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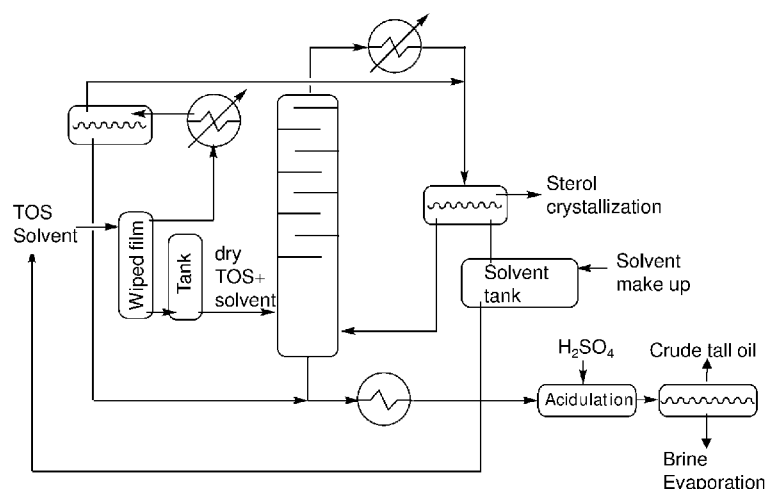
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(54) Title: PROCESS FOR SEPARATING UNSAPONIFIABLES FROM TALL OIL SOAP

Fig 1



(57) Abstract: The present invention relates to a process for separating unsaponifiabiles from tall oil soap (TOS) using co-distillation. The invention also enables the production of tall oil with high acid number.

PROCESS FOR SEPARATING UNSAPONIFIABLES FROM TALL OIL SOAP

Field of the invention

The present invention relates to a process for separating unsaponifiables
5 from tall oil soap (TOS) using co-distillation. The invention also enables the production of tall oil with high acid number.

Background

10 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
15 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
20 (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
25 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
- 5 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
- 10 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,
- 15 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 seen as problematic in these processes. Also, recycling highly water soluble solvents such as acetone and methanol from water mixtures is very complicated.
- 20
- Further examples of methods of obtaining sterols are described in US2005/0107582, WO2009/106696, CA2319230, US6297353, US6465665, US6462210, US7078544, US7087402 and US20020107168.
- 25 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.
- 30 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 process for separating unsaponifiables
5 from tall oil soap using co-distillation, to produce tall oil with high acid number.

In a first step, a molecular solvent having a boiling point higher than 160°C
and in which sterols are essentially insoluble is added to the soap and most
or all the water of the soap is evaporated using e.g. a wipe-film evaporator or
10 any other distillation technique applicable. Alternatively, water is distilled
along the chosen molecular solvent. The water can be removed in
atmospheric or under reduced pressure. The molecular solvent can be e.g.
ethylene glycol, propylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-
butanediol, glycerol or a mixture thereof.

15

In a second step, after the water removal, the mixture is distilled, for example
in atmospheric or under reduced pressure using e.g. a wipe-film evaporator or
any other distillation technique applicable for the present mixture.

Phytosterols are co-distilled (the distillation temperature is below the boiling
20 point of phytosterols) with the molecular solvent but are not soluble in the
chosen solvent. When the distillate is collected and the distillate temperature
is reduced, phytosterols are insoluble and can be isolated either by phase
separation or after precipitation by sedimentation, filtration, centrifugation or
any combination thereof. The phytosterol depleted distilled molecular solvent
25 can be returned back to the distillation vessel or purified and recycled by
further distillation.

The distillation condenser temperature can be controlled in order to avoid
solidification of the phytosterols which could lead to clogging of the
30 condenser. The condenser temperature is chosen according to the molecular
solvent used. Preferably, the chosen molecular solvent can perform as the

crystallization solvent and produce high purity sterol mixture. Alternatively, the crude sterols can be purified using methods known in the art.

5 After the distillation of the unsaponifiables, most of the molecular solvent still present in the residue can be distilled off with remaining phytosterols and the distillation residue is acidified using the standard acid cooking in order to produce high acid number tall oil. The residual molecular solvent still present in the distillation residue dissolves into the water fraction and high quality tall oil can be separated using the standard procedure.

10

Thus, 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.

15 Thus, the present invention is directed to a process for isolation of phytosterols and/or other neutral compounds from tall oil soap using co-distillation wherein added molecular solvent is used to achieve the co-distillation of phytosterols, comprising the steps of:

- 20 a) adding the molecular solvent having a boiling point higher than 160°C, and in which sterols are essentially insoluble at 25°C, to tall oil soap;
- b) distilling the mixture obtained in step a) at a distillation temperature below the boiling point of phytosterols; and
- 25 c) collecting the distillate, reducing the temperature of the distillate and isolating the phytosterols and/or other neutral compounds.

The molecular solvent used in step a) is a solvent that is miscible with water. The molecular solvent used in step a) is a polar solvent.

30

In one embodiment of the invention, the molecular solvent used in step a) has a boiling point higher than 170°C, such as 180°C or 190°C or 195°C or 200°C or 205°C or 210°C or 215°C.

In one embodiment of the invention, the molecular solvent is selected from ethylene glycol, propylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, glycerol or a combination thereof. Further examples of groups of solvents from which a molecular solvent for use in step a) can be selected include sulfoxides, sulfones and ketones.

The term “essentially insoluble” as used herein means that the sterols concerned are only partly soluble, such as less than 1% of the sterols being soluble in the molecular solvent or the sterols are completely insoluble in the molecular solvent concerned.

The distillation in step b) may be carried out in atmospheric pressure or under reduced pressure.

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

In one embodiment of the present invention, in or prior to step a), most or all water is removed from the tall oil soap before step b). In one embodiment, the water is removed by evaporation. The water can be removed at atmospheric or reduced pressure.

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

d) acidulating the remaining tall oil soap from step c) and optionally washing the molecular solvent from the tall oil to obtain high acid number tall oil.

The optional washing in step d) is typically done with water.

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. The acid number can be determined using methods known in the art. One aspect of the present invention is tall oil is obtainable by the process according to the present
5 invention.

Brief description of the figures

10 Fig 1: illustrates a process according to the present invention. The molecular solvent having a boiling point higher than 160°C, and in which sterols are essentially insoluble at 25°C, is added to tall oil soap (TOS). The mixture is distilled at a distillation temperature below the boiling point of phytosterols. The distillate is collected, the temperature of the distillate is reduced and the
15 phytosterols and/or other neutral compounds are isolated. The figure also illustrates the step of acidulating the remaining tall oil soap.

Detailed description

20 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
25 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, stigmastanol,
30 clionastanol, and brassicastanol. Phytosterols isolated by the methods of the invention may be quantified by any means known in the art.

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
5 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.

10

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.

15

Claims

1. A process for isolation of phytosterols and/or other neutral compounds from tall oil soap using co-distillation wherein added
5 molecular solvent is used to achieve the co-distillation of phytosterols, comprising the steps of
- a) adding the molecular solvent having a boiling point higher than 160°C, and in which sterols are essentially insoluble at 25°C, to tall oil soap;
- 10 b) distilling the mixture obtained in step a) at a distillation temperature below the boiling point of phytosterols; and
- c) collecting the distillate, reducing the temperature of the distillate and isolating the phytosterols and/or other neutral compounds.
- 15
2. A process according to claim 1, wherein the molecular solvent in step a) is selected from ethylene glycol, propylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, glycerol or a combination thereof.
- 20
3. A process according to claim 1 or 2, wherein the distillation in step b) is carried out in a wiped film evaporator.
4. A process according to any one of claims 1-3, wherein, in or prior
25 to step a), most or all water present in the tall oil soap is removed before step b).
5. A process according to claim 4, wherein the water is removed by evaporation at atmospheric or reduced pressure.
- 30
6. A process according to any one of claims 1 to 5, further comprising the step of

d) acidulating the remaining tall oil soap from step c) and optionally washing the molecular solvent from the tall oil to obtain high acid number tall oil.

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

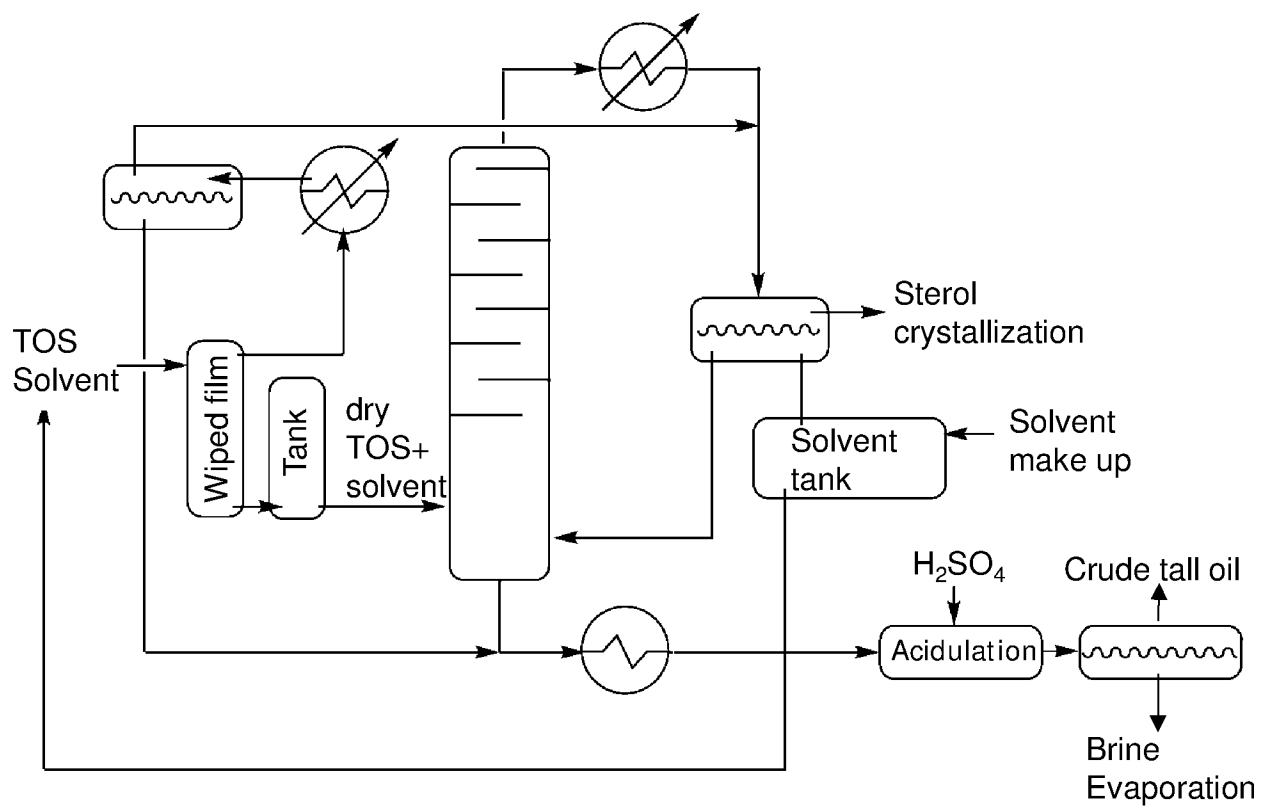
8. Tall oil having an acid number of at least 170.

10 9. Tall oil according to claim 8, having acid number of at least 180.

10. Tall oil obtainable by the process according to any one of claims 1 to 6.

15

Fig 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/056060

A. CLASSIFICATION OF SUBJECT MATTER														
IPC: see extra sheet														
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)														
IPC: C11B														
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched														
SE, DK, FI, NO classes as above														
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)														
EPO-Internal, PAJ, WPI data														
C. DOCUMENTS CONSIDERED TO BE RELEVANT														
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.												
X	US 20020107168 A1 (HAMUNEN ANTTI), 8 August 2002 (2002-08-08); abstract; paragraphs [0013]-[0031], [0035]-[0036], [0042]-[0044], [0058]-[0059]; claim 1 --	7-10												
X	US 2503772 A (RUST JOHN B), 11 April 1950 (1950-04-11); column 1, line 1 - line 7; column 3, line 54 - line 62 --	7-10												
X	RU 2507230 C1 (KRONOS SPB AOOT), 20 February 2014 (2014-02-20); Epodoc abstract --	7-10												
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.														
<table border="0"> <tr> <td>* Special categories of cited documents:</td> <td>"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</td> </tr> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"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</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"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</td> </tr> <tr> <td>"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)</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			* Special categories of cited documents:	"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	"A" document defining the general state of the art which is not considered to be of particular relevance	"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	"E" earlier application or patent but published on or after the international filing date	"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	"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)	"&" document member of the same patent family	"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	
* Special categories of cited documents:	"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													
"A" document defining the general state of the art which is not considered to be of particular relevance	"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													
"E" earlier application or patent but published on or after the international filing date	"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													
"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)	"&" document member of the same patent family													
"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														
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/056060

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 20050197490 A1 (ROJAS ALEJANDRO M ET AL), 8 September 2005 (2005-09-08); abstract; claims; Example 5 and Table 3 --	7-10
A	CA 2319230 A1 (WONG ALFRED), 13 March 2002 (2002-03-13); abstract; figures; claims --	1-10
A	US 20060166951 A1 (SANBOM ALEXANDRA J), 27 July 2006 (2006-07-27); abstract; figures; claims --	1-10
A	US 3965085 A (HOLMBOM BJARNE ET AL), 22 June 1976 (1976-06-22); abstract; claims -- -----	1-10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/056060

Box No. II 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).

Box No. III 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:

Invention 1: Claims 1-7, and 10 concerning a process for isolation of phytosterol and/or other neutral compounds from tall oil soap.

Invention 2: Claims 8-9 concerning tall oil having an acid number of at least 170. This invention does not appear to be linked to the process.

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 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. ☐ 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.:

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.

Continuation of: second sheet
International Patent Classification (IPC)
C11B 13/02 (2006.01)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/IB2017/056060

US	20020107168 A1	08/08/2002	US	6780831 B2	24/08/2004
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			SE	7407901 A	30/12/1974