(54) Title: POLYMERIZATION INHIBITOR FOR 1,3-BUTADIENE AND A METHOD OF INHIBITING POLYMERIZATION OF 1,3-BUTADIENE BY IMPUTING THEREOF

(57) Abstract: Disclosed are a polymerization inhibitor of 1,3-butadiene comprising alklyphenol based anti-fouling agent containing one to two hydroxyl groups, amine based anti-fouling agent and organic solvent and a method of inhibiting polymerization of 1,3-butadiene by using the above inhibitor. The polymerization inhibitor and the method of inhibiting polymerization of 1,3-butadiene of the present invention with excellent inhibition of polymerization and prevention of fouling make it possible to extract and distill 1,3-butadiene product with high purity by inhibiting polymerization of 1,3-butadiene in a wide range of temperature from liquid phase to gaseous phase, prevent operational stoppage of a factory for manufacturing 1,3-butadiene in emergency possible to occur due to fouling, and to ensure stable operation thereof for a long term.

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Description

POLYMERIZATION INHIBITOR FOR 1,3-BUTADIENE AND A METHOD OF INHIBITING POLYMERIZATION OF 1,3-BUTADIENE BY INPUTTING THEREOF

Technical Field

[1] The present invention relates to a polymerization inhibitor for 1,3-butadiene and a method of inhibiting polymerization of 1,3-butadiene by introducing the same, and more particularly, to a novel polymerization inhibitor for blocking and preventing fouling from occurring in a process for manufacturing 1,3-butadiene, and a method of inhibiting polymerization of 1,3-butadiene by introducing the above inhibitor in an extractive distillation column.

Background Art

[2] In factories for manufacturing styrene monomer and isoprene as well as 1,3-butadiene, which belongs to a mixed C4 raffinate and is used as a crude material of various synthetic resins, products are unsaturated hydrocarbons that are liable to undergo polymerization and occur significant problems such as fouling of organic materials even during a normal operation. For example, it was known that fouling generated in an extractive distillation column may occur clogging or blocking of trays in the column to decrease efficiency of the column, or close pathway of an upper condenser to decrease efficiency of heat transfer or cause equipments of the column to be broken off.

[3] With regard to a mechanism for occurring fouling of organic materials, the fouling is occurred by reaction of free radicals. It is generally known that the free radical is an atom or atom group with lack of an electron and has a natural tendency of supplement the lack of electron to form a stable electron pair, therefore, the reactivity of the radical reaction is remarkably high. The free radical is generated by heat, reaction with peroxides or oxygen, or catalytic reaction of metals. Such generated free radical reacts rapidly with unsaturated hydrocarbons to produce resins or rubber type polymers, and has an increased molecular weight in case that the reaction is continued by prolonging residual time of reactant materials in a reactor or processing at high temperature. Polymerization of the free radical is completed by collision of two of the free radicals or reacting the free radical with a compound having higher reactivity, and forms a greatly stable compound without activity leading to the fouling in the process.

[4] The fouling in the extractive distillation process of 1,3-butadiene production factories is mostly an organic fouling to produce popcorn type of polymers by the free radical.
More particularly, a reaction of generating polymers in the production of 1,3-butadiene is the free radical reaction that initiates with radicals of peroxides and iron oxides and is accelerated by oxygen, iron oxides presented in the production process, thereby producing the popcorn type polymers.

To solve the above problem of occurring the organic fouling, residual oxygen and metal ingredients are removed by chemical treatment during the periodical maintenance of equipments. Also, it is conventionally known that 4-tertiary-butylcate chol (hereinafter referring to TBC), butylhydroxy toluene (hereinafter referring to BHT), quinone based compounds such as hydroxyquinone and N,N-diethyl hydroxyl amine (hereinafter referring to DEHA), and stable free radical (hereinafter referring to SFR) are used alone as a fouling-proof agent during the normal operation.

However, a polymerization inhibitor formed of single component described above lacks a function of preventing generation of polymers under liquid and gaseous conditions in a polymerization process and exhibits substantially no effect in removing polymers already formed. Also, 4-TBC, BHT, hydroxyquinone and DEHA which are normally produced by using water as a solvent have an adverse effect of occurring the fouling due to introduction of undesired moisture in the polymerization process.

Specifically, the above described polymerization inhibitor formed of single component has disadvantages as follows:

In contrast with most of popcorn type polymers generated in gaseous state, it has been believed that 4-TBC, BHT and hydroxyquinone have a lower vacuum pressure and are difficult to express the effect for inhibiting the polymerization in gaseous processes. Moreover, TBC, BHT and hydroxyquinone that are used alone do not stop progress of the polymerization of popcorn type polymers which are already generated. Also, TBC, BHT and hydroxyquinone in solid state are dissolved in 15% by weight of water and used, therefore, have disadvantages that the free radical reaction thereof is accelerated typically by water to progress the polymerization and increases the fouling on the contrary.

In case of using DEHA alone, although it enables removal of oxygen from the process and represents somewhat of the effect for inhibiting the polymerization if DEHA is used in the gaseous process, the same used in liquid or gaseous-liquid processes exhibits very slight effect.

In case of using SFR alone which is a polar reaction terminator, it shows better effect in liquid state compared with TBC, BHT and hydroxyquinone. However, gaseous SFR has no effect for preventing generation of the popcorn type polymer and is expensive.

At present, with development of equipments, operational and maintenance techniques in petroleum chemical industries, it intends to prolong a period of the
periodical maintenance and improve productivity and economical effect. However, a stable operation till the periodical maintenance period cannot be expected unless it overcomes conventionally technical problems described above.

Furthermore, due to operational interruption of a factory beyond expectation by a great amount of organic fouling, it may occur enormous expense and even an explosion danger of equipments in the factory. Since the operational stoppage of the factory for manufacturing 1,3-butadiene greatly affects operational rate of each of upper and lower factories in view of a process flow diagram for the petroleum chemical industry. Accordingly, it still requires an improved polymerization preventing agent to ensure 1,3-butadiene manufacturing equipments stably operated.

**Disclosure of Invention**

**Technical Problem**

In order to solve the above described problems, the present invention has an object to provide a polymerization inhibitor for preventing occurrence of fouling in a 1,3-butadiene manufacturing process, which comprises: removing free radicals, peroxides, water and oxygen in a wide range of temperature from gaseous phase to liquid phase in an extractive distillation step of a process for manufacturing 1,3-butadiene with high purity in order to inhibit polymerization of 1,3-butadiene and block generation of polymer, thereby preventing occurrence of fouling, and a method of inhibiting polymerization of 1,3-butadiene by introducing the above inhibitor in an extractive distillation column.

Accordingly, the present invention has purposes that operational stoppage of a factory for manufacturing 1,3-butadiene in emergency possible to occur due to the fouling is prevented beforehand and stable operation thereof is ensured for a long term.

**Technical Solution**

After intensive and extensive research and investigation by inventors, the object of the present invention has been accomplished by providing a polymerization inhibitor for preventing generation of popcorn type polymers, that is, occurrence of fouling, and eliminating activity of the popcorn type polymers already produced to produce 1,3-butadiene product with high purity.

In accordance with the present invention, there is provided a method of inhibiting polymerization of 1,3-butadiene which comprises: introducing one-component type of polymerization inhibitor in an extractive distillation column during an extractive distillation step of the method to extract and distill out 1,3-butadiene from a mixed C4 raffinate in the column, the one-component type inhibitor being prepared by combining alkylphenol based anti-fouling agent containing one to two hydroxyl groups and/or amine based anti-fouling agent with an organic solvent.
Advantageous Effects

[18] As described above, the polymerization inhibitor of the present invention with excellent inhibition of polymerization and prevention of fouling makes it possible to extract and distill 1,3-butadiene product with high purity by inhibiting polymerization of 1,3-butadiene in a wide range of temperature from liquid phase to gaseous phase in a process for manufacturing 1,3-butadiene that is a crude material of various rubber and synthetic resins and separated from a mixed C4 raffinate.

[19] Further, the method for inhibiting polymerization of 1,3-butadiene of the present invention has advantages that operational stoppage of a factory for manufacturing 1,3-butadiene in emergency possible to occur due to fouling is prevented beforehand and stable operation thereof is ensured for a long term.

Brief Description of the Drawings

[20] Fig. 1 is a flow diagram illustrating an extractive distillation process in a method for manufacturing 1,3-butadiene including introduction of a polymerization inhibitor according to the present invention.

Best Mode for Carrying Out the Invention

[21] The present invention relates to a polymerization inhibitor of 1,3-butadiene which comprises alkylphenol based anti-fouling agent containing one to two hydroxyl groups, amine based anti-fouling agent and an organic solvent.

[22] The alkylphenol based anti-fouling agent containing one to two hydroxyl groups used in the present invention preferably includes, but is not limited to, any one selected from a group consisting of 2,6-di-tertiary-butyl-4-methylphenol, 2,6-di-tertiary-buthyl-ethylphenol, 2,6-di-cyclopentyl-4-methylphenol, 4-tertiary-buthylcatechol, 2,6-di-tertiary-butyl-methoxyphenol, 2,5-di-tertiary-butylhydroquinone, 2,6-diphenyl-4-octadecyloxylphenol and bis(3,5-di-tertiary-butyl)-4-hydroxyphenol. More preferably used are 4-tertiary-butyl-catechol (that is, TBC) and butylhydroxytoluene (that is, BHT).

[23] The amine based anti-fouling agent used in the present invention includes, but is not limited to, any one selected from a group consisting of diethylhydroxamine, N,N-di-secondary-butyl-p-phenylenediamine, 4-n-butylaminophenol, 4-butrylaminophenol, 4-nonanoyl aminophenol and 2,6-di-tertiary-butyl-4-dimethyl aminomethylphenol. More preferably used is diethylhydroxamine (that is, DEHA).

[24] The polymerization inhibitor according to the present invention preferably comprises 9.0 to 30.0% by weight of the alkylphenol based anti-fouling agent containing one to two hydroxyl groups, 50.0 to 90.0% by weight of the amine based anti-fouling agent and 1.0 to 20.0% by weight of the organic solvent, so that the inhibitor can efficiently remove polymerization initiators such as free radicals, oxygen
and the like by introducing the polymerization inhibitor in a distillation part of an extractive distillation column, which contains both of gaseous and liquid phases together, to be naturally admixed with upper stream of the distillation part, and can eliminate activity of polymer already under polymerization.

[25] The organic solvent is preferably selected from solvents that have an excellent solubility of the alkylphenol based anti-fouling agent containing one to two hydroxyl groups such as TBC, BHT, hydroxyquinone and/or the amine based anti-fouling agent such as DEHA and do not affect purity of 1,3-butadiene as a final product. More preferably used is the organic solvent selected from alcohols having three to five carbon atoms. Most preferably used is isobutyl alcohol (hereinafter referring to IBA) containing a structure represented by the following formula 1, or isopropyl alcohol (hereinafter referring to IPA) containing a structure represented by the following formula 2:

[26] Formula 1

[27]

[28] Formula 2

[29]

[30] IBA and IPA may dissolve both of the alkylphenol based anti-fouling agent containing one to two hydroxyl groups such as 4-tertiary-butylcatechol and diethyl hydroxylamine and the amine based anti-fouling agent such as DEHA and show no adverse effect to the manufacturing process and product.

[31] Preferably illustrative alkylphenol based anti-fouling agent containing one to two hydroxyl groups is TBC which has a structure represented by the following formula 3:

[32] Formula 3

[33]
TBC has a molecular formula of $\text{C}_6\text{H}_2(\text{OH})\text{C(CH}_3\text{)}_3$ in solid state with white to pale yellow colors, a boiling point of 285°C, a melting point of 53°C, a specific gravity of 1.049 at 60°C and a viscosity of 36 cps at 60°C. TBC is generally used alone as the polymerization inhibitor for liquid 1,3-butadiene and styrene products and prepared by using raw materials including catechol, isobutylene, p-tertiary-butyphenol, chlorine, sodium hydroxide, etc. More particularly, TBC may be manufactured by a catechol process that proceeds butylation of catechol with isobutylene in the presence of Lewis acid based catalyst, or a PTBP process that chlorinates p-t-PTBP to give 2-chloro-4-tertiary-butyphenol and substitutes chlorine in the obtained product with hydroxyl group using sodium hydroxide.

TBC has a lower vapor pressure and displays polymerization inhibiting effect in liquid phase processes.

Another preferable example of the alkylphenol based anti-fouling agent containing one to two hydroxyl groups is BHT which has a structure represented by the following formula 4:

Formula 4

BHT has a molecular formula of $\text{C}_6\text{H}_2(\text{OH})\text{(CH}_3\text{)(C(CH}_3\text{)}_3$ in solid state with white to pale yellow colors, a boiling point of 265°C, a melting point of 70°C, and a specific gravity of 1.05 at 25°C.
Still a further preferable example of the alkylphenol based anti-fouling agent containing one to two hydroxyl groups is hydroxyquinone which has a structure represented by the following formula 5:

[41] Formula 5

[43] Hydroxyquinone has a molecular formula of C₆H₄(OH)₂ in white solid state, a boiling point of 285°C, a melting point of 170°C and a specific gravity of 1.332 at 25°C.

[44] A preferable example of the amine anti-fouling agent is DEHA which has a structure represented by the following formula 6:

[45] Formula 6

[47] DEHA has a molecular formula of (C₅H₁₀)₅NOH in liquid state, which is widely used as a deoxygenating agent or an oxygen adsorbent for boiler water or in petroleum chemical processes.

[48] DEHA that can remove oxygen partially in the process exhibits the polymerization inhibiting effect in the gaseous phase processes.

[49] Also, the present invention provides a method of inhibiting polymerization of 1,3-butadiene which prevents generation of 1,3-butadiene polymer in an extractive distillation step of a process for manufacturing 1,3-butadiene.

[50] Specially, the present invention provides the method for inhibiting polymerization of 1,3-butadiene which prevents generation of polymer under gaseous and liquid
conditions and, in addition, removes activity of the polymer already produced. More particularly, the present invention provides the method for inhibiting polymerization of 1,3-butadiene that introduces one-component type of polymerization inhibitor in an extractive distillation column to extract and distill 1,3-butadiene from a mixed C4 raffinate in the column, the one-component type inhibitor being prepared by combining an alkylphenol based anti-fouling agent containing one to two hydroxyl groups and/or an amine based anti-fouling agent with an organic solvent.

[51]

The alkylphenol based anti-fouling agent containing one to two hydroxyl groups used in the present invention preferably includes, but is not limited to, any one selected from a group consisting of 2,6-di-tertiary-butyl-4-methylphenol, 2,6-di-tertiary-butyl-ethylphenol, 2,6-di-cyclopentyl-4-methylphenol, 4-tertiary-butylcatechol, 2,6-di-tertiary-butyl-methoxyphenol, 2,5-di-tertiary-butylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol and bis(3,5-di-tertiary-butyl)-4-hydroxyphenol. More preferably used are 4-tertiary-butyl-catechol (that is, TBC) and butylhydroxyl toluene (that is, BHT).

[52]

The amine based anti-fouling agent used in the present invention includes, but is not limited to, any one selected from a group consisting of diethylhydroxyamine, N,N-di-secondary-butyl-p-phenylenediamine, 4-n-butylaminophenol, 4-butryryaminophenol, 4-nonanoyl aminophenol and 2,6-di-tertiary-butyl-4-dimethyl aminomethylphenol. More preferably used is diethylhydroxyamine (that is, DEHA).

[53]

The organic solvent is preferably selected from alcohols having three to five carbon atoms, which can dissolve both of the alkylphenol based anti-fouling agent containing one to two hydroxyl groups such as TBC, BHT, hydroxyquinone and/or the amine based anti-fouling agent such as DEHA and do not affect the process or the product. Most preferably used is isobutyl alcohol (that is, IBA) or isopropyl alcohol (that is, IPA).

[54]

The polymerization inhibitor according to the present invention preferably comprises 9.0 to 30.0% by weight of the alkylphenol based anti-fouling agent containing one to two hydroxyl groups, 50.0 to 90.0% by weight of the amine based anti-fouling agent and 1.0 to 20.0% by weight of the organic solvent, so that the inhibitor can efficiently remove polymerization initiators such as free radicals, oxygen, etc. by introducing the inhibitor in a distillation part of the extractive distillation column, which contains both of gaseous and liquid phases together, to be naturally admixed with upper stream of the distillation part, and eliminate activity of polymer already under polymerization.

**Mode for the Invention**

[55]

The present invention will be described in detail with reference to accompanying
FIG. 1 is a flow diagram illustrating a method of manufacturing 1,3-butadiene including an introduction process of polymerization inhibitor according the present invention. The method of inhibiting polymerization of 1,3-butadiene which is included in the 1,3-butadiene manufacturing method of the present invention is described in detail as follows.

As shown in FIG. 1, an extractive distillation column 1 is composed of 61 stages of trays and 2 stages of chimney trays 1-a and 1-b. The mixed C4 raffinate introduced in the column 1 comprises 83 to 84wt.% of 1,3-butadiene, vinyl acetylene, ethyl acetylene, 1,2-butadiene, methyl acetylene and a mixed C5 raffinate in a gaseous phase and, is introduced in a first chimney tray 1-a of the column 1 through an inlet 2 for feeding the mixed C4 raffinate at a flow rate ranged from 27 to 28 tones/hour. Alternatively, an extraction solvent such as dimethylformamide is introduced into another inlet 3 for feeding dimethylformamide, which is formed on 11th stage of the trays in the column 1, at a flow rate ranged from 45 to 47 tones/hour.

The polymerization inhibitor of the present invention is transported from a storage tank 4 of the inhibitor to an upper transportation pipe of the column 1 by a feeding pump 5. Alternatively, the inhibitor is entered into a pipe for feeding dimethylformamide and through the inlet 3 for feeding dimethylformamide into the column 1 as combined with dimethylformamide.

Among the mixed C4 raffinate introduced in the column 1, 1,3-butadiene having a lower solubility to the extractive solvent, that is, dimethylformamide is firstly refined in the solvent and transferred to top of the column 1. Concentration of 1,3-butadiene in top of the column 1 ranges from 95 to 98%. Top portion of the column 1 has a temperature of 36 to 38.5°C and a pressure of 3.10 to 3.15kg/cm²G.

On the other hand, other ingredients such as vinyl acetylene, ethyl acetylene, 1,2-butadiene, methyl acetylene and the mixed C5 raffinate which have a higher solubility to dimethylformamide as the extractive solvent in spite of the boiling point similar to that of 1,3-butadiene among the mixed C4 raffinate are dissolved in the solvent and transferred to bottom of the column 1. Concentration of 1,3-butadiene in bottom of the column 1 ranges from 5.3 to 5.5%. Bottom portion of the column 1 has a temperature of about 130°C and a pressure of 3.9 to 4.0kg/cm²G.

The refined C4 raffinate from top of the column 1 is phase-changed into liquid state in a condenser 6 and temporarily stayed in a condensation drum 7. Following then, The raffinate migrates to a reflux pump strainer 8 with a capacity of 4 liters, in which 1,3-butadiene polymer (fouling material) generated is removed from the refined C4 raffinate. Subsequently, a part of the refined C4 raffinate is returned and entered again into the column 1 by the reflux pump 4 to control the concentration of 1,3-butadene
among the raffinate existed in top portion of the column 1 in a range of 95 to 98%. On the other hand, most of the refined C4 raffinate is transported to a further 1,3-butadiene refining process A.

A mixture containing dimethylformamide, 1,3-butadiene, vinyl acetylene, ethyl acetylene, 1,2-butadiene, methyl acetylene, C5 raffinate and the like out of bottom of the column 1 migrates to a bottom built-in strainer 10 in which 1,3-butadiene polymer (fouling material) is removed. After then, the mixture of an extractive solvent and the mixed C4 raffinate without the fouling material leads to a further process B for recovering 1,3-butadiene under pressure in order to recover 5.3 to 5.5% of residual 1,3-butadiene in the mixture.

Because internal condition of the column 1 cannot be observed by naked eyes, condition and accumulated amount of the polymer generated in the reflux pump strainer 8 and the bottom strainer 10, which are possible to be opened during the normal operation, are criteria for determining degrees of polymerization and fouling of 1,3-butadiene by the extractive distillation column.

If any suitable measure is not taken to inhibit polymerization of 1,3-butadiene, an extractive distillation column 1 may be blocked or clogged by resin type or rubber type of polymers (fouling materials) which are generated by polymerization of 1,3-butadiene on top or bottom of the column 1, thereby leading to explosion or stoppage of the extractive distillation column 1 and even abnormally stopping operation of related factories.

When the polymerization inhibitor of the present invention is introduced in top of the column 1 by any feeding means, it requires to combine the inhibitor with top fluid (gas and liquid) of the column in a preferable composition ratio so that the inhibitor can more efficiently remove polymerization initiators such as free radicals, oxygen, etc. and activity of a polymer under polymerization in advance on top portion of the column 1, and can inhibit polymerization of 1,3-butadiene and activity of the polymer under polymerization in advance on bottom portion of the column 1. Accordingly, in accordance with the method of inhibiting polymerization of 1,3-butadiene of the present invention, one-component type of polymerization inhibitor that comprises 9.0 to 30.0wt.% of the alkylphenol based anti-fouling agent containing one to two hydroxyl groups such as TBC, BHT or hydroxyquinone, 50.0 to 90.0wt.% of the amine based anti-fouling agent such as DEHA and 1.0 to 20.0wt.% of the organic solvent is preferably introduced in the column 1.

The present invention will be described in more detail by the following examples and comparative examples, which are not intended to limit the scope of the invention thereto but illustrative embodiments of the present invention.

**Example 1**
30ppm of a polymerization inhibitor comprising 15wt.% of TBC, 75wt.% of DEHA and 10wt.% of IBA relative to total amount introduced of a C4 mixture was entered into top of an extractive distillation pump containing both of liquid and gaseous phases together through a feeding pump for the polymerization inhibitor, and under a periodical evaluation to examine condition and amount of polymer accumulation. The results are shown in Table 1.

**Example 2**

The condition and amount of polymer accumulation were periodically examined in the same manner as in Example 1 except for changing composition and combination ratio of the polymerization inhibitor such that the inhibitor comprised 15wt.% of TBC, 75wt.% of DEHA and 10wt.% of IPA. The results are shown in Table 1.

**Example 3**

The condition and amount of polymer accumulation were periodically examined in the same manner as in Example 1 except for changing composition and combination ratio of the polymerization inhibitor such that the inhibitor comprised 15wt.% of BHT, 75wt.% of DEHA and 10wt.% of IPA. The results are shown in Table 1.

**Example 4**

The condition and amount of polymer accumulation were periodically examined in the same manner as in Example 1 except for changing composition and combination ratio of the polymerization inhibitor such that the inhibitor comprised 15wt.% of hydroxyquinone, 75wt.% of DEHA and 10wt.% of IPA. The results are shown in Table 1.

**Comparative Example 1**

The condition and amount of polymer accumulation were periodically examined in the same manner as in Example 1 except for using no polymerization inhibitor. The results are shown in Table 1.

**Comparative Example 2**

The condition and amount of polymer accumulation were periodically examined in the same manner as in Example 1 except that the polymerization inhibitor formed of TBC only was entered into top of the column through the feeding pump in an amount of 30ppm relative to total amount of the C4 mixture. The results are shown in Table 1.

**Comparative Example 3**

The condition and amount of polymer accumulation were periodically examined in the same manner as in Example 1 except that the polymerization inhibitor formed of DEHA only was entered into top of the column through the feeding pump in an amount of 30ppm relative to total amount of the C4 mixture. The results are shown in Table 1.

Table 1
<table>
<thead>
<tr>
<th>Example</th>
<th>Accumulated amount</th>
<th>Condition of polymer</th>
<th>Condition of process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1</td>
<td>1 liter / 14 months</td>
<td>Fluidizing rubber type</td>
<td>Normal operation</td>
</tr>
<tr>
<td>Example 2</td>
<td>1 liter / 13 months</td>
<td>Fluidizing rubber type</td>
<td>Normal operation</td>
</tr>
<tr>
<td>Example 3</td>
<td>1 liter / 13 months</td>
<td>Fluidizing rubber type</td>
<td>Normal operation</td>
</tr>
<tr>
<td>Example 4</td>
<td>1 liter / 13 months</td>
<td>Partially including resin type</td>
<td>Regular maintenance after 11 months</td>
</tr>
<tr>
<td>Comparative Example 1</td>
<td>1 liter / 0.5 months</td>
<td>Resin type</td>
<td>Abnormal stoppage of operation after 2 months</td>
</tr>
<tr>
<td>Comparative Example 2</td>
<td>1 liter / 2 months</td>
<td>Rubber type</td>
<td>Abnormal stoppage of operation after 17 months</td>
</tr>
<tr>
<td>Comparative Example 3</td>
<td>1 liter / 1 month</td>
<td>Resin type</td>
<td>Abnormal stoppage of operation after 11 months</td>
</tr>
</tbody>
</table>

[82] (Result of evaluation)

With regard to an extractive distillation process of 1,3-butadiene, the condition of polymer (fouling material) is classified into the fluidizing rubber type with smaller molecular weight, the rubber type with moderate molecular weight and the resin type with larger molecular weight depending upon degree of polymerization of 1,3-butadiene. It has been evaluated that the smaller the molecular weight of the polymer generated (fouling material), the lower the degree of polymerization of 1,3-butadiene.

[84] As illustrated in Comparative Example 1, it was demonstrated that the resin type polymer has been rapidly generated in case of using no polymerization inhibitor and, after 2 months, operation of a factory was abnormally stopped for safety due to the increase of pressure in the extractive distillation column.

[85] As illustrated in Comparative Example 2, it was demonstrated that the rubber type polymer has been generated in case of introducing only TBC and, after 17 months, operation of the factory was abnormally stopped for safety due to the increase of pressure in the extractive distillation column.

[86] As illustrated in Comparative Example 3, it was demonstrated that the resin type polymer has been generated in case of introducing only DEHA and, after 11 months, operation of the factory was abnormally stopped for safety due to the increase of pressure in the extractive distillation column.
On the other hand, when the polymerization inhibitor of the present invention comprising any one of anti-fouling agents selected from TBC, BHC and hydroxyquinone, DEHA, and an alcohol based organic solvent such as IPA or IBA was introduced in the extractive distillation column as illustrated in Examples 1 to 4, they demonstrated the effect for inhibiting polymerization of 1,3-butadiene in both of gas and liquid conditions noticeably superior over Comparative Examples 2 and 3 which applied only one-component polymerization inhibitor. As a result, the extractive distillation column was at full work until it was stopped for a periodical maintenance after 3 years.

Industrial Applicability

As described in detail above, the polymerization inhibitor of the present invention with excellent inhibition of polymerization and prevention of fouling makes it possible to extract and distill 1,3-butadiene product with high purity by inhibiting polymerization of 1,3-butadiene in a wide range of temperature from liquid phase to gaseous phase in a process for manufacturing 1,3-butadiene that is a crude material of various rubber and synthetic resins and separated from a mixed C4 raffinate.

Additionally, the method for inhibiting polymerization of 1,3-butadiene of the present invention has advantages that operational stoppage of a factory for manufacturing 1,3-butadiene in emergency possible to occur due to fouling is prevented beforehand and stable operation thereof is ensured for long term.

While the present invention has been described with reference to exemplary embodiments thereof, it will be understood by those skilled in the art that various modifications and variations may be made therein without departing from the scope of the present invention as defined by the appended claims.
Claims

[1] A polymerization inhibitor of 1,3-butadiene comprising alkylphenol based anti-fouling agent containing one to two hydroxyl groups, amine based anti-fouling agent and organic solvent.

[2] The inhibitor according to claim 1, wherein the alkylphenol based anti-fouling agent containing one to two hydroxyl groups is selected from a group consisting of 2,6-di-tertiary-butyl-4-methylphenol, 2,6-di-tertiary-buty1-ethylphenol, 2,6-di-cyclopentyl-4-methylphenol, 4-tertiary-butylcatechol, 2,6-di-tertiary-butyl-methoxyphenol, 2,5-di-tertiary-butylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol and bis(3,5-di-tertiary-butyl)-4-hydroxyphenol.

[3] The inhibitor according to claim 1, wherein the amine based anti-fouling agent is selected from a group consisting of diethylhydroxyamine, N,N-di-secondary-butyl-p-phenylenediamine, 4-n-butylaminophenol, 4-butryrlyaminophenol, 4-nonanoyl aminophenol and 2,6-di-tertiary-butyl-4-dimethyl aminomethylphenol.

[4] The inhibitor according to claim 1, wherein the inhibitor has a combination ratio of 9.0 to 30.0% by weight of the alkylphenol based anti-fouling agent containing one to two hydroxyl groups, 50.0 to 90.0% by weight of the amine based anti-fouling agent and 1.0 to 20.0% by weight of the organic solvent.

[5] The inhibitor according to claim 1 or 4, wherein the organic solvent is any one of alcohols having 3 to 5 carbon atoms.

[6] The inhibitor according to claim 5, wherein the alcohol is isopropyl alcohol or isobutyl alcohol.

[7] A method of inhibiting polymerization of 1,3-butadiene which comprises: introducing one-component type of polymerization inhibitor in an extractive distillation column to extract and distill out 1,3-butadiene from a mixed C4 raffinate in the column, the one-component type inhibitor being prepared by combining alkylphenol based anti-fouling agent containing one to two hydroxyl groups and amine based anti-fouling agent with an organic solvent.

[8] The method according to claim 7, wherein the alkylphenol based anti-fouling agent containing one to two hydroxyl groups is selected from a group consisting of 2,6-di-tertiary-butyl-4-methylphenol, 2,6-di-tertiary-buty1-ethylphenol, 2,6-di-cyclopentyl-4-methylphenol, 4-tertiary-butylcatechol, 2,6-di-tertiary-butyl-methoxyphenol, 2,5-di-tertiary-butylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol and bis(3,5-di-tertiary-butyl)-4-hydroxyphenol.
[9] The method according to claim 7, wherein the amine based anti-fouling agent is selected from a group consisting of diethylhydroxyamine, N,N-di-secondary-butyl-p-phenylenediamine, 4-n-butylaminophenol, 4-butyralaminophenol, 4-nonanoyl aminophenol and 2,6-di-tertiary-butyl-4-dimethyl aminomethylphenol.

[10] The method according to claim 7, wherein the inhibitor has a combination ratio of 9.0 to 30.0% by weight of the alkylphenol based anti-fouling agent containing one to two hydroxyl groups, 50.0 to 90.0% by weight of the amine based anti-fouling agent and 1.0 to 20.0% by weight of the organic solvent.

[11] The method according to claim 7 or 10, wherein the organic solvent is any one of alcohols having 3 to 5 carbon atoms.

[12] The method according to claim 11, wherein the alcohol is isopropyl alcohol or isobutyl alcohol.
A. CLASSIFICATION OF SUBJECT MATTER

C08F 2/38(2006.01)j

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F 2/38, C07C 7/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Patents and applications for inventions since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Date of mailing of the international search report
27 APRIL 2006 (27.04.2006)

Authorized officer
HUR, Soo Joon
Telephone No. 82-42-481-5595

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### INTERNATIONAL SEARCH REPORT

**Information on patent family members**

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<th>Publication date</th>
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