COMPOSITION FOR REMOVING IRON SULFIDE

Provided is a composition for removing iron sulfide, containing, as an active ingredient, an α,β-unsaturated aldehyde represented by the following general formula (1):

\[ R^1 \rightarrow R^2 \rightarrow R^3 \]

wherein R\(^1\) to R\(^3\) each independently represent a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, an alkenyl group having 2 to 10 carbon atoms, or an aryl group having 6 to 12 carbon atoms, provided that R\(^1\) may be connected to R\(^2\) or R\(^3\), to constitute an alkyene group having 2 to 6 carbon atoms; and that R\(^1\) and R\(^2\) are not a hydrogen atom at the same time.
The present invention relates to a composition for removing iron sulfide and a method for removing iron sulfide, which includes using the same.

Hydrogen sulfide that often exists in hydrocarbons, such as fossil fuels and refined petroleum products, for example, natural gas, liquefied natural gas, sour gas, crude oil, naphtha, heavy aromatic naphtha, gasoline, kerosene, diesel oil, light oil, heavy oil, FCC slurry, asphalt, and oil field concentrates, corrodes iron which is used in excavation facilities, etc., to cause generation of iron sulfide. The iron sulfide is accumulated as a deposit within production facilities of fossil fuels and refined petroleum products, to lower operational efficiency of instruments in heat exchanger, cooling tower, reactor, transmission pipeline, furnace, etc., or disturb precise measurement for facility maintenance, and therefore, it is desired to remove this.

As a method for removing iron sulfide, a method of dissolving iron sulfide with acrolein is known, and announcement regarding the removal of iron sulfide with acrolein as an active ingredient is also made in SPE Annual Technical Conference and Exhibition SPE 146080, held in the city of Denver, Colorado, USA on October 30 to November 2, 2011 (NPL 1). However, the acrolein is a compound which is strongly toxic and whose concentration is strictly regulated from the viewpoint of occupational safety and from the viewpoint of environmental safety, so that it involves such a problem that attention is required for handling. In addition to the above, the acrolein is problematic from the viewpoint that it is extremely easily polymerized and lacks in thermal stability and also from the viewpoint that it lacks in pH stability, so that its abundance gradually decreases depending upon the pH of the environment to be used.

In the light of the above, in using acrolein for the purpose of removing iron sulfide, there are problems from the viewpoint of safety and thermal stability and also from the viewpoint of pH stability, and therefore, a safer and more stable compound is desired as a substitute therefor. Now, an object of the present invention is to provide a composition containing an active ingredient with high thermal stability and pH stability and being capable of removing iron sulfide safely and efficiently.

In accordance with the present invention, the aforementioned object is achieved by the following [1] to [7].

[1] A composition for removing iron sulfide, containing, as an active ingredient, an α,β-unsaturated aldehyde represented by the following general formula (1) (hereinafter referred to as “aldehyde (1)“):

\[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{R}^3 \\
\end{array}
\]

\((1)\)

wherein R¹ to R³ each independently represent a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, an alkenyl group having 2 to 10 carbon atoms, or an aryl group having 6 to 12 carbon atoms, provided that R¹ may be...
connected to R² or R³, to constitute an alkylene group having 2 to 6 carbon atoms; and that R¹ and R² are not a hydrogen atom at the same time.

[2] The composition of [1], wherein R¹ to R³ are each independently a hydrogen atom or an alkyl group having 1 to 5 carbon atoms.


[5] The method of [4], wherein the aldehyde (1) in the composition is added in an amount of 0.1 to 100 parts by mass based on 1 part by mass of iron sulfide.

[6] The method of [4] or [5], including bringing the aldehyde (1) in the composition into contact with iron sulfide in a range of from -30°C to 150°C.


Advantageous Effects of Invention

[0007] Since the composition of the present invention contains the aldehyde (1), an excellent removal performance of iron sulfide is exhibited.

[0008] In particular, as compared with a conventional iron sulfide remover containing acrolein, the composition of the present invention has such an advantage that it is extremely low in toxicity and high in thermal stability and pH stability. Though the reasons for this are not elucidated yet, it may be considered as one of factors that since the aldehyde (1) has at least one of an alkyl group, an alkenyl group, and an aryl group at the β-position thereof, an addition reaction to the β-position of a bulky molecule, such as a biomolecule and a propagating chain, is hard to occur as compared with acrolein not having a substituent at the β-position thereof. Meanwhile, with respect to the removal of iron sulfide, it may be considered that the aldehyde (1) comes to bond to hydrogen sulfide that is existent in an equilibrium state with iron sulfide to thereby remove hydrogen sulfide, dissolution of iron sulfide is promoted, and as a result, the iron sulfide is removed; and while the aldehyde (1) has a substituent at the β-position thereof, an attack from hydrogen sulfide that is in general a small molecule is not hindered so much, whereby the removal performance of iron sulfide is kept.

Brief Description of Drawings

[0009]

Fig. 1 is a graph showing pH stability of senecioaldehyde (SAL).

Fig. 2 is a graph showing pH stability of acrolein.

Description of Embodiments

[0010] The composition of the present invention includes the aldehyde (1) as an active ingredient.

[0011] In the aldehyde (1), the alkyl group having 1 to 10 carbon atoms, which R¹ to R³ each independently represent, may be linear, branched, or cyclic, and examples thereof include a methyl group, an ethyl group, a n-propyl group, an isopropyl group, a n-butyl group, an isobutyl group, a t-butyl group, a n-pentyl group, a n-hexyl group, a n-octyl group, a n-decyl group, a n-dodecyl group, and a cyclopentyl group. Above all, from the viewpoint of removal performance of iron sulfide, a methyl group, an ethyl group, or a n-propyl group is preferred, a methyl group or an ethyl group is more preferred, and a methyl group is still more preferred.

[0012] The alkenyl group having 2 to 10 carbon atoms, which R¹ to R³ each independently represent, may be linear, branched, or cyclic, and examples thereof include a vinyl group, an allyl group, a 1-penten-1-yl group, a 4-methyl-3-penten-1-yl group, a 4-penten-1-yl group, a 1-hexen-1-yl group, a 1-octen-1-yl group, and a 1-decen-1-yl group. Above all, an alkenyl group having 1 to 8 carbon atoms is preferred, and an alkenyl group having 1 to 6 carbon atoms is more preferred.

[0013] Examples of the aryl group having 6 to 12 carbon atoms, which R¹ to R³ each independently represent, include a phenyl group, a tolyl group, an ethylphenyl group, a xyl group, a trimethylphenyl group, a naphthyl group, a biphenyl group. Above all, an aryl group having 6 to 10 carbon atoms is preferred.

[0014] In the case where R¹ is connected to R² or R³, to constitute an alkylene group having 2 to 6 carbon atoms, examples of the alkylene group include an ethylene group, a n-propylene group, a n-butylene group, a n-pentylene group, a hexylene group, a 2-methylethylene group, a 1,2-dimethylethylene group, a 2-methyl-n-propylene group, a 2,2-dimethyl-n-propylene group, and a 3-methyl-n-pentylene group.

[0015] It is preferred that R¹ to R³ are each independently a hydrogen atom or an alkyl group having 1 to 5 carbon atoms.

[0016] From the viewpoint of exhibiting removal performance of iron sulfide and keeping thermal stability and pH
stability, it is preferred that at least one of \( R^1 \) and \( R^2 \) is a methyl group, and it is still more preferred that both \( R^1 \) and \( R^2 \) are a methyl group.

[0017] From the viewpoint of promoting the reaction with hydrogen sulfide and efficiently removing iron sulfide, it is preferred that \( R^3 \) is a hydrogen atom.

[0018] Examples of the aldehyde (1) include 2-butenal, 2-pentenal, 2-hexenal, 2-heptenal, 2-octenal, 2-nonenal, 2-decenal, 2-dodecenal, 2-tridecenal, 4-methyl-2-pentenal, 4-methyl-2-hexenal, 5-methyl-2-hexenal, 4,4-dimethyl-2-pentenal, 6-methyl-2-heptenal, 4-ethyl-2-hexenal, 2-methyl-2-butenal, 2-methyl-2-pentenal, 2-methyl-2-hexenal, 2-methyl-2-heptenal, 2-methyl-2-octenal, 2-methyl-2-propenal, 2,4-dimethyl-2-pentenal, 2,4-dimethyl-2-hexenal, 2,4-dimethyl-2-heptenal, 2,5-dimethyl-2-hexenal, 2,6-dimethyl-2-heptenal, 2,4,4-trimethyl-2-pentenal, 2-ethyl-2-butenal, 2-ethyl-2-hexenal, 2-ethyl-2-heptenal, 2-ethyl-2-octenal, 2-ethyl-4-methyl-2-pentenal, 2-ethyl-4-methyl-2-hexenal, 2-propyl-2-butenal, 2-propyl-2-pentenal, 2-propyl-2-heptenal, 2-propyl-4-methyl-2-pentenal, 2-propyl-5-methyl-2-hexenal, 2-isopropyl-2-butenal, 2-isopropyl-4-methyl-2-pentenal, 2-isopropyl-4-methyl-2-hexenal, 2-isopropyl-5-methyl-2-hexenal, 2-butyl-2-butenal, 2-butyl-2-pentenal, 2-butyl-2-heptenal, 2-butyl-2-octenal, 2-isobutyl-2-butenal, 2-isobutyl-6-methyl-2-heptenal, 2-pentyl-2-butenal, 2-pentyl-2-pentenal, 2-pentyl-2-heptenal, 2-pentyl-2-octenal, 2-methyl-2-butenal, 2-methyl-2-pentenal, 2-methyl-2-hexenal, 2-methyl-2-heptenal, 2-methyl-2-octenal, 3-methyl-2-pentenal, 3-methyl-2-hexenal, 3-methyl-2-heptenal, 3-methyl-2-octenal, 3-methyl-2-nonenal, 3-methyl-2-decenal, 3-methyl-2-dodecenal, 3-methyl-2-tridecenal, 3-ethyl-2-pentenal, 3,4-dimethyl-2-pentenal, 3,4,4-trimethyl-2-pentenal, 3-isopropyl-4-methyl-2-pentenal, 3-ethyl-2-hexenal, 3-propyl-2-hexenal, 3,5-dimethyl-2-hexenal, 3-(t-buty1)-4,4-dimethyl-2-pentenal, 3-butyl-2-heptenal, 2,3-dimethyl-2-butenal, 2-ethyl-3-methyl-2-butenal, 2-isopropyl-3-methyl-2-butenal, 2,3-dimethyl-2-pentenal, 2,3,4-trimethyl-2-hexenal, 2-isobutyl-3-methyl-2-butenal, 3-methyl-2-pentyl-2-pentenal, 2,3-diethyl-2-pentenal, 2-(1,1-dimethylpropyl)-3-methyl-2-butenal, 3,5,5-trimethyl-2-hexenal, 2,3,4-trimethyl-2-pentenal, 2-cyclopropylpyridenedepropanal, 2-cyclopentenyldienehexenal, 2-cyclohexyldieneheptenal, 2-cyclohexyldienehexanal, 1-formylcyclobutene, 1-formyl-3,3-dimethylcyclobutene, 1-cyclopropyl-2-formylcyclobutene, 1-formylcyclopentene, 5-ethyl-1-formylcyclopentene, 1-formyl-3-methylcyclopentene, 1-formyl-4-methylcyclopentene, 1-formyl-5-methylcyclopentene, 1-formyl-3,3-dimethylcyclopentene, 1-formyl-4,5-dimethylcyclopentene, 1-formyl-2,5,5-trimethylcyclopentene, 1-formyl-2,5,5-trimethylcyclopentene, 1-formyl-4-methylcyclohexene, 1-formyl-5-methylcyclohexene, 1-formyl-6-methylcyclohexene, 1-formyl-3,3-dimethylcyclohexene, 1-formyl-5,5-dimethylcyclohexene, 1-formyl-2,2,2-trimethylcyclohexene, 2-cyclopropylpyridenedeprpanal, 2-cyclopentenyldienehexenal, 2-cyclohexyldienehexenal, 2-cyclohexyldieneheptenal, 2-cyclohexyldienehexanal, 1-formylcyclobutene, 1-formyl-3,3-dimethylcyclobutene, 1-cyclopropyl-2-formylcyclobutene, 1-formylcyclopentene, 5-ethyl-1-formylcyclopentene, 1-formyl-3-methylcyclopentene, 1-formyl-4-methylcyclopentene, 1-formyl-5-methylcyclopentene, 1-formyl-3,3-dimethylcyclopentene, 1-formyl-4,5-dimethylcyclopentene, 1-formyl-2,5,5-trimethylcyclopentene, 1-formyl-3,3-dimethylcyclohexene, 1-formyl-5,5-dimethylcyclohexene, 1-formyl-2,2,2-trimethylcyclohexene, 1-formyl-2,4,6,6-tetramethylcyclohexene, 1-formylcycloheptene, 1-formyl-2-methylcycloheptene, 1-formyl-3-methylcycloheptene, 1-formylcyclooctene, 2,4-pentadienal, 2,4-hexadienal, 2,5-hexadienal, 5-methyl-2,4-hexadienal, 2,4-heptadienal, 2,4-octadienal, 2,7-octadienal, 3,7-dimethyl-2,6-octadienal (citral), 2,4,6-octatrienal, 7-methyl-2,4,6-octatrienal, 2,4-nonadienal, 2,6-nonadienal, 4,8-dimethyl-2,7-nonadienal, 2,4-decadienal, 2,4-undecadienal, 2,4-dodecadienal, 2,4-tridecadienal, 2,4,7-tridecatrienal, 3-phenylpropenal, 3-phenyl-2-methylpropenal, 3-(o-tolyl)propenal, 3-(p-tolyl)propenal, and 3-naphthylpropenal. Above all, 3-methyl-2-butenal, 3-methyl-2-pentenal, 3-methyl-2-hexenal, 3-methyl-2-heptenal, 3-methyl-2-octenal, 3,7-dimethyl-2,6-octadienal (citral), 3-ethyl-2-pentenal, 3-ethyl-2-heptenal, and 3-propyl-2-heptenal are preferred; 3-methyl-2-butenal, 3-methyl-2-pentenal, and 3-ethyl-2-pentenal are more preferred; and 3-methyl-2-butenal (senecioaldehyde, hereinafter referred to simply as "SAL") is still more preferred.

[0019] With respect to compounds having a trans-isomer and a cis-isomer, either one of them may be used, or a mixture of the both isomers may also be used. In the case of using a mixture, those having an arbitrary mixing ratio can be used.

[0020] As for the aldehyde (1), a commercially available product may be used, or it may be synthesized through an oxidative dehydrogenation reaction of a corresponding \( \alpha,\beta \)-unsaturated alcohol (see, for example, JP 60-224652 A).

[0021] Though a content proportion of the aldehyde (1) that is an active ingredient in the composition of the present invention can be properly set according to the use embodiment, it is typically 1 to 99.9% by mass, and from viewpoint of cost-effectiveness, it is preferably 5 to 99.9% by mass, and more preferably 5 to 95% by mass.

[0022] The composition of the present invention may contain other iron sulfide remover, such as acrolein, tetrais(hydroxymethyl)phosphine or a corresponding phosphonium salt, hydrochloric acid, and formic acid, as long as the effects of the present invention are not impaired.

[0023] The composition of the present invention may contain an appropriate solvent, such as cyclohexane, toluene, xylene, a heavy aromatic naphtha, and a petroleum distillate; and a monoalcohol or dialcohol having 1 to 10 carbon atoms, e.g., methanol, ethanol, and ethylene glycol.

[0024] The composition of the present invention may contain, in addition to the aldehyde (1), a component, such as a surfactant, a corrosion inhibitor, an oxygen scavenger, an iron control agent, a crosslinking agent, a breaker, a coagulant, a temperature stabilizer, a pH adjuster, a dehydration regulator, a swelling prevention agent, a scale inhibitor, a biocide, a friction reducer, a defoaming agent, an agent for preventing a lost circulation of mud water, a lubricating agent, a clay dispersant, a weighting agent, and a gelling agent, as long as the effects of the present invention are not impaired.

[0025] The composition of the present invention is not particularly limited with respect to its production method, and
it can be, for example, produced by adding and mixing the aldehyde (1) with the aforementioned arbitrary component, such as an iron sulfide remover and a solvent.

[0026] Though the composition of the present invention is suitably a liquid, it may be converted in a solid form, such as a powder and a fluid, upon being properly supported on a carrier, etc., according to a form to be used for the purpose of removing iron sulfide.

[0027] As a preferred embodiment of the present invention, the treatment is performed by adding the composition of the present invention in an amount sufficient for the removal of iron sulfide to a liquid containing iron sulfide. In the method of removing iron sulfide by using the composition of the present invention, the composition of the present invention is added such that the amount of the aldehyde (1) contained in the composition of the present invention is preferably 0.1 to 100 parts by mass, and more preferably 2 to 100 parts by mass based on 1 part by mass of iron sulfide. A temperature on the occasion of performing the treatment in which the composition of the present invention is added to and brought into contact with a liquid containing iron sulfide is preferably in a range of from 0°C to 150°C, and more preferably from 20°C to 130°C.

Examples

[0028] The present invention is hereunder specifically described by reference to Examples and the like, but it should be construed that the present invention is by no means limited by the following Examples. SAL, citral, and acrolein used in the Examples and Comparative Example are those mentioned below.

SAL: One synthesized from prenol in conformity with the method described in JP 60-224652 A (purity: 98.1%)  
Citral: Product available from Kuraray Co., Ltd. (purity: 98.0%, trans/cis = 51/49 to 57/43 (molar ratio))  
Acrolein: Product available from Tokyo Chemical Industry Co., Ltd., which contains hydroquinone as a stabilizer

[0029] <Example 1> Removal Test of Iron Sulfide (SAL)

[0030] In a 1L three-necked flask equipped with a thermometer, a stirrer, and a condenser, 500 mL of distilled water, 1 mL of 1 mol/L hydrochloric acid, 120.0 mg (0.5 mmol) of sodium sulfide nonahydrate, and 138.2 (0.5 mmol) of iron sulfate heptahydrate were added and stirred. As a result, iron sulfide was produced as a fine black precipitate. 126.3 mg (1.5 mmol) of SAL was added thereto, and the reaction solution was subjected to temperature rise to 50°C while stirring at 500 rpm. The point of time at when SAL was added was defined as 0 hour, and the behavior of iron sulfide was observed. As a result, after elapsing 4 hours, the iron sulfide was dissolved, and the reaction solution became colorless transparent.

<Example 2> Removal Test of Iron Sulfide (Citral)

[0031] The same test as in Example 1 was carried out, except that citral was used in place of SAL. After elapsing 7 hours, iron sulfide was dissolved, and the reaction solution became colorless transparent.

<Comparative Example 1> Removal Test of Iron Sulfide (Acrolein)

[0032] The same test as in Example 1 was carried out, except that acrolein was used in place of SAL. After elapsing 4 hours, iron sulfide was dissolved, and the reaction solution became colorless transparent.

<Test Example 1> Thermal Stability Test

[0033] 50 mL of each of SAL and acrolein was charged in three-necked flask, and the contents were subjected to temperature rise to 50°C in a nitrogen atmosphere. On the occasion when the content of each of SAL and acrolein immediately after the temperature rise was defined as 100%, a change of the content ratio was observed according to the calibration curve method by means of gas chromatography with an internal standard. The results are shown in Table 1.

[Gas Chromatography Analysis]

[0034] Analysis instrument: GC-14A (available from Shimadzu Corporation)  
Detector: FID (hydrogen flame ionization detector)  
Column used: DB-1701 (length: 50 m, film thickness: 1 μm, inner diameter: 0.32 mm) (available from Agilent...
Technologies)

Analysis conditions: Injection temperature: 250°C, detection temperature: 250°C
Temperature rise conditions: 70°C → (temperature rise at 5°C/min) → 250°C
Internal standard substance: Diglyme (diethylene glycol dimethyl ether)

<table>
<thead>
<tr>
<th>Table 1: Results of thermal stability test</th>
</tr>
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<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>SAL</td>
</tr>
<tr>
<td>Acrolein</td>
</tr>
</tbody>
</table>

[0035] After elapsing 10 hours, SAL remained in a ratio of 99.9%, whereas nevertheless acrolein contained hydroquinone as a stabilizer, it was lost in a ratio of 3.4%. It is noted from these results that SAL is extremely high in the thermal stability as compared with acrolein.

<Test Example 2> pH Stability Test

[0036] Each of SAL and acrolein was dissolved in 0.5 mol/L of phosphoric acid buffer solutions having a pH different from each other, thereby preparing 0.1 wt% solutions. 50 mL of each of the solutions was charged in a sample vial in a nitrogen atmosphere and stored at 23±2°C. On the occasion when the content of each of SAL and acrolein at the time of preparation was defined as 100%, a change of the content ratio was observed according to the absolute calibration curve by means of high-performance liquid chromatography analysis. The results are shown in Figs. 1 and 2.

[0037] It is noted from these results that SAL is extremely high in the pH stability as compared with acrolein.

[Preparation of Phosphoric Acid Buffer Solution]

[0038]

pH 1.7: 4.9 g of 75% phosphoric acid and 7.8 g of sodium dihydrogen phosphate dihydrate were dissolved in 200 mL of distilled water.

pH 6.2: 7.8 g of sodium dihydrogen phosphate dihydrate and 7.1 g of disodium hydrogen phosphate were dissolved in 200 mL of distilled water.

pH 8.1: 0.3 g of sodium dihydrogen phosphate dihydrate and 13.9 g of disodium hydrogen phosphate were dissolved in 200 mL of distilled water.

[High-Performance Liquid Chromatography Analysis]

[0039]

Analysis instrument: Prominence System (available from Shimadzu Corporation)
Column used: Cadenza CD-C18 (length: 150 m, inner diameter: 4.6 mm)
Developing solution: H2O/MeOH = 45/55 (volume ratio), H3PO4 = 1 mol/L
Flow rate: 1 mL/min

<Reference Example>

[0040] SAL, citral, and acrolein are each an existing compound, and the information regarding the safety is disclosed. For reference, the information regarding the safety is shown in Table 2. SAL and citral are extremely low in the toxicity and safe as compared with acrolein.

<table>
<thead>
<tr>
<th>Table 2: Information regarding safety of SAL, citral, and acrolein</th>
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<tr>
<td>Fire Service Act</td>
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<tr>
<td>Category IV, Class II petroleum Hazardous grade III, water-insoluble</td>
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It is noted from the aforementioned Examples, Comparative Example, and Reference Example that the aldehyde (1), such as SAL, has an iron sulfide removal ability equivalent to acrolein and is higher in the thermal stability and the pH stability and safer than acrolein.

Industrial Applicability

The composition of the present invention is useful in view of the fact that it is high in the thermal stability and the pH stability and is able to remove iron sulfide safely and efficiently.

Claims

1. A composition for removing iron sulfide, comprising, as an active ingredient, an α,β-unsaturated aldehyde represented by the following general formula (1):

   ![Chemical Structure](image)

   wherein R¹ to R³ each independently represent a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, an alkenyl group having 2 to 10 carbon atoms, or an aryl group having 6 to 12 carbon atoms, provided that R¹ may be connected to R² or R³, to constitute an alkylene group having 2 to 6 carbon atoms; and that R¹ and R² are not a hydrogen atom at the same time.

2. The composition according to claim 1, wherein R¹ to R³ each independently represent a hydrogen atom or an alkyl group having 1 to 5 carbon atoms.

3. The composition according to claim 1 or 2, wherein R³ is a hydrogen atom.

4. A method for removing iron sulfide, comprising bringing the composition of any of claims 1 to 3 into contact with iron sulfide.

5. The method according to claim 4, wherein the α,β-unsaturated aldehyde in the composition is added in an amount of 0.1 to 100 parts by mass based on 1 part by mass of iron sulfide.
6. The method according to claim 4 or 5, comprising bringing the \( \alpha,\beta \)-unsaturated aldehyde in the composition into contact with iron sulfide in a range of from \(-30^\circ\text{C}\) to \(150^\circ\text{C}\).

7. Use of the composition according to any of claims 1 to 3, for removing iron sulfide.
[Fig. 1]

**SAL**

Retention

- 100%
- 90%
- 80%
- 70%
- 60%
- 50%
- 40%
- 30%
- 20%
- 10%
- 0%

Time (hr)

- pH 1.72
- pH 6.20
- pH 8.13

[Fig. 2]

**Acrolein**

Retention

- 100%
- 90%
- 80%
- 70%
- 60%
- 50%
- 40%
- 30%
- 20%
- 10%
- 0%

Time (hr)

- pH 1.72
- pH 6.20
- pH 8.13
## INTERNATIONAL SEARCH REPORT

**International application No.**

PCT/JP2017/022837

### A. CLASSIFICATION OF SUBJECT MATTER

C23G1/24(2006.01)i, C10G75/02(2006.01)i, C23G5/00(2006.01)i

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)

C23G1/24, C10G75/02, C23G5/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996
Jitsuyo Shinan Toroku Koho 1996-2017
Kokai Jitsuyo Shinan Koho 1971-2017
Toroku Jitsuyo Shinan Koho 1994-2017

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

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>JP 60-224652 A (Kuraray Co., Ltd.), 09 November 1985 (09.11.1985), (Family: none)</td>
<td>1-7</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special documents of cited documents:
  
  "A" document defining the general state of the art which is not considered to be of particular relevance
  
  "E" earlier application or patent but published on or after the international filing date
  
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  "O" document referring to an oral disclosure, use, exhibition or other means
  
  "P" document published prior to the international filing date but later than the priority date claimed

1. "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

2. "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

3. "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

4. "K" document member of the same patent family

Date of the actual completion of the international search

07 July 2017 (07.07.17)

Date of mailing of the international search report

18 July 2017 (18.07.17)

Name and mailing address of the ISA/

Japan Patent Office

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Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)
REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

• JP 60224652 A [0020] [0028]

Non-patent literature cited in the description

• SPE Annual Technical Conference and Exhibition SPE 146080, held in the city of Denver, 30 October 2011 [0003]
• SPE Annual Technical Conference and Exhibition SPE 146080, 2011, 10.2118/146080-MS [0004]