

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 August 2002 (08.08.2002)

PCT

(10) International Publication Number
WO 02/061184 A1

(51) International Patent Classification⁷: **C25D 1/08**,
1/04, 1/10, H01M 4/70, 4/74, F24J 2/48

(21) International Application Number: PCT/NL02/00064

(22) International Filing Date: 28 January 2002 (28.01.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1017213 29 January 2001 (29.01.2001) NL

(71) Applicant (for all designated States except US): **STORK
SCREENS B.V.** [NL/NL]; Raamstraat 3, NL-5831 AT
Boxmeer (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BLANKENBORG,
Stephanus, Gerardus, Johannes** [NL/NL]; Veemarkt
10, NL-6511 ZD Nijmegen (NL). **MACHIELSE, Jacob,
Joost** [NL/NL]; Van Vlattenstraat 151, NL-5975 SE
Sevenum (NL).

(74) Agent: **VOLMER, J., C.**; Exter Polak & Charlouis B.V.,
P.O. Box 3241, NL-2280 GE Rijswijk (NL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, 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, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

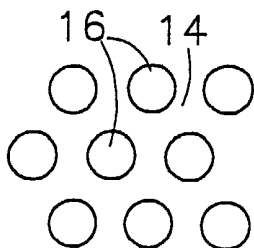
(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Published:

- with international search report
- with amended claims

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

(54) Title: METHOD FOR PRODUCING ELECTRICAL CONDUCTORS, A SOLAR COLLECTOR, AN ELECTROCHEMICAL CELL AND USE OF CONDUCTORS PRODUCED IN THIS WAY



(57) Abstract: Conductors for use in batteries, storage batteries, and solar collectors are produced by means of electrolysis. According to the invention, a method of this type for the production of an electrical conductor, which conductor comprises a copper-containing screen material, comprises the steps of using electrodeposition to deposit a copper skeleton on conductive parts of an electroforming matrix in an electrodeposition bath, and removing the deposited copper skeleton from the electroforming matrix, and if desired further growing of the skeleton, the screen material having a density of openings which lies in the range of 1-20,000/cm² and allows of an open surface area which is larger than a defined minimum.

WO 02/061184 A1

Method for producing electrical conductors, a solar collector, an electrochemical cell and use of conductors produced in this way

The invention relates to a method for producing an electrical conductor suitable for use in a device for conversion of energy.

Copper screen material, which if desired may be nickel-plated, for use as current conductors in batteries and storage batteries is
5 known per se in the art. For example, US Patent 4,328,293 discloses a positive electrode for an electrochemical cell (generator), which electrode comprises a conductive substrate which comprises, for example, a perforated and nickel-plated copper strip. Furthermore, US-A-4,228,224 discloses a copper screen material of 80 mesh which is
10 used in a positive electrode.

These screen materials for use as electrodes are usually formed by stamping/punching or etching of a solid copper strip. However, stamping and punching leave behind sharp knurled or cut edges, which causes problems for further processing and handling. Etching is a
15 less accurate process, and consequently the uniformity of the thickness and the hole size is unsatisfactory. Furthermore, these production techniques impose undesirable limitations on the number of openings per unit surface area, which is disadvantageous with regard to the volume for and to the contact surface with an active chemical
20 material, such as an electrolyte paste, to be applied thereto, and with regard to adhesion.

From JP-A-51136535 a porous metal, for example, copper, foil is known for use as electrode material, which is obtained by the electroforming of a mechanically roughened substrate to form a metal
25 foil with a thickness ranging from a few tens to a few hundreds of micrometers. The foil formed in this way is peeled off the substrate, or the substrate is dissolved. However, the reproducibility of machining of the substrate is low, so that products with different characteristics of the pores, such as the dimensions thereof, and
30 therefore also of the overall conductivity, are in each case obtained. Moreover, it is unclear how the pores are obtained in accordance with this Japanese Patent Application.

The present invention is based on the general object of avoiding the above drawbacks. In particular, it is an object of the

invention to provide electrical conductors having a large volume, contact surface area and good adhesion for active chemical material. Additionally, it is an object of the invention to provide an alternative way of roughening the conductor.

5 To this end, according to the invention, a method for the production of an electrical conductor, which conductor comprises a copper-containing screen material, is characterized in that the method comprises the steps of:

10 a) using electrodeposition to deposit a copper skeleton on conductive parts of an electroforming matrix in an electrodeposition bath, and

b) removing the deposited copper skeleton from the electroforming matrix, the screen material having a density of openings which lies in the 15 range of 1-20,000/cm².

For the higher mesh numbers, it is advantageous to apply a step c) of further growth of the skeleton by electrodeposition after step b).

20 Preferably, the method according to the invention comprises after step c) a step d) of further growth of the skeleton by electrodeposition of lead to form screen material. For example, by introducing the screen material in an electrodeposition bath containing leadmethanesulphonate and methanesulphonic acid.

25 In the method according to the invention, in a first step a skeleton of screen material is deposited on an electroforming matrix which is connected as cathode, from a suitable electrodeposition bath for the deposition of copper. An electroforming matrix of this type, which may, for example, be flat or cylindrical, comprises a surface which includes conductive parts, generally in the form of a regular 30 network of interconnected metal dykes, which dykes are delimited by nonconductive parts made from an insulating material, for example photoresist. In this way, a skeleton of copper screen material is formed, the screen openings being delimited by copper dykes corresponding to the pattern of the electroforming matrix. Depending 35 on the conditions, some lateral overgrowth over the nonconductive parts of the electroforming matrix may occur. If desired, after removal of the skeleton, it can be grown further until it reaches the desired thickness, taking into account the requirements with regard to density of holes and passage area (open surface area/total of open

and closed surface area). The open surface area of the screen material obtained will be preferably at least equal to a minimum open surface area, which is determined experimentally in order to obtain the desired advantageous characteristics of the conductor. The lower
5 the density of holes, the higher the minimum open surface area.

Here it should be noted that a method of forming a sieve material by thickening a previously formed, electrically conducting sieve skeleton by metal deposition in an electrolysis bath is known per se from EP-A1-0 492 731. As starting materials of the
10 electrically conducting skeleton nickel and iron are mentioned in the preferred embodiments, while in principle all electrolytically depositable metals can be used in the thickening step. The sieve material thus produced is suitable for various purposes such as screen printing and sieving. Although copper is mentioned as one of
15 the electrolytically depositable metals it is not used in printing screens, because copper will dissolve in the printing ink and pastes conveniently used in screen printing.

The copper bath used may be a conventional electrodeposition bath, such as acidic Cu baths, or baths with an electrolyte such as
20 copper sulphate, copper cyanide, copper fluoroborate, copper pyrophosphate and the like. An example of a bath of this type comprises:

	CuSO ₄ .5H ₂ O	150-250 g/l
	H ₂ SO ₄	50-100 g/l
25	Cl ⁻	0-50 mg/l.

The current density is in the range 1-70 A/dm², preferably 10-50 A/dm².

When step c) is not applied, the thickness of the skeleton, and
30 therefore of the screen material, is preferably in the range of 10-45 micrometers. This level of thickness offers sufficient strength to remove the skeleton from the matrix.

The dimensions and shape of the openings may vary. In the case of openings which are circular in cross section, the diameter
35 preferably lies in the range of 50-100 micrometers. This preferred range is determined by factors such as open surface area, mesh number and technical feasibility.

When the optional step c) is applied, the skeleton is grown further by conventional deposition techniques by deposition of a

metal which is preferably selected from the group comprising Ag, Zn, Cd, Ni, Pb and Cu or alloys, Cu and Pb being the more preferred metals of this group. The skeleton is advantageously further grown with Cu in an electrodeposition bath, the skeleton being
5 (electrically) connected as cathode. A further growth of the skeleton with Pb may be accomplished by introducing the screen material in an electrodeposition bath containing leadmethanesulphonate and methanesulphonic acid. The final thickness of the screen material is then advantageously over 15 micrometers, preferably in the range of
10 20-70 micrometers, so that the screen material is still easy to deform, for example to wind. With regard to this deformation, it can be stated in general terms that the thinner the material, the easier the deformation.

Advantageously, the further growth accomplished by step c) and,
15 if applicable by step d), complies with the condition $0.5 \leq (a+b)/(c+d) \leq 5$, wherein $a+b$ denotes the further growth in the thickness direction of the skeleton and $c+d$ denotes the further growth in the plane of the skeleton. Screen material which complies with this condition allows of the application of electrically
20 conductive paste in the screen openings from one side. If the values are higher, i.e. a relatively thick further growth, the application of paste, even from two sides, becomes more difficult, with a high probability of air bubbles being included in the paste. This is undesirable with regard to conductivity.

25 This further growth can be controlled by adding additives (brightening agents) to the composition of the electrodeposition bath, by applying a forced flow of liquid, which for example passes through the openings in the skeleton, and by adjusting the current density. Examples of these effects are described in EP-A-0,038,104,
30 in the name of the present applicant.

An electrical conductor which is produced using the method according to the invention does not have any sharp edges and is therefore easy to handle as an electrode compared to punched or stamped electrode materials. Compared to etched electrode material,
35 an electrical conductor produced in accordance with the invention is characterised by a more uniform thickness, hole shape and hole size. The method according to the invention also allows the production of electrodes with finer grids of openings.

When used as an electrode, the screen material provides more

space for active chemical material, and the contact surface between screen material and active chemical material is greater. For instance, a copper foil with a thickness of 35 micrometers and a grid of hexagonal openings of 155 mesh and an open surface area of approx. 5 10% (approx. 3800 openings/cm²) has an additional contact surface area of approximately 15% compared to solid material.

Furthermore, this contact surface area is further enhanced by the roughening effect of the method according to the invention on the resultant surface of the conductor. This roughening effect is 10 particularly strong when lead is deposited as a surface layer. In general, the roughening effect is dependent on the working conditions of the method according to the invention.

Advantages are also obtained during the assembly of the electrode, such as better adhesion of the active chemical material 15 and the possibility of applying it on one side only, compared to copper products that are currently used for this purpose.

The invention also relates to a solar collector comprising a current collector, made of an electroformed screen material comprising a copper skeleton wherein the screen material has a 20 density of openings that lies in the range of 1-20,000 openings/cm².

The invention furthermore relates to an electrochemical cell comprising an electrode made of an electroformed screen material comprising a copper skeleton wherein the screen material has a density of openings that lies in the range of 1-20,000 openings/cm².

25 The electrical conductors produced using the method according to the invention, can be used as electrically conductive electrode material in batteries and storage batteries, including types based on lithium-ion, lithium-polymer, nickel-cadmium, nickel-metal hydride, zinc-air, nickel-zinc and lead. Another possible application is as a 30 current collector in solar collectors.

The invention is explained below with reference to the appended drawing, in which:

Fig. 1 shows a cross section of a dyke of a further grown skeleton in accordance with the first aspect of the invention;

35 Fig. 2-9 show examples of a pattern of openings in a conductor produced in accordance with the invention;

Fig. 10 shows the open surface area as a function of the density of holes for an embodiment of an electrical conductor according to the invention; and

With reference to Fig. 1, this figure shows a skeleton dyke 10 in cross section. For the sake of clarity, only this skeleton web is depicted in hatched form. This skeleton has been produced in the manner described above in accordance with the first aspect of the invention. The planar underside of the skeleton dyke 10 is the side which has been grown onto the metal conductors of the electroforming matrix and includes, as it were, an impression of the shape of the conductor. After the skeleton formed has been removed from the matrix applied, this skeleton is grown further in an electrodeposition bath while a forced flow of liquid is maintained through the openings of the skeleton, to form a screen material with copper dykes 12. As a result, the further growth in the direction of the flow of liquid, i.e. the thickness direction of the skeleton, denoted by a and b, is greater than the further growth in a direction perpendicular to the flow of liquid, in this figure indicated by c and d.

Fig. 2-9 show examples of patterns of interconnected conductive dykes 14 which are separated by nonconductive islands 16, as may be provided in a matrix which is used in a method according to the first aspect. As is clearly apparent, the nonconductive islands 16, which correspond to the openings which are to be formed, may adopt various shapes and dimensions, even within a pattern.

The pattern depicted in Fig. 9 shows a grid with slot shaped openings 16 between dykes 14, wherein the arrow 32 indicates the orientation of high conductance of the conductor and arrow 30 of low conductance of the conductor, respectively. Such a discrimination in conductance by the pattern of the conductor is of interest when the conductor is used in powertools and EV's, for instance.

The table I below shows the maximum open surface area as a function of the number of holes/cm² for screen materials with a total thickness of 20 micrometers which have been produced on an electroforming matrix with a minimum dyke width of 15 micrometers and a hexagonal grid, as shown in Fig. 2.

Table I

Holes/cm ²	Mesh No.	Dyke Width Matrix (μm)	Skeleton Thickness (μm)	Skeleton Open Surface Area (%)	
				Min.	Max.
1	2.4	100	20	40	97
10	7.5	100	20	30	92
100	24	70	20	20	80
1000	75	30	20	10	63
10000	235	15	20	5	24
10000	235	15	10 ^a	5	45
20000	335	15	20	3	7.5
20000	335	15	10 ^a	3	30

a : further grown to 20 micrometers in a following step

Fig. 10 shows a graph representing this information. A conductor according to the invention has a minimum value for the open surface area (MIN. OPEN SURFACE AREA) in combination with a specific thickness and mesh number, since otherwise the advantages compared to solid material are only marginal. The maximum value is determined by the technique employed. As can be seen, the open surface area can be increased, which offers advantages in particular for the higher mesh numbers (generally a density of holes which is greater than or equal to 10,000), by producing the screen material in two steps. Obviously, even when using the two-step method, a conductor obtained has to comply with the condition relating to the minimum open surface area.

The maximum open surface area (OA) can be calculated for a screen material with a hexagonal grid by applying formula 1:

$$OA = \frac{(d - dyke - 2 \cdot th)^2}{(d)^2} 100\% \quad (1)$$

wherein $d = \frac{25400}{\text{mesh no.}}$ (μm)

$dyke$ = dyke width (μm)

th = thickness of skeleton (μm)

The maximum open surface area is delimited by practical limitations.

C L A I M S

1. Method for producing an electrical conductor suitable for use in a device for conversion of energy, which conductor comprises a copper-containing screen material (12), which method comprises the steps of:
- 5 a) using electrodeposition to deposit a copper skeleton (10) on conductive parts (14) of an electroforming matrix in an electrodeposition bath, and
- b) removing the deposited copper skeleton (10) from the electroforming matrix,
- 10 the screen material (12) having a density of openings which lies in the range of 1-20,000/cm².
2. Method according to claim 1, characterized in that after step b) the method comprises a step c) of further growth of the skeleton
- 15 (10) by electrodeposition to form screen material (12).
3. Method according to claim 2, characterized in that after step c) the method comprises a step d) of further growth of the skeleton (10) by electrodeposition of lead to form screen material (12).
- 20
4. Method according to claim 1, characterized in that the thickness of the skeleton (10) is in the range of 10-45 micrometers.
5. Method according to one of the preceding claims, characterized
- 25 in that the diameter of the openings in the screen material (12) is in the range of 50-100 micrometers.
6. Method according to claim 2 or 3, characterized in that in step c) the skeleton (10) is further grown by deposition of a metal which
- 30 is selected from the group comprising Ag, Zn, Cd, Ni, preferably Cu and Pb, or alloys thereof.
7. Method according to claim 2 or 3, characterized in that in step c) - and when applicable - the further growth complies with the
- 35 condition $0.5 \leq (a+b)/(c+d) \leq 5$, wherein $a+b$ denotes the further growth in the thickness direction of the skeleton and $c+d$ denotes the further growth in the plane of the skeleton (10).

8. Solar collector comprising a current collector, made of an electroformed screen material comprising a copper skeleton wherein the screen material has a density of openings that lies in the range of 1-20,000 openings/cm².

5

9. Electrochemical cell comprising an electrode made of an electroformed screen material comprising a copper skeleton wherein the screen material has a density of openings that lies in the range of 1-20,000 openings/cm².

10

10. Use of an electrical conductor obtained using the method according to one of the preceding claims 1-7, in batteries, storage batteries or solar collectors.

AMENDED CLAIMS

**[Received by the International Bureau on 28 June 2002 (28.06.02):
original claims 1-10 replaced by amended claims 1-9 (2 pages)]**

1. Method for producing an electrical conductor suitable for use in a device for conversion of energy, which conductor comprises a copper-containing screen material (12), which method comprises the steps of:
- 5 a) using electrodeposition to deposit a copper skeleton (10) on conductive parts (14) of an electroforming matrix in an electrodeposition bath, and
- b) removing the deposited copper skeleton (10) from the electroforming matrix,
- 10 d) a further growth of the skeleton (10) by electrodeposition of lead to form the screen material (12)
- the screen material (12) having a density of openings which lies in the range of 1-20,000/cm².
- 15 2. Method according to claim 1, characterized in that the method comprises between step b) and step d), an intermediate step c) of further growth of the skeleton (10) by electrodeposition.
3. Method according to claim 1, characterized in that the
- 20 thickness of the skeleton (10) is in the range of 10-45 micrometers.
4. Method according to one of the preceding claims, characterized in that the diameter of the openings in the screen material (12) is in the range of 50-100 micrometers.
- 25 5. Method according to claim 1 or 2, characterized in that in the intermediate step c) the skeleton (10) is further grown by deposition of a metal which is selected from the group comprising Ag, Zn, Cd, Ni, preferably Cu and Pb, or alloys thereof.
- 30 6. Method according to claim 1 or 2, characterized in that in step d) the further growth complies with the condition $0.5 \leq (a+b)/(c+d) \leq 5$, wherein a+b denotes the further growth in the thickness direction of the skeleton and c+d denotes the further growth in the plane of the

skeleton (10).

7. . Solar collector comprising a current collector, made of an electroformed screen material comprising a copper skeleton wherein the screen material has a density of openings that lies in the range
5 of 1-20,000 openings/cm².

8. Electrochemical cell comprising an electrode made of an electroformed screen material comprising a copper skeleton wherein the screen material has a density of openings that lies in the range
10 of 1-20,000 openings/cm².

9. Use of an electrical conductor obtained using the method according to one of the preceding claims 1-6, in batteries, storage
15 batteries or solar collectors.

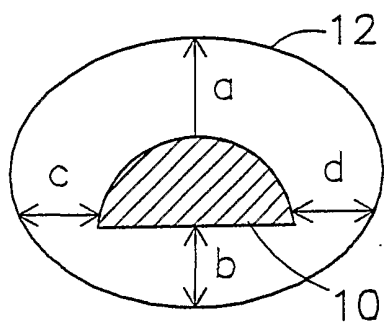


Fig 1

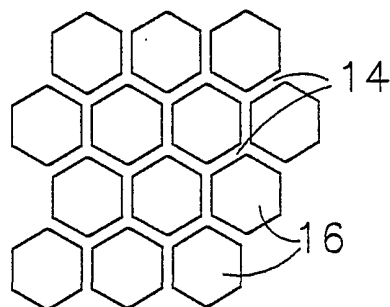


Fig 2

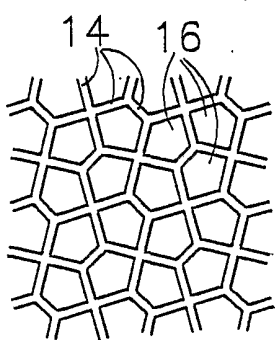


Fig 3

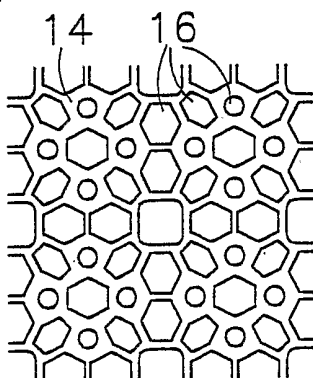


Fig 4

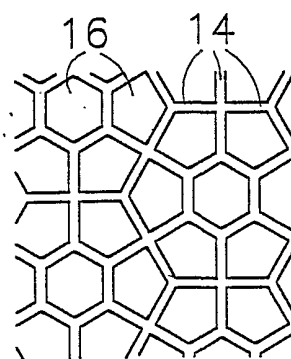


Fig 5

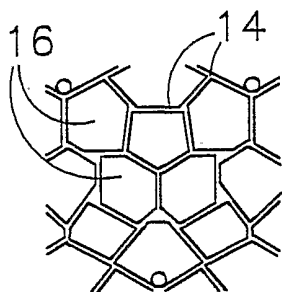


Fig 6

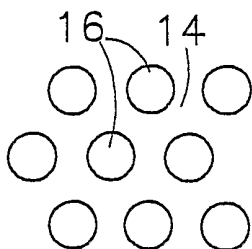


Fig 7

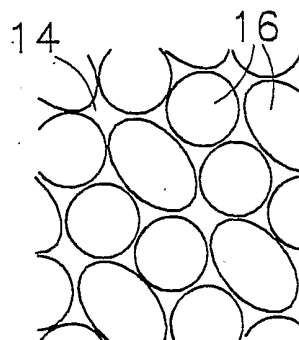


Fig 8

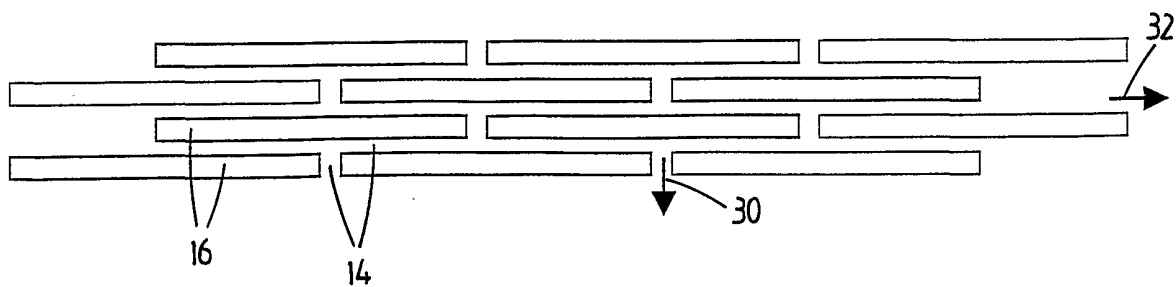


Fig 9

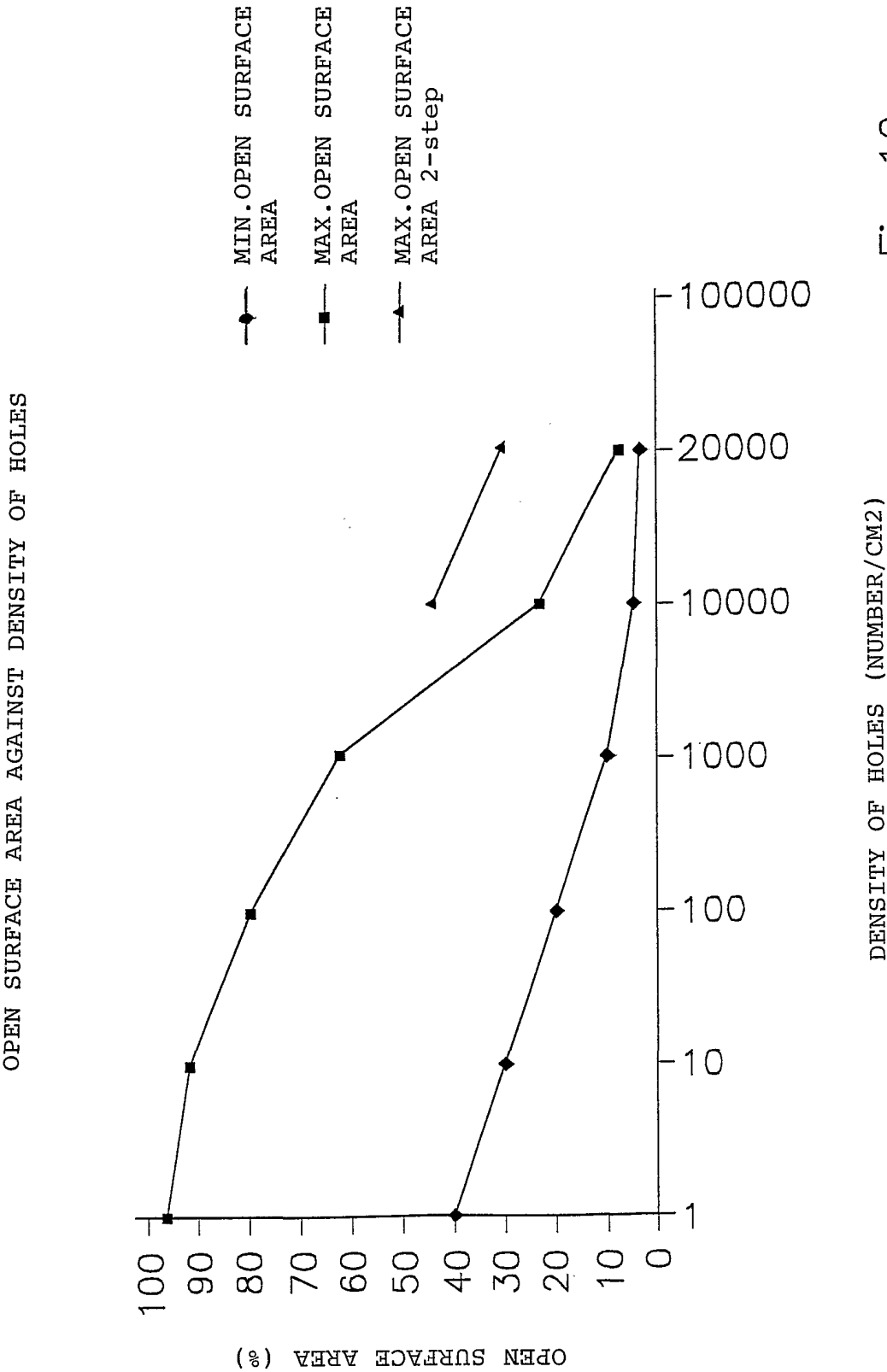


Fig 10

INTERNATIONAL SEARCH REPORT

PCT/NL 02/00064

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C25D1/08 C25D1/04 C25D1/10 H01M4/70 H01M4/74
F24J2/48

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 C25D H01M F24J

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, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 492 731 A (STORK SCREENS BV) 1 July 1992 (1992-07-01) cited in the application the whole document ----	1,2,4-7
A	US 4 228 224 A (HEREDY LASZLO A ET AL) 14 October 1980 (1980-10-14) cited in the application example 1 ----	9,10
A	DE 28 19 339 A (VECO BEHEER ELECTRO PHOTO) 8 November 1979 (1979-11-08) -----	



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

23 April 2002

Date of mailing of the international search report

29/04/2002

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

Van Leeuwen, R

INTERNATIONAL SEARCH REPORT

PCT/NL 02/00064

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0492731	A	01-07-1992	NL 9002866 A	16-07-1992
			AT 135754 T	15-04-1996
			AU 634920 B2	04-03-1993
			AU 8979391 A	25-06-1992
			BR 9105530 A	01-09-1992
			CA 2058109 A1	25-06-1992
			CN 1062772 A ,B	15-07-1992
			DE 69118147 D1	25-04-1996
			DE 69118147 T2	05-09-1996
			DK 492731 T3	15-04-1996
			EP 0492731 A1	01-07-1992
			ES 2085958 T3	16-06-1996
			FI 916090 A ,B,	25-06-1992
			GR 3020278 T3	30-09-1996
			HK 210796 A	06-12-1996
			JP 2079996 C	09-08-1996
			JP 4311594 A	04-11-1992
			JP 7091673 B	04-10-1995
			KR 127832 B1	26-12-1997
			NO 304385 B1	07-12-1998
			NZ 241124 A	26-05-1993
			PT 99884 A ,B	28-02-1994
			US 5282951 A	01-02-1994
			ZA 9109874 A	30-09-1992
US 4228224	A	14-10-1980	CA 1149444 A1	05-07-1983
			DE 3014037 A1	23-10-1980
			GB 2046504 A	12-11-1980
DE 2819339	A	08-11-1979	DE 2819339 A1	08-11-1979