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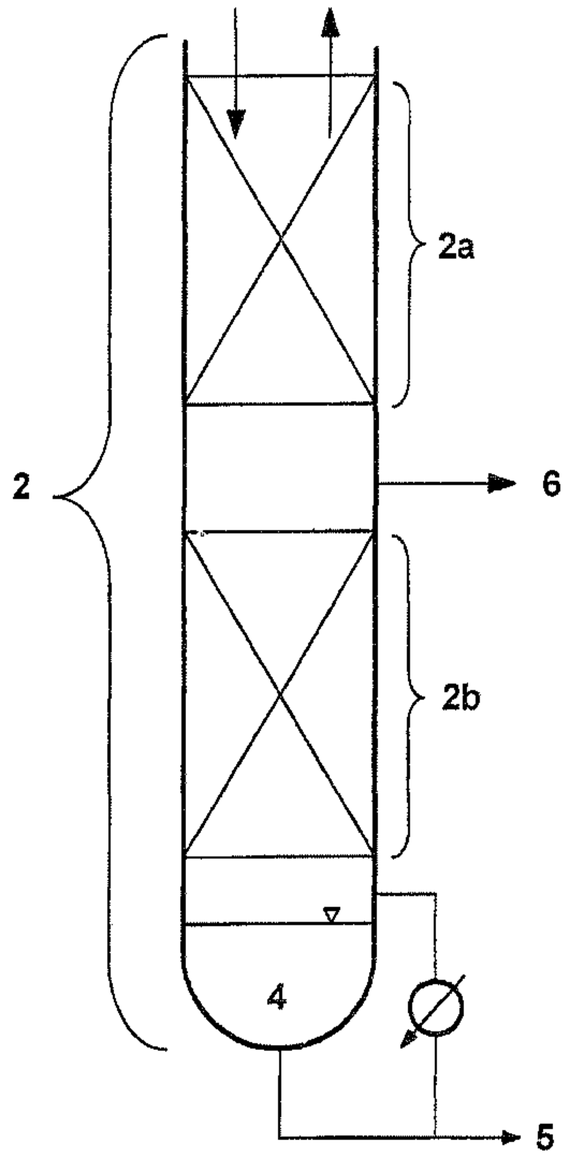
(54) **Titre : PROCEDE DE PURIFICATION DE COMPOSES POLYMERISABLES**
(54) **Title: PROCESS FOR PURIFYING POLYMERIZABLE COMPOUNDS**



(57) **Abrégé/Abstract:**
Process for distillatively purifying polymerizable compounds using a high-boiling, inert, thermally longterm-stable substance as a boiling oil, characterized in that the boiling oil is disposed in the bottom of a rectification column.

Abstract:

Process for distillatively purifying polymerizable compounds using a high-boiling, inert, thermally long-term-stable substance as a boiling oil, characterized in that the boiling oil is disposed in the bottom of a rectification column.

Process for purifying polymerizable compounds

FIELD OF THE INVENTION

The invention describes a process for distillatively purifying polymerizable compounds and the use of a boiling oil for the distillative purification of polymerizable compounds.

BACKGROUND OF THE INVENTION

DE-A-2136396 describes a process for obtaining anhydrous acrylic acid by countercurrent scrubbing of the reaction gases in an absorber column with a high-boiling, inert, extremely hydrophobic solvent. Suitable solvents are hydrocarbons of the middle oil fraction, heat carrier oils with boiling points above 170°C (at standard pressure) or diphenyl ether, diphenyl and/or mixtures thereof. The solvent is fed in via the top of the column. For the absorption, a minimum temperature of 30-80°C at standard pressure is established.

EP-A-188775 discloses a process for obtaining anhydrous methacrylic acid, in which the reaction gases obtained are scrubbed with an inert, high-boiling, hydrophobic, organic solvent, especially by countercurrent scrubbing in an absorber column. The solvent, such as diphenyl, diphenyl ether, dibenzofuran and/or mixtures thereof, is added via the top of the column. The absorption temperature is 40-120°C at standard pressure.

A disadvantage of the aforementioned processes is that, to obtain anhydrous acrylic acid or methacrylic acid, further desorption and distillation steps have to follow in order to remove the target product from the solvent used again.

SUMMARY OF THE INVENTION

In one embodiment, there is provided a process for distillatively purifying polymerizable compounds using a high-boiling, inert, thermally long-term-stable substance as a boiling oil, characterized in that the boiling oil is disposed in the bottom of a rectification column, and the boiling oil remains in the bottom of the rectification column and can be recycled without further purification.

In another embodiment, there is provided a use of a high-boiling, inert, thermally long-term-stable substance as a boiling oil in the bottom of a rectification column for the distillative purification of polymerizable compounds, wherein the boiling oil remains in the bottom of the rectification column and can be recycled without further purification.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic representation of an embodiment of the process according to the present invention.

DETAILED DESCRIPTION

It is an object of the present invention to provide a process for distillatively purifying polymerizable compounds, in which the substances used as assistants can be recycled into the plant without further purification, and not more than 10% of the assistant, based on the target product, is discharged. In addition, the process shall ensure in particular that polymerization of the target product is avoided. The object is achieved by performing the distillative purification of the polymerizable compound in the presence of a high-boiling, inert, thermally long-term-stable substance, this substance referred to as a boiling oil being present in the bottom of a rectification

column. This rules out long residence times of the polymerization-prone target product in the bottom, since the concentration of the polymerization-prone compound decreases greatly as a result of the heat exchange with the boiling oil vapours in the direction of the bottom and hence in the direction of increasing temperature, which largely averts the risk of polymerization.

The invention therefore provides a process for distillatively purifying polymerizable compounds using a high-boiling, inert, thermally long-term-stable substance as a boiling oil, characterized in that the boiling oil is disposed in the bottom of a rectification column.

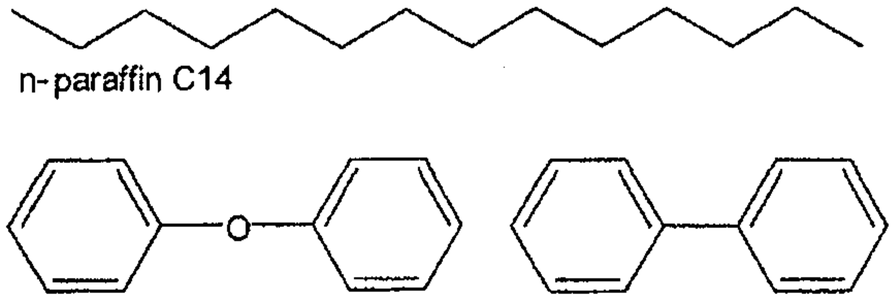
For the process according to the invention, the boiling oil used is a high-boiling, inert, thermally long-term-stable substance having a boiling point higher than the boiling point of the pure target product, in order to ensure its distillative removal. The boiling point of the boiling oil should, though, not be too high either, in order to reduce the thermal stress on the pure polymerizable compound.

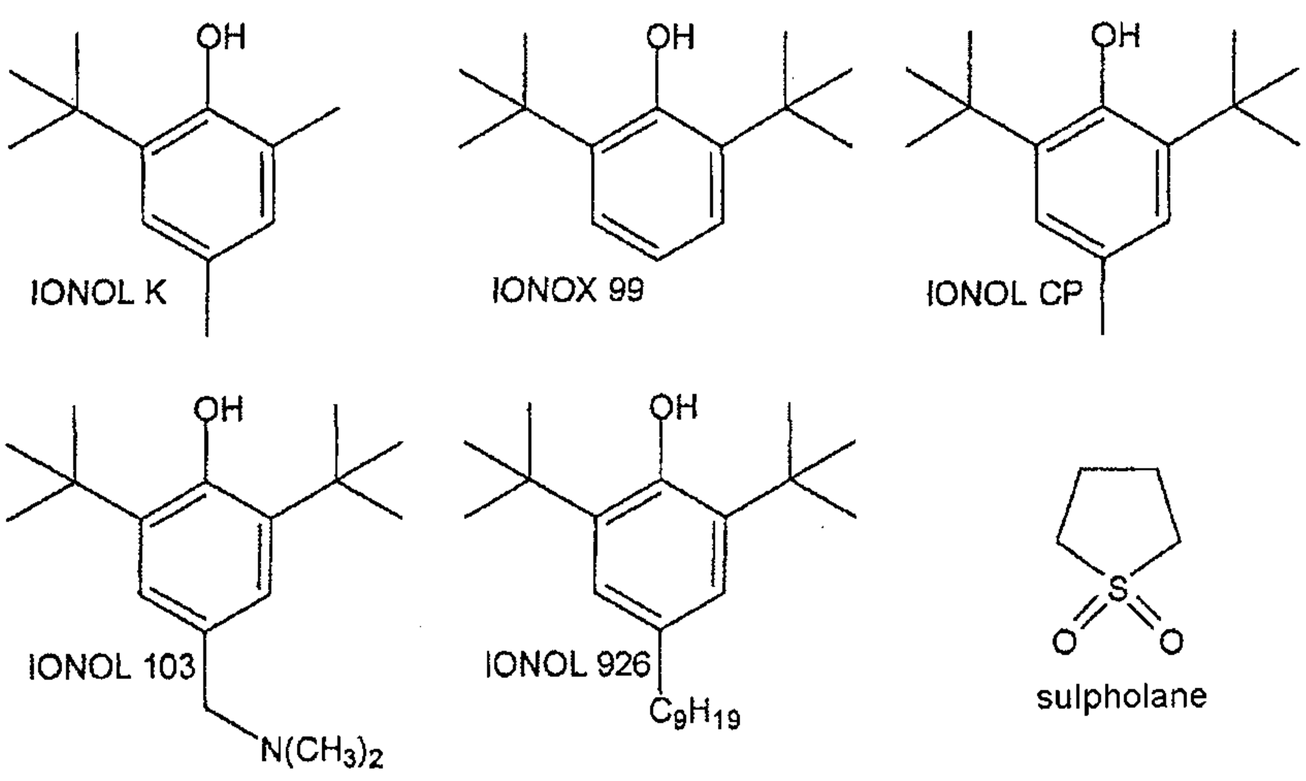
In general, the boiling point of the boiling oil at standard pressure (1013 mbar) is 150 to 400°C, in particular 200 to 300°C.

Suitable boiling oils include relatively long-chain unbranched paraffins having 12-20 carbon atoms, aromatic compounds such as Diphyl (eutectic mixture of

75% biphenyl oxide and 25% biphenyl), alkyl-substituted phenols or naphthalene compounds, sulpholane (tetrahydrothiophene 1,1-dioxide) or mixtures thereof.

Suitable examples are the boiling oils shown below:





Particular preference is given to using 2,6-di-tert-butyl-para-cresol, 2,6-di-tert-butylphenol, sulpholane, Diphyl or mixtures thereof, very particular preference to using sulpholane.

For the process according to the invention, any rectification column which has preferably 5 to 50 separating stages can be used. In the present invention, the number of separating stages refers to the number of trays in a tray column multiplied by the tray efficiency, or the number of theoretical plates in the case of a column with structure packing or a column with random packing.

Examples of a rectification column with trays include those such as bubble-cap trays, sieve trays, tunnel-cap trays, valve trays, slot trays, slotted sieve trays, slotted bubble-cap trays, jet trays, centrifugal trays; examples of a rectification column with random packings include those such as Raschig rings, Lessing rings, Pall rings, Berl saddles, Intalox saddles; and examples of a rectification column with structured packings include those of the Mellapak (Sulzer), Rombopak (Kühni), Montz-Pak (Montz) types, and structured packings with catalyst pockets, for example Katapak (Sulzer).

A rectification column with combinations of regions of trays, of regions of random packings and/or of regions of structured packings may likewise be used.

Preference is given to using a rectification column with random packings and/or structured packings. The rectification column can be produced from any material suitable therefor. These include stainless steel and inert materials.

The rectification column is preferably operated under reduced pressure at an absolute pressure of 1 to 500 mbar, preferably at an absolute pressure of 1 to 100 mbar. The temperature in the bottom of the rectification column is determined by the boiling oil used and the system pressure which exists.

Polymerizable compounds are generally understood to mean monomers with at least one reactive double bond or other reactive functional groups. They include compounds having carbon-carbon multiple bonds (olefins, alkynes, vinyl, (meth)acryloyl compounds), cyclic ethers, esters or amides (oxiranes, lactones, lactams), unsaturated cyclic hydrocarbons, and also those with isocyanate or H-acidic amino, hydroxyl or carboxyl groups. Suitable polymerizable compounds are known to

those skilled in the art from the literature, for example from J. Brandrup, E.H. Immergut and E.A. Grulke, Polymer Handbook, 4th ed., Hoboken, John Wiley and Sons, 1999, pages III-1 to III-41.

The polymerizable compound to be purified is fed in preferably above the middle region of the column. Low-boiling impurities are drawn off at the top of the column; high-boiling impurities are discharged from the column bottom. The pure target product is preferably discharged at a side draw below the middle region of the column.

The column may also be connected to other apparatus, for example further apparatus for substance separation and/or a reactor. A reaction region may also be arranged within the column. The column may also be divided into a plurality of separating segments which fulfil different tasks.

In order to avoid undesired polymerizations of the polymerizable compound to be purified, a polymerization inhibitor is optionally added. The polymerization inhibitors usable with preference include octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, phenothiazine, hydroquinone, hydroquinone monomethyl ether, 4-hydroxy-2,2,6,6-tetramethylpiperidinooxyl (TEMPOL), 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert-butylphenol, 2,6-di-tert-butyl-4-methylphenol, para-substituted phenylenediamines, for example N,N'-diphenyl-p-phenylenediamine, 1,4-benzoquinone, 2,6-di-tert-butyl-alpha-(dimethylamino)-p-cresol, 2,5-di-tert-butylhydroquinone or mixtures of two or more of these stabilizers.

The inhibitor is metered in preferably at the top of the column. From the column bottom, high boilers such as added inhibitors can be discharged by customary methods, for example by means of a thin-film evaporator

or an apparatus which performs similar tasks, which recycles evaporating substances into the rectification column and discharges non-evaporating high boilers.

The invention further provides for the use of the abovementioned high-boiling, inert, thermally long-term-stable substance as a boiling oil in the bottom of a rectification column for the distillative purification of polymerizable compounds.

The process according to the invention enables the polymerizable compound to be obtained without losses by undesired polymerization in high purity by simple removal, and the boiling oil used can be recycled into the plant without further purification.

One embodiment of the process according to the invention is shown schematically in Figure 1.

The monomer to be purified = crude monomer (1) passes into the lower section of a rectification column (2). Here, the removal of components which have a lower boiling point (3) than the monomer to be purified takes place in the separating region (2a). In the separating region (2b) of the column, the monomer is separated from the boiling oil (4) present in the bottom and from components which have a higher boiling point than the monomer to be purified. High boilers present in the bottom can be discharged by customary methods (5), for example by means of a thin-film evaporator or an apparatus which performs similar tasks, which recycles evaporating substances into the rectification column and discharges non-evaporating high boilers. The highly pure monomer (6) is drawn off, preferably in gaseous form, between separating region (2a) and (2b).

The examples which follow illustrate the process according to the invention without restricting it.

Example 1: Purification of methacrylic anhydride

The purification of methacrylic anhydride was performed in the lower section of a rectification column according to Figure 1.

The rectification column had twelve separating stages in the separating region (2a) and eight separating stages in the separating region (2b). This column had an internal diameter of 100 mm and was equipped with Sulzer CY structured packings (separating region 2a) and Montz BSH 400 structured packings (separating region 2b). The pressure in the column bottom was 35 mbar. Under steady-state conditions, a temperature profile of 164°C (bottom) to 66°C (upper end of the separating region 2a) was established. The discharge of methacrylic anhydride at the side draw (between separating region 2a and 2b) and the heating steam output of the bottom evaporator were effected under temperature control in the particular regions.

In the bottom of the rectification column, 6 kg of sulpholane were used as the boiling oil (4). The evaporator used was a falling-film evaporator.

At the side draw, methacrylic anhydride was withdrawn with a purity of 99.7% (GC analysis).

Example 2: Purification of acrylic anhydride

The purification of acrylic anhydride was performed as explained in Example 1 in the same lower section of a rectification column according to Figure 1. The pressure in the column bottom was 35 mbar. Under steady-state conditions, a temperature profile of 164°C (bottom) to 54°C (upper end of the separating region 2a) was established. The discharge of acrylic anhydride at the side draw (between separating region 2a and 2b) and the heating steam output of the bottom evaporator were effected under temperature control in the particular regions.

In the bottom of the rectification column, 6 kg of sulpholane were used as boiling oil (4). The evaporator used was a falling-film evaporator.

At the side draw, acrylic anhydride was withdrawn with a purity of 99.7% (GC analysis).

Claims:

1. Process for distillatively purifying polymerizable compounds using a high-boiling, inert, thermally long-term-stable substance as a boiling oil, characterized in that the boiling oil is disposed in the bottom of a rectification column, and the boiling oil remains in the bottom of the rectification column and can be recycled without further purification.

2. The process according to claim 1, wherein not more than 10% of boiling oil, based on the polymerizable compounds, are discharged.

3. The process according to Claim 1 or 2, wherein the boiling point of the boiling oil at 1013 mbar is 150 to 400°C.

4. The process according to any one of Claims 1 to 3, wherein the boiling point of the boiling oil at 1013 mbar is 200 to 300°C.

5. The process according to any one of Claims 1 to 4, wherein the high-boiling, inert, thermally long-term-stable substances used are relatively long-chain unbranched paraffins having 12-20 carbon atoms, aromatic compounds, alkyl-substituted phenols or naphthalene compounds, sulpholane or mixtures thereof.

6. The process according to Claim 5 wherein an aromatic compound is used and the aromatic compound is Diphyl.

7. The process according to any one of Claims 1 to 5, wherein the high-boiling, inert, thermally long-term-stable

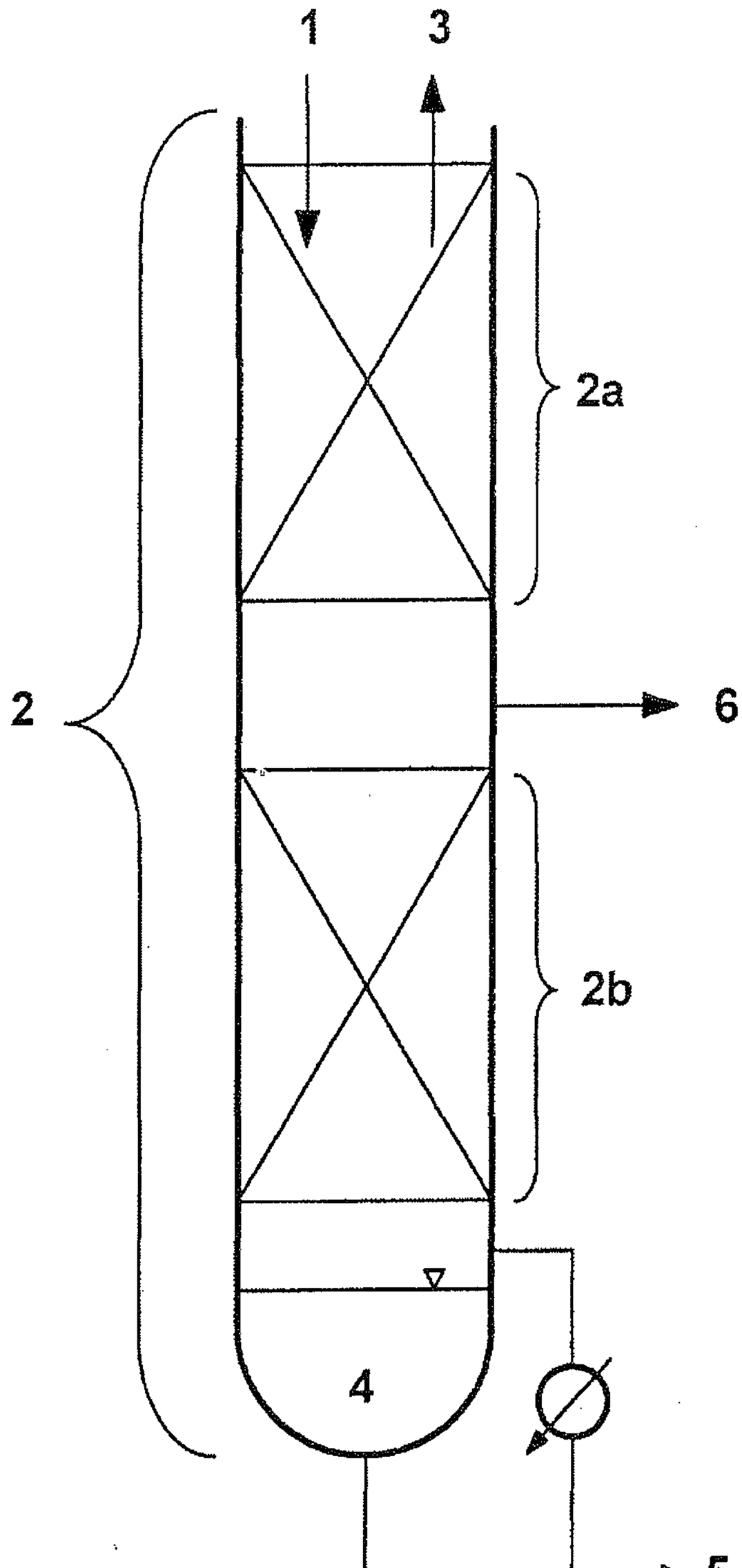
substance used is 2,6-di-tert-butyl-para-cresol, 2,6-di-tert-butylphenol, sulpholane, Diphyl, or mixtures thereof.

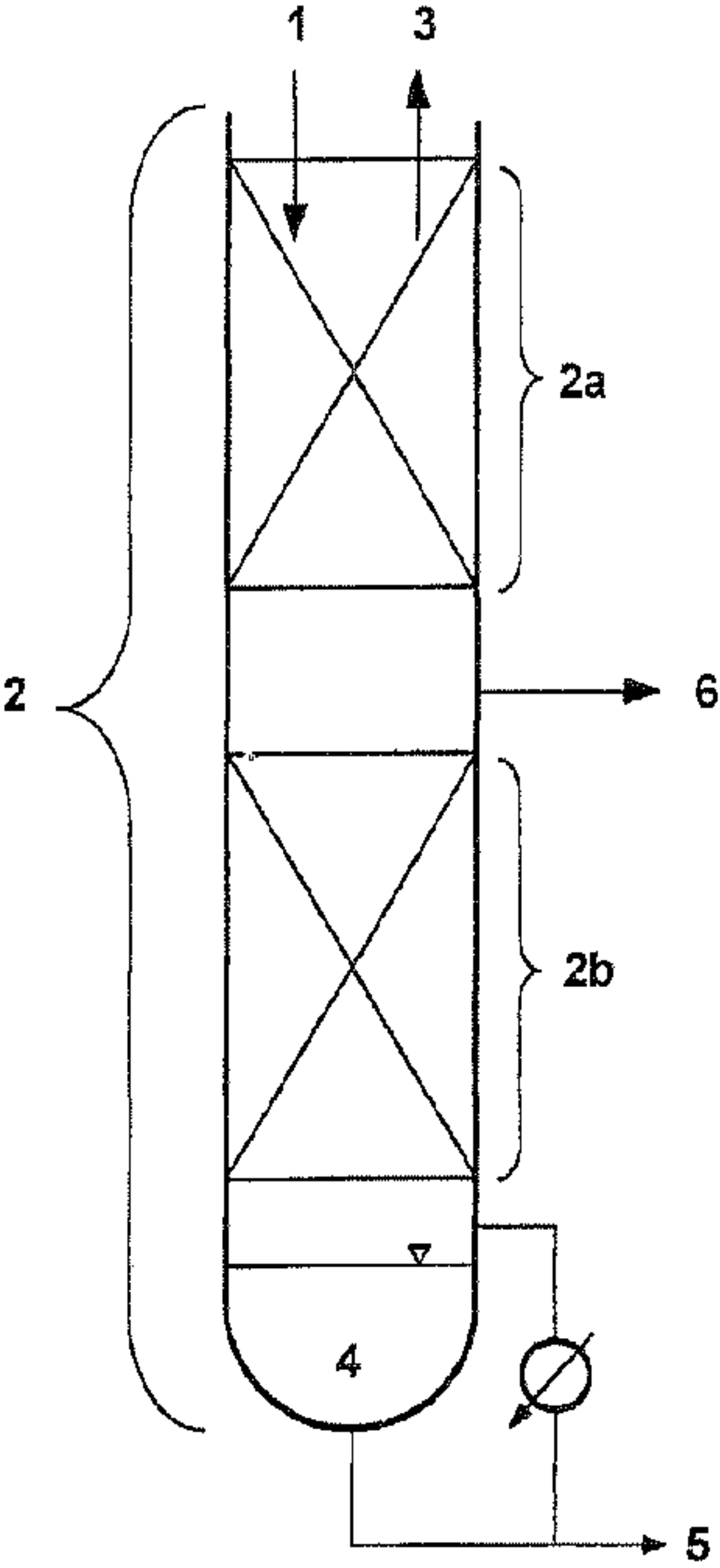
8. The process according to any one of Claims 1 to 5 or 7, wherein the high-boiling, inert, thermally long-term-stable substance used is sulpholane.

9. Use of a high-boiling, inert, thermally long-term-stable substance as a boiling oil in the bottom of a rectification column for the distillative purification of polymerizable compounds, wherein the boiling oil remains in the bottom of the rectification column and can be recycled without further purification.

10. The use of claim 9 wherein not more than 10% of boiling oil, based on the polymerizable compounds, are discharged.

Figure 1

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