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(54) Title: METHOD OF INCREASING LIGNIN SOLUBILITY

(57) Abstract

The solubility of lignin may be increased by means of a surfactant.

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METHOD OF INCREASING LIGNIN SOLUBILITY

TECHNICAL FIELD

This invention relates to a method of preparing a solution of lignin at high concentration, to a method of preparing a binder using said solution, and to a method of producing a wood composite using said binder.

BACKGROUND ART

It is known from US 4,432,921 to treatment of lignin with a phenol oxidizing enzyme to prepare a binder, and to use this binder for coating wood particles to produce a particle board. The enzymes are known to be active at weakly acidic to neutral pH.

In order to obtain a strong particle board, it is desirable to use a high lignin concentration, but lignin is only sparingly soluble in water at weakly acidic to neutral pH.

STATEMENT OF THE INVENTION

We have found that, surprisingly, the solubility of lignin can be increased by incorporating a surfactant.

Accordingly, the invention provides a method of increasing the solubility of lignin, characterized by incorporating a surfactant and a lignin solution, characterized by comprising a surfactant. Further, the invention also provides a method for producing a binder for wood products from lignin, characterized by comprising treatment of such a lignin solution with a phenol oxidizing enzyme system. Finally, the invention provides a method of producing a wood composite from wood fibre material, characterized by comprising production of a binder in this way, coating the wood fibre material with said binder, followed by pressing and heating.

DETAILED DESCRIPTION OF THE INVENTION

Lignin

The invention is applicable to any quality of lignin, particularly non-sulfonated lignin such as indulin which results in a strong binder when treated with a phenol-oxidizing system, but has a low solubility in water at weakly acidic to neutral pH where these enzymes are mostly active.

Lignin can be used in an amount of 25-250 g/l, and solutions containing above 100 g/l of lignin can be obtained.

Surfactant

The surfactant used in the invention may be nonionic, anionic, cationic or zwitterionic (amphoteric). Examples of suitable nonionics are alkyl glycosides, alkyl glycoside esters and ethoxylated alcohols and phenols.

The alkyl glycoside (ester) used in the invention consists of an alkyl group linked to a saccharide moiety through a glycosidic bond. The saccharide moiety may optionally be esterified. The saccharide moiety is a mono- or oligosaccharide, preferably a mono-, di- or trisaccharide, preferably consisting of hexose units, particularly of aldose units. Some preferred saccharide moieties are of the type G_n where G is a glucose group, n is 1, 2 or 3, and the glucose units are linked through α-1,4 bonds, i.e. glucose, maltose or maltotriose. The alkyl glycoside preferably contains a straight-chain saturated unsubstituted C_6-C_{18} alkyl, particularly C_8-C_{12}. The alkyl glycoside ester is preferably a monoester and preferably contains a C_1-C_4 alkyl group and a straight-chain saturated unsubstituted C_6-C_{18} acyl group, particularly C_8-C_{12}. The ester group is preferably attached to the C atom in the 6-position of a glucose moiety. The glycoside bond may be in the α- or β-conformation, or a mixture of the two may be used.

Examples of suitable anionic surfactants are linear alkylbenzene sulfonate (LAS), alcohol ether sulfate (AES) and alkyl ether phosphate. Examples of suitable cationic surfactants are quaternary ammonium salts. Examples of suitable

zwitterionic (amphoteric) surfactants are substituted betaines, e.g. alkylamide propyl betaine.

The surfactant is generally added in an amount of 5-100 g/l.

Phenol oxidizing enzyme system

The enzyme system used in the invention consists of a suitable oxidase together with O_2 or a suitable peroxidase together with H_2O_2. Suitable enzymes are those which oxidize and polymerize aromatic compounds such as phenols and lignin.

Examples of suitable enzymes are catechol oxidase (EC 1.10.3.1), laccase (EC 1.10.3.2) and peroxidase (EC 1.11.1.7). Some preferred enzymes are peroxidase derived from a strain of *Coprinus*, e.g. *C. cinereus* or *C. macrorhizus*, peroxidase from *Bacillus*, e.g. *B. pumilus* and laccase from *Trametes*, e.g. *T. versicolor* (previously called *Polyporus*). It may be preferable to use two different phenol oxidizing enzymes together.

The amount of enzyme should generally be in the range 10-10,000 PODU or laccase units per g of lignin solid (activity units defined below).

Molecular oxygen from the atmosphere will usually be present in sufficient quantity. A suitable amount of H_2O_2 will usually be in the range 0.01-10 mM, particularly 1-10 mM.

Production of binder

Suitable conditions for the enzymatic treatment of lignin to produce binder are known in the art. Typical conditions are 20-60°C and pH 5-6 for laccase, and 20-60°C and pH 7-8 for peroxidase.

Production of wood composite

Application of the binder to wood fibre material and pressing under heat to produce a wood composite can be done by methods known in the art. A typical example is production of particle board from wood particles. Typically, the binder is applied by spraying in an amount of 40-100 g/kg of wood fibre material, and

pressing is typically done by compressing for 2-4 minutes at a pressure of 20-40 kg/cm^2 (2-4 Pa) with temperature rising form 35 to 190°C in 20 seconds.

EXAMPLES

EXAMPLE 1

125 g/l of indulin in 0.1 N buffer (Britton & Robinson) was adjusted to an initial pH as shown in the Table below, 50 g/l of alkyl glycoside was added, and the mixture was held for 15 minutes at 80°C with stirring. pH was measured after heating. The samples were then centrifuged for 5 minutes at 10,000 rpm, and the amount of lignin in solution was then determined by measuring OD 280 nm. The alkyl glycosides tested were 1-O-ethyl-6-O-decanoyl-glucose (Ethyl-glucose-C_{10}) and alkyl polyglucoside (APG, Plantaren 600, product of Henkel). A reference experiment was made in the same way, but without alkyl glycoside. The results (corrected for the absorbance of the alkyl glycoside) are shown in the following table.

It is seen from the table that APG increases the lignin solubility particularly at acid pH, and glucose-C_{10} particularly at alkaline pH.

Alkyl glycoside	None (reference)		APG		Ethyl-glucose-C_{10}	
Initial pH	Final pH	Solubility g/l	Final pH	Solubility g/l	Final pH	Solubility g/l
4.0	4.0	5.9	5.4	12.1	5.4	4.7
5.0	5.8	8.4	5.6	16.2	5.7	8.2
6.0	6.0	11.1	5.9	19.5	5.9	15.9
7.0	6.4	18.5	6.2	23.8	6.1	26.1
8.0	6.6	23.6	6.4	27.6	6.3	31.0
9.0	6.8	27	6.6	31.6	6.5	37.6
10.0	7.0	30	6.7	35.0	6.6	42.3

EXAMPLE 2

Solubilization

To a suspension of indulin in 0.1 M Universal buffer pH 7.0 were added 5% Empigen BS (alkyl amide propyl betaine), 5% Nansa 1169/P (C_{12} LAS), 5% Berol 121 (C_{12-14} alkyl ethoxylate EO=5.5), 0.1% Tween 80 (polyethoxy sorbitan oleate EO=20), 5% C-10 glycolipid and 5% APG, respectively. Solubilization was carried out substantially as described in Example 1. A reference experiment with no surfactant added was carried out in the same manner.

The results appear from Fig. 1 which shows the solibility of indulin in the presence of surfactants as a function of pH. It appears that at pH 7, the solubility of indulin is 12.7 mg/ml in the absence of surfactant, and 39, 45 and 29 mg/ml in the presence of 5% Empigen, 5% Nansa 1169/P and 5% APG, respectively.

EXAMPLE 3

Production of binder (polymerization)

To a suspension of indulin and lignin 6 (another non-sulfonated lignin), respectively, in 0.1 M Universal buffer pH 7.0 also containing 0.1% surfactant was added 400 PODU/ml *Coprinus cinereus* peroxidase, and the polymerization reaction was started by adding 10 mM H_2O_2 x 3. After reaction, the mixture was centrifuged to separate the soluble and insoluble lignin before measuring the degree of polymerization by HPLC-GPC. The surfactants used in the experiments were Berol 121, Tween 80, APG, Empigen BS, C-10 glycolipid and Nansa 1169/P.

The results appear from Figs. 2 and 3 which show that APG, Tween 80 and Berol 121 (non-ionic surfactants) have a positive effect on the degree of polymerization of indulin (Fig. 2), and that Empigen BS (zwitter-ionic surfactant) has a positive effect on the degree of polymerization of lignin 6.

CLAIMS

1. A method of increasing the solubility of lignin, characterized by incorporating a surfactant.

2. A method according to Claim 1 wherein the surfactant is incorporated at a concentration of 5-100 g/l.

3. A method according to Claim 1 or 2 wherein the surfactant is a nonionic surfactant, preferably an alkyl glycoside, an alkyl glycoside ester or an ethoxylated alcohol or phenol.

4. A method according to Claim 3 wherein the alkyl glycoside is a C_6-C_{18} saturated alkyl glycoside.

5. A method according to Claim 3 wherein the alkyl glycoside ester contains a C_1-C_4 alkyl group and a straight-chain saturated unsubstituted C_6-C_{18} acyl group, particularly C_8-C_{12}.

6. A method according to Claim 3 or 4 wherein the sugar moiety of the alkyl glycoside (ester) is glucose or a glucose oligosaccharide.

7. A method according to Claim 1 or 2 wherein the surfactant is an anionic surfactant, preferably a linear alkyl benzene sulfonate, an alcohol ether sulfate or an alkyl ether phosphate.

8. A method according to Claim 1 or 2 wherein the surfactant is a cationic surfactant, preferably a quaternary ammonium salt.

9. A method according to Claim 1 or 2 wherein the surfactant is a zwitterionic surfactant, preferably a substituted betaine.

10. A lignin solution, characterized by comprising a surfactant.

11. A solution according to Claim 9, further characterized as in any of claims 2-8.

12. A method for producing a binder for wood products from lignin, characterized by comprising treatment of a lignin solution according to Claim 9 or 10 with a phenol oxidizing enzyme system.

13. A method of producing a wood composite from wood fibre material, characterized by comprising production of a binder according to the previous claim, coating the wood fibre material with said binder, followed by pressing and heating.

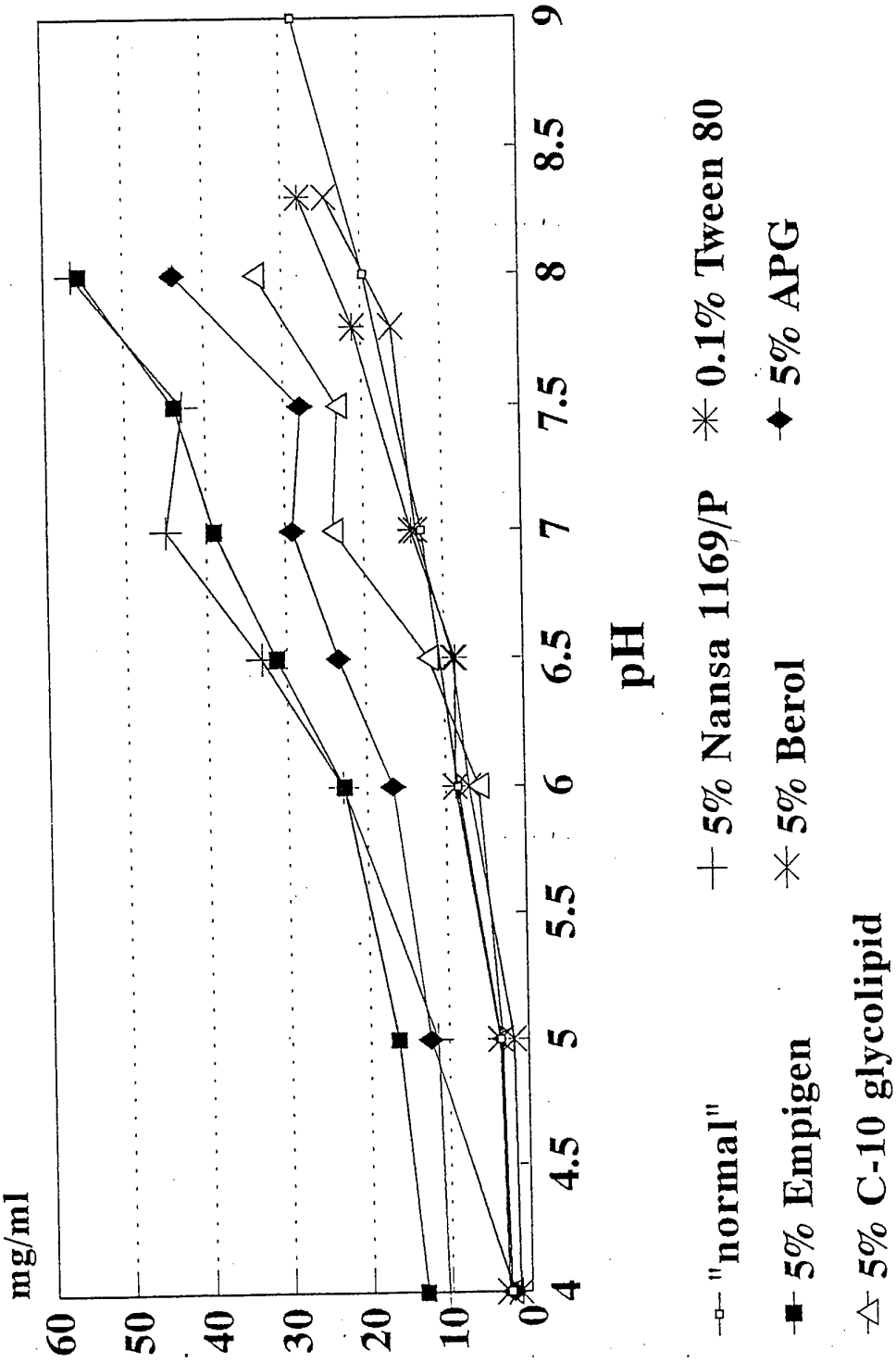
mg/ml
60
50
40
30
20
10
0
4
4.5
5
5.5
6
6.5
7
7.5
8
8.5
9
pH
"normal"
5% Nansa 1169/P
0.1% Tween 80
5% Empigen
5% Berol
5% APG
5% C-10 glycolipid

FIG. 1

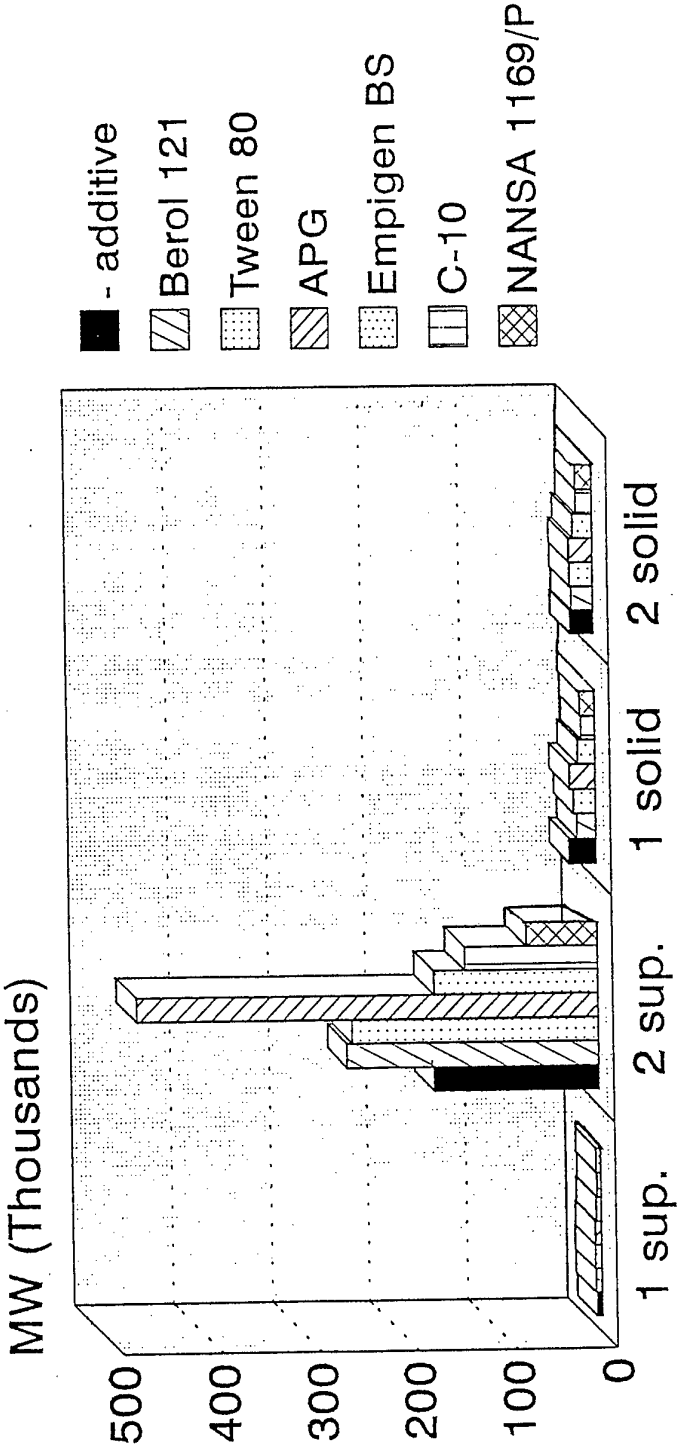
- additive
Berol 121
Tween 80
APG
Empigen BS
C-10
NANSA 1169/P
MW (Thousands)
500
400
300
200
100
0
1 sup.
2 sup.
1 solid
2 solid
1: Blind, pH 7
2: POD, 400 PODU/ml, 10 mM H_2O_2 x 3, pH 7

FIG. 2

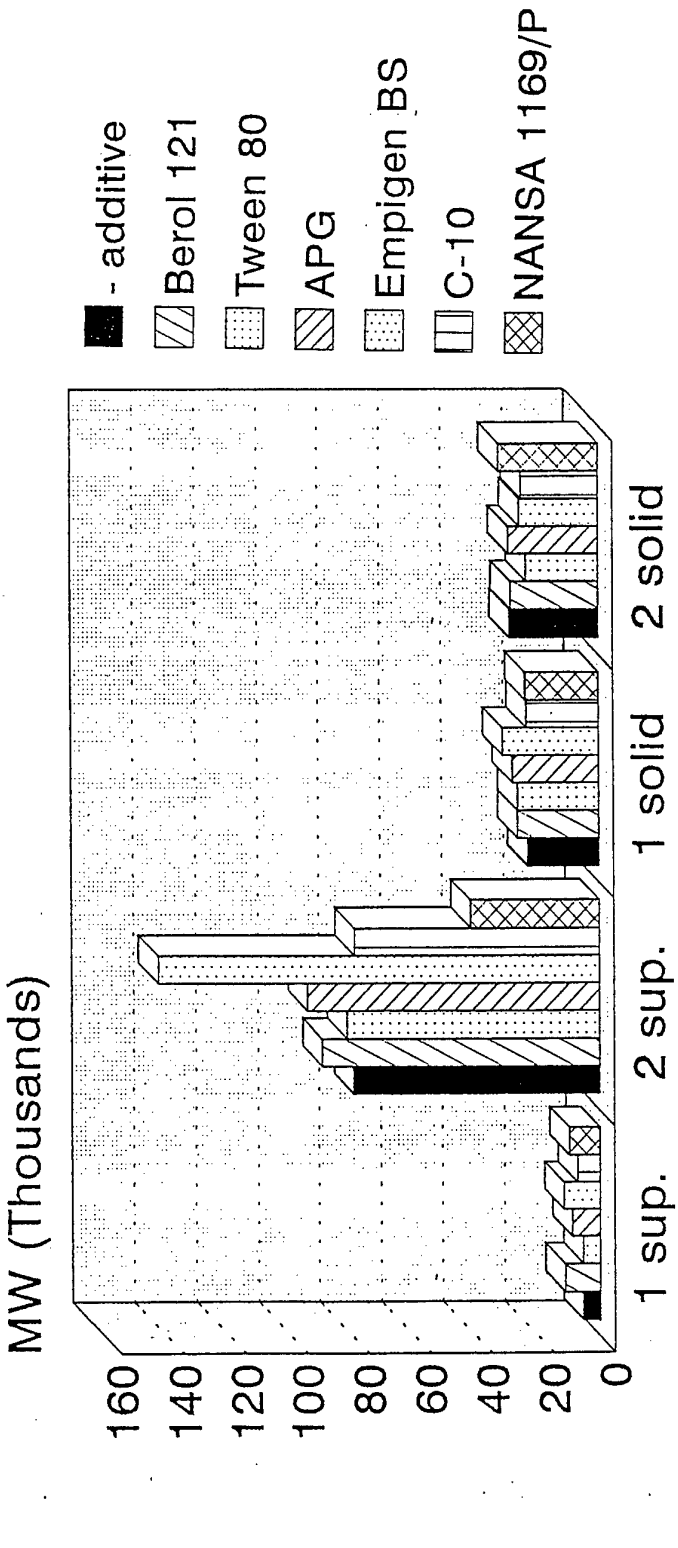
MW (Thousands)
160
140
120
100
80
60
40
20
0
1 sup.
2 sup.
1 solid
2 solid
- additive
Berol 121
Tween 80
APG
Empigen BS
C-10
NANSA 1169/P
1: Blind, pH 7
2: POD, 400 PODU/ml, 10 mM H_2O_2 x 3, pH 7

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/DK 93/00199

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C08L 97/00
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)

IPC5: C08L, C08H, C07G, C09J

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

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Electronic data base consulted during the international search (name of data base and, where practicable, 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.
A	Chemical Abstracts, Volume 97, No 24, 13 December 1982 (13.12.82), (Columbus, Ohio, USA), Heikki Palonen et al, "Surfactant behavior of wood resin components. The solubility of rosin and fatty acid soaps in water and in salt solutions", page 93, THE ABSTRACT No 199768n, Sven. Papperstidn. 1982, 85 (12), 93-99 --	1-11
A	Chemical Abstracts, Volume 71, No16, 20 October 1969 (20.10.69), (Columbus, Ohio, US), Shpenzer N.P. et al, "Solubility of natural resins", THE ABSTRACT No 72139r, Tr. Leningrad. Tekhnol. Inst. Tsellyul.-Bum. Prom. 1968, 21, 265-74 --	1-11

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

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Date of the actual completion of the international search	Date of mailing of the international search report
13 Sept 1993	15 -09- 1993
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International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A2, 0275544 (G.A. PFLEIDERER), 27 July 1988 (27.07.88) --	12-13
A	US, A, 4357454 (KRISTER HOLMBERG ET AL), 2 November 1982 (02.11.82) --	12-13
A	DE, C2, 3037992 (GESELLSCHAFT FüR BIOTECHNOLOGISCHE FORSCHUNG MBH(GBF)), 19 August 1982 (19.08.82) --	12-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

26/08/93

International application No.
PCT/DK 93/00199

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0275544	27/07/88	SE-T3- 0275544	
		DE-C- 3644397	05/05/88
US-A- 4357454	02/11/82	JP-A- 57076056	12/05/82
		SE-B,C- 436888	28/01/85
		SE-A- 8006100	03/03/82
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