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(71) Applicant *(for all designated States except US)*: WESTVACO CORPORATION [US/US]; 299 Park Avenue, New York, NY 10171 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: ROBINSON, Philip, L. [US/US]; 29 28th Avenue, Isle of Palms, SC 29451 (US). CUFF, Thomas, J. [US/US]; 50–1/2 Smith Street, Charleston, SC 29401 (US). BYRNE, Jane, F. [US/US]; 1349 National Drive, Mt. Pleasant, SC 29464 (US). YAN, Zhiquan, Q. [US/US]; 2056 Prospect Hill Drive, Mt. Pleasant, SC 29464 (US).

(74) Agent: SCHEINER, Burton; Dennison, Meserole, Scheiner & Schultz, Suite 612, 1745 Jefferson Davis Highway, Arlington, VA 22202 (US).

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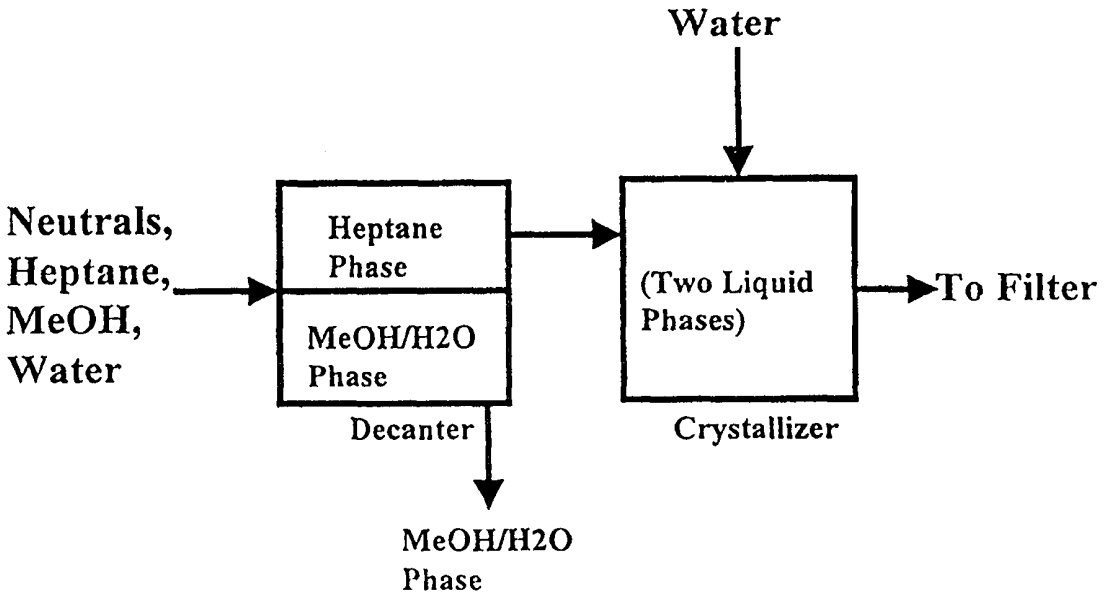

(57) Abstract

Sterols from the neutrals fraction of tall oil pitch are disclosed to be isolated and purified by a process of a liquid–liquid extraction where the hydrocarbon extraction stream is washed with an aqueous methanol solution to remove methanol–soluble impurities. After the hydrocarbon and aqueous phases are separated, water is added to the hydrocarbon phase to facilitate crystallization of sterols.

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ISOLATION AND PURIFICATION OF STEROLS FROM NEUTRALS FRACTION OF TALL OIL PITCH BY SINGLE DECANTATION PRECIPITATION

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention is related to methods of isolating and purifying the valuable constituents from Crude Tall Oil (CTO) recovered from the black liquor residue of wood pulping processes, primarily used in making paper. More particularly, the present invention is related to methods of extraction of valuable constituents from the neutrals fraction of CTO. Most particularly, the present invention is related to methods of isolation and purification of extracted or distilled constituents of the neutrals fraction of CTO which, upon said purification and subsequent modification, are useful as a dietary supplement in foods to reduce cholesterol levels in humans.

Description of Related Art

It has long been appreciated that the black liquor residue from wood pulping contains valuable chemicals, which make up the CTO, with various industrial applications. The black liquor

contains the soaps of rosin and fatty acids, as well as sodium lignate and the spent cooking chemicals for reuse. The CTO is recovered by partially evaporating the black liquor, for concentration purposes, and then skimming off the tall oil soaps which float to the top of a skimming tank. The soap skimmings are converted to CTO by reaction with sulfuric acid and then separated from the simultaneously-formed spent acid by batch cooking, continuous centrifuging, or continuous decanting. The CTO is normally divided into various fractions by distillation which first extracts the pitch (or bottoms). The depitched CTO is then separated into fractions of heads, tall oil rosin (TOR), tall oil fatty acids (TOFA), and distilled tall oil (DTO). A major ingredient of the neutral fraction of CTO, concentrated in the pitch fraction thereof, is a class of compounds known as sterols, including sitosterol. It is known, however, that a better place to obtain these sterols is via solvent extraction of tall oil soap, which is done commercially in Scandinavia.

Recently, U.S. Patent No. 5,502,045 disclosed the use (by ingestion) of a ß-sitostanol fatty acid ester for reducing serum cholesterol level. The patent's assignee, Raisio, a Finnish manufacturer of foodstuffs, grain, and specially chemicals, has developed a cholesterol-reducing margarine called Benecol®. The active ingredient (in cholesterol reduction) in Benecol® is the claimed fat-soluble stanol ester which prevents cholesterol from being absorbed into the human digestive system. The stanol ester is produced from plant-derived sterols (phytosterols) via hydrogenation and trans-esterification reactions. Cholesterol

reductions (LDL and HDL) of 10-15% are common for individuals with diets containing Benecol®.

Therefore, the value of recovering plant-derived sterols has become enhanced and the particular problems associated with recovering sitosterol from tall oil pitch worthy of investigation. A viable commercial process must achieve a high percent recovery of neutrals and/or sterols (greater than 70% recovery is preferable) and achieve high final sterol purity (higher than 95% is desirable). Past attempts to extract neutrals/sterols from one or more fractions of CTO are reported in the following patents:

Patent No.	Inventor	Title
US 2,499,430	Vogel et al.	"Obtaining Sterols of High Purity"
US 2,530,809	Christenson et al.	"Fractionation of Tall Oil"
US 2,530,810	Christensen, et al.	"Separation of Unsaponifiable Matter from Tall Oil Residue"
US 2,547,208	Hasselstrom et al.	"Method for the Refining of Tall Oil Residue"
US 2,715,638	Albrecht et al.	"Production of Sterols from Tall Oil Pitch"
US 2,835,682	Steiner et al.	"Sterol Recovery Process"
US 2,866,781	Chase et al.	"Separating Non-acids from Soap Stocks"
US 2,866,797	Berry et al.	"Improved Process of Isolating Sterols"
US 3,840,570	Julian et al.	"Process for Preparing Sterols from Tall Oil Pitch"
US 3,879,431	Clark et al.	"Purification of Sterols by Distillation"
US 3,965,085	Holmbom et al.	"Method for Refining of Soaps Using Solvent Extraction"
US 4,044,031	Johansson et al.	"Process for the Separation of Sterols"
US 4,124,607	Beaton et al.	"Preparation of Sterol Substrates for Bioconversion"
US 4,153,622	Lamminkari et al.	"Process for the Recovery of Beta-Sitosterol"

Patent No.	Inventor	Title
US 4,420,427	Hamunen	"Process for the Separation of Sterols or Mixtures of Sterols"
US 4,422,974	Hamunen	"Process for the Purification of Beta-Sitosterol Isolated from the Unsaponifiables in Crude Soap from the Sulphate Cellulose Process"
US 4,422,966	Amer	"Separation of Neutrals from Tall Oil Soaps"
US 4,496,478	Kulkarni et al.	"Process for Separating Unsaponifiables from Fatty and Rosin Acids"
US 4,524,024	Hughes	"Processes of Recovering Fatty Acids and Sterols from Tall Oil Pitch"
US 4,849,112	Barder et al.	"Adsorption Separation of Sterols from Tall Oil Pitch with Carbon Adsorbent"
US 4,935,168	Sjöberg et al.	"Process for the Preparation of Alcohols"
US 5,097,012	Thies et al.	"Solvent Extraction of Fatty Acid Stream with Liquid Water and Elevated Temperatures and Pressures"

These approaches have failed to provide both a high percent recovery of neutrals and/or sterols and a high final sterol purity. It is an object of this invention, therefore, to provide a method for recovering the single-solvent extraction or distilled neutral fraction of saponified tall oil pitch and isolating a high percentage of the sterol component thereof. It is a further object of this invention to obtain the isolated sterols at a high purity.

SUMMARY OF THE INVENTION

The above-stated objects of the invention are achieved by isolating the sterol component of the neutrals fraction of saponified tall oil pitch. The isolation is accomplished by a liquid-liquid extraction where the hydrocarbon extraction stream is washed with an aqueous methanol solution to remove methanol-soluble impurities. After the hydrocarbon and aqueous phases

are separated, water is added to the hydrocarbon phase to facilitate crystallization of sterols.

BRIEF DESCRIPTION OF THE DRAWING

The Figure represents a flow diagram of the claimed process of isolation and purification of sterols from the neutrals fraction of tall oil pitch by single decantation precipitation.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The first step in the isolation and purification of sterols from an extracted neutrals fraction of tall oil pitch by a preferred embodiment of the invention process involves dissolving the concentrated (solventless) neutrals in a hydrocarbon solvent, preferably heptane, in a ratio between 2 and 5 parts hydrocarbon to 1 part neutrals fraction. In the next step, a solution of an alcohol solvent, preferably methanol, and water are combined with the neutrals in heptane at 40-50°C so that impurities, presumably dimer fatty acids, can be removed selectively from the neutrals solution. (The higher temperature prevents sterols from crystallizing in the heptane phase during the washing procedure.) Once phase separation has occurred, the sterol-rich heptane phase is isolated and allowed to cool to room temperature.

At this point, water is added to the heptane with vigorous agitation of the layers, which causes precipitation of solid sterols from the solution. Vacuum filtration of the solid sterol crystals followed by a heptane wash provides a good yield of sterols with high purity (typically >70% recovery of the available sterols with >90% total sterol content). This step, in which water is used to crystallize the sterols from heptane,

appears to be critical to achieving the excellent yield and purity. Simply cooling the heptane layer (without water induced crystallization) results in a low yield (45-50%) of sterol crystals. Examples of the invention process were conducted, and the sterol yields and purities therefrom are given in Table I.

TABLE I

Sterol Crystallization Data for Single Decantation Precipitation (SDP) Process

Example	Reference	Conditions	Sterol Yield	Sterol Purity
1	RSV 7253-59A	2.0:4.0:0.5 heptane:MeOH:H2O @ 50°C	64.7%	96.0%
2	RSV 7253-59B	2.0:4.0:0.5 heptane:MeOH:H2O @ 50°C	73.7%	94.4%
3	RSV 7253-89A	2.0:4.0:0.5 heptane:MeOH:H2O @ 50°C	74.4%	96.0%
4	RSV 7253-90A	2.0:4.0:0.5 heptane:MeOH:H2O @ 50°C	76.5%	93.5%
5	RSV 7253-71B	5.5:1.0:0.1 heptane:MeOH:H2O @ 40°C	78.8%	96.2%
6	RSV 7253-85	5.5:1.0:0.1 heptane:MeOH:H2O @ 40°C	70.8%	97.7%
7	RSV 7253-90B	5.5:1.0:0.1 heptane:MeOH:H2O @ 40°C	77.1%	93.4%
8	RSV 7253-93A	5.5:1.0:0.1 heptane:MeOH:H2O @ 40°C	77.7%	94.2%
9	RSV 7255-10	5.5:1.0:0.1 heptane:MeOH:H2O @ 40°C	75.5%	93.1%

In another set of experiments, the single decantation precipitation (SDP) process begins with dissolving the dry (solventless) neutrals by heating to near reflux in heptane at ratios between two and five parts heptane to one part SSE neutrals. Next, a blend of methanol (1 to 4 parts) and water (0.1 to 0.5 parts) are combined with the heptane solution of neutrals at 40°C. Once the heptane phase has been isolated, it

is allowed to cool to the final crystallization temperature where water (1 part) is added quickly with a specified agitation rate and agitation time for precipitation. Finally, the sterol granules that precipitate are filtered from the two liquid phases, and the solid is washed with an additional two parts heptane on the Buchner funnel. The sterols are then dried, weighed, and analyzed for mass yield, sterol yield, and sterol purity.

The key variables listed in the stated general procedure are the heptane content, methanol content, water content, crystallization temperature, crystallization agitation time, and crystallization agitation rate. The high, low, and center point values are listed for each variable in Table II.

TABLE II

Ranges for Variables in Single Decantation Precipitation (SDP) Process

Factor[a]	High	Low	Center Point
Heptane Content (parts)	5.0	2.0	3.5
Methanol Content (parts)	4.0	1.0	2.5
Wash Water (parts)	0.5	0.1	0.3
Crystallization Temperature (°C)	30	20	25
Agitation Time (min)	20	1	10.5
Agitation Rate rad/s (rpm)	104.7 (100)	10.5 (10)	62.8 (60)

(a) Parts refers to the relative weight ratio of the variable to the amount of neutrals used in the experiment. For example, experiments performed with the high heptane value were run with five parts heptane to one part neutrals.

The results from 22 additional experiments for the SDP process (Examples 10-31) are given in Table III, below. The mass yields range from 0 to 85.2%; sterol yields range from 0 to 78.4%; and the purities range from 0 to 98.4%. Unfortunately, two experiments (runs 9 and 16) produced an emulsion that did not settle well, therefore, very low sterol yields were obtained. The data show that these two experiments are atypical. Both runs were done with high heptane, high methanol, and low wash water conditions, which obviously leads to problems.

TABLE III

Example	Heptane Content	MeOH Content	Wash Water	Crystal-ization Temp (°C)	Agitation Rate rad/s (rpm)	Agitation Time (min)	Grams Re-Covered	Avail. Sterols (g)	Mass Yield (%)	Purity (%)	Sterol Yield (%)
10	2.0	1.0	0.1	20	20.9 (20)	1.0	2.2	3.3	66.1	92.6	61.2
11	3.5	2.5	0.3	25	62.8 (60)	10.5	2.4	3.3	72.1	96.5	69.6
12	3.5	2.5	0.3	25	62.8 (60)	10.5	2.7	3.4	79.7	93.4	74.4
13	2.0	4.0	0.5	20	20.9 (20)	1.0	2.8	3.5	80.9	90.0	72.8
14	2.0	4.0	0.5	30	104.7 (100)	1.0	2.2	3.4	65.2	96.2	62.7
15	3.5	2.5	0.3	25	62.8 (60)	10.5	2.4	3.3	73.3	96.7	70.9
16	3.5	2.5	0.3	25	62.8 (60)	10.5	2.7	3.3	80.6	95.0	76.6
17	5.0	4.0	0.5	20	20.9 (20)	20.0	2.9	3.4	85.2	92.0	78.4
18	5.0	4.0	0.1	30	20.9 (20)	1.0	0.1	3.3	1.8	90.1	1.6
19	5.0	1.0	0.5	30	20.9 (20)	1.0	2.2	3.3	67.5	94.7	63.9
20	5.0	1.0	0.1	30	104.7 (100)	20.0	2.5	3.3	74.2	95.2	70.6
21	3.5	2.5	0.3	25	62.8 (60)	10.5	2.4	3.3	71.8	97.8	70.2
22	2.0	4.0	0.1	20	104.7 (100)	20.0	1.7	3.3	50.6	91.0	46.0
23	3.5	2.5	0.3	25	62.8 (60)	10.5	2.1	3.3	63.9	98.4	62.9
24	2.0	1.0	0.1	30	104.7 (100)	1.0	1.6	3.3	48.3	98.4	47.5
25	5.0	4.0	0.1	20	104.7 (100)	1.0	0.0	0.0	0.0	0.0	0.0
26	5.0	1.0	0.5	20	104.7 (100)	1.0	2.5	3.4	73.9	96.9	71.6
27	5.0	1.0	0.1	20	20.9 (20)	20.0	2.4	3.4	69.0	96.7	66.7
28	2.0	1.0	0.5	20	104.7 (100)	20.0	2.7	3.4	79.2	95.7	75.8
29	2.0	1.0	0.5	30	20.9 (20)	20.0	2.4	3.3	72.6	97.6	70.9
30	5.0	4.0	0.5	30	104.7 (100)	20.0	2.4	3.3	72.5	97.9	71.0
31	2.0	4.0	0.1	30	20.9 (20)	20.0	1.2	3.4	34.3	98.7	33.9
						Mean and standard deviation center points =			73.6±5.6	96.3±1.7	70.8±4.3

Mass Yield = grams recovered/available sterols
Sterol Yield = mass yield x purity
Neutral sSource (32.9% sterols)

The center point in the design was replicated six times to give an assessment of the reproducibility of the experiment. The mean and standard deviation for the six center point experiments were 73.6 ± 5.6% for mass yield, 70.8 ± 4.3% for sterol yield, and 96.3 ± 1.7% for sterol purity. The high sterol yield and purity for these center point replicates meet the desirable values for the crystallization process.

The subject matter of the invention is:

(1) A method for the isolation of sterols from the neutrals fraction of tall oil pitch comprising the steps of:

(a) dissolving said dry neutrals by heating with a hydrocarbon solvent in a ratio of two to five parts hydrocarbon solvent to one part neutrals;

(b) blending the hydrocarbon solution of neutrals with a 1-4:0.1-0.5 mixture, respectively, of an alcohol solvent and water at a temperature from about 40°C to about 50°C;

(c) upon isolation of the hydrocarbon solution phase, it is cooled to a final crystallization temperature from about 20°C to about 30°C;

(d) upon reaching said final crystallization temperature, an equal part of water is added with agitation to precipitate sterol granules; and

(e) the sterol granules are recovered by filtering;

(2) The method of (1) wherein the extraction neutrals of tall oil pitch are derived by a process selected from the group consisting of solvent extraction and distillation;

(3) The method of (1) wherein the hydrocarbon solvent is selected from the group consisting of straight- and branched-chain hydrocarbons with from about 5 to about 10 carbons;

(4) The method of (3) wherein the hydrocarbon solvent is selected from the group consisting of pentane, hexane, heptane, and iso-octane;

(5) The method of (1) wherein the alcohol solvent is an aliphatic alcohol; and

(6) The method of (5) wherein the alcohol solvent is selected from the group consisting of methanol, ethanol, propanol, butanol, and iso-propanol.

(7) A method for the isolation of sterols from a hydrocarbon solution of tall oil pitch neutrals comprising the steps of:

(a) blending the hydrocarbon solution of neutrals with a 1-4:0.1-0.5 mixture, respectively, of an alcohol solvent and water at a temperature from about 40°C to about 50°C;

(b) upon isolation of the hydrocarbon solution phase, it is cooled to a final crystallization temperature from about 20°C to about 30°C;

(c) upon reaching said final crystallization temperature, an equal part of water is added with agitation to precipitate sterol granules; and

(d) the sterol granules are recovered by filtering.

Modifications to this invention will occur to those skilled in the art. Therefore, it is to be understood that this

invention is not necessarily limited to the particular embodiments disclosed; rather, it is intended to cover all modifications which are within the true spirit and scope of this invention, as disclosed and claimed herein.

What is claimed is:

1. A method for the isolation of sterols from the neutrals fraction of tall oil pitch comprising the steps of:

(a) dissolving said dry neutrals by heating with a hydrocarbon solvent in a ratio of two to five parts hydrocarbon solvent to one part neutrals;

(b) blending the hydrocarbon solution of neutrals with a 1-4:0.1-0.5 mixture, respectively, of an alcohol solvent and water at a temperature from about 40°C to about 50°C;

(c) upon isolation of the hydrocarbon solution phase, it is cooled to a final crystallization temperature from about 20°C to about 30°C;

(d) upon reaching said final crystallization temperature, an equal part of water is added with agitation to precipitate sterol granules; and

(e) the sterol granules are recovered by filtering.

2. The method of claim 1 wherein the extraction neutrals of tall oil pitch are derived by a process selected from the group consisting of solvent extraction and distillation.

3. The method of claim 1 wherein the hydrocarbon solvent is selected from the group consisting of straight- and branched-chain hydrocarbons with from about 5 to about 10 carbons.

4. The method of claim 3 wherein the hydrocarbon solvent is selected from the group consisting of pentane, hexane, heptane, and iso-octane.

5. The method of claim 1 wherein the alcohol solvent is an aliphatic alcohol.

6. The method of claim 5 wherein the alcohol solvent is selected from the group consisting of methanol, ethanol, propanol, butanol, and iso-propanol.

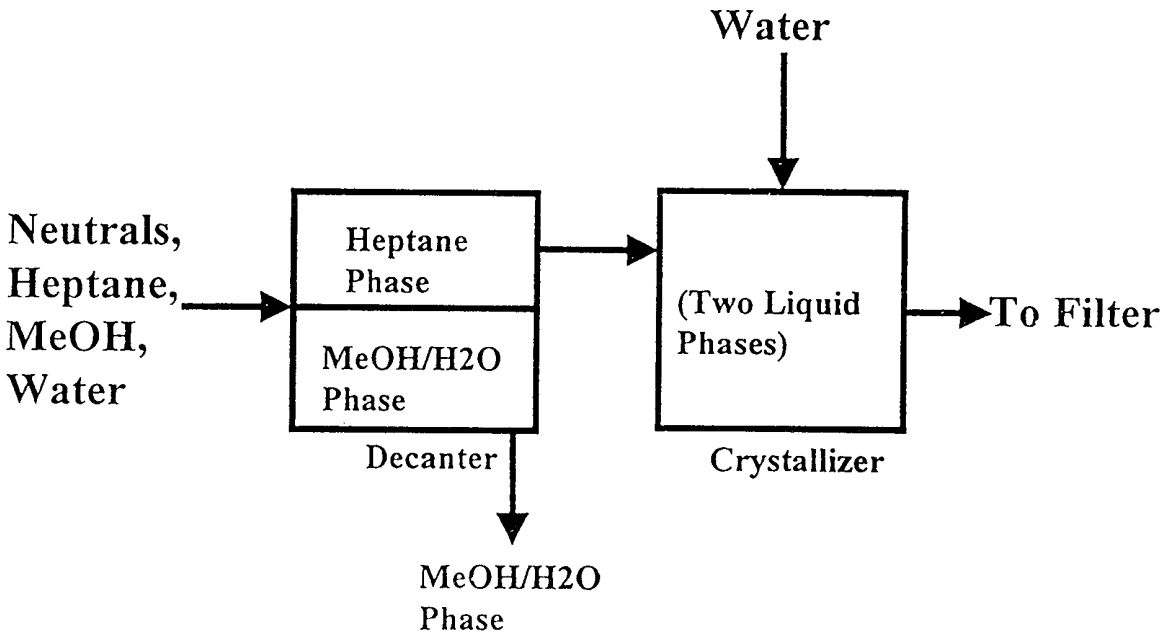
7. A method for the isolation of sterols from a hydrocarbon solution of tall oil pitch neutrals comprising the steps of:

(a) blending the hydrocarbon solution of neutrals with a 1-4:0.1-0.5 mixture, respectively, of an alcohol solvent and water at a temperature from about 40°C to about 50°C;

(b) upon isolation of the hydrocarbon solution phase, it is cooled to a final crystallization temperature from about 20°C to about 30°C;

(c) upon reaching said final crystallization temperature, an equal part of water is added with agitation to precipitate sterol granules; and

(d) the sterol granules are recovered by filtering.


Water
Neutrals,
Heptane,
MeOH,
Water
Heptane
Phase
MeOH/H2O
Phase
Decanter
(Two Liquid
Phases)
Crystallizer
To Filter
MeOH/H2O
Phase

Figure

ITERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07J9/00 C11B13/00

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 7 C07J 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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2 530 810 A (R. M. CHRISTENSON ET AL) 21 November 1950 (1950-11-21) examples A,IX,,X	1-7
Y	US 4 044 031 A (JOHANSSON AKE ALLAN ET AL) 23 August 1977 (1977-08-23) example 1	1-7
Y	US 3 691 211 A (JULIAN DONALD V) 12 September 1972 (1972-09-12) whole document, in particular example 1 and claim 1	1-7
Y	US 3 840 570 A (JULIAN D) 8 October 1974 (1974-10-08) whole document, in particular claim 1 and examples 1, 2	1-7

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[X] Further documents are listed in the continuation of box C.

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27 September 1999	06/10/1999

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PCT/US 99/14139

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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