclosed separation and recovery method for an unsaturated hydrocarbon, it is preferable that at least one of the trays is an oxide-coated tray. By using an oxide-coated tray as a tray when the distillation column illustrated in FIG. 1 is used, blocking of holes in the tray due to deposition of polymerized product can be prevented, and good flow of gas, in particular, can be maintained even when distillation is performed continuously over a long period.

[0039] -Oxide-coated component-

The coating of the oxide-coated component contains a metal oxide and/or a metalloid oxide. Examples of the metal oxide include chromium oxide such as chromium(II) oxide, chromium(III) oxide, chromium(IV) oxide, and chromium(VI) oxide; aluminum oxide such as alumina (Al_2O_3); tin oxide

such as tin(II) oxide and tin(VI) oxide; zirconium oxide such as zirconia (ZrO_2); and yttrium oxide such as yttrium(III) oxide. Examples of the metalloid oxide include boron oxide such as diboron trioxide (B_2O_3); silicon oxide such as silica (SiO_2); germanium oxide such as germanium(IV) oxide; 5 arsenic oxide such as diarsenic trioxide (As_2O_3) and diarsenic pentaoxide (As_2O_5); tellurium oxide such as tellurium dioxide (TeO_2) and tellurium trioxide (TeO_3); and polonium oxide such as polonium monoxide (PoO), polonium dioxide (PoO_2), and polonium trioxide (PoO_3). One of these metal oxides and metalloid oxides may be used individually, or two or more of these 10 metal oxides and metalloid oxides may be used in combination. Of these metal oxides and metalloid oxides, at least one of chromium oxide and silicon oxide is preferably contained in the coating, and chromium oxide is more preferably contained in the coating from a viewpoint of further inhibiting adhesion of polymerized product to the component.

15 **[0040]** Although no specific limitations are placed on the average thickness of the coating of the oxide-coated component, the average thickness is preferably 0.5 μm or more, more preferably 10 μm or more, and even more preferably 30 μm or more from a viewpoint of further inhibiting adhesion of polymerized product to the component. On the other hand, the average 20 thickness of the coating of the oxide-coated component is preferably 100 μm or less, and more preferably 50 μm or less when the balance of cost with the aforementioned effect of inhibiting polymerized product adhesion is taken into account.

[0041] The type of base material that the coating is formed on is not 25 specifically limited. For example, a base material containing iron and/or titanium can suitably be used. The thickness of the base material can be adjusted as appropriate in consideration of the type of component in which the base material on which the coating is formed is used, and also the production cost and rigidity of the oxide-coated component.

30 The oxide-coated component preferably has a contact angle with water of 70° or less. When the contact angle of the surface of the oxide-coated component with water is 70° or less, adhesion of polymerized product to the component can be further inhibited, and handling of the unsaturated hydrocarbon can be performed efficiently over a longer period. Although no

specific limitations are placed on the lower limit of the contact angle of the oxide-coated component with water, the contact angle is normally 30° or more.

5 [0042] No specific limitations are placed on the method by which a coating of an oxide is provided at the surface of the base material. For example, a coating of an oxide may be provided at the surface of the base material by immersing the base material in a solution containing a metal oxide and/or metalloid ion oxide, subsequently performing baking of the base material, and further repeating immersion and baking. Note that through inclusion of
10 metaphosphoric acid or the like in the solution used for immersion, the contact angle with water can be reduced, and adhesion of polymerized product can be further inhibited.

Examples of methods by which a coating of an oxide may be provided on the surface of the base material include methods described in JP S63-57783
15 A, JP H10-18052 A, and JP 3220012 B, for example.

[0043] (Separation and recovery apparatus for unsaturated hydrocarbon)

The presently disclosed separation and recovery apparatus for an unsaturated hydrocarbon can suitably be used in separation and recovery of an unsaturated hydrocarbon for a starting material using the presently disclosed
20 separation and recovery method for an unsaturated hydrocarbon set forth above. In one example, the presently disclosed separation and recovery apparatus may have a configuration such as illustrated in FIG. 2, for example. The following describes the separation and recovery apparatus illustrated in FIG. 2 using an example in which the starting material is a C₄ hydrocarbon
25 mixture and the unsaturated hydrocarbon that is a target for separation and recovery is 1,3-butadiene.

[0044] A separation and recovery apparatus 100 illustrated in FIG. 2 includes an extractive distillation section 10 that obtains a fraction (A) containing 1,3-butadiene and an extract (B) through extractive distillation of the C₄
30 hydrocarbon mixture used as the starting material, a stripping section 20 that recovers 1,3-butadiene and solvent contained in the extract (B) obtained in the extractive distillation section 10, and an impurity removal section 30 that removes impurities other than 1,3-butadiene from the fraction (A) obtained in the extractive distillation section 10. The previously described distillation

column including an oxide-coated component is used as a distillation column in at least one of the extractive distillation section 10, the stripping section 20, and the impurity removal section 30 of the separation and recovery apparatus 100. In the separation and recovery apparatus 100, it is preferable that a distillation column including an oxide-coated component is used as an extractive distillation column in the extractive distillation section 10, and more preferable that a distillation column including an oxide-coated tray is used as an extractive distillation column in the extractive distillation section 10. The following describes a case in which a distillation column including an oxide-coated tray is used as an extractive distillation column in the extractive distillation section 10.

[0045] <Extractive distillation section>

The extractive distillation section 10 includes, for example, an evaporation column 11 that gasifies the C₄ hydrocarbon mixture, a first extractive distillation column 12 (distillation column including oxide-coated tray; e.g., having structure illustrated in FIG. 1) that separates the C₄ hydrocarbon mixture gasified in the evaporation column 11 into a fraction (C) and an extract (D) by extractive distillation, a stripping column 13 that removes solvent from the extract (D), a compressor 14 that pressurizes a fraction obtained through removal of solvent from the extract (D), and a second extractive distillation column 15 (distillation column including oxide-coated tray; e.g., having structure illustrated in FIG. 1) that separates the fraction pressurized by the compressor 14 into a fraction (A) and an extract (B) by extractive distillation.

[0046] In the first extractive distillation column 12, by supplying solvent from an upper stage relative to a supply stage of the C₄ hydrocarbon mixture and performing extractive distillation of the C₄ hydrocarbon mixture, a fraction (C) containing butanes, butenes, and the like that have lower solubility than 1,3-butadiene with respect to the solvent is distilled from the top of the column and an extract (D) containing 1,3-butadiene and vinylacetylene is drained from the bottom of the column. The solvent that is supplied into the first extractive distillation column 12 may be a known solvent that is used in extractive distillation of C₄ hydrocarbon mixtures (for example, dimethylformamide (DMF)) such as described in JP 2003-128595 A,

for example. Moreover, an alkali metal salt such as previously described is preferably supplied into the first extractive distillation column 12 from a viewpoint of further inhibiting adhesion of polymerized product to a component. In addition, a known polymerization inhibitor (exclusive of those
5 corresponding to the alkali metal salt) may be supplied into the first extractive distillation column 12 from a viewpoint of suppressing production of polymerized product. Although no specific limitations are placed on the method by which the alkali metal salt and the polymerization inhibitor are supplied, it is preferable that the alkali metal salt and the polymerization
10 inhibitor are dissolved in the solvent and are supplied into the first extractive distillation column 12 together with the solvent.

[0047] In the stripping column 13, solvent is drained from the bottom of the column and a fraction containing 1,3-butadiene and vinylacetylene is distilled from the top of the column. Note that solvent that is recovered in the stripping
15 column 13 may optionally be reused in the first extractive distillation column 12, the second extractive distillation column 15, or the like.

[0048] In the second extractive distillation column 15, by supplying solvent from an upper stage relative to a supply stage of the fraction containing 1,3-butadiene and vinylacetylene that is distilled from the stripping column 13 and performing extractive distillation of the fraction containing 1,3-butadiene
20 and vinylacetylene, a fraction (A) containing 1,3-butadiene is distilled from the top of the column and an extract (B) containing vinylacetylene and the like that have higher solubility than 1,3-butadiene with respect to the solvent is drained from the bottom of the column. The solvent that is supplied into the
25 second extractive distillation column 15 may be a known solvent that is used in extractive distillation of C₄ hydrocarbon mixtures (for example, DMF) such as described in JP 2003-128595 A, for example. Moreover, an alkali metal salt such as previously described is preferably supplied into the second extractive
30 distillation column 15 from a viewpoint of further inhibiting adhesion of polymerized product to a component. In addition, a known polymerization inhibitor (exclusive of those corresponding to the alkali metal salt) may be supplied into the second extractive distillation column 15 from a viewpoint of suppressing production of polymerized product. Although no specific limitations are placed on the method by which the alkali metal salt and the

polymerization inhibitor are supplied, it is preferable that the alkali metal salt and the polymerization inhibitor are dissolved in the solvent and are supplied into the second extractive distillation column 15 together with the solvent.

[0049] <Stripping section>

5 The stripping section 20 includes, for example, a first stripping column 21 for recovering 1,3-butadiene that is mixed into the extract (B) and a second stripping column 22 that recovers solvent from the extract (B) after recovery of 1,3-butadiene.

10 **[0050]** In the first stripping column 21, a fraction containing 1,3-butadiene that was mixed into the extract (B) is distilled from the top of the column and a bottom liquid containing vinylacetylene and the like is drained from the bottom of the column. The fraction containing 1,3-butadiene that is distilled from the top of the first stripping column 21 may optionally be returned to the second extractive distillation column 15.

15 **[0051]** In the second stripping column 22, a fraction (high VA fraction) containing vinylacetylene and the like that were contained in the bottom liquid from the first stripping column 21 is distilled from the top of the column and solvent is drained from the bottom of the column. Note that solvent that is recovered in the second stripping column 22 may optionally be
20 reused in the first extractive distillation column 12, the second extractive distillation column 15, or the like.

[0052] <Impurity removal section>

 The impurity removal section 30 includes, for example, a low boiling point substance removal column 31 that removes impurities having a lower
25 boiling point than 1,3-butadiene that are contained in the fraction (A) obtained in the second extractive distillation column 15 and a high boiling point substance removal column 32 that removes impurities having a higher boiling point than 1,3-butadiene.

30 **[0053]** In the low boiling point substance removal column 31, a fraction (low boiling point fraction) containing low boiling point impurities such as methylacetylene is distilled from the top of the column and a bottom liquid in which 1,3-butadiene is enriched is drained from the bottom of the column.

[0054] In the high boiling point substance removal column 32, a fraction in which 1,3-butadiene is further enriched is distilled from the top of the column

and a fraction (high boiling point fraction) containing high boiling point impurities such as 1,2-butadiene is drained from the bottom of the column.

[0055] Although the presently disclosed separation and recovery apparatus for an unsaturated hydrocarbon is described above using one example, the presently disclosed separation and recovery apparatus for an unsaturated hydrocarbon is not limited to the preceding example. For example, although 1,3-butadiene is separated and recovered from a C₄ hydrocarbon mixture used as a starting material in the previously described example, a C₅ hydrocarbon mixture may be used as a starting material and isoprene may be separated and recovered from this starting material in the presently disclosed separation and recovery apparatus for an unsaturated hydrocarbon, or a crude mixture containing unreacted unsaturated hydrocarbon that is recovered after any polymerization reaction may be used as a starting material and a desired unsaturated hydrocarbon may be separated and recovered from this starting material in the presently disclosed separation and recovery apparatus for an unsaturated hydrocarbon.

EXAMPLES

[0056] The following provides a more detailed description of the present disclosure through examples. However, the present disclosure is not limited to these examples.

[0057] (Example 1)

<Oxide-coated tray>

A tray including a coating containing chromium(III) oxide as a main component (base material: SUS (stainless steel); average thickness of coating: 30 μ m) was prepared as an oxide-coated tray. The contact angle of the oxide-coated tray with water was measured to be 63°.

<Separation and recovery of 1,3-butadiene>

Separation and recovery of 1,3-butadiene from a C₄ hydrocarbon mixture formed from a C₄ fraction obtained in production of ethylene through cracking of naphtha was performed using a separation and recovery apparatus that was the separation and recovery apparatus 100 illustrated in FIG. 2 and that included a distillation column including the previously described oxide-coated tray as the second extractive distillation column 15. The specific

procedure was as follows.

[0058] [Extractive distillation step]

First, a C₄ fraction (1,3-butadiene concentration: 40 mass%) used as a starting material was supplied into the evaporation column 11 and was
5 gasified.

Next, the gasified C₄ fraction was supplied into the first extractive distillation column together with DMF (containing NaNO₂ (sodium nitrite) in a concentration of 20 ppm by weight) as an extractant (solvent). The supply position of the C₄ fraction was taken to be a roughly middle stage in the first
10 extractive distillation column 12 and the supply position of the DMF was taken to be an upper stage relative to the supply position of the gasified C₄ fraction. In accompaniment to supply of the C₄ fraction and the solvent, heating was performed by a reboiler located at the bottom of the first extractive distillation column 12 in order to perform a first stage of extractive
15 distillation. A fraction (C) containing butanes, butenes, and the like was removed from the top of the first extractive distillation column 12. On the other hand, an extract (D) containing 1,3-butadiene and vinylacetylene was removed from the bottom of the first extractive distillation column 12.

The removed extract (D) was supplied at a roughly middle stage in the
20 stripping column 13 and was heated by a reboiler located at the bottom of the stripping column 13 in order to perform distillation. DMF that was separated from the extract (D) was discharged from the bottom of the stripping column 13. On the other hand, a fraction containing large quantities of 1,3-butadiene and vinylacetylene was removed from the top of the stripping column 13.

25 Next, the fraction containing 1,3-butadiene and vinylacetylene was supplied near a lower stage of the second extractive distillation column 15 together with DMF (containing NaNO₂ (sodium nitrite) in a concentration of 20 ppm by weight) as an extractant (solvent) and was heated by a reboiler located at the bottom of the second extractive distillation column 15 in order
30 to perform a second stage of extractive distillation. The distillation column 1 illustrated in FIG. 1 was used as the second extractive distillation column 15. (However, note that the number of trays was 60 and all of the trays were oxide-coated trays such as previously described.) The supply position of the fraction was taken to be a roughly middle stage in the second extractive

distillation column 15 and the supply position of the DMF was taken to be an upper stage relative to the supply position of the fraction. The pressure at the bottom of the second extractive distillation column 15 was maintained at an absolute pressure of 5 atm and the temperature at the bottom of the second
5 extractive distillation column 15 was controlled to 128°C. The temperature at the top of the second extractive distillation column 15 was 45°C. A gas containing 1,3-butadiene in a high concentration was removed from the top of the second extractive distillation column 15 as a fraction (A). On the other hand, impurities having lower volatility (solubility) than butadiene, such as
10 vinylacetylene, were removed from the bottom of the second extractive distillation column 15 as an extract (B).

The extract (B) was fed to the stripping section 20, where a fraction containing 1,3-butadiene that was mixed into the extract (B) was recovered in the first stripping column 21. This 1,3-butadiene-containing fraction was
15 returned to the second extractive distillation column 15 from the first stripping column 21. In the second stripping column 22, a high VA fraction containing vinylacetylene in a high concentration was discharged from the top of the column and separated DMF was discharged from the bottom of the column.

20 **[0059]** [Impurity removal step]

The fraction (A) removed in the previously described extractive distillation step was supplied at a roughly middle stage in the low boiling point substance removal column 31 and was heated by a reboiler located at the bottom of the low boiling point substance removal column 31 in order to
25 perform distillation. The pressure at the bottom of the low boiling point substance removal column 31 was maintained at an absolute pressure of 4 atm and the temperature at the bottom of the low boiling point substance removal column 31 was maintained at 50°C. A bottom liquid in which 1,3-butadiene was enriched was removed from the bottom of the low boiling point substance
30 removal column 31. On the other hand, methylacetylene (impurity having a lower boiling point than butadiene) was removed from the top of the low boiling point substance removal column 31 as a low boiling point fraction.

Next, the removed bottom liquid was supplied at a roughly middle stage in the high boiling point substance removal column 32 and was heated

by a reboiler located at the bottom of the high boiling point substance removal column 32 in order to perform distillation. The pressure at the bottom of the high boiling point substance removal column 32 was maintained at an absolute pressure of 5 atm and the temperature at the bottom of the high boiling point substance removal column 32 was maintained at 60°C. Impurities having a higher boiling point than butadiene (for example, cis-2-butene and pentene) were removed from the bottom of the high boiling point substance removal column 32 as a high boiling point fraction. On the other hand, a fraction in which 1,3-butadiene was further enriched was removed from the top of the high boiling point substance removal column 32. The concentration of 1,3-butadiene in the fraction obtained from the top of the high boiling point substance removal column 32 was confirmed to be 99 mass% or more.

[0060] [Continuous operation]

The trays in the second extractive distillation column 15 were inspected after performing the previously described extractive distillation step and impurity removal step continuously for 300 days. The amount of polymerized product adhered to the surface of each of the trays was very small and blocking of holes in the trays was not observed.

[0061] (Comparative Example 1)

An extractive distillation step and an impurity removal step were performed in the same way as in Example 1 with the exception that an extractive distillation column including trays made of SUS that was not coated by an oxide instead of oxide-coated trays was used as the second extractive distillation column 15. The contact angle of the trays made of SUS with water was measured to be 80°.

The trays in the second extractive distillation column 15 were inspected after performing the previously described extractive distillation step and impurity removal step continuously for 300 days. The amount of polymerized product adhered to the surface of each of the trays was greater than (roughly double) the amount in Example 1 and blocking of holes in the trays was observed.

INDUSTRIAL APPLICABILITY

[0062] According to the present disclosure, it is possible to provide a method

and an apparatus for handling an unsaturated hydrocarbon that enable efficient separation and recovery of the unsaturated hydrocarbon over a long period.

REFERENCE SIGNS LIST

5	[0063]	1	distillation column
		2	column main body
		3	condenser
		4	reflux drum
		5	reflux line
10		6	reboiler
		7	tray
		10	extractive distillation section
		11	evaporation column
		12	first extractive distillation column
15		13	stripping column
		14	compressor
		15	second extractive distillation column
		20	stripping section
		21	first stripping column
20		22	second stripping column
		30	impurity removal section
		31	low boiling point substance removal column
		32	high boiling point substance removal column
		100	separation and recovery apparatus

CLAIMS

1. A method for handling an unsaturated hydrocarbon comprising a step of handling a composition containing the unsaturated hydrocarbon using
5 at least one piece of equipment selected from the group consisting of a distillation column, a heat exchanger, a reactor, a pump, a pipe, and a valve, wherein at least one component of the equipment that comes into contact with the composition is a component including a coating containing at least one of a metal oxide and a metalloid oxide.
- 10 2. The method according to claim 1, wherein the unsaturated hydrocarbon is an unsaturated hydrocarbon having a carbon number of at least 4 and not more than 10.
- 15 3. The method according to claim 1 or 2, wherein the composition is a hydrocarbon mixture having a 1,3-butadiene concentration of at least 0.1 mass% and not more than 99.9 mass% or a hydrocarbon mixture having an isoprene concentration of at least 0.1 mass% and not more than 99.9 mass%.
- 20 4. The method according to any one of claims 1 to 3, wherein the coating has an average thickness of at least 0.5 μm and not more than 100 μm .
5. The method according to any one of claims 1 to 4, wherein the metal oxide is at least one selected from the group consisting of chromium
25 oxide, aluminum oxide, tin oxide, zirconium oxide, and yttrium oxide, and the metalloid oxide is at least one selected from the group consisting of boron oxide, silicon oxide, germanium oxide, arsenic oxide, tellurium oxide, and polonium oxide.
- 30 6. The method according to any one of claims 1 to 5, wherein the component including a coating containing at least one of a metal oxide and a metalloid oxide includes a base material and the coating on a surface of the base material, and the base material contains at least one of iron and titanium.

7. The method according to any one of claims 1 to 6, wherein the component including a coating containing at least one of a metal oxide and a metalloid oxide has a contact angle with water of 70° or less.

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8. The method according to any one of claims 1 to 7, wherein the composition further contains an alkali metal salt.

9. The method according to claim 8, wherein the alkali metal salt is at least one selected from the group consisting of NaNO₃, NaNO₂, Na₃PO₄, Na₂HPO₄, NaH₂PO₄, Na₂SO₄, KNO₃, KNO₂, K₃PO₄, K₂HPO₄, KH₂PO₄, and K₂SO₄.

10. The method according to any one of claims 1 to 9, wherein the method is a method for separating and recovering an unsaturated hydrocarbon that is a target from a starting material, and the step of handling the composition is a step of performing distillation of a mixture containing the unsaturated hydrocarbon.

11. The method according to claim 10, wherein the starting material is a C₄ fraction or a C₅ fraction.

12. The method according to claim 10 or 11, wherein the step of performing distillation of the mixture is a step of performing extractive distillation.

13. An apparatus for handling an unsaturated hydrocarbon comprising equipment that handles a composition containing the unsaturated hydrocarbon, wherein

the equipment is at least one selected from the group consisting of a distillation column, a heat exchanger, a reactor, a pump, a pipe, and a valve, and

at least one component of the equipment that comes into contact with the composition is a component including a coating containing at least one of

a metal oxide and a metalloid oxide.

14. The apparatus according to claim 13, wherein the coating has an average thickness of at least 0.5 μm and not more than 100 μm .

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15. The apparatus according to claim 13 or 14, wherein the metal oxide is at least one selected from the group consisting of chromium oxide, aluminum oxide, tin oxide, zirconium oxide, and yttrium oxide, and the metalloid oxide is at least one selected from the group consisting of boron oxide, silicon oxide, germanium oxide, arsenic oxide, tellurium oxide, and polonium oxide.

16. The apparatus according to any one of claims 13 to 15, wherein the component including a coating containing at least one of a metal oxide and a metalloid oxide includes a base material and the coating on a surface of the base material, and the base material contains at least one of iron and titanium.

17. The apparatus according to any one of claims 13 to 16, wherein the component including a coating containing at least one of a metal oxide and a metalloid oxide has a contact angle with water of 70° or less.

18. The apparatus according to any one of claims 13 to 17, wherein the apparatus is an apparatus for separating and recovering an unsaturated hydrocarbon, the equipment is a distillation column, and the distillation column performs distillation of a mixture containing the unsaturated hydrocarbon.

19. The apparatus according to claim 18, wherein the distillation column is an extractive distillation column.

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