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(54) **ANODE AND METHOD FOR ELECTROLYTICALLY DEPOSITING A METAL LAYER ONTO A METAL SUBSTRATE**

(57) The invention relates to an anode for use in method for electrolytically depositing a metal layer onto a metal substrate and to a process for electrolytically depositing a metal layer onto a metal substrate using said anode.

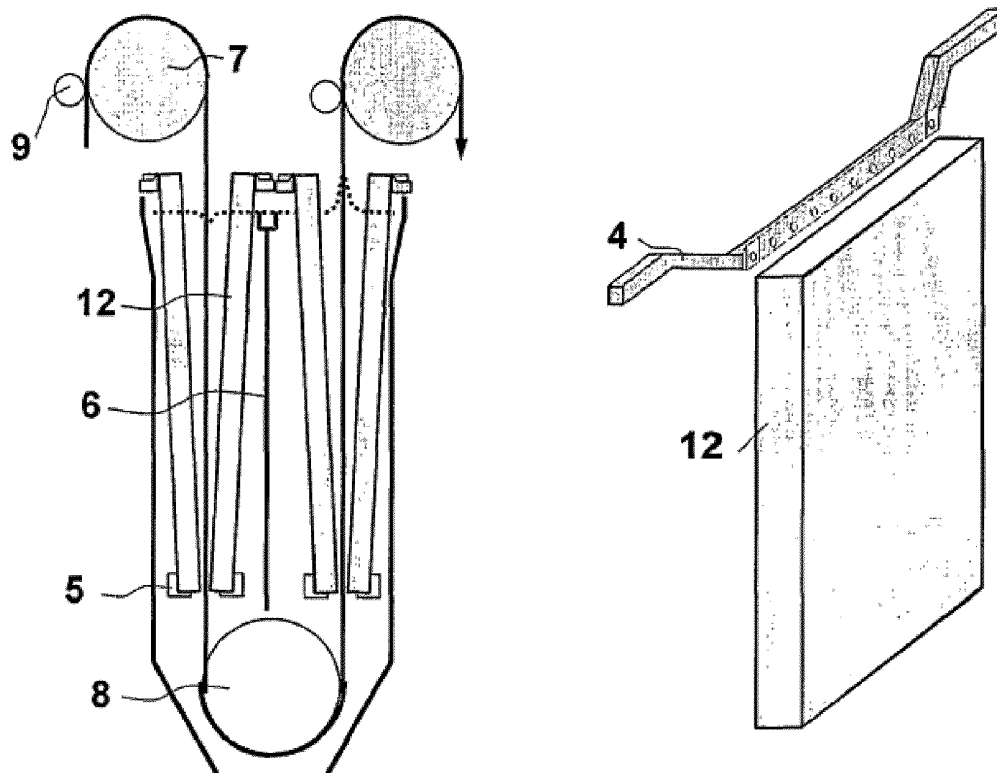


Figure 3

Description**Field of the invention**

- 5 **[0001]** The invention relates to an anode for use in method for electrolytically depositing a metal layer onto a metal substrate and to a process for electrolytically depositing a metal layer onto a metal substrate using said anode.

Background of the invention

- 10 **[0002]** Electrolytically depositing a metal layer onto a substrate, or electroplating, is a process that uses an electric current to reduce dissolved metal cations in an electrolyte so that they form a thin coherent metal coating on an electrically conductive substrate.

- [0003]** A process for electroplating a tin layer onto a steel substrate is known from practice and is described in detail e.g. in the handbook "The Making, Shaping and Treating of Steel", 10th ed., pp. 1146-1153, where a description of a typical commercial tinplating process called FERROSTAN is given which description is incorporated herein by reference.

- 15 **[0004]** In case of tinplating in an electroplating line the electrolyte is replenished with tin cations by anodically dissolving tin into the electrolyte. As known, see also Fig. 36-5 of said handbook, in the said known process the tin is dissolved into the electrolyte from anode bars hanging in the electrolyte from an anode bar (see Figure 1). The anode bars must be replaced regularly, and the anode bar positions have to be adjusted regularly along the anode bridge to ensure that the distance between the anode bar surface and the steel strip to be plated remains constant (See Figure 2). This continuous handling of the anode bars is labour intensive because of the weight of the anode bars of typically 50 kg, potentially hazardous in view of fumes, strong acids and high electrical currents and deteriorates the uniform tin coating thickness over the strip width. Since optimal placement of the anodes is important for stable and uniform plating, the anode positions must be adjusted regularly.

- 25 **[0005]** When the anode bars are spent to an agreed minimum thickness, they are removed from the plating section and recycled in a remelting process for new cast anodes.

- [0006]** To dispense with the continuous replacing of the anode bars, so-called dimensionally stable soluble anodes were developed. EP1699949 discloses such a DSSA. The anode bars and the anode bridge onto which the anode bars are mounted were replaced by a DSSA, e.g. in the form of a titanium basket filled with tin pellets (See Figure 3). The baskets are resistant to the plating conditions, and the pellets dissolve anodically into the electrolyte through openings (holes, gauze, etc.) in the basket where the pellets contact the electrolyte.

- 30 **[0007]** The high electrical resistance of the steel strip is enough to cause an appreciable voltage (IR) drop in the steel strip. Because the current is fed from the top (via the conductor roll 7 in Figure 3), the current density will be higher at the top of the pass than at the bottom. This can be largely overcome by tilting the anode so that it is closer to the strip at the bottom than at the top. This is also schematically depicted in Figure 3. By doing so, the current density is more uniform along the strip between the tilted anodes compared to using anodes that are not tilted.

- 35 **[0008]** Anode baskets can also be used in electroplating processes for depositing zinc, chromium, iron, copper, cobalt and nickel plating, as well as for depositing alloys thereof, such as brass.

40 **Objectives of the invention**

- [0009]** It is an object of the invention to provide an anode for a process for depositing a metal layer onto a metal substrate in a continuous high-speed metal strip electroplating line that can provide a uniform current density distribution on the metal substrate to be plated during plating.

- 45 **[0010]** It is also an object of the invention to provide a process for depositing a metal layer onto a metal substrate in a continuous electroplating line that has a uniform current density distribution along the strip when travelling between the anodes.

- [0011]** It is also an object of the invention to provide a process for depositing a metal layer onto a metal substrate in a continuous electroplating that has a uniform current density distribution along the substrate when travelling between the anodes which is less sensitive or even insensitive for the distance between the strip and the anodes.

50 **Description of the invention**

- [0012]** One or more of the objects is reached with a dimensionally stable anode or dimensionally stable soluble anode for use in a continuous plating line for depositing a metal layer onto a metal substrate wherein, in use, the distance between the anode and the cathode (x) is given by:

$$x = x_0 + x_A(y) \pm c \cdot (x_L(y) - x_A(y)) \quad \text{eq.1}$$

And

$$x_A(y) = \frac{\rho_s \cdot y^2}{\rho_e \cdot d} \quad \text{eq.2}$$

wherein

x = distance between anode and metal substrate (=cathode) [m]

x_A = distance of cathode to ideal anode [m]

x_L = distance of cathode to tilted anode [m]

x_0 = offset at $y=0$ [m]

y = vertical position on cathode [m]

ρ_s = resistivity of strip [Ω m]

ρ_e = resistivity of electrolyte [Ω m]

d = thickness (gauge) of strip [m]

c = constant [-]

wherein c = between 0 and 0.75.

[0013] It is noted that the metal substrate to be plated acts as the cathode in a continuous plating line, and is provided in the form of a metal strip.

[0014] It is also noted that the invention is described for the situation where the strip (cathode) moves between the anode(s) in a substantially vertical direction. This is the most used configuration in continuous plating lines. However, the invention is also applicable for plating lines where the strip (cathode) moves between the anode(s) in a different reaction, e.g. horizontally. The situation is schematically depicted in Figure 4 for a vertical (i.e. the most used) configuration.

[0015] The inventors found that for an anode to have a uniform current density along the anode, the distance of the anode surface facing the cathode to the cathode is given by (eq. 2):

$$x_A(y) = \frac{\rho_s \times y^2}{\rho_e \times d}$$

[0016] The inventors found that this is the case in any electrodeposition process. By means of non-limiting examples reference is made to the deposition of tin in a tinplating line, nickel in a nickel-plating line or chromium in a chromium plating line, nickel-cobalt or brass in an alloy plating line.

[0017] Eq. 2 describes the ideal shape of the anode surface, and it is a parabolic shape. It is noted that the anode surface facing the cathode according to the invention is parallel to the cathode for values of $y=0$. However, any anode that has a shape which can be described by this equation for values of y from 0 to h benefits from the advantage of uniform current density and insensitivity for the distance between the anode and the cathode. For example, an anode surface facing the cathode with a distance to the cathode as prescribed by eq. 2 having a length of $\frac{1}{2}h$ and running from $y=0.25h$ to $y=0.75h$ will also provide the benefits of the invention, albeit that the anode is shorter, and therefore less metal will be deposited as compared to a full length anode running from $y=0$ to $y=h$, wherein h is the maximum height of the anode. The maximum height of the anode depends on the specific installation, and is different for each installation, but the principle as described herein above is the same.

[0018] To maintain the shape of the anode it is important that the anode is a dimensionally stable anode (DSA): an anode that preserves its shape and voltage characteristics even under the most severe conditions prevailing in electrolysis. An anode that dissolves during plating has the ideal shape only at the beginning of its lifetime and is thus not ideal.

[0019] A DSA may be provided in one of two different types:

a. A dimensionally stable anode (DSA): an anode with an anode surface that, in use, faces the cathode, has the desired shape, which is dimensionally stable and does not dissolve under the operating conditions, wherein the concentration of the metal cations is kept constant by replenishing the metal cations in the electrolyte by known means, or by using

b. A dimensionally stable soluble anode (DSSA): an anode basket with a surface that, in use, faces the cathode, has the desired shape containing metal pellets. The basket does not dissolve and is dimensionally stable, and its contents (suitable metal pellets) anodically dissolve into the electrolyte.

[0020] A suitable material for a DSSA that does not dissolve under most operating conditions is titanium. Other known DSSA basket materials that may be suitable depending on the plating conditions and the electrolyte are zirconium, niobium, stainless steel, carbon steel and monel. A suitable material for a DSA that does not dissolve under most operating conditions is titanium provided with a catalytic coating such as platinum or a mixed metal oxide for promoting the oxygen evolution reaction.

[0021] DSSA are like DSA in the sense that these also preserve their shape and voltage characteristics even under the most severe conditions prevailing in electrolysis, but additionally serve as receptacles for metal pellets which dissolve into the electrolyte and enter the solution as metal cations available to be deposited onto the metal strip.

[0022] Pellets in the sense of the invention intend to encompass metal pellets, chunks, lumps, particles, balls, and the like, which can be deposited into the DSSA, e.g. by means of an automated feeder system or otherwise.

[0023] In the following DS(S)A will be used to refer to both DSA and DSSA.

[0024] By shaping the surface of the DS(S)A facing the cathode such that the distance between the anode surface and the strip (cathode) is given by eq. 1 for $c=0$ the system becomes insensitive for the exact placement of the anode. In the ideal case the offset value x_0 is as small as possible. The minimum value is limited because too small an offset value could result in the cathode touching the anode which would lead to short circuiting and damage to strip and installation. When the strip moves between the anodes there is always a risk of some sideways movement due to flutter of the moving strip or deviations in strip shape.

[0025] If the offset is smaller, then the voltage between anode and cathode is also smaller. For any larger value of the offset x_0 the current density is also homogeneous at the cathode if the anode has the ideal shape according to the invention. Whether the anode is placed close to the strip or further away, the current density at the strip is the homogeneous along its length when it is between the anodes. Consequently, the ideal shape of the anode face facing the strip is given by eq. 2 because it ensures a constant current density along its length, and the system is insensitive for the distance between the strip and the anode.

[0026] Of course, the resistance of the system increases or decreases depending on the placement of the anode because the distance between the anode and the strip changes. Consequently, the voltage between the anode and the cathode will increase or decrease accordingly.

[0027] As a reference point the distance between the cathode and the tilted straight anode is defined as $x_L(y)$. The distance between the cathode and the surface facing the cathode of the ideal DS(S)A is defined as $x_A(y)$ (see Figure 4).

[0028] The inventors found that deviations from the ideal shape of the DS(S)A still result in an improvement compared to the tilted straight DS(S)A. Although the optimum result is obtained for $c=0$, the benefits of the invention are still obtained for values of c larger than 0. The smaller the value of c , the more the current density approaches the ideal situation of complete uniformity between the anode and the cathode. Consequently, the invention is embodied in a DS(S)A that is provided with a surface that, in use, faces the cathode (i.e. the strip to be plated) wherein the surface of the anode facing the cathode is curved such that, in use, the distance between the anode and the cathode, x , is between $x_0 + x_A(y) \pm c \cdot (x_L(y) - x_A(y))$, where c is between 0 and 0.75, wherein $x_L(y) - x_A(y)$ is 0 at $y=0$ and at $y=h$, wherein h is the height of the anode.

[0029] Using a DS(S)A with this shape of the surface facing the cathode results in a significantly improved homogeneity of the current density at the cathode.

[0030] The homogeneity of the current density at the cathode is ideal by providing the DS(S)A with a surface that, in use, faces the cathode (i.e. the strip to be plated) wherein the surface is curved such that, in use, the distance between the anode and the cathode, x , is given by $x_A(y)$. Using such a DS(S)A provides the best homogeneity of the current density at the anode, and the homogeneity is also not dependent on the distance between the anode and the cathode. For cases where $c \neq 0$ the homogeneity depends on the distance between the anode and the cathode and some optimisation is needed to determine the optimal distance, whereas for the case where $c=0$ this is not needed from a homogeneity point of view. The distance does affect the voltage needed to execute the plating process, but not the homogeneity at the cathode.

[0031] The homogeneity of the current density at the cathode can be further improved by providing the DS(S)A with a surface that, in use, faces the cathode (i.e. the strip to be plated) wherein the surface is curved such that, in use, the distance between the anode and the cathode, x , is in the range of $x_A(y) \pm c \cdot (x_L(y) - x_A(y))$, where c is between 0 and 0.50 or still further if c is between 0 and 0.25, wherein $x_L(y) - x_A(y)$ is 0 at $y=0$, and at $y=h$, wherein h is the height of the anode.

[0032] The homogeneity of the current density at the cathode can be even further improved by providing the DS(S)A with a surface that, in use, faces the cathode (i.e. the metal strip to be plated) wherein the surface is curved such that, in use, the distance between the anode and the cathode, x , is in the range of $x_A(y) \pm c \cdot (x_L(y) - x_A(y))$, where c is between 0 and 0.10, or even between 0 and 0.05, wherein $x_L(y) - x_A(y)$ is 0 at $y=0$, and at $y=h$, wherein h is the height of the anode.

[0033] Although an anode with a value of $c=0$ is ideal, the producibility and maintenance of these large anodes, and potentially some distortion of the anode ideal shape during use, allow for some deviation from the ideal shape, and therefore a value of $c=0.15$, 0.10 or even 0.05 is achievable consistently in practice.

[0034] The invention is also embodied in an electrolytic plating line comprising one or more DS(S)A's. The principle of the DS(S)A according to the invention is such that straight tilted anodes (DS(S)A or conventional replaceable anodes) can be easily replaced by the DS(S)A's according to the invention. The dimensions are comparable to the conventional tilted anodes. However, the use of the anodes according to the invention will result in the line providing a more homogeneous current density during the plating.

[0035] In an embodiment the anode or anodes according to the invention are used in a continuous plating line operating at a line speed of at least 10 m/min. The benefit of these anodes is also useful in continuous high speed plating line operating at much higher line speeds of between 50 and 750 m/min. Preferably the line speed is at least 75 m/min, more preferably at least 100 m/min, even more preferably at least 150 m/min.

Experiments

[0036] To calculate the primary current distribution two differential equations have to be solved numerically: Ohm's law ($i = -\kappa \nabla \phi$) and Laplace's equation ($\nabla^2 \phi = 0$), where ' ϕ ' is the local potential [V], ' i ' is the current density [$A\ m^{-2}$] and ' κ ' is the electrolyte conductivity [$\Omega^{-1}\ m^{-1}$] (∇ is the well-known del or nabla vector differential operator).

[0037] Both differential equations have been solved numerically by using a Boundary Element Method (BEM). The calculations were performed with the software package EISy2D Version 2016 for a closed geometry consisting of line segments (see Figure 6). In practice, there are two anodes on the opposite sides of the steel strip. In the EISy2D model, the plating cell was cut in half along its symmetry axis (i.e. the steel strip) and the actual thickness of the steel strip was divided by 2.

[0038] Each line segment becomes either an insulator or an electrode as defined by the user. The cell geometry is shown in Figure 6. In this figure, line segment 3 is the anode and line segment 5 is the cathode (i.e. the strip). Within EISy2D, the voltage drop over an electrode is calculated by assigning a value for the resistivity and the thickness of the electrode and the contact point of the electrode, which is either the 'Begin' or the 'End' of the line segment. The line segments are divided into a number of elements and the local current density is calculated for each element. In order to obtain a unique numerical solution, at least one electrode should receive an imposed potential.

Description of the drawings

[0039] The invention will now be explained by means of the following, non-limiting figures.

[0040] A typical soluble anode system for a tinplating line is illustrated in Figure 1. In Figure 1 tin is supplied by tin anode 1 which has an anode gap 2 and an anode notch 3. Each of a series of tin anodes 1 is supported by an anode bridge 4 at a top portion near its anode notch 3 and at a bottom portion in anode box 5. Isolated plate 6 separates two tinning sections in one plating cell. Electrical power is supplied to the strip via conductor roll 7. Near the bottom of the plating cell the strip is guided by sink roll 8. Hold-down roll 9 is also shown. Anode bridge 4 comprises an insulated parking space 10 for a fresh tin anode 1. The tin anodes 1 are connected to the anode bridge 4 via contact strip 14.

[0041] The thickness of the worn anodes is regularly checked with a thickness gauge. When the anode thickness becomes too small, the anode is detached from the anode bridge and placed on the nearest insulated parking space, see Figure 2 where the arrows indicate how the anodes "move" along the anode bridge. On the other side a new anode is placed on the insulated parking space and transferred to the anode bridge. After each replacement, anodes need to be repositioned again. In Figure 2 a fresh tin anode is designated with N and a worn one with W.

[0042] Figure 3 shows, instead of individual tin bars, anode baskets 12 mounted on the anode bar 4 via contact strip 14. The contact strips 14, made of copper in the experiments according to this example, may be coated on their surface contacting the anode basket 12 with a noble metal like Au or Pt. The anode baskets 12 in Figure 6 were filled with tin pellets and, to replenish anodic substance, tin pellets are supplied regularly, which can be done while the plating line is fully operational. The anode baskets 12 can be made of titanium and are designed and positioned.

[0043] Figure 4 shows a schematic drawing of the geometry of the cathode and the anode (tilted and ideal) shown on one side. It shows the offset value x_0 at $y=0$ and the values of x_A and x_L as well as the difference in distance between the ideally curved anode and the tilted linear anode: $(x_L - x_A)$. From this figure it is also clear that a value of $c=1$ describes the distance between the linear anode and the cathode, and a value of $c=0$ describes the distance between the cathode and the ideal curved anode.

[0044] Figure 5a shows a schematic drawing of a strip moving downwardly as a cathode in a plating cell with a straight tilted anode shown on one side, which is distanced from the cathode at a distance b at the top and at a distance a at the bottom of the anode. The distance between the top and the bottom of the anode as seen by the cathode is h . The distance from the anode to the cathode between the top and the bottom of the anode is given by x_L . The value of x_L is

b at the top and x_0 at the bottom of the anode.

[0045] Figure 5b shows a schematic drawing of a strip moving downwardly as a cathode in a plating cell with an anode according to the invention shown on one side, which is distanced from the cathode at a distance b at the top and at a distance x_0 at the bottom of the anode. The distance between the top and the bottom of the anode as seen by the cathode is h. The distance from the anode to the cathode between the top and the bottom of the anode is given by x_A . The value of $x(y)$ is $b=x_0 + x_A(h)$ at the top and x_0 at the bottom of the anode (because $x_A=0$). Figure 5c and 5d schematically show that it is also possible to use anodes wherein the surface facing the cathode is described is only a section (as indicated by the dashed box) of the complete surface as described in figure 5b.

[0046] Figure 6 shows the definition of the system for the BEM calculations.

[0047] Figure 7 shows the value of $x(y)$ for the linear tilted anode (dashed line) and the anode according to the invention (ideal), as well as for three variations on the ideal line. The lines indicated with the circles enclose the shapes that cover values of $x(y) = x_A(y) \pm 0.25 \cdot (x_L(y) - x_A(y))$ ($x_0=30$ mm) and as such cover the ideal shape of the anode as well as a deviation thereof. The line indicated with the triangle described by the line $x = x_A(y) - 0.5 \cdot (x_L(y) - x_A(y))$;

[0048] Figure 8 shows the results of the calculations of the current density divided by the average current density. If the value is 1, then the current density is equal to the average current density.

Claims

1. Dimensionally stable anode or dimensionally stable soluble anode for use in a continuous plating line for depositing a metal layer onto a metal substrate wherein, in use, the distance between the anode and the cathode (x) is given by:

$$x = x_0 + x_A(y) \pm c \cdot (x_L(y) - x_A(y)) \quad \text{eq.1}$$

And

$$x_A(y) = \frac{\rho_s \times y^2}{\rho_e \times d} \quad \text{eq.2}$$

wherein

- x = distance between anode and metal substrate (=cathode) [m]
- x_A = distance of cathode to ideal anode [m]
- x_L = distance of cathode to tilted anode [m]
- x_0 = offset at $y=0$ [m]
- y = vertical position on cathode [m]
- ρ_s = resistivity of strip [Ω m]
- ρ_e = resistivity of electrolyte [Ω m]
- d = thickness (gauge) of strip [m]
- c = constant [-]

wherein c = between 0 and 0.75.

2. Anode as claimed in claim 1 wherein c is between 0 and 0.50.
3. Anode as claimed in claim 1 wherein c is between 0 and 0.10.
4. Anode as claimed in any one of claims 1 to 3 wherein the anode is a dimensionally stable soluble anode.
5. Anode as claimed in any one of claims 1 to 3 wherein part of the side or sides of the anodes is masked out using adjustable masking means that are controlled and guided dependent on strip width and/or coating thickness distribution.
6. Anode as claimed in claim 5, **characterised in that** the masking means comprise a shutter or blind.

7. Anode as claimed in any one of claims 1 to 6 wherein the anode is composed mainly of titanium or of titanium coated with a catalytic coating.
8. Process for electrolytically depositing a metal layer onto a metal substrate in a continuous plating line comprising one or more of dimensionally stable anodes and/or dimensionally stable soluble anodes wherein, in use, the distance between the surface of the anode facing the metal substrate cathode and the metal substrate (x) is given by:

$$x = x_0 + x_A(y) \pm c \cdot (x_L(y) - x_A(y)) \quad \text{eq.1}$$

And

$$x_A(y) = \frac{\rho_s \times y^2}{\rho_e \times d} \quad \text{eq.2}$$

Wherein

- x = distance between anode and metal substrate (=cathode) [m]
- x_A = distance of cathode to ideal anode [m]
- x_L = distance of cathode to tilted anode [m]
- x_0 = offset at y=0 [m]
- y = vertical position on cathode [m]
- ρ_s = resistivity of strip [Ω m]
- ρ_e = resistivity of electrolyte [Ω m]
- d = thickness (gauge) of strip [m]
- c = constant [-]

wherein c = between 0 and 0.75.

9. Process as claimed in claim 8 wherein c is between 0 and 0.50.
10. Process as claimed in claim 9 wherein c is between 0 and 0.10.
11. Process as claimed in any one of claims 8 to 10 wherein the anode is a dimensionally stable soluble anode.
12. Process as claimed in any one of claims 8 to 11 for plating a metal strip with tin, zinc, nickel, chromium, cobalt, molybdenum, copper, zinc or alloys thereof, such as brass.
13. Process as claimed in claim 12 wherein a tin layer is electroplated onto a steel strip.
14. Process as claimed in claim 13 wherein a chromium layer is electroplated onto a steel strip from a trivalent chromium based electrolyte.
15. Process as claimed in any of the claims 8 to 14 wherein the anode is, or the anodes are, composed mainly of titanium or of titanium coated with a catalytic coating.

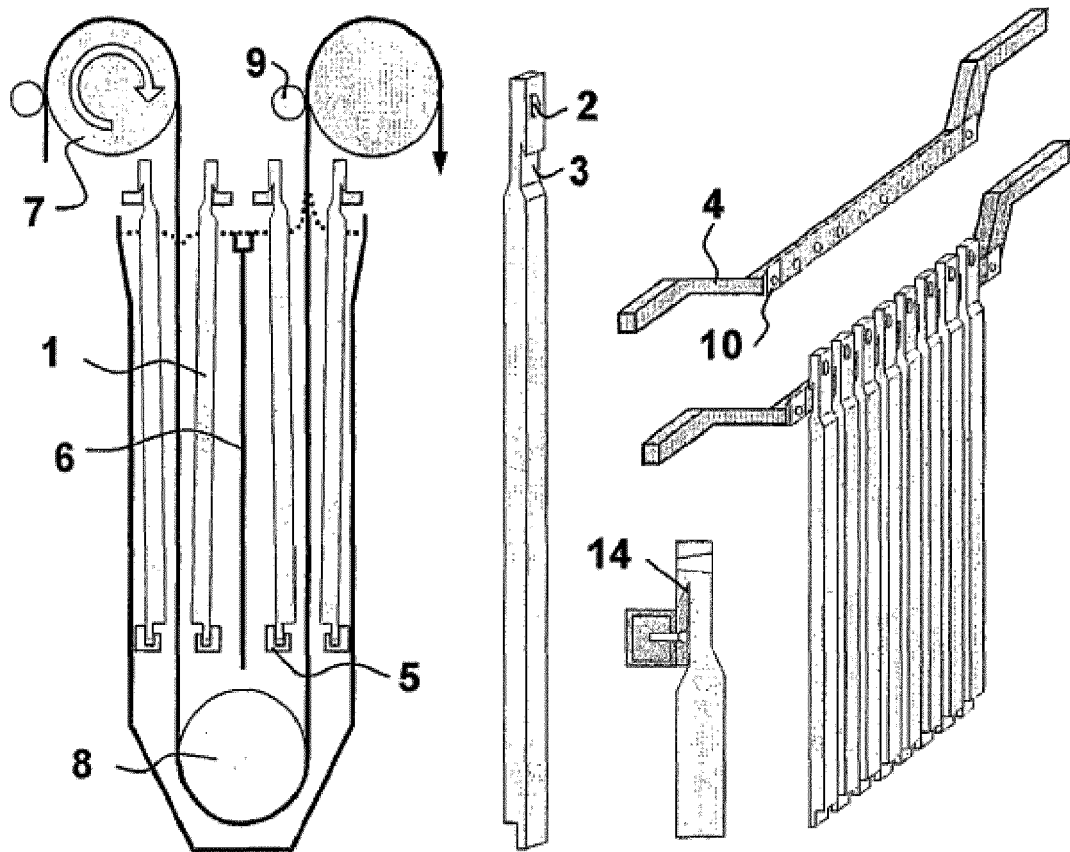


Figure 1

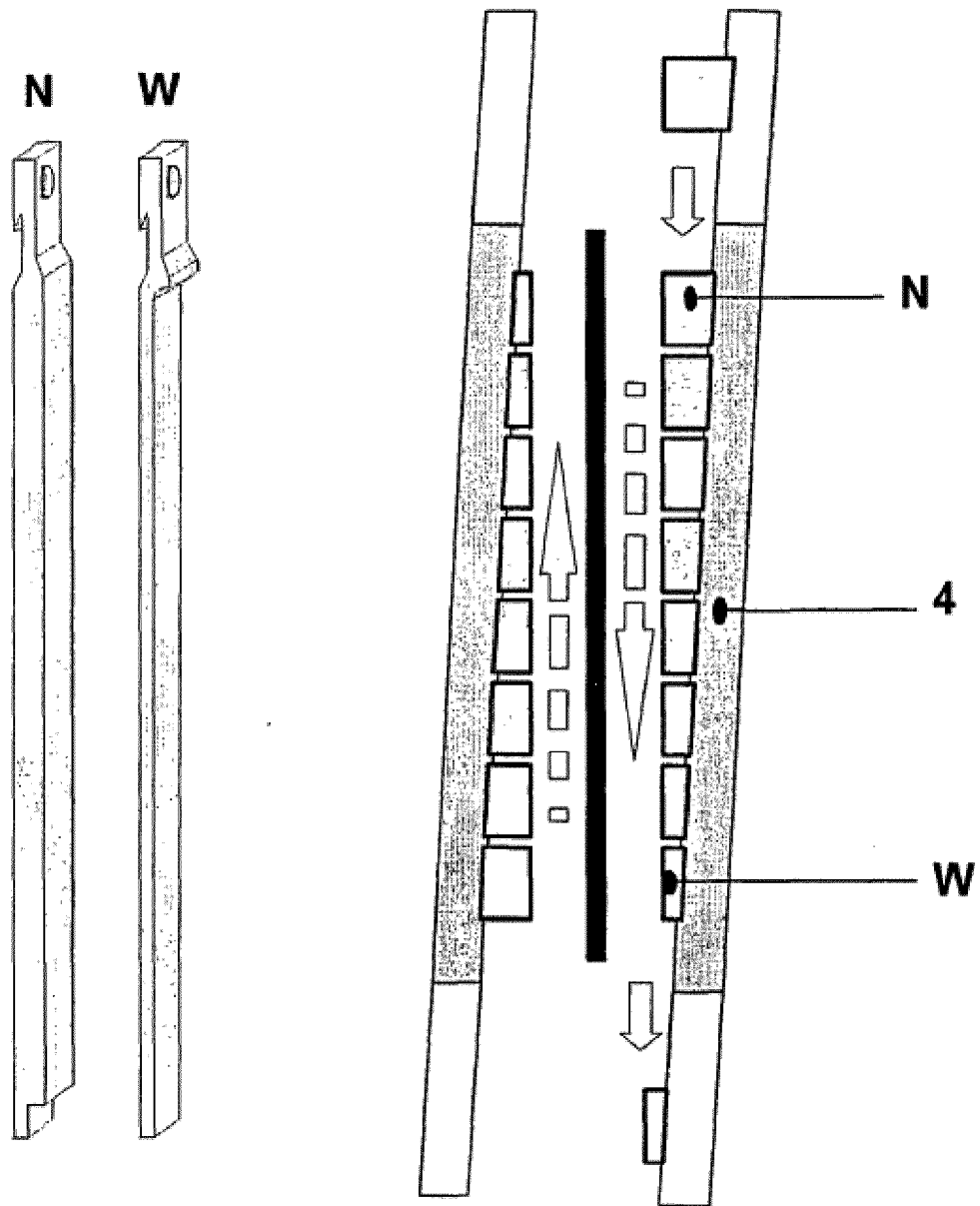


Figure 2

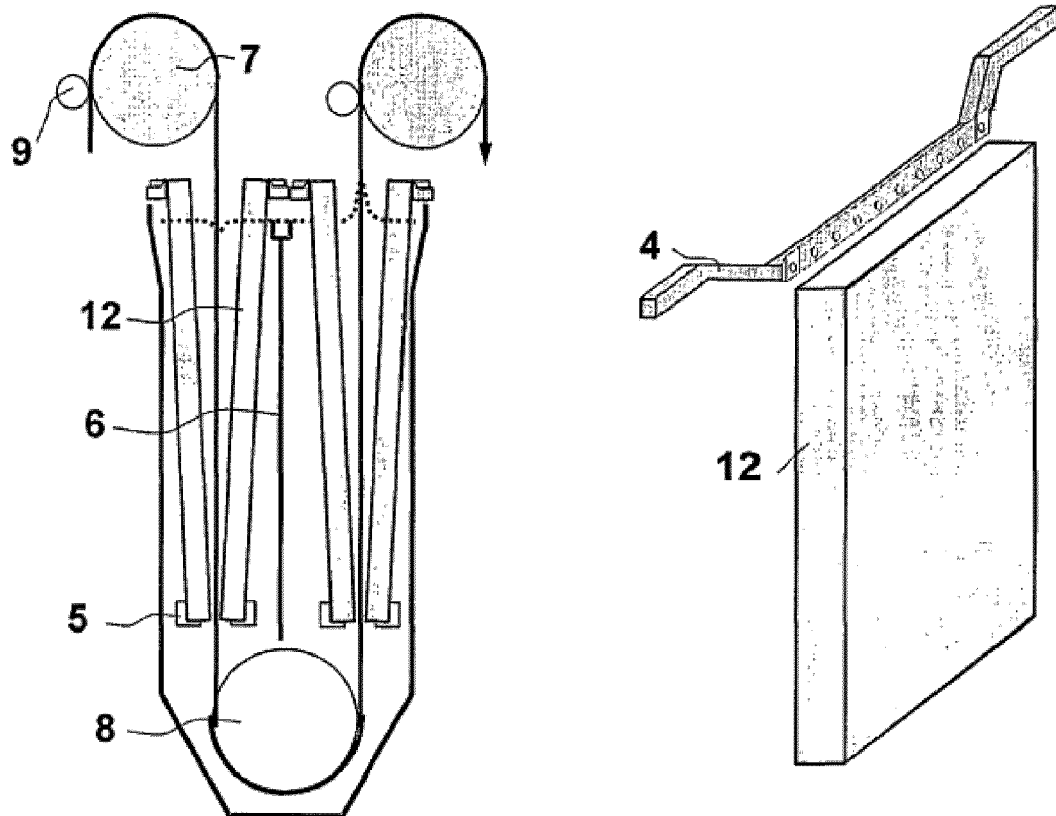


Figure 3

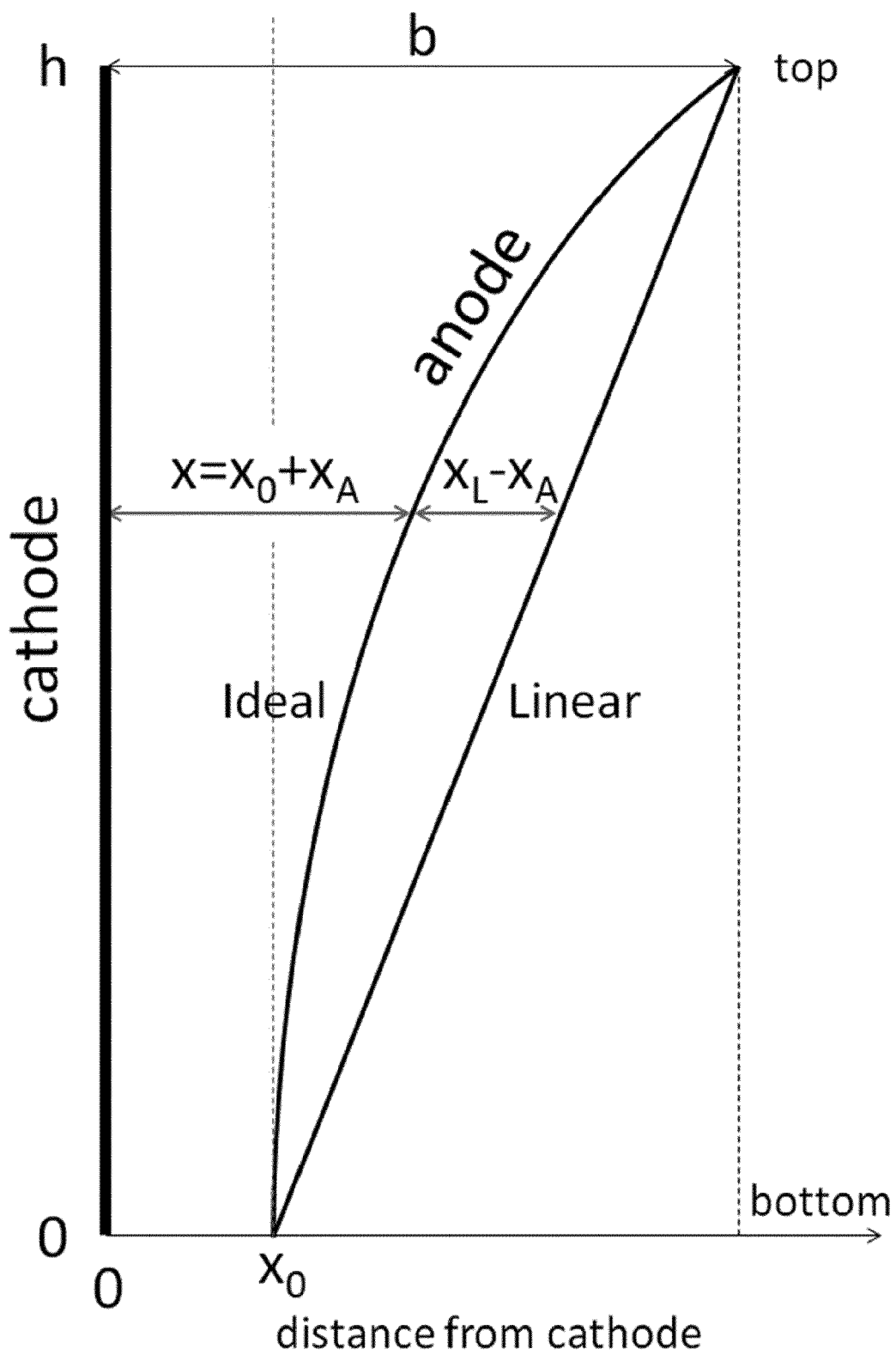


Figure 4

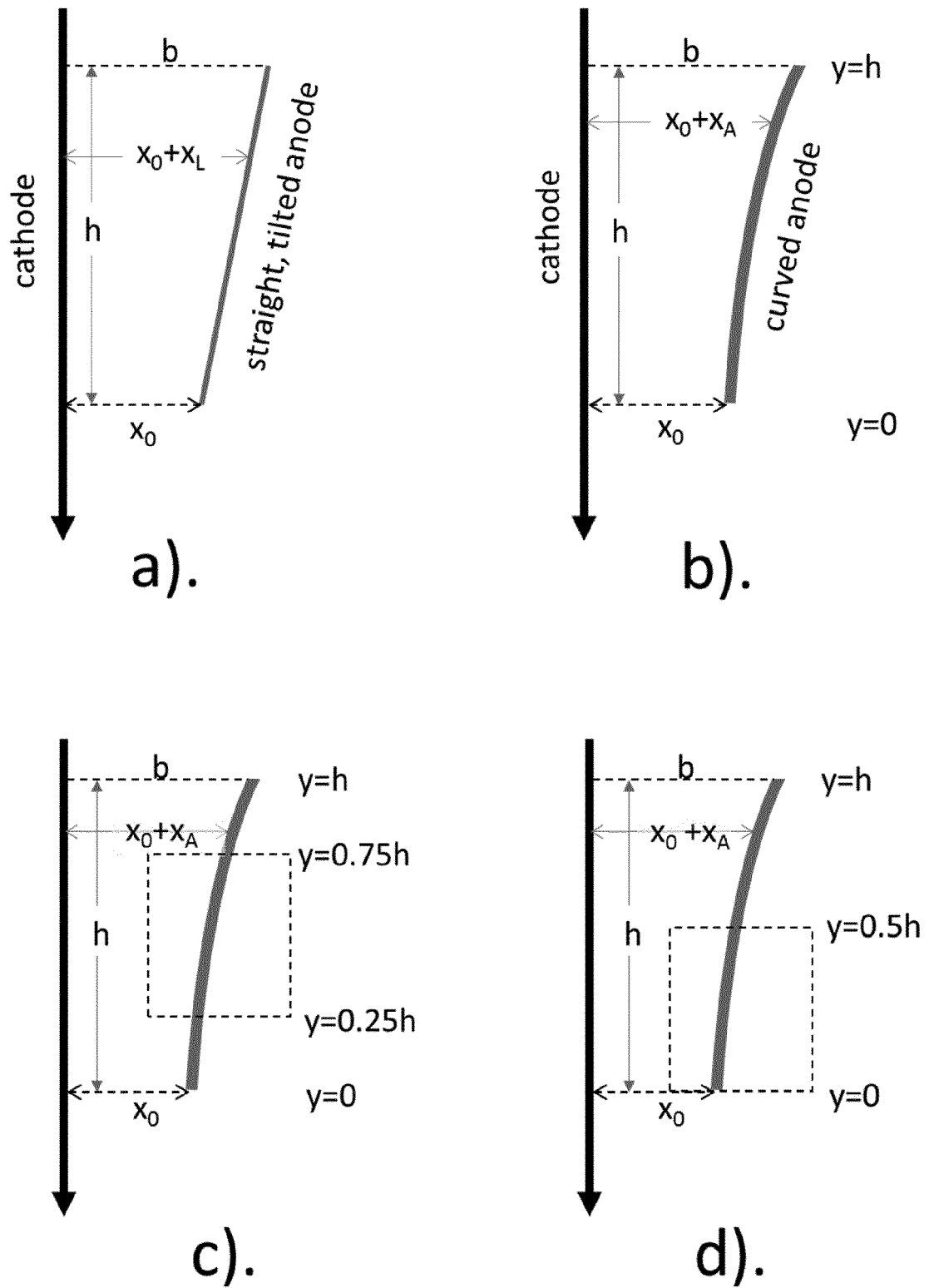


Figure 5

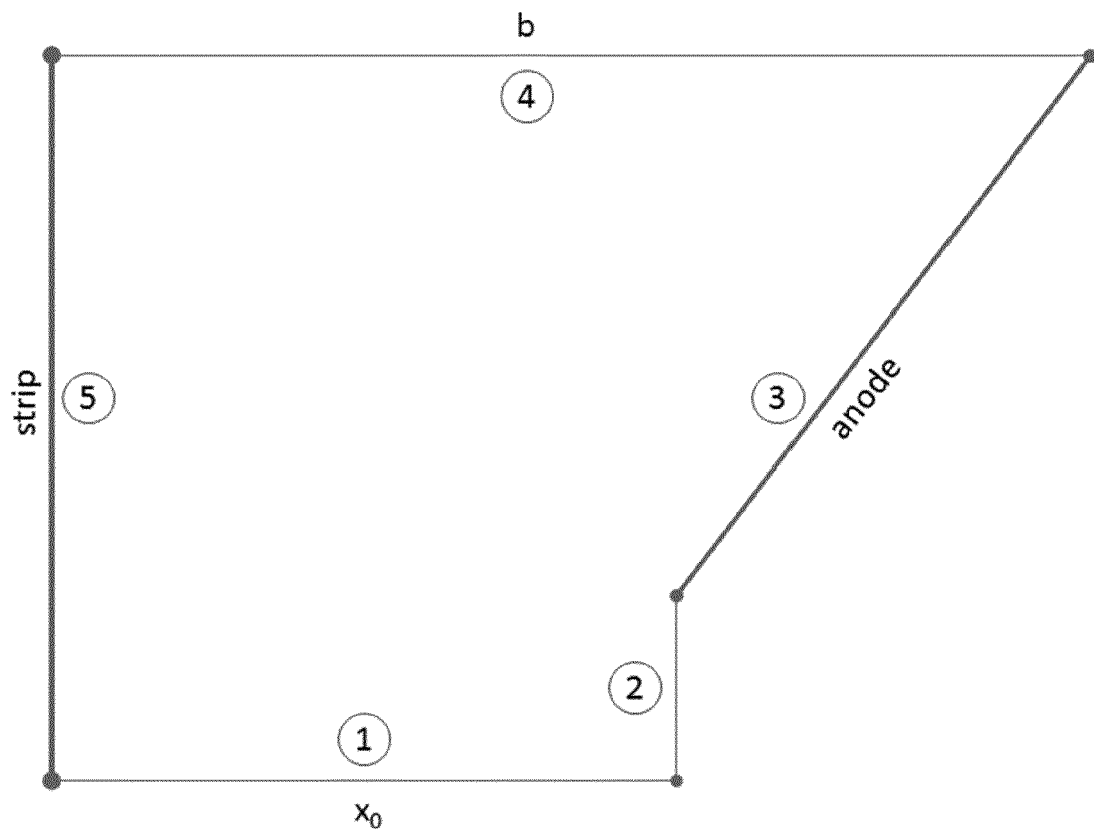


Figure 6

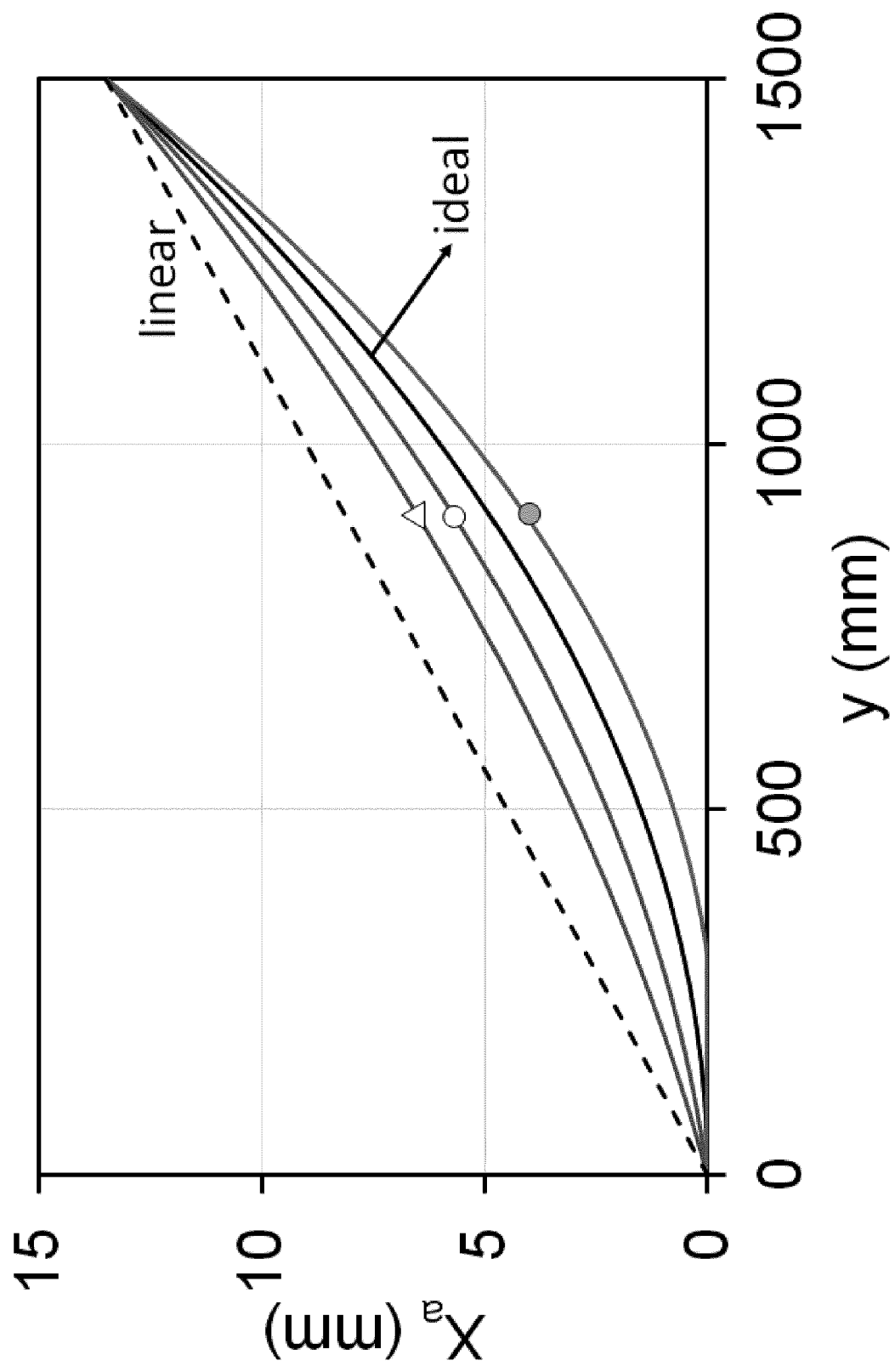


Figure 7

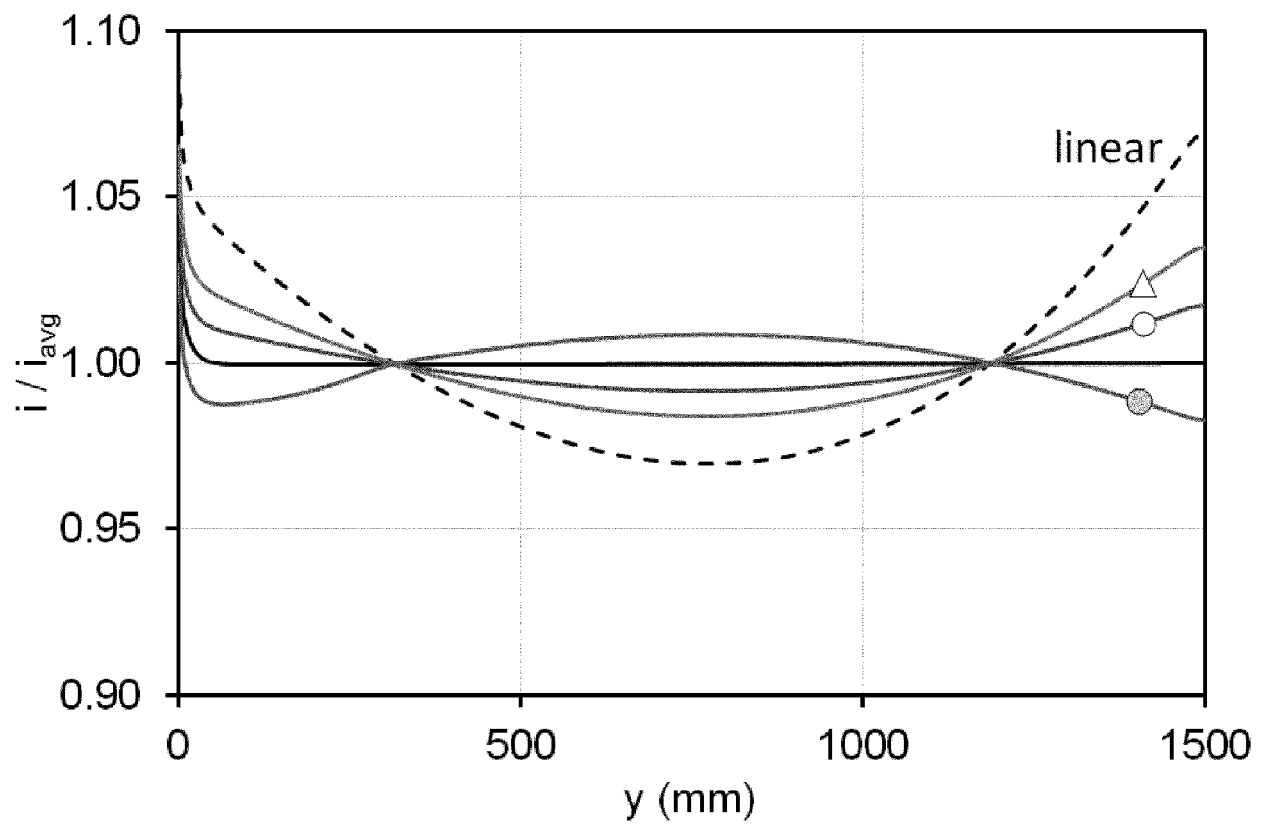


Figure 8



EUROPEAN SEARCH REPORT

Application Number
EP 19 18 5454

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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			TECHNICAL FIELDS SEARCHED (IPC)
			C25D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 15 January 2020	Examiner Crottaz, Olivier
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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