

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
10 March 2005 (10.03.2005)

PCT

(10) International Publication Number
WO 2005/021476 A1

(51) International Patent Classification⁷: **C07C 29/62**,
31/36

(21) International Application Number:
PCT/CZ2004/000049

(22) International Filing Date: 23 August 2004 (23.08.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PV 2003-2346 1 September 2003 (01.09.2003) CZ

(71) Applicant (for all designated States except US): **SPOLEK
PRO CHEMICKOU A HUTNI VYROBU, AKCIOVA
SPOLECNOST** [CZ/CZ]; Revolucni 86, 400 32 Usti nad
Labem (CZ).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KUBICEK, Pavel**
[CZ/CZ]; Za bazantnici 1786/9, 405 02 Decin (CZ).
SLADEK, Petr [CZ/CZ]; 403 02 Sebusin 28 (CZ). **BURI-
COVA, Ivana** [CZ/CZ]; Mosnova 1369/30, 400 01 Usti
nad Labem (CZ).

(74) Agents: **JIROTKOVA, Ivana** et al.; Rott, Ruzicka &
Guttmann, Patent, Trademark & Law Office, Nad Stolou
12, 170 00 Praha 7 (CZ).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,
SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF PREPARING DICHLOROPROPANOLS FROM GLYCERINE

(57) Abstract: A method of highly selective catalytic hydrochlorination of glycerine and/or monochloropropanediols to the dichloro-
propanol products 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol, carried out in at least one continuous reaction zone at reac-
tion temperatures in the range of 70-140 °C and with continuous removing of the water of reaction, the liquid feed containing at least
50 % by weight of glycerine and/or monochloropropanediols. The method can be carried out in a continuously operating one-step
circulation reactor or a cascade of continuous flow reactors of the liquid-gas type.



WO 2005/021476 A1

Method of preparing dichloropropanols from glycerine

Technical Field

5 This invention relates to the technology of production of epichlorohydrin, the field of chemical engineering. Epichlorohydrin is an important raw material for the production of epoxide resins, synthetic elastomers, sizing agents for paper-making industry and the like.

Background Art

10

In the industrial production of epichlorohydrin, a technology is mostly worldwide used, which comprises:

15

- high temperature radical substitutive chlorination of propene to allyl chloride;
- preparation of dichloropropanols by addition of hypochlorous acid to allyl chloride; and
- dehydrochlorination of dichloropropanols with an alkali aqueous solution to epichlorohydrin.

The basic features of this technology are, above all:

20

- relatively mediocre total yield of the synthesis based on the starting propylene of ca. 73 %;
- low yield of the synthesis based on chlorine of ca. 38 %;
- high unit consumption of energy;
- high unit volume of waste water of ca. 35 m³/t of epichlorohydrin, pollution AOX (Adsorbable Organic Halides), DIS (Dissolved Inorganic Salts) and COD (Chemical Oxygen Demand); and
- use of hazardous propene and evaporated chlorine in the process.

25

The technology of Showa-Denko (e.g., USP 5,011,980, USP 5,227,541 or USP 4,634,784), comprising:

30

- palladium-catalyzed oxidation of propene with acetic acid to allyl acetate;
- catex-catalyzed hydrolysis of allyl acetate to allyl alcohol;
- catalytic chlorination of allyl alcohol to dichloropropanol; and
- alkaline dehydrochlorination of dichloropropanol to epichlorohydrin

is worldwide used to only minor extents.

In both cases, the basic starting materials are propene, chlorine and an alkali, for example calcium hydroxide or sodium hydroxide.

Accordingly, for economic, environmental, and safety reasons, new synthetic routes are being sought worldwide. For several years, attempts have been made to manage a process of direct catalytic oxidation of allyl chloride to epichlorohydrin with hydrogen peroxide, or organic hydroperoxides, with use of catalysts based on titanium silicalites (e.g., USP 5,466,835, USP 6,187,935, USP 6,288,248, or USP 6,103,915) but without any commercial application to date.

One of further possible synthetic routes has been known since the beginning of the 20th century; its principle resides in catalytic hydrochlorination of glycerine by means of anhydrous hydrogen chloride according to the German patent to Boehringer, C.F. und Söhne, Waldhof b. Mannheim: Verfahren zur Darstellung von Mono- und Dichlorhydrin aus Glycerin und gasformiger Salzsäure, DE Patent No. 197308, 1906.

The principle is a reaction of glycerine with hydrogen chloride in the presence of carboxylic acids as catalysts, providing 1,3-dichloro-2-propanol and water. The said reaction is carried out in the liquid phase under temperatures of around 100 °C. Pressure can be either atmospheric or elevated, for increasing the solubility of gaseous HCl in the reaction mixture. An optimal concentration of the homogeneous acetic acid catalyst is ca. 1 – 2 % by weight; at higher concentrations undesired by-products are formed to a greater extent, which lower the yields. Besides acetic acid, the Patent mentions other carboxylic acids, propionic acid having been tested. The published yield of the batch arrangement without separation of water amounts to, in a control recalculation, ca. 75 %. In order to increase the yield and reduce the hydrogen chloride loss a basic problem is removal of the water of reaction for shifting the equilibrium towards emerging dichloropropanol.

US Patent No. USP 2,144,612 has tried to solve the problem of sufficient removal of the reaction water at a suitable reaction temperature by the use of various kinds of inert, water immiscible solvents such di-n-butyl ether, ethylene dichloride, propylene dichloride or chlorobenzol, which allow to remove the reaction water as an acid distillate. The patent mentions that only the little amount of residues is formed, the reaction may be readily carried to completion, the solution of glycerol-dichlorohydrin obtained as a reaction product is substantially free from water and loss of glycerol-dichlorohydrin in hardly separable aqueous acid solution is minimized. Also the higher content of catalyst in range of 5 % based on glycerine input is mentioned.

US Patent No. USP 2,198,600 has tried to solve the problem of the purification and the recovery of dichloropropanol from acid distillate by extraction using a suitable organic solvent for dichloropropanol, preferably di-n-butyl ether.

5 All the above mentioned methods described in the respective patents were developed as discontinuous batch processes.

In industrial scale such methods are not feasible for high losses of hydrogen chloride, the necessity of several batch reaction steps with long residence times of the order of hours to tens of hours, and hence high demands on the size of apparatuses, the logistics of raw materials and products, sanitation of waste streams, labour hygiene and the like. Also the use
10 of significant portion of inert solvents required for the suitable results acceptable in the industrial scale significantly increases the reactor volumes and needs a lot of additional equipments for solvents handling, treatment, recovery etc.

For these reasons a method of continuous preparation of a mixture of 1,3-dichloro-2-propanol and/or 2,3-dichloro-1-propanol, characterized by high conversion of the starting
15 materials, high yields of the products and high selectivity of the reaction system has been developed.

Disclosure of Invention

20 This invention consists in a method of preparing the dichloropropanols 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol by hydrochlorination of glycerine and/or monochloropropanediols with gaseous hydrogen chloride with catalysis of a carboxylic acid, wherein said hydrochlorination is carried out in at least one continuous reaction zone at reaction temperatures in the range of 70-140 °C and with continuous removing of the water of
25 reaction, the liquid feed containing at least 50 % by weight of glycerine and/or monochloropropanediols.

This method does not need any additional compounds like solvents to reach industrially acceptable yields. The mixture of products, which apart from dichloropropanols contains also the reaction water and the small amount of catalyst acetic acid and unreacted
30 hydrogen chloride, can be favourably used without any treatment for the next reaction step in epichlorohydrin synthesis, e.g. for the alkaline dehydrochlorination.

Preferably, the liquid feed contains 80 – 100 % by weight of glycerine, and the carboxylic acid catalyst is preferably acetic acid.

The reaction temperature is preferably 100-110 °C.

The hydrochlorination can be carried out in a continuously operating one-step circulation reactor or in a cascade of continuous flow reactors of the liquid-gas type.

For achieving favourable conversions of the starting glycerine to the dichloropropanol
5 product it is also necessary, apart from the presence of a catalyst, to remove the water of reaction from the reaction environment for the reason of chemical equilibrium, preferably by distillation under reduced pressure.

In case of a circulation reactor, the raw materials glycerine, hydrogen chloride and the acetic acid catalyst can be fed into external circulation upstream the reactor itself and, for
10 primary collection of the dichloropropanol product and the water of reaction, a distillation device can be located in the circulation, preferably a distillation column operated at reduced pressure. The remaining balance of the reaction mixture can be also secondarily collected from the circulation and, after recovery of the dichloropropanol product and the monochloropropanediol reactive intermediate, which are returned to the reaction, the residue
15 containing a mixture of undesired products is further processed. The recovery can be advantageously carried out by distillation under reduced pressure, wherein the undesired higher-boiling waste products leave as the distillation residue.

By balancing the set of parameters of the circulation reactor such as the ratio between the quantity of reactor circulation and glycerine input, the ratio between the quantity of the
20 secondary collection and glycerine input, the reactor temperature, the value of reduced pressure in the continuous primary distillation in the reactor circulation, etc., optimization of the process and its yields can be achieved.

In case of a cascade of the continuous flow reactors the number of members of the cascade can range from one to five, preferably three. The raw materials glycerine, hydrogen
25 chloride and the acetic acid catalyst are fed into the first member of the cascade; hydrogen chloride and a supplement for the loss of the catalyst are in turn fed into the other members. Distillation of the water of reaction is always located between the individual members of the cascade. After distilling off the water of reaction and a part of the dichloropropanol product the distillation residue is subjected to hydrochlorination in the next member of the cascade. It
30 is advisable, for increasing the total yield, to recover dichloropropanols and the reactive intermediates monochloropropanediols from the distillation residue after distilling off the water of reaction and dichloropropanol from the last member of the cascade. The recovery can preferably be carried out by distillation under reduced pressure, wherein higher boiling waste

products are separated as the distillation residue and the distillate is dichloropropanols and monochloropropanediols, recycled back to the reactor, preferably into the first member of the cascade.

Generally, any reactor for the reaction of the liquid-gas type can be chosen for the reaction itself, such as a stirrer reactor, a bubble tower (column), variously filled columns for the liquid-gas contact, ejector reactors and the like.

For dispersing the gaseous hydrogen chloride, any dispersing means can be used, such as nozzles, perforated plates or pipes, microporous plates, ejectors and the like.

Pressures in the reactors can be atmospheric, or elevated for better solubility of hydrogen chloride in the reaction mixture. Temperatures in the reactors can range between 70 and 140 °C, preferably 100-110 °C.

The total mean residence time of the system can be selected in the range of 5-40 hours according to the required total conversion of glycerine and total yield of the dichloropropanol product.

For the distillation under reduced pressure to separate the water of reaction any device for distillation can be used, such as evaporators of various constructions with or without a source of heat, rectification columns with various internals such as trays, structured packing, random packing and the like.

As devices for recovery distillation, generally known apparatuses for distillation can be used, such as various types of evaporators or distillation systems.

Starting material glycerine can be of various quality with the various glycerine content and various kinds of the impurities. Distilled glycerine with the various contents of glycerine can be used; content of 90.0-99.9 % being preferred. Also crude glycerine with various contents of glycerine can be used; content of 80.0-90.0 % being preferred.

Alternatively, the glycerine feed can be, partially or totally, replaced by monochloropropanediol (especially 3-chloro-1,2-propanediol, and/or 2-chloro-1,3-propanediol), optionally prepared by other methods, such as hydrochlorination of glycerine with a solution of hydrochloric acid.

Examples

Example 1

According to the described disclosure of the invention the following experiment was conducted. In a circulation column reactor, consisting of a vertical cylinder with external

circulation of the reaction mixture, a feed of glycerine, containing 97.5 % of glycerine, 2 % of acetic acid and 0.5 % of water, was fed into the external circulation upstream the reactor itself in the amount of 5.0 kg/h. Gaseous hydrogen chloride was fed directly into the bottom of the reactor through classical dispersing devices in the amount of 4.6 kg/h. In the external
5 circulation there was inserted a vacuum rectification column downstream the reactor; a mixture of the dichloropropanol product, the reaction water and the residual hydrogen chloride was collected as the distillate in the amount of 9.3 kg/h. The distillation residue was pumped back to the reactor. The residual balance of the reaction mixture was also collected from the circulation downstream the rectification column in the amount of 1.4 kg/h and this was
10 subjected to vacuum distillation in an evaporator in order to recover the dichloropropanol product and the monochloropropanediol reactive intermediate, which were returned back to the reaction in the amount of 1.2 kg/h together with the glycerine feed. The distillation residue from the recovery, containing a mixture of undesired products, was collected as waste in a tank. The basic parameters and results are illustrated in the following Table:

Parameter	
Reaction temperature	106 °C
Pressure in the reactor	101 kPa
Conversion of glycerine	99.8 %
Yield of 1,3-dichloro-2-propanol+2,3-dichloro-1-propanol	95.6 %

15

Example 2

According to the described disclosure of the invention the following experiment was conducted. A cascade of continuous flow reactors with 3 reactors of the cascade without final
20 recovery of the monochloropropanediol reactive intermediate was sequentially modelled. A feed of glycerine, containing 97.5 % of glycerine, 2 % of acetic acid and 0.5 % of water, was continuously fed into the first member of the cascade – a tower reactor of the liquid-gas type; as was hydrogen chloride through classical dispersing devices. The product, containing a mixture of dichloropropanols, monochloropropanediols and other side products, was collected
25 into a tank. After the selected time of continuous run the reaction was interrupted; the product was subjected to one-step equilibrium vacuum distillation to distil off the reaction water, a part of dichloropropanol and excess hydrogen chloride. The distillation residue was then used as injection into the next member of the sequentially designed cascade. The distillates together

with the reaction mixture from the last member of the cascade were the output of the whole system. The basic parameters and results of the 3-member cascade are illustrated in the following Table:

Parameter	
Reaction temperature	95 °C
Pressure	101 kPa
Conversion of glycerine	99.9 %
Yield of 1,3-dichloro-2-propanol+2,3-dichloro-1-propanol	83.1 %

5

Example 3

According to the described disclosure of the invention the following experiment was conducted. In a circulation column reactor, consisting of a vertical cylinder with external circulation of the reaction mixture, a feed of glycerine, containing 88.7 % of glycerine, 2 % of acetic acid and 9.3% of water was fed into the external circulation upstream the reactor itself in the amount of 5.4 kg/h. Gaseous hydrogen chloride was fed directly into the bottom of the reactor through classical dispersing devices in the amount of 4.3 kg/h. In the external circulation there was inserted a vacuum rectification column downstream the reactor; a mixture of the dichloropropanol product, the reaction water and the residual hydrogen chloride was collected as the distillate in the amount of 9.3 kg/h. The distillation residue was pumped back to the reactor. The residual balance of the reaction mixture was also collected from the circulation downstream the rectification column in the amount of 1.4 kg/h and this was subjected to vacuum distillation in an evaporator in order to recover the dichloropropanol product and the monochloropropanediol reactive intermediate, which were returned back to the reaction in the amount of 1.1 kg/h together with the glycerine feed. The distillation residue from the recovery, containing a mixture of undesired products, was collected as waste in a tank. The basic parameters and results are illustrated in the following Table:

Parameter	
Reaction temperature	107 °C
Pressure in the reactor	101 kPa
Conversion of glycerine	99.6 %
Yield of 1,3-dichloro-2-propanol+2,3-dichloro-1-propanol	90.9 %

Example 4

According to the described disclosure of the invention the following experiment was conducted. In a circulation column reactor, consisting of a vertical cylinder with external circulation of the reaction mixture, a feed of crude glycerine, containing 84.9% of glycerine, 2% of acetic acid, 4.7% of water and 8.4% of non-volatile compounds, was fed into the external circulation upstream the reactor itself in the amount of 5.5 kg/h. Gaseous hydrogen chloride was fed directly into the bottom of the reactor through classical dispersing devices in the amount of 4.5 kg/h. In the external circulation there was inserted a vacuum rectification column downstream the reactor; a mixture of the dichloropropanol product, the reaction water and the residual hydrogen chloride was collected as the distillate in the amount of 8.9 kg/h. The distillation residue was pumped back to the reactor. The residual balance of the reaction mixture was also collected from the circulation downstream the rectification column in the amount of 2.0 kg/h and this was subjected to vacuum distillation in an evaporator in order to recover the dichloropropanol product and the monochloropropanediol reactive intermediate, which were returned back to the reaction in the amount of 1.0 kg/h together with the glycerine feed. The distillation residue from the recovery, containing a mixture of undesired products, was collected as waste in a tank. The basic parameters and results are illustrated in the following Table:

Parameter	
Reaction temperature	103 °C
Pressure in the reactor	101 kPa
Conversion of glycerine	99.5 %
Yield of 1,3-dichloro-2-propanol+2,3-dichloro-1-propanol	89.3%

Claims

1. A method of preparing the dichloropropanols 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol by hydrochlorination of glycerine and/or monochloropropanediols with gaseous hydrogen chloride with catalysis of a carboxylic acid, characterized in that said hydrochlorination is carried out in at least one continuous reaction zone at reaction temperatures in the range of 70-140 °C and with continuous removing of the water of reaction, the liquid feed containing at least 50 % by weight of glycerine and/or monochloropropanediols.
2. The method according to claim 1, characterized in that the liquid feed contains 80-100 % by weight of glycerine.
3. The method according to claim 1, characterized in that the liquid feed contains, as the monochloropropanediols, 3-chloro-1,2-propanediol and/or 2-chloro-1,3-propanediol.
4. The method according to any of the preceding claims, characterized in that the catalysis is made with acetic acid.
5. The method according to any of the preceding claims, characterized in that the reaction is carried out at a temperature of 100-110 °C.
6. The method according to any of the preceding claims, characterized in that the removing of the water of reaction is made by distillation.
7. The method according to claim 6, characterized in that the distillation is carried out at a reduced pressure in a rectification zone linked to the reaction zone.
8. The method according to claim 6 or 7, characterized in that, together with the removing of the water of reaction by distillation, at least partial primary collection of the product dichloropropanols is made.
9. The method according to any of claims 6-8, characterized in that secondary collection is made, from which dichloropropanols and monochloropropanediols are recycled to the process.
10. The method according to claim 9, characterized in that the secondarily collected residual balance of the reaction mixture is subjected to distillation under reduced

pressure in order to separate the higher boiling waste products as the distillation residue and the dichloropropanols and monochloropropanediols, recycled to the reactor, as the distillate.

- 5 11. The method according to any of claims 1-6, characterized in that it is carried out in a cascade of continuous flow reaction zones wherein the water of reaction is collected, together with partial collection of the product dichloropropanols, by distillation, located always downstream the individual reaction zones of the cascade, and the distillation residue is fed into the next zone of the cascade.
- 10 12. The method according to claim 11, characterized in that the reaction mixture exiting from the last step of the cascade is subjected to a two-step distillation, wherein in the first step the water of reaction is separated together with the dichloropropanol reaction product as the distillate and in the second step the higher boiling waste products are separated as the distillation residue and the dichloropropanols and monochloropropanediols are separated as the distillate and are recycled back to the process, preferably into the first step of the cascade.
- 15 13. An apparatus for carrying out the method of any of claims 1-10, wherein the apparatus comprises a circulation reactor with external circulation, in which there is located a distillation device.
- 20 14. An apparatus for carrying out the method of claims 11 or 12, wherein the apparatus comprises a cascade of continuous flow reactors, in which there are distillation devices located downstream the individual steps of the cascade.
15. The apparatus of claim 14, wherein the number of the members of the cascade is 1 to 5.
16. The apparatus of claim 14 or 15, wherein the number of the members of the cascade is 3.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CZ2004/000049

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C29/62 C07C31/36

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 C07C

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)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X, Y	US 2 144 612 A (BRITTON EDGAR C ET AL) 24 January 1939 (1939-01-24) cited in the application page 3, right-hand column, lines 25-48	1-12
X	WO 02/50014 A1 (BASF AKTIENGESELLSCHAFT; MARTIN, FRIEDRICH-GEORG; NESTLER, GERHARD; SC) 27 June 2002 (2002-06-27) page 7, lines 1-28; fig. 1;	13
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 202 (C-0834), 23 May 1991 (1991-05-23) & JP 03 056430 A (DAISO CO LTD), 12 March 1991 (1991-03-12) fig. abstract -/--	13

☒ Further documents are listed in the continuation of box C

☒ Patent family members are listed in 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 document 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

- *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
- *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
- *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
- *&* document member of the same patent family

Date of the actual completion of the international search

28 January 2005

Date of mailing of the international search report

15/02/2005

Name and mailing address of the ISA

European Patent Office, P B 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Grammenoudi, S

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CZ2004/000049

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	-& JP 03 056430 A (DAISO CO LTD) 12 March 1991 (1991-03-12) fig. 1 and 2 -----	13
X	EP 0 781 760 A1 (GENERAL ELECTRIC COMPANY) 2 July 1997 (1997-07-02) page 8, lines 1-26; fig. 1 -----	14
X	US 6 072 076 A (SCHMIDT ET AL) 6 June 2000 (2000-06-06) column 5, lines 4-42; fig. 1 -----	14
Y	US 2 198 600 A (BRITTON EDGAR C ET AL) 30 April 1940 (1940-04-30) cited in the application example 1 -----	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CZ2004/000049

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2144612	A	24-01-1939	NONE	
WO 0250014	A1	27-06-2002	DE 10063175 A1	20-06-2002
			WO 02055472 A1	18-07-2002
			EP 1345886 A1	24-09-2003
			EP 1343748 A1	17-09-2003
			US 2004019235 A1	29-01-2004
			US 2004024241 A1	05-02-2004
JP 03056430	A	12-03-1991	JP 1915566 C	23-03-1995
			JP 6043353 B	08-06-1994
JP 3056430	A	12-03-1991	JP 1915566 C	23-03-1995
			JP 6043353 B	08-06-1994
EP 0781760	A1	02-07-1997	JP 9176094 A	08-07-1997
			CN 1157813 A	27-08-1997
			DE 69623429 D1	10-10-2002
			DE 69623429 T2	17-04-2003
			ES 2182955 T3	16-03-2003
			SG 87749 A1	16-04-2002
US 6072076	A	06-06-2000	DE 19604253 A1	07-08-1997
			CA 2196913 A1	07-08-1997
			CZ 9700309 A3	15-10-1997
			DE 59704095 D1	30-08-2001
			EP 0795536 A1	17-09-1997
			ID 16433 A	25-09-1997
			JP 9208519 A	12-08-1997
			SG 80565 A1	22-05-2001
US 2198600	A	30-04-1940	NONE	