Title: DISTILLATION OF NEUTRAL COMPOUNDS FROM TALL OIL SOAP

Abstract: The present invention relates to isolation of phytosterols and other neutral compounds from alkaline tall oil soap (TOS) which is obtained from the Kraft process black liquor by skimming. The invention also enables the production of tall oil with high acid number.
DISTILLATION OF NEUTRAL COMPOUNDS FROM TALL OIL SOAP

Field of the invention

The present invention relates to isolation of phytosterols and other neutral compounds from alkaline tall oil soap (TOS) which is obtained from the Kraft process black liquor by skimming. The invention also enables the production of tall oil with high acid number.

Background

Tall oil soap (TOS) is a by-product of the Kraft process. The soap consists mainly of sodium salts of fatty acids, sodium salts of diterpenic (rosin) acids, free fatty acids, free rosin acids and unsaponifiable neutral compounds such as fatty alcohols, sterols, steryl esters and waxes. The water content of neat soap is typically 25 to 45%, such as 30 to 35%. The pH of the soap is typically in the range of 11 to 13, arising from the presence of entrained black liquor. In industrial practice, soap is routinely acidulated with sulphuric acid to produce crude tall oil (CTO), an article of commerce.

Crude tall oil can be refined by distillation into heads, tall oil fatty acids (TOFA), tall oil rosin acids (TOR) and tall oil pitch (TOP) fractions. Distillation is done at low pressure and at high temperature which is somewhat detrimental to sterols. The sterols which survive the harsh distillation conditions are esterified with either rosin or fatty acids. Despite the loss of some sterols and the formation of sterol esters in the distillation phase the TOP is currently used as the primary source of pine based phytosterols.

Sterols, in particular phytosterols, have several uses, including the use as food additives and as precursors for steroids. Several methods have been reported for the isolation of sterols from tall oil soap. The general method
involves the extraction of neat soap with a variety of organic solvents. The presence of entrained black liquor promotes and stabilizes the unwanted water-oil emulsion, which is known to be extremely difficult to break. Consequently, the efficiency of solvent extraction of neat soap for the isolation of sterols is greatly reduced. Holmbom et al. teach in US Patent 3,965,085 the extraction of a mixture of acetone-water soap slurry, with a water-immiscible solvent such as hexane. The aqueous phase contains mainly sodium salts of fatty and resin acids. The organic phase contains mostly unsaponifiables including sterols. In US Patent 4,044,031, Johansson et al. teach the dissolution of soap in a water-immiscible mixture comprising hexane and acetone, extraction of the water-immiscible phase with another solvent mixture comprising methanol, hexane, acetone and water, and isolation of sterols from the methanolic phase by evaporative crystallization. In US Patent 5,770,749, Kutney et al. teach the use of a mixture of ketones, hydrocarbons and water to extract sterols from soap. The hydrocarbon extract is further processed with methanol. However, the complexity of recovering the multi-component spent solvent is very problematic in these processes. Also, recycling highly water soluble solvents such as acetone and methanol from water mixtures is very complicated.


The methods known in the art for separation of phytosterols and other neutral compounds from alkaline tall oil soap are generally complex and the methods using distillation suffer from the drawbacks of solidification of water depleted distillation residue and the distillate.

There is thus a need for a more efficient method of obtaining phytosterols from tall oil soap.
Summary of the invention

The present invention is directed to a two stage treatment of tall oil soap in order to separate unsaponifiables and finally produce tall oil with high acid number.

First, the tall oil soap is dried. The drying can be performed using a wiped film evaporator or other suitable technique. Before, during or directly after the water removal, a diluent is added in order to prevent the solidification of the distillation residue or the intended distillate. The diluent concentration is chosen between 1 to 100 weight% (based on the wet soap). A suitable diluent can be any chemically inert high boiling oil or solvent e.g. silicon oil, mineral oil, paraffin oil etc., or mixture thereof which preferably does not dissolve the residue compounds at lower than working distillation temperature.

Second, the dried tall oil soap is subjected to a short path distillation procedure. Since the distillate consists of high melting compounds like phytosterols, the distillate may solidify to the condensing part of the apparatus. According to the present invention, a washing condenser system is used to avoid solidification of the distillate. The washing solvent chosen must have a high boiling point but must be liquid in the condenser temperature or in direct surrounding temperature and must be able to dissolve the distillate in whole at the condenser or direct surrounding temperature. Examples of such washing solvents are chemically inert high boiling oil or solvent e.g. silicon oil, mineral oil, paraffin oil etc., or mixtures thereof.

Third, the washing solvent is either used directly as crystallization solvent for the purification of the phytosterols or separated prior to crystallization process.
Fourth, after the distillation of unsaponifiables, the diluent is separated from the residue by filtration, washing, centrifugation, extraction or any combination thereof.

Finally, the neutral compound depleted tall oil soap can be acidified to produce tall oil with high acid number.

To summarize, through the advanced distillation sequence presented herein, both isolation of phytosterols from tall oil soap and production of tall oil with high acid number can be achieved.

Thus, the present invention is directed to a process for isolation of phytosterols and/or other neutral compounds from alkaline tall oil soap comprising the steps of

a) drying the tall oil soap;
b) adding a diluent to prevent solidification of the distillation residue or the distillate before, during or directly after step a);
c) subjecting the dried tall oil soap to a short path distillation using a washing condenser system wherein the washing solvent has a boiling point such that it is liquid in the condenser temperature and able to dissolve the distillate at the condenser temperature; and
d) isolating the phytosterols and/or other neutral compounds.

In one embodiment of the present invention, the drying in step a) is carried out in a wiped film evaporator.

In one embodiment of the present invention, the diluent is a chemically inert high boiling oil or solvent such as a silicon oil, mineral oil, paraffin oil or mixtures thereof.

In one embodiment of the present invention, the diluent is a mineral oil.
In one embodiment of the present invention, the diluent is a silicon oil.

In one embodiment of the present invention, the diluent is a paraffin oil.

In one embodiment of the present invention, the process also comprises the steps of

e) removing the diluent from the distillation residue by washing using an organic solvent; and
f) acidulating the remaining washed residue from step e) and removing the water phase to obtain essentially water-free tall oil.

One embodiment of the present invention is a distillation residue obtainable by the process according to the present invention.

One embodiment of the present invention is tall oil having an acid number of at least 170, such as at least 175 or at least 180. In one embodiment, the tall oil is obtainable by the process according to the present invention.

**Detailed description**

The term "phytosterol" is intended to mean a sterol derived from plants and encompasses all plant sterols and the saturated forms of phytosterols thereof (i.e., phytostanols). Plant sterols fall into one of three categories: 4-desmethylsterols (lacking methyl groups); 4-monomethylsterols (one methyl group); and 4,4-dimethylsterols (two methyl groups) and include, but are not limited to, sitosterol (e.g., [alpha] and [beta] sitosterol), campesterol, stigmasterol, taraxasterol, and brassicasterol. The term "phytostanol" is intended to mean a saturated phytosterol and encompasses, but is not limited to, sitostanol (e.g., [alpha] and [beta] sitostanol), campestanol, stigmasteranol, clionastanol, and brassicastanol. Phytosterols isolated by the methods of the invention may be quantified by any means known in the art.
Suitable diluents include heavy mineral oils, silicon oil, polyethyleneoxides and paraffin oil.

A washing condenser is defined herein as an internal condenser used in a short path distillatory which is continuously wetted with liquid in which the distillate dissolves.

The phytosterol crystallization can be performed using methods known in the art, including cooling, concentration by removing some of the solvent by distillation, evaporation to dryness followed by introduction of a solvent or solvent mixture in which the phytosterols only dissolve at elevated temperature followed by cooling or through seeding with phytosterol crystals.

The process according to the present invention may be carried out as a batch process or as a continuous process.

In view of the above detailed description of the present invention, other modifications and variations will become apparent to those skilled in the art. However, it should be apparent that such other modifications and variations may be effected without departing from the spirit and scope of the invention.
Claims

1. A process for isolation of phytosterols and/or other neutral compounds from alkaline tall oil soap comprising the steps of
   a) drying the tall oil soap;
   b) adding a diluent to prevent solidification of the distillation residue or the distillate before, during or directly after step a);
   c) subjecting the dried tall oil soap to a short path distillation using a washing condenser system wherein the washing solvent has a boiling point such that it is liquid in the condenser temperature and able to dissolve the distillate at the condenser temperature; and
   d) isolating the phytosterols and/or other neutral compounds.

2. A process according to claim 1, wherein the drying in step a) is carried out in a wiped film evaporator.

3. A process according to claim 1 or 2, wherein the diluent is a chemically inert high boiling oil or solvent such as a silicon oil, mineral oil, paraffin oil or mixtures thereof.

4. A process according to claim 3, wherein the diluent is a mineral oil.

5. A process according to claim 3, wherein the diluent is a silicon oil.

6. A process according to claim 3, wherein the diluent is a paraffin oil.

7. Distillation residue obtainable by the process according to any one of claims 1 to 6.

8. A process according to any one of claims 1 to 6, also comprising the steps of
   e) removing the diluent from the distillation residue by washing using an organic solvent; and
f) acidulating the remaining washed residue from step e) and removing the water phase to obtain essentially water-free tall oil.

9. Tall oil having an acid number of at least 170.

10. Tall oil according to claim 9, having acid number of at least 180.

11. Tall oil obtainable by the process according to claim 8.
### INTERNATIONAL SEARCH REPORT

**PCT/IB2017/050694**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. B01D3/12 B01D3/14 B01D1/22 C11B13/00

**ADD.**

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)

B01D C11B

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

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

EPO-Internal, WPI Data, COMPENDEX, FSTA

**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>
</thead>
<tbody>
<tr>
<td>A</td>
<td>paragraph [0026]</td>
<td>1-8</td>
</tr>
<tr>
<td>A</td>
<td>paragraph [0036]</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>example 5; table 2</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>US 6 462 210 B1 (DIAZ MIGUEL ANGEL FUENZALIDA [CL] ET AL) 8 October 2002 (2002-10-08) cited in the application claim 1; figures 1-3 column 1, lines 33-43 column 11, line 16 - column 12, line 15</td>
<td>1-8,11</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories 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
  - *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - *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

**Date of the actual completion of the international search**

10 April 2017

**Date of mailing of the international search report**

16/06/2017

**Name and mailing address of the ISA/ European Patent Office, P.B. 5018 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016**

Goetz, Michael
<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>
</thead>
<tbody>
<tr>
<td>A</td>
<td>MILENA ROUSKOVÁ ET AL: &quot;Extraction of phytosterols from tall oil soap using selected organic solvents&quot;, CHEMICAL PAPERS, SP VERSITA, HEIDELBERG, vol. 65, no. 6, 26 August 2011 (2011-08-26), pages 805-812, XP019957867, ISSN: 1336-9075, DOI: 10.2478/S11696-011-0077-3 the whole document</td>
<td>1-8,11</td>
</tr>
</tbody>
</table>
INTERNATIONAL SEARCH REPORT

Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. [ ] Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. [ ] Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. [x] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

   1-8, 11

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

[ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

[ ] No protest accompanied the payment of additional search fees.
This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-8, 11

   Process for the isolation of phytosterols from alkaline tall oil soap, using a particular distillation method; tall oil obtainable by the said method.

   ---

2. claims: 9, 10

   Tall oil having an acid number of at least 170.

   ---