



(86) Date de dépôt PCT/PCT Filing Date: 2012/11/23
 (87) Date publication PCT/PCT Publication Date: 2013/05/30
 (85) Entrée phase nationale/National Entry: 2014/04/03
 (86) N° demande PCT/PCT Application No.: EP 2012/073527
 (87) N° publication PCT/PCT Publication No.: 2013/076277
 (30) Priorité/Priority: 2011/11/24 (IT MI2011A002136)

(51) Cl.Int./Int.Cl. *C25D 7/06* (2006.01),
C25B 11/02 (2006.01), *C25B 11/04* (2006.01),
C25C 7/02 (2006.01), *C25D 17/00* (2006.01),
C25D 17/10 (2006.01), *C25D 17/12* (2006.01)
 (71) Demandeur/Applicant:
 INDUSTRIE DE NORA S.P.A., IT
 (72) Inventeurs/Inventors:
 GOMES DE ABREU, JOSE EDUARDO, BR;
 OISHI, TAKASHI, BR;
 CALDERARA, ALICE, IT
 (74) Agent: MACRAE & CO.

(54) Titre : STRUCTURE ANODIQUE POUR CELLULES HORIZONTALES UTILISEE DANS DES PROCEDES DE
 DEPOT ELECTROLYTIQUE DE METAL
 (54) Title: HORIZONTAL CELL ANODIC STRUCTURE FOR METAL ELECTROPLATING PROCESSES

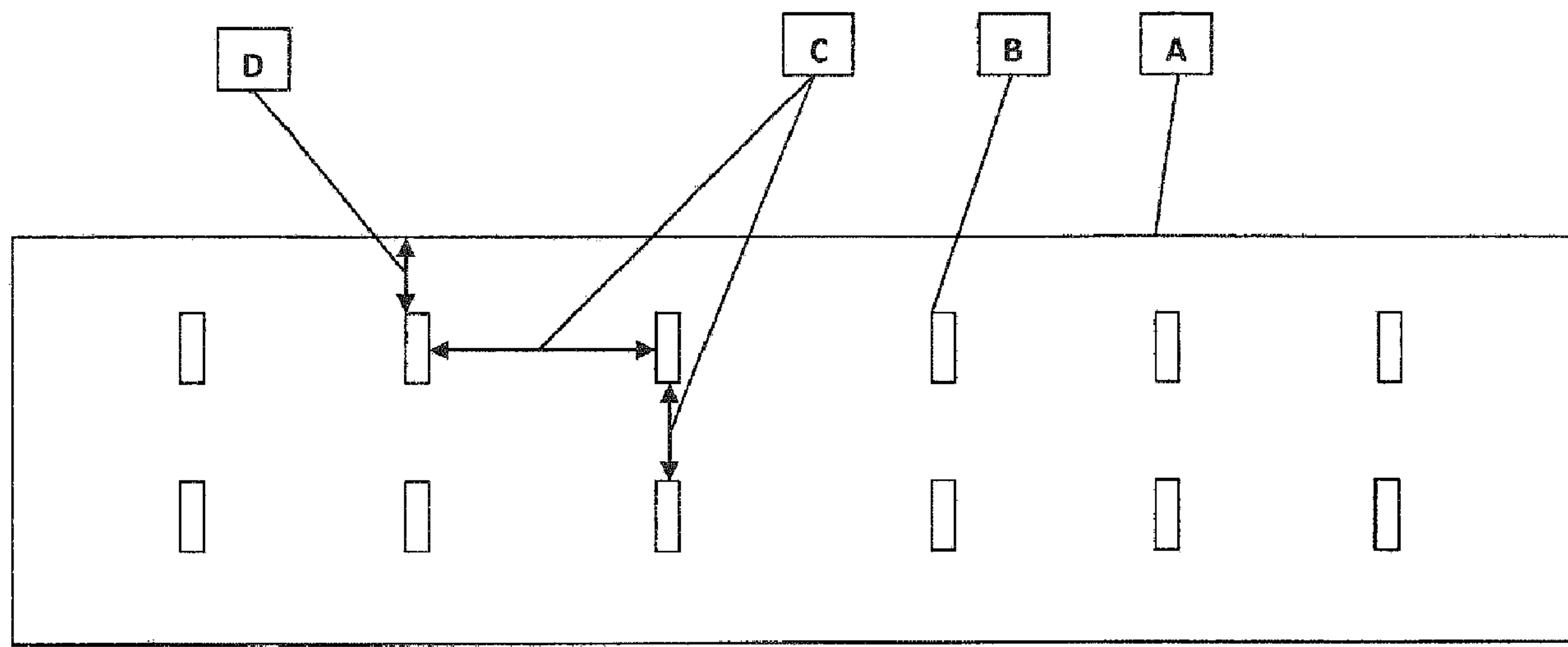


Fig. 1

(57) **Abrégé/Abstract:**
 The present invention concerns an electrode for oxygen evolution in electroplating plants comprising a valve metal substrate and an outer catalytic layer, the substrate consisting of a metal plate provided with slits of area ranging from 2 to 8 cm², said slits being spaced apart by a distance of 5 to 25 cm. The invention also concerns a horizontal electrochemical cell for electroplating processes comprising at least one of said electrodes, and an electroplating plant equipped with at least one of said cells. The invention also concerns an electroplating process comprising the step of anodically evolving oxygen on the surface of said electrode.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau(10) International Publication Number
WO 2013/076277 A3(43) International Publication Date
30 May 2013 (30.05.2013)

(51) International Patent Classification:

C25D 7/06 (2006.01) C25C 7/02 (2006.01)
C25D 17/00 (2006.01) C25B 11/02 (2006.01)
C25D 17/10 (2006.01) C25B 11/04 (2006.01)
C25D 17/12 (2006.01)

(21) International Application Number:

PCT/EP2012/073527

(22) International Filing Date:

23 November 2012 (23.11.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

MI2011A002136 24 November 2011 (24.11.2011) IT

(71) Applicant: INDUSTRIE DE NORA S.P.A. [IT/IT]; Via Bistolfi 35, I-20134 Milan (IT).

(72) Inventors: GOMES DE ABREU, José Eduardo; Rua Benedito Ayres da Silva, 40, CEP-Piedade (SP), Estado de Sao Paulo (BR). OISHI, Takashi; Rua Almeida Filho, 95, CEP-Parque Sao Domingos, Sao Paulo (BR). CALDERARA, Alice; Via della Vittoria, 34, I-26020 Agnadello (CR) (IT).

(74) Agent: REITSTÖTTER KINZEBACH; Sternwartstraße 4, 81679 Munich (DE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(88) Date of publication of the international search report:

1 August 2013

(54) Title: ANODIC STRUCTURE FOR HORIZONTAL CELLS FOR PROCESSES OF METAL ELECTRODEPOSITION

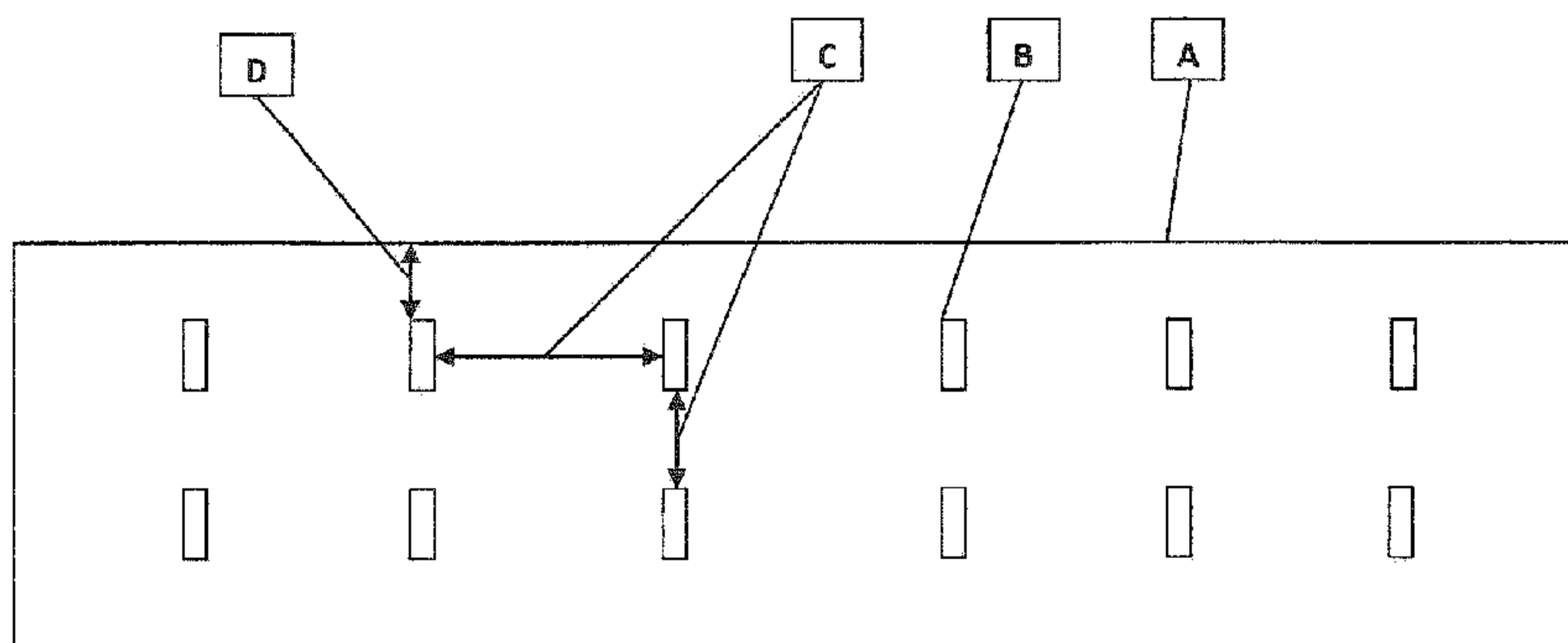


Fig. 1

(57) Abstract: The present invention concerns an electrode for oxygen evolution in electroplating plants comprising a valve metal substrate and an outer catalytic layer, the substrate consisting of a metal plate provided with slits of area ranging from 2 to 8 cm², said slits being spaced apart by a distance of 5 to 25 cm. The invention also concerns a horizontal electrochemical cell for electroplating processes comprising at least one of said electrodes, and an electroplating plant equipped with at least one of said cells. The invention also concerns an electroplating process comprising the step of anodically evolving oxygen on the surface of said electrode.

WO 2013/076277 A3

HORIZONTAL CELL ANODIC STRUCTURE FOR METAL ELECTROPLATING PROCESSES

FIELD OF THE INVENTION

5

The invention relates to an electrode structure for oxygen evolution suitable for plants of galvanic electrodeposition of metals equipped with horizontal cells.

BACKGROUND OF THE INVENTION

10

The use of non consumable anodes in processes of galvanic electrodeposition of metals in horizontal cells as a replacement of heavier and less performant lead anodes is a well-known practice in the art. Insoluble anodes allow in fact a higher flexibility in plant design and consequent operation mode. Non consumable anodes also allow operating at higher current density than lead anodes with consequent advantages on productivity. In traditional metal electrodeposition, such as in electrochemical zinc or zinc alloy plating, oxygen is produced as the result of the anodic reaction. Operating at higher current density making use of non-consumable anodes brings about however an increased oxygen production on the anode surface. In many cases, electrodeposition plants are equipped with horizontal cells; in such case, a metal ribbon or wire used as cathode is transported across an electrolytic bath between rows of anodes arranged parallel to each other. In this case, an increased oxygen production generally implies problems associated with gas stagnation with consequent increase of local current density which negatively affects homogeneity of deposition.

25

It would therefore be desirable to provide an electrode with enhanced mechanical characteristics, suitable for facilitating the release of oxygen and improve the solution refreshment rate – thus favouring an adequate cation feed to the cathode – as well as the electrode-to-solution contact.

30

SUMMARY OF THE INVENTION

Various aspects of the invention are set out in the accompanying claims.

35

Under one aspect, the invention relates to an electrode for oxygen evolution in electroplating plants equipped with horizontal cells, comprising a valve metal substrate and an outer catalytic layer, said substrate consisting of a metal sheet provided with slits of area ranging from 2 to 8

cm², said slits being spaced apart by a distance of 5 to 25 cm. In one embodiment, the slits are arranged in an evenly spaced apart configuration.

Inventors surprisingly observed that the addition of suitably sized slits arranged at an adequate distance has the effect of remarkably increasing the operative lifetime of an electrode for anodic evolution of oxygen used in electroplating processes in plants with horizontal cells.

In one embodiment the electrode has a rectangular shape and said slits have an elongated shape, optionally with the major side arranged parallel to the short side of the electrode.

In another embodiment, the electrode for oxygen evolution in electroplating plants equipped with horizontal cells is provided with slits regularly spaced apart and having an area of 3 to 5 cm².

Inventors surprisingly observed that the production of metal does not show any advantage with slits having a lower size than the one specified and spaced apart by a larger distance. This could happen because too small and spaced apart slits do not allow a sufficient gas release and recirculation. Conversely, too large and tightly spaced slits entail a loss of active area negatively affecting the homogeneity of deposition.

Under another aspect, the valve metal of the oxygen-evolving electrode in electroplating plants equipped with horizontal cells is titanium and the catalytic layer comprises oxides of iridium, tantalum and titanium.

Under another aspect, the present invention relates to a horizontal electrochemical cell for electroplating processes comprising at least one electrode as hereinbefore described. So long as the anodic section is structured in two parallel rows of anodes with the metal ribbon of wire acting as cathode being transported therebetween, slits may be present on one row of anodes only, preferably the upper one. Under another aspect the invention relates to a cell comprising an upper row of anodes and a lower row of anodes, arranged one above the other, and a cathode consisting of a continuous metal ribbon or wire subject to an advancing motion between the upper row of anodes and the lower row of anodes, said direction of advancement being parallel to said parallel rows of anodes and said at least one electrode being an anode of said upper row of anodes. Under yet another aspect the invention relates to a cell having slits arranged with the major side perpendicular to the direction of advancement of the metal ribbon or wire used as the cathode.

Under yet another aspect, the present invention relates to an electroplating plant equipped with at least one horizontal electrochemical cell for electroplating processes comprising at least one electrode as hereinbefore described.

5 Some implementations exemplifying the invention will now be described with reference to the attached drawing, which has the sole purpose of illustrating the reciprocal arrangement of the different elements relatively to said particular implementations of the invention; in particular, drawings are not necessarily drawn to scale.

10 BRIEF DESCRIPTION OF THE DRAWING

Figure 1 shows a top view of a possible embodiment of an anode according to the invention provided with twelve slits.

15 Figure 2 shows a side view of a possible embodiment of a horizontal cell according to the invention.

DETAILED DESCRIPTION OF THE DRAWING

20 Figure 1 shows a top view of a possible embodiment of an anode A having twelve slits B mutually spaced apart by distance C and at distance D from the periphery.

Figure 2 shows a side view of a possible embodiment of a horizontal cell having eight anodes L with twelve slits each, arranged in two parallel rows through which a metal ribbon I acting as the
25 cathode is transported. There are also indicated electrolyte bath inlet E, depleted electrolyte bath outlet F, discharge of oxygen produced at the anodes G and level of electrolyte bath H.

The following examples are included to demonstrate particular embodiments of the invention, whose practicability has been largely verified in the claimed range of values. It should be
30 appreciated by those of skill in the art that the compositions and techniques disclosed in the examples which follow represent compositions and techniques discovered by the inventors to function well in the practice of the invention; however, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the scope of
35 the invention.

EXAMPLE 1

5 Sixteen anodes of 1380 mm x 200 mm x 6 mm size consisting of a titanium substrate provided with a catalytic coating consisting of two distinct layers, namely a first (internal) layer based on oxides of tantalum and iridium in a 65:35 weight ratio (corresponding to a molar ratio of about 63.6:36.4), at an overall iridium loading of 10 g/m², and a second (external) layer based on oxides of iridium, tantalum and titanium in a 78:20:2 weight ratio (corresponding to a molar ratio of about 72.6:19.9:7.5), at an overall iridium loading of 35 g/m², were subdivided into two
10 groups of eight anodes each and arranged parallel in two corresponding rows on either side of a sheet to be zinc-plated. Each anode was provided with 12 elongated slits of 400 mm² area, arranged with the short side oriented parallel to the length of the sheet, mutually spaced apart by 198 mm and at a distance of 25 mm from the periphery of the sheet. Anodes were tested in a zinc-plating plant with horizontal cells at a current density of 13 kA/m² with an electrolytic bath
15 containing 100 g/l of zinc, at a temperature of 50°C and pH 2. Anode deactivation occurred after depositing 210 tons of zinc. In the context of the present description and in accordance with a convention commonly accepted in many zinc-plating plants, an anode is considered to be deactivated when the slope of the ohmic drop in the electrolyte bath increases in time by 20% with respect to the initial value. In fact, at the onset of a partial deactivation of anodes, current
20 distribution becomes uneven with current concentrating in correspondence of the most active zones of the anodes: the concentration of current determines an increase of ohmic drop in the electrolyte bath which hence becomes a representative parameter of the state of conservation of anodes.

25 COUNTEREXAMPLE 1

Sixteen anodes of 1380 mm x 200 mm x 6 mm size consisting of a titanium substrate provided with a catalytic coating consisting of two distinct layers, namely a first (internal) layer based on oxides of tantalum and iridium in a 65:35 weight ratio (corresponding to a molar ratio of about
30 63.6:36.4), at an overall iridium loading of 10 g/m², and a second (external) layer based on oxides of iridium, tantalum and titanium in a 78:20:2 weight ratio (corresponding to a molar ratio of about 72.6:19.9:7.5), at an overall iridium loading of 35 g/m², were subdivided into two groups of eight anodes each and arranged parallel in two corresponding rows on either side of a sheet to be zinc-plated. Anodes were tested in a zinc-plating plant with horizontal cells at a
35 current density of 13 kA/m² with an electrolytic bath containing 100 g/l of zinc, at a temperature of 50°C and pH 2. Anode deactivation occurred after depositing 100 tons of zinc.

EXAMPLE 2

5 Sixteen anodes of 1380 mm x 200 mm x 6 mm size consisting of a titanium substrate provided with a catalytic coating consisting of two distinct layers, namely a first (internal) layer based on oxides of tantalum and iridium in a 65:35 weight ratio (corresponding to a molar ratio of about 63.6:36.4), at an overall iridium loading of 10 g/m², and a second (external) layer based on oxides of iridium, tantalum and titanium in a 78:20:2 weight ratio (corresponding to a molar ratio of about 72.6:19.9:7.5), at an overall iridium loading of 35 g/m², were subdivided into two
10 groups of eight anodes each and arranged parallel in two corresponding rows on either side of a sheet to be zinc-plated. Each anode was provided with 12 elongated slits of 400 mm² area, arranged with the short side oriented parallel to the length of the sheet, mutually spaced apart by 198 mm and at a distance of 25 mm from the periphery of the sheet. Anodes were tested in a zinc-plating plant with horizontal cells at a current density of 10 kA/m² with an electrolytic bath
15 containing 100 g/l of zinc, at a temperature of 50°C and pH 2. Anode deactivation occurred after depositing 180 tons of zinc.

COUNTEREXAMPLE 2

20 Sixteen anodes of 1380 mm x 200 mm x 6 mm size consisting of a titanium substrate provided with a catalytic coating consisting of two distinct layers, namely a first (internal) layer based on oxides of tantalum and iridium in a 65:35 weight ratio (corresponding to a molar ratio of about 63.6:36.4), at an overall iridium loading of 10 g/m², and a second (external) layer based on oxides of iridium, tantalum and titanium in a 78:20:2 weight ratio (corresponding to a molar ratio
25 of about 72.6:19.9:7.5), at an overall iridium loading of 35 g/m², were subdivided into two groups of eight anodes each and arranged parallel in two corresponding rows on either side of a sheet to be zinc-plated. Anodes were tested in a zinc-plating plant with horizontal cells at a current density of 10 kA/m² with an electrolytic bath containing 100 g/l of zinc, at a temperature of 50°C and pH 2. Anode deactivation occurred after depositing 140 tons of zinc.

30

The previous description shall not be intended as limiting the invention, which may be used according to different embodiments without departing from the scopes thereof, and whose extent is solely defined by the appended claims.

35 Throughout the description and claims of the present application, the term "comprise" and variations thereof such as "comprising" and "comprises" are not intended to exclude the presence of other elements, components or additional process steps.

The discussion of documents, acts, materials, devices, articles and the like is included in this specification solely for the purpose of providing a context for the present invention. It is not suggested or represented that any or all of these matters formed part of the prior art base or
5 were common general knowledge in the field relevant to the present invention before the priority date of each claim of this application.

CLAIMS

1. Electrode for oxygen evolution in electroplating plants comprising a valve metal substrate and an outer catalytic layer, the substrate consisting of a metal plate provided with slits of area ranging from 2 to 8 cm², said slits being spaced apart by a distance of 5 to 25 cm.
2. The electrode according to claim 1 wherein said slits are regularly spaced apart.
3. The electrode according to claim 1 or 2 wherein said slits have an elongated shape.
4. The electrode according to one of claims 1 to 3 wherein said slits have an area of 3 to 5 cm².
5. The electrode according to one of claims 1 to 4 wherein said valve metal is titanium and said catalytic layer comprises oxides of iridium, tantalum and titanium.
6. A horizontal electrochemical cell for electroplating processes comprising at least one electrode according to one of the previous claims.
7. Cell according to claim 6, wherein said at least one electrode comprises elongated slits arranged with the major side perpendicular to the direction of advancement of a metal ribbon or wire used as the cathode.
8. Cell according to claim 6, comprising:
 - a. an upper row of anodes and a lower row of anodes, arranged one above the other; and
 - b. a cathode consisting of a continuous metal ribbon or wire subject to an advancing motion between said upper row of anodes and said lower row of anodes, the direction of advancement being parallel to said parallel rows of anodes,wherein said at least one electrode is one anode of said upper row of anodes.

9. Electroplating plant equipped with at least one cell according to claim 6, 7 or 8.
10. Electroplating process comprising the step of anodically evolving oxygen on the
5 surface of an electrode according to one of claims 1 to 5.

1/1

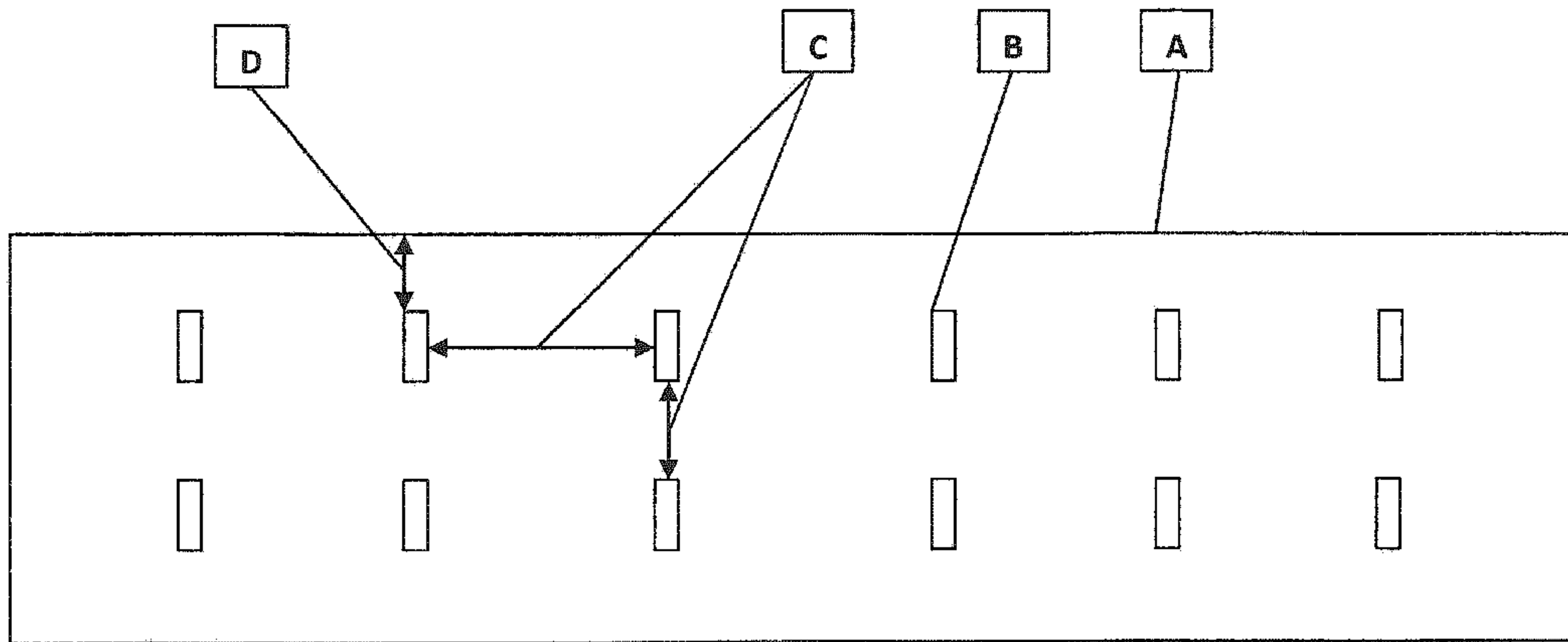


Fig. 1

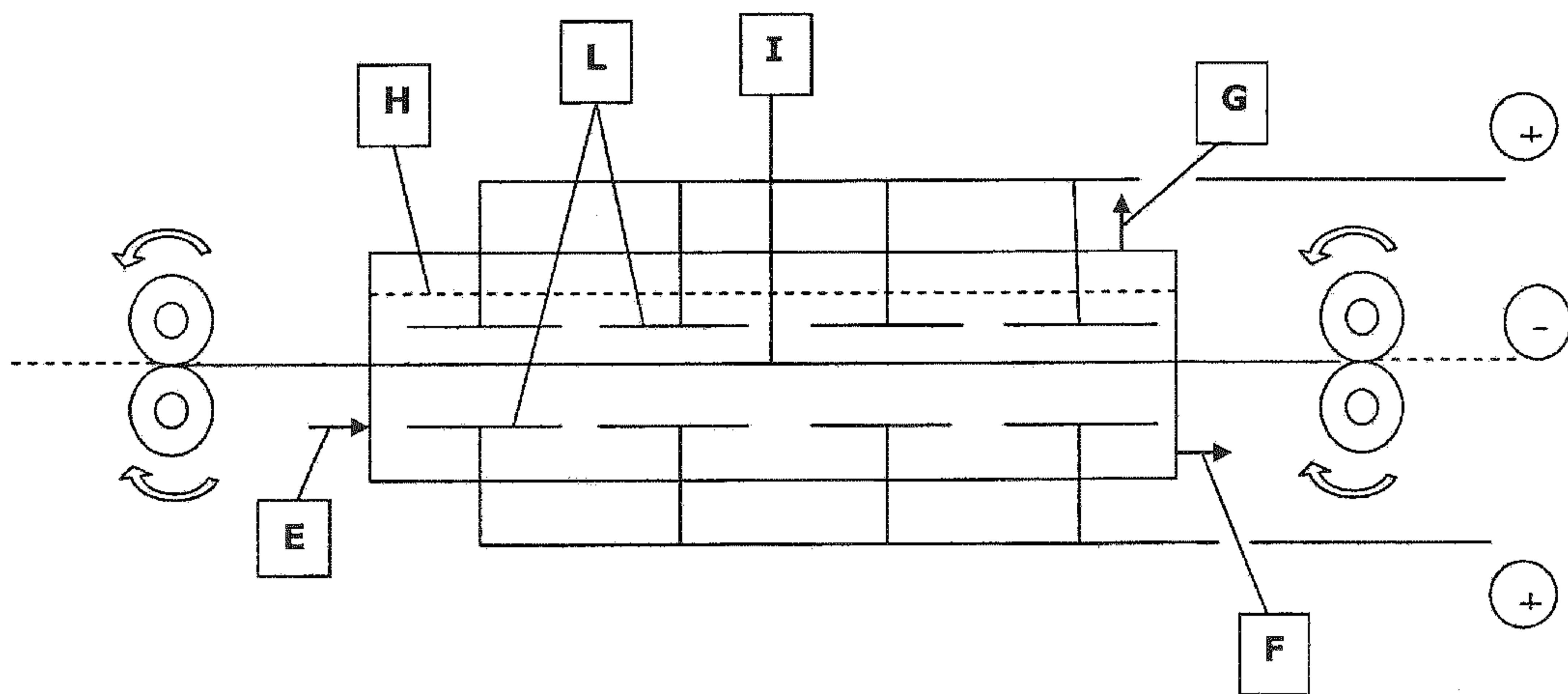


Fig. 2

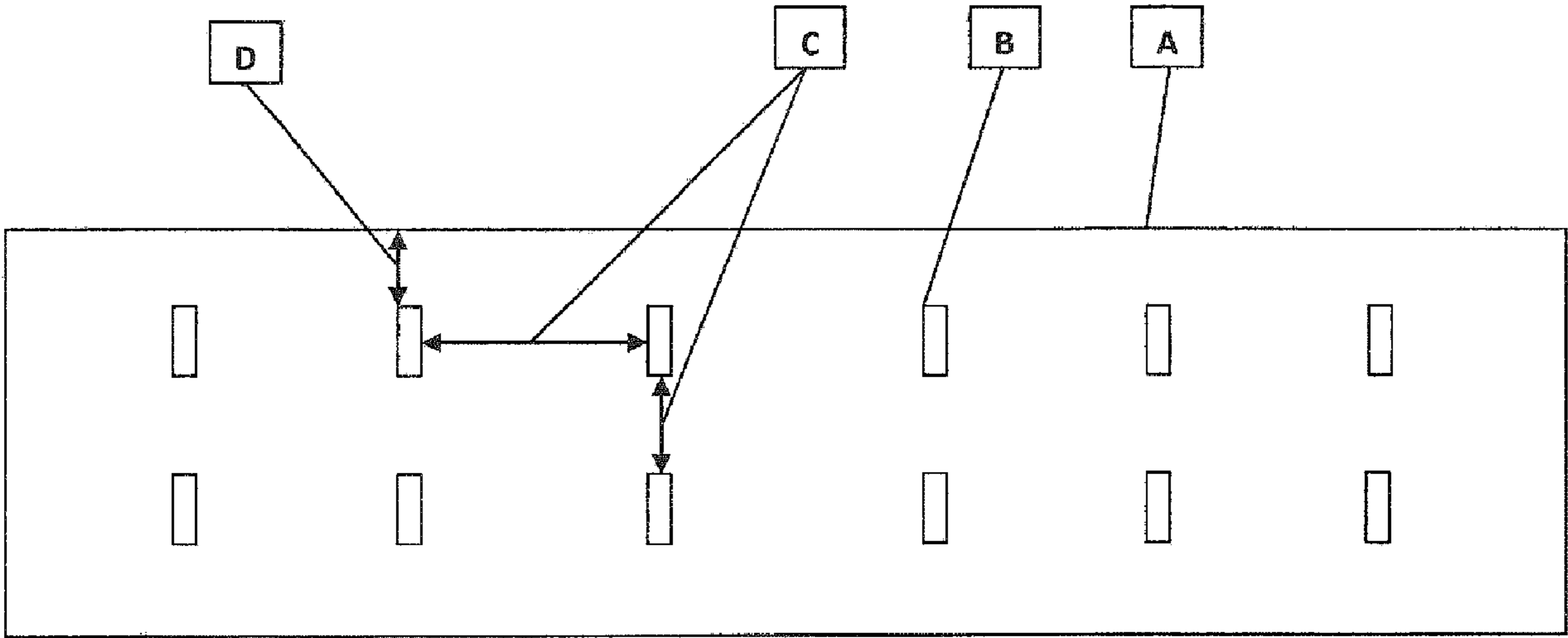


Fig. 1