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(54) **ELECTROWINNING SYSTEM WITH INTERCONNECTABLE INTERCELL BARS**

(57) Electrowinning system with interconnectable intercell bars, used in electro-deposition systems, featuring at least three cells connected to each other in series by means of a set of two or three bars: one central main bar and one or two lateral bars placed between each pair of consecutive cells. The main bar provides support and electrical connection to one end of all the cathode hangers of the preceding cell and to one end of all the anode hangers of the next cell. The system includes electrical switches capable of periodically creating an electrical bridge between said bars for a short period of time, causing a temporary reversal of current.

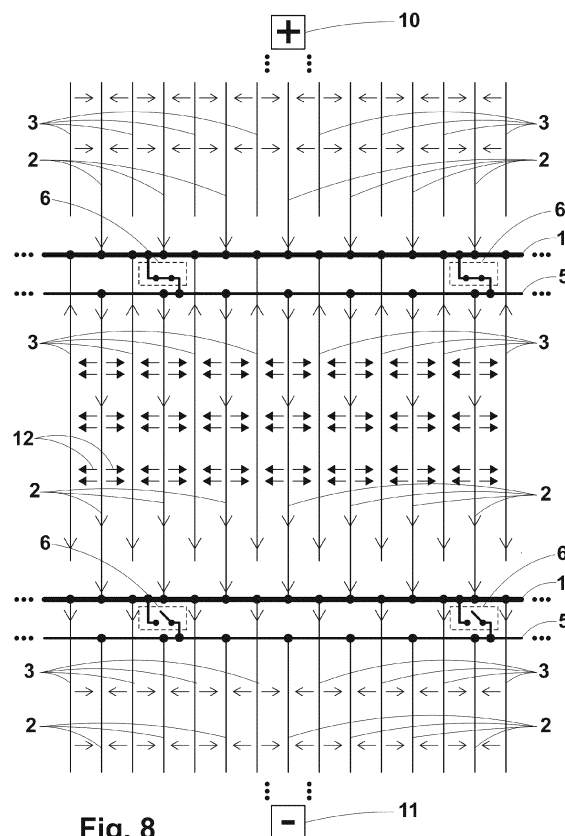


Fig. 8

Description

[0001] This specification pertains, as indicated by its title, to an electrowinning system with interconnectable intercell bars. An electrowinning system refers to an electro-deposition system used for the selective and pure recovery of the metals contained in a solution. The system comprises at least three cells connected in a series circuit between the positive and negative poles of a rectifier. The electrical connection between each cell and the next one is established via a set of at least two bars: a main bar and one or two side bars placed between each pair of consecutive cells and positioned parallel to each other a few centimetres apart.

[0002] The main bar acts in a conventional way and gives support and electrical connection to one of the ends of all the hangers of the cathodes of the preceding cell in the series of cells, where the first cell is the one connected to the positive pole of the rectifier, this main bar also gives support and electrical connection to one of the ends of all the hangers of the anodes of the next cell. One of the two mentioned side bars, the upper side bar, if there is one, provides support and connection to all the anodes of the preceding cell, while the other bar, the lower side bar, if there is one, provides support and connection to all the cathodes of the next cell.

[0003] Several high-current electrical switches, installed uniformly along these bars, endow them with the capability of being connectable bars. These switches can create an electrical bridge or connection between the bars, which is done periodically for a short period of time, causing the desired temporary current reversal in the electrodes of a cell. At this point, we say that the cell is in a state of reversal. During a period of tens of times longer, the switches remain open or without establishing the connection. During this period with the switches open, the cell remains in its conventional production state.

Field of the invention

[0004] The invention relates to the field of metal electro-deposition plants and processes, particularly electrowinning, where production cells containing the electrodes and electrolyte are connected or can be connected to each other via an inter-cell electrical bar.

State of the art

[0005] For more than a hundred years, metal electro-deposition processes have been widely used industrially, especially for electrowinning. When they are used to create thin coating layers, they are also often referred to as "coatings" or "plating".

[0006] The conventional electrical system or connection of electro-deposition of metals, as illustrated in Figures 1 and 2, consists of a grouping of cells connected in series, wherein we highlight as main elements:

- the positive pole of the rectifier that feeds the series circuit of cells,
- the negative pole of the rectifier that feeds the series circuit of cells,
- the anode hanger bars, with the anode electrode plate located underneath,
- the cathode hanger bars, with the cathode electrode plate located underneath,
- the conventional inter-cell bar, and
- the liquid electrolyte occupying the space between the anodes and the cathodes.

[0007] The metal deposited on the cathode is obtained by circulating a direct current between the anode and the cathode. On an industrial scale, in a production plant, this means tens of thousands of amps applied to thousands of electrodes. The continuous circulation of these amps for hours (amps x hours) causes the deposition of the millions of tons of metal produced annually in these plants.

[0008] These electrowinning processes can produce very high-quality metals with very high purity and fineness. However, since their origins a century ago, they have intrinsically presented serious technical challenges with natural limitations that significantly increase the cost and complexity of their operation, while also making these processes more contaminating.

[0009] The current density, and consequently the density and manufacturing capacity, have very strict technical limits, above which quality is lost, contamination increases and energy costs skyrocket. In addition, the electrochemistry of the process is very vulnerable to small and inevitable deviations in the composition of the minerals and process variables.

[0010] It has been more than a hundred years since the construction of the first industrial plants using conventional intercell bars, called "Walker bars", with their different versions or profiles. During this time, extensive research and efforts have been undertaken to mitigate and overcome the identified difficulties and technical problems.

Short circuits or direct anode-cathode contacts

[0011] Accidental short circuits may occur due to positioning error, due to the non-alignment of the electrodes in parallel, or due to their physical deformations. It is evident that an improvement in the work discipline of their placement and in the quality of the plates involved can resolve and has resolved this accidental difficulty.

[0012] But, in addition to this, during the metal deposition process, protrusions appear, naturally and unpredictably, in the flat layer of metal generated, on the cathode plate, which usually has a surface of approximately one square meter. These irregularities quickly grow in the form of dendrites and can easily come into contact with the anode, which is located just five centimetres from the cathode. These contacts cause short circuits with high, destructive currents, which reduce production, destroy

the physical integrity of the electrodes, contaminating the electrolyte and thus the metal produced, and ultimately impact the environment.

[0013] A solution adopted from the beginning to this important problem is to detect the overcurrent as soon as possible and manually eliminate the short-circuit contact. Given the thousands of electrodes involved, and in a very hostile and dangerous environment, it has the disadvantage that it is a high-cost and low-efficiency task.

[0014] Another palliative procedure consists of the application of additives that refine the granulation of the deposited metal crystal and reduce the likelihood of dendrite formation. However, these additives are somewhat contaminant, expensive and only relatively effective.

[0015] More sophisticated solutions are known, such as the application of segmented titanium anodes such as those described in patent WO2015/079072 "*Anode structure for metal electrowinning cells*", but have the drawback that they have a high cost as they require a coating composed of scarce materials given their high demand, such as ruthenium, iridium or rhodium. These anodes automatically disconnect the partial section where the short-circuit contact occurs, thus avoiding high currents. However, as a result of the disconnection of the anode segment, a small collateral issue inevitably appears: the disconnected anode segment becomes coated with a layer of copper. This copper coating dissolves naturally once the dendrite is removed. Although this is a lesser issue, this solution should be operational. However, its real implementation and industrial validation face unexpected difficulties.

Quality and capacity

[0016] Electrode plates work efficiently at very low current densities, around 300 Amps per m² (or 30 mA per cm²), in contrast to a copper conductor of a few millimetres, which can carry tens of thousands of mA. As a consequence, this requires working in very large plants with a high construction and operating cost. Exceeding current density limits in the interest of greater productivity or productive concentration means paying the price of poorer metal quality, a drastic increase in dendrite short circuits as described above, a loss of performance and greater contamination.

[0017] It is surprising and very interesting to know that for decades there have been clear and conclusive studies that show and propose a recognized technical solution to all the natural difficulties of these electrochemical processes, eliminating the root of the intrinsic background limitation suffered by these electro-deposition processes, as for example described in patent US4140596 "*Process for the electrolytic refining of copper*". This solution consists of the periodic reversal of the electric current in electrodes, as proposed in the patent, for 0.355 seconds, followed by 7.1 seconds of direct productive operation. This would apparently mean cycli-

cally reversing or undoing 5 percent of what was previously manufactured. However, reality proves, and theories justify, that on the contrary, this short current reversal clears the barriers of electrochemical potentials that cake and are the source of all the natural difficulties pointed out above for these processes.

[0018] There are established and accepted studies by the scientific community that explain this phenomenon through the study of the ionic layers that originate on or near the surface of the electrodes. These studies also demonstrate the effectiveness of periodic current reversal, or, in other words, the application of periodically repeated current pulses and/or reverse pulses. Thus appears the concept of the existence of a capacitive ionic layer, the Helmholtz layer, whose creation would be the root of the severe limitations of these processes described above.

[0019] The theoretical procedure of applying a current in the opposite direction to that of the production current periodically seems to be the solution, but the real technical problem is the serious difficulty of how to make it a reality or how to implement it practically and operationally on a large scale in a real industrial production plant. In a laboratory with cathode plates of a few square centimetres operating under a few amps, it is easy to implement an electrical system that allows us to experiment, find and apply a highly satisfactory solution. However, in an industrial plant the few square centimetres are converted into thousands and thousands of square meters of electrode surface, and a few amps into tens of thousands of amps.

[0020] The sudden and periodic change of direction of these high currents, which reach tens of thousands of amps, has been tried to obtain by superimposing or adding an alternating current to the conventional direct current. This standard alternating current, with a sinusoidal temporal profile that reaches our homes and is also used in the industry, which in its negative peak exceeds the amplitude of the always positive direct current, resulting in the sum of both having a long period of positive values against a reverse current moment, as described in patents WO2015056121 "*Metal-electrowinning or -electrorefining process comprising the application of an electrical power signal formed of an alternating current superimposed on a direct current*" and WO2015075634 "*Method of superimposing alternating current on direct current for methods for the electrowinning or electrorefining of copper or others products, wherein the alternating current source is connected between two consecutive cells of the electrolytic cell group using an inductor for injecting alternating current and a capacitor for closing the electric circuit*". The problem with these solutions is the extreme magnitude of the electrical devices necessary to couple both alternating and direct currents, with large capacitors and enormous coils operating at thousands of hertz. The technical challenges that they entail make their practical industrial implementation currently infeasible. These solutions, in addition, require an external supplementary

energy supply in alternating current.

[0021] Another solution is also known, as described in patent P201930869 "*Electro-deposition system with active intercell bars*", corresponding to a SAIB or BIAI type system that also uses periodic current reversal, and which, like our current invention, makes use of the internal energy stored in the production process. This is done by dividing or distributing the magnitude of the problem into millions of switching microdevices inserted into the intercell bars of the plant, in each of them we work with amplitudes affordable for today's modern transistors. This is a viable solution although it has the disadvantage of constructive complexity, given the very high number of production switch devices that have to be integrated into the copper of the intercell connection bars, which forces a complex manufacture of these bars, and complicates their maintenance and/or repair.

Description of the invention

[0022] In order to solve the currently existing problem caused by the intrinsic background limitation of these industrial processes, dendrite short circuits and performance losses in metal electro-deposition systems, the interconnectable intercell bar electrowinning system object of the present invention has been devised, which comprises

- at least three cells connected in series between the positive and negative poles of a rectifier, each cell comprising a plurality of anodes and cathodes supported on their respective hangers, the first cell being the one connected to the positive pole of the rectifier,
- a set of at least two electrical connection bars arranged parallel to each other between each cell and the next, being a main bar and at least one side bar, which may be an upper side bar, a lower side bar, or both, and being placed at a sufficient distance so that there is no risk of electrical contact, normally a few centimetres at the usual working voltages,
- a plurality of high-current electrical switches, which can be remotely activated and deactivated via communication means, electrically connected between the main bar and the side bar(s) and evenly distributed along the electrical connection bars, and
- at least one control equipment equipped with means of communication with the electrical switches, preferably being a configurable computer and/or electronic equipment, in charge of giving the periodic orders of activation/deactivation of the electrical switches,
- each main bar serving as both mechanical support and electrical connection for one end of all the cathode hangers of the preceding cell in the series and also as a mechanical support and electrical connection for one end of all the anode hangers of the next cell,

- each upper side bar, if any, serving as both a mechanical support and electrical connection of all the anodes of the preceding cell, and

- each lower side bar, if any, serving as both a mechanical support and electrical connection of all the cathodes of the next cell.

[0023] We refer generically to at least three cells, the first cell, any intermediate cell and the last cell, to represent in the simplest way a conventional industrial plant composed of hundreds of cells and explain the invention applied to it. This requirement is not exclusive for the operation of our invention, as a single cell, or two cells, could also be directly benefited by our invention, although it does not represent an actual industrial system.

[0024] The electric switches may be either solid-state electronic switches, power electromechanical switches or relays, or any combination of both. They can be associated with a printed circuit board featuring a microcontroller capable of communication via digital communication protocols with the control system, and optionally include current sensors as well.

[0025] High-current electrical switches allow electrical connections to be selectively established between the bars associated with a cell. These connections are periodically activated and deactivated by establishing for a short period of time an electrical contact between some of the bars adjacent to a cell, which causes a temporary reversal of current in the electrodes of said cell with natural discharge of the Helmholtz ionic layer without the need for external energy supply, and, for a period tens of times longer, the contacts of the electrical switches remain open. For example, one second of contact or connection and twenty seconds open without connection.

[0026] The activation of the reversal switches must be applied periodically to each cell of the cell series circuit. Closing the switches of all the cells at the same time would cause a short circuit collapse in the general rectifier. If we let it be the chance of non-synchronized clocks, or let the various controllers of the different cells randomly trigger the instant of connection or reversal, we will obtain a statistical distribution in the form of the known binomial distribution that would result in a naturally homogeneous performance for large numbers. But we would face infrequent but safe coincidences of simultaneous reversals that could produce some small instability in the general rectifier.

[0027] As a result of the above lines, an orderly and simple deterministic action is proposed for the current reversal procedure in the circuit cells.

[0028] We act in an orderly manner using an index "i" which is the cell number to which we apply the short inversion period, that is, with switches activated, so that when cell one finishes its reversal state, cell two starts it, and so on ($i = i + 1$), one by one. Once the reversal has reached the last cell, it would start again.

[0029] If the number of cells is large, which is the most common case in an industrial facility, it is clear that we may need to reverse cell one again before reaching the last cell. We must establish some parameters to analyse the problem and its solution:

- E1 is the state wherein the electrical switches of a cell are activated, and therefore in electrical conduction. It applies to the electrodes during the reversal process.
- T1 is the configurable time in the control equipment wherein the electrical switches are in E1 state in each cycle,
- E0 is the state wherein the electrical switches of a cell are deactivated, and therefore there is no electrical conduction. It applies to the electrodes during production.
- T0 is the configurable time in the control equipment during which the electrical switches remain in the E0 state in each cycle, and
- NC is the number of cells that make up the series circuit between the positive and negative poles,

[0030] The sweep time for the reversal wave across the NC cells of the circuit, by sequentially connecting the electrical switches of the cells, is $NC \times T1$ following the explained sequence.

[0031] The time it takes for cell one to request its second or next reversal is $T0 + T1$.

[0032] As mentioned, the problem arises when the number of cells is large and $NC \times T1 > T0 + T1$. In this case, it becomes necessary to reach the E1 state in more than one cell at a time.

[0033] When $NC \times T1 = T0 + T1$, just at the end of E1 in cell NC (last cell), cell one will enter E1. If NC is cleared, and now using NCP as the number of cells per package, we have the formula $NCP = (T0 + T1) / T1$, always adjusting decimals of T0 and T1 to be an integer.

[0034] The number of cell packages on which the cycle should be performed will be $NP = NC / NCP$

If p is referred to as the cell package number, each package p will be composed of cells $(p-1) \times NCP + i$, where i ranges from $i=1$ to $i=NCP$. If NP is not an integer, it is rounded up: $NP = \text{truncate}(NP) + 1$.

[0035] Thus, in general, the sweep of cells in reversal E1 will be:

$$\text{Cell number in E1 reversal} = (p-1) \times NCP + i,$$

where i ranges from $i = 1$ to $i = NCP$, and p ranges from $p = 1$ to $p = NP$. In this way, at all times there are NP cells with switches closed, in a stable way, avoiding fluctuations in the supply of the rectifier.

[0036] Applying the formulation to the example proposed above with the times of $T0 = 7.1$ sec. and $T1 = 0.355$ sec. yields $NCP = (7.1 + 0.355) / 0.355 = 21$.

[0037] In a case of a circuit of, for example, 63 cells, then $NP = 63 / 21 = 3$. 3 packages of 21 cells each are

considered. Each package will be applied the same sequence procedure:

Package 1, with the circuit cells 1,2,3...21

Package 2, with the circuit cells 22,23,24...42

Package 3, with the circuit cells 43,44,45...63

When $i=1$ and $p=1$, cell 1 is reversed

When $i=1$ and $p=2$, cell 22 is reversed

When $i=1$ and $p=3$, cell 43 is reversed

When $i=2$ and $p=1$, cell 2 is reversed

When $i=2$ and $p=2$, cell 23 is reversed

When $i=2$ and $p=3$, cell 44 is reversed

When $i=21$ and $p=3$, cell 63 is reversed

[0038] Following this sequence, there would be 3 cells at a time with the switches closed making the reversal, but never consecutive, with which the process would be carried out in a stable manner, avoiding fluctuations.

[0039] To explain the interconnection between the bars that causes the reversal of currents in the electrodes of a cell, we will first name the bars for reference.

- Each cell is preceded (according to the direction of the electrical current flow, from the positive pole to the negative pole, in the cell series circuit) by a set of three bars that we will call preceding bars: a preceding main bar and two lateral preceding bars that are the preceding upper side bar and the preceding lower side bar.
- Each cell is followed (according to the direction of the electrical current flow, from the positive pole to the negative pole, in the cell series circuit) by a set of three bars that we will call following bars: a following main bar and two lateral preceding bars that are the following upper side bar and the following lower side bar.

[0040] In this electrowinning system, the current reversal switches for the electrodes of a cell are placed between the preceding main bar and the preceding lower side bar, if any, and between the following main bar and the following upper side bar, if any. Embodiments with two and three bars are planned. These switches will be activated and deactivated simultaneously in each cell, causing a current reversal in the electrodes of the cell.

[0041] The typical operation procedure is as follows, which is carried out simultaneously in each cell package, in the event that there are several cell packages:

- the number of cells per package being $NCP = (T0 + T1) / T1$,
- i being the cell index in each package, which will start with $i=1$,

the following sequence is performed:

- in a first step, the electrical switches of cell i are set to state E1 (closed), while the electrical switches of all

- other cells in the package are kept in state E0 (open),
- in a second step, time T1 is allowed to elapse,
 - in a third step, the electrical switches of cell i of the package are set to state E0 a,
 - the value of i is incremented by 1 ($i=i+1$) and the previous steps are repeated sequentially for the following cells, from 1 to NCP, simultaneously in each package, if there are several packages.

[0042] Thus, when $i=1$ we set the first cell in all packages to E1, when $i=2$ we set the second cell in all packages to E1,... when $i = \text{NCP}$ we set the last cell to all packages to E1.

[0043] Obviously, in case the number of cells is not high, only one cell package would be considered to exist.

Advantages of the invention

[0044] The great value of this invention consists in the substantial improvements in quality and productivity that its application causes in the annual production of millions of tons of metals, such as copper, nickel, zinc..., together with the simplicity and robustness of the mechanism that supports it, which make it immediately industrially applicable.

[0045] This intercell bar system with current reversal applies the periodic reversal of currents through an arrangement of high-current electronic switches that provides multiple advantages over the systems currently available, the most important being that it improves the current state of the art, especially the electro-deposition systems with active intercell bars that require millions of switching microdevices inserted into the intercell bars of the plant, one for each segment.

[0046] Unlike solutions known in the state of the art that require an external supplementary energy supply in alternating current, the present invention has the great advantage that it makes use of its own switching strategy that makes use of the natural energy stored in the electrowinning process for the generation of a reverse current and elimination or discharge of the harmful Helmholtz ionic layer, through the high-current switch plates acting between the three bars in a convenient way.

[0047] Among these improvements, we must highlight the increased operational robustness and safety, since the main transistors or switches that require, in an enormous amount, the electro-deposition systems with known active intercell bars, intercept the passage of the total production current, so their potential breakage or breakdown affects production until their repair or replacement, operations that are very complicated and delicate since these switches are embedded within the intercell bars. This is solved in the present invention since the electrical switches act in parallel with the main current, and do so only for the short period of time that the investment lasts, so in case of breakage, it does not affect the production current.

[0048] Another advantage is that, when operating the

electrical switches in parallel, the neighbouring switch devices, which are suitably oversized, provide sufficient reverse current for effective operational continuity. Thus, the system is fault-tolerant, in terms of its subsequent replacement by not being embedded in the intercell bar, but simply coupled and installed on it. This makes this operation much more feasible and straightforward.

[0049] It is also important to note that electrical switches, as they do not have to withstand the load of the plant through them, and only contribute or superimpose the reversal current for a short period, are significantly reduced in number and also in their ease of system, reducing both the economic cost of the system, which is reduced by almost half, and the probability of failures and breakdowns.

[0050] Another notable advantage is that the control system is much simpler and more general, as it does not necessarily require wireless and low-power activity for control. Given its simplicity and the reduced number of switches required, wiring through the bar itself is possible using the plastic channel that supports the secondary intercell bars. This avoids the consumption of thousands and thousands of batteries and the difficult management of such a complex synchronized control through a radio network, which is required in the known electro-deposition systems with active intercell bars.

[0051] Finally, we must highlight the ease of initial system and commissioning, unlike the known electro-deposition systems with active intercell bars. This allows for even subsequent maintenance to be handled by the clients themselves or by a company with low-control specialization, as required in facilities in the mining environment.

Description of the figures

[0052] In order to better understand the object of the present invention, the attached drawing shows a conventional system and two practical embodiments of an electrowinning system with interconnectable intercell bars. In the relevant figures, the symbol of an open-headed arrow ($>$) has been used to represent the production currents, and a closed-headed arrow (\blacktriangleright) to represent the reverse currents that can be obtained with this invention.

Figure -1- shows a representative section of a conventional electro-deposition system for electrowinning consisting of three sections of three cells.

Figure -2- shows a representative section of a conventional electro-deposition system, including the direction of the production currents through the hanger bars and the electrolyte during normal operation.

Figure -3- shows a representative section of an electro-deposition system, in an embodiment with

three intercell bars, with the electrical switches open and not activated.

Figure -4- shows a representative section of an electro-deposition system, in an embodiment with three intercell bars, including the direction of the currents during normal or production operation, with the electrical switches open and not activated.

Figure -5- shows a representative section of an electro-deposition system, in an embodiment with three intercell bars, where the electrical switches of the central cell in the bar system have been closed, allowing the generation of reverse currents. The electrical switches corresponding to the central cell are closed, i.e. activated.

Figure -6- shows a representative section of an electro-deposition system, in an embodiment with two intercell bars with a lower sidebar, including the direction of the currents during normal or production operation, with the electrical switches open and not activated.

Figure -7- shows a representative section of an electro-deposition system, in an embodiment with two intercell bars and an upper sidebar, including the direction of the currents during normal or production operation, with the electrical switches open and not activated.

Figure -8- shows a representative section of an electro-deposition system, in an embodiment with two intercell bars and a lower side bar, where the electrical switches of the central cell in the bar system have been closed, allowing the generation of reverse currents. The electrical switches corresponding to the central cell are closed, i.e. activated.

Figure -9- shows a representative section of an electro-deposition system, in an embodiment with three intercell bars, but where only two of them-the main and the upper bars-are used to generate reverse currents. In this set-up, the electrical switches of the central cell in the bar system have been closed, allowing the generation of reverse currents. The electrical switches corresponding to the central cell are closed, i.e. activated.

Figure -10- represents in a simplified way the control equipment connected via the appropriate communication means to the electrical switches of the cells, in an embodiment with three intercell bars.

Figure -11- represents in a simplified way the control equipment connected via the appropriate communication means to the electrical switches of the cells, in an embodiment with two intercell bars and a lower

side bar.

Figure -12- represents in a simplified way the control equipment connected via the appropriate communication means to the electrical switches of the cells, in an embodiment with two intercell bars and an upper side bar.

Preferred embodiment of the invention

[0053] The constitution and characteristics of the invention may be better understood with the following description made with reference to the attached figures.

[0054] To understand the invention, it is advisable to take into account the configuration of representative elements of a conventional electro-deposition system, which is the same for electrowinning or electrorefining metals, as illustrated in Figures 1 and 2. In it we can see the main elements of a conventional system:

- the positive pole (10) of the rectifier that feeds the series circuit of cells,
- the negative pole (11) of the rectifier that feeds the series circuit of cells,
- the anode hanger bars (3), with the anode electrode plate located underneath,
- the cathode hanger bars (2), with the cathode electrode plate located underneath,
- the conventional inter-cell bar (8),

and the liquid electrolyte representing the area surrounding and between the anodes (3) and the cathodes (2).

[0055] Figure 2 shows the direction of the productive currents through the hanger bars and through the electrolyte in its normal operation.

[0056] As can be seen in Figures 3, 4, 5, 6, 7, 8, 9 and 10, it is illustrated as an electrowinning system with interconnectable intercell bars with current reversal object of this invention comprises

- at least three cells connected in series between the positive (10) and negative (11) poles of a rectifier, each cell comprising a plurality of anodes (3) and cathodes (2) supported on their respective hangers, with the first cell connected to the positive pole of the rectifier,
- a set of at least two electrical connection bars arranged parallel to each other between each cell and the next, being a main bar (1) and at least one side bar, which may be an upper side bar (4), a lower side bar (5), or both, and being placed at a sufficient distance so that there is no risk of electrical contact, normally a few centimetres at the usual working voltages,
- a plurality of high-current electrical switches (7), which can be remotely activated and deactivated via communication means, electrically connected between the main bar (1) and the side bar(s) (4, 5)

and evenly distributed along the electrical connection bars (1, 4, 5), and

- at least one control equipment (13) equipped with means of communication with the electrical switches (7),
- each main bar (1) serving as both mechanical support and electrical connection for one end of all the cathode hangers (2) of the preceding cell in the series and also as a mechanical support and electrical connection for one end of all anode hangers (3) of the next cell,
- each upper side bar (4), if any, serving as both a mechanical support and electrical connection of all the anodes (3) of the preceding cell, and
- each lower side bar (5), if any, serving as both a mechanical support and electrical connection of all the cathodes (2) of the next cell.

[0057] To facilitate the understanding of the operation, we will take the convention that:

- each cell is preceded in the series of cells circuit, according to the direction of current flow, from the positive pole to the negative pole, by a set of bars, either two or three, which we will call preceding bars: a preceding main bar (1), the upper preceding side bar (4), where appropriate, and the lower preceding side bar (4), where appropriate.
- each cell is followed in the series of cells circuit, according to the direction of current flow, from the positive pole to the negative pole, by a set of bars, either two or three, which we will call following bars: a following main bar (1), the upper following side bar (4), where appropriate, and the lower following side bar (4), where appropriate.

[0058] In this electrowinning system, in a preferred embodiment with three bars, as illustrated in Figures 3, 4 and 5, the electrical switches (7) associated with each cell are electrically connected between the preceding main bar (1) and the lower preceding side bar (5) and between the following main bar (1) and the following upper side bar (4). These electrical switches (7) establish electrical bridges between the main bar (1) and the side bars (4, 5) associated with a cell, causing the current to reverse in the cell electrodes. In Figure 4 we see the electrical switches (7) open and in Figure 5 we see the electrical switches (7) closed in the central cell.

[0059] An alternative, simpler embodiment of the electrowinning system is possible with just two bars, as illustrated in Figures 6, 7, and 8, wherein the electrical switches (7) associated with each cell are electrically connected either between the main preceding bars (1) and the preceding side bars (5), as shown in Figures 6 and 8, or between the main following bars (1) and the

upper following side bars (4), as illustrated in Figure 7. It is also possible to use three intercell bars, but only to use the electrical switches (7) between the main bars (1) and one of the side bars (4, 5), as illustrated in Figure 9. These electrical switches (7) establish electrical bridges between the main bar (1) and the side bars (4, 5) associated with a cell, causing the current to reverse in the cell electrodes. In Figures 4, 6 and 7 we see the electrical switches (7) in the open position, while in Figures 5, 8 and 9, the electrical switches (7) are closed in the central cell.

[0060] In an electrowinning system, the existing side bars (4,5) will preferably have a section of at least 200 mm², while the main bar (1) may be the one usually used in the plant, which typically ranges from 575 mm² to 1280 mm², depending on whether more complex bar profiles are used. In an electrowinning system, the amplitude of the reverse currents (12) generated, although of short duration, is very intense, approximately 2.5 times the production current. For this purpose, 32 electrical switches (7) will preferably be installed per cell, 16 on each side of the cell. These electrical switches (7) are oversized for robustness, ideally featuring a contact resistance between 2.5 and 5 micro-ohms.

[0061] The means of communication between the control equipment (13) and the electrical switches (7) are preferably selected from the group consisting of wired or wireless options.

[0062] The electric switches (7) may be either solid-state electronic switches, power electromechanical switches or relays, or any combination of both. It is envisaged that, in an alternative embodiment, the electrical switches (7) will be associated with a printed circuit board equipped with a microcontroller capable of communication via digital communication protocols with the control equipment (13). Optionally, the printed circuit boards associated with the electrical switches (7) will also have current sensors.

[0063] The high-current electrical switches (7) allow to establish electrical connections selectively between the bars (1, 4, 5). These connections are periodically activated and deactivated by establishing an electrical contact between said bars for a short period of time, which causes a temporary reversal of current with natural discharge of the Helmholtz ionic layer, without the need for external energy supply. During a period of tens of times longer, the contacts of the electrical switches (7) remain open.

[0064] This system involves a characteristic current reversal procedure, aimed at ensuring the stability of the general power supply to the series circuit of cells, wherein,

- E1 is the state wherein the electrical switches (7) associated with a cell are activated, and therefore in electrical conduction. It applies to the electrodes during the reversal process.
- T1 is the configurable time in the control equipment wherein the electrical switches are in E1 state in each

cycle,

- E0 is the state wherein the electrical switches (7) associated with a cell are deactivated, and, therefore, there is no electrical conduction. It applies to the electrodes during production.
- T0 is the configurable time in the control equipment during which the electrical switches (7) remain in the E0 state in each cycle, and
- NC is the number of cells that make up the series circuit between the positive and negative poles,
- NCP is the number of cells per package, calculated as $NCP = (T0 + T1) / T1$, always rounding the decimals of T0 and T1 so that it results in an integer,
- i is the cell index in each package, which will start with i=1,

the following sequence is carried out simultaneously in each of the cell packages:

- in a first step, the electrical switches (7) associated with cell i are set to the E1 state (closed), while the electrical switches associated with all other cells in the package remain in the E0 state (open),
- in a second step, time T1 is allowed to elapse,
- in a third step, the electrical switches (7) associated with cell i of the package are set to the E0 state,
- the value of i is incremented by 1 ($i = i+1$) and the previous steps are repeated sequentially for the following cells, from 1 to NCP, simultaneously in each package, if there are several packages.

[0065] Thus, when $i=1$ we set the first cell in all packages to E1, when $i=2$ we set the second cell in all packages to E1,... when $i = NCP$ we set the last cell to all packages to E1.

[0066] Obviously, in case the number of cells is not high, only one cell package would be considered to exist.

[0067] The objective we aim to achieve and have accomplished is the periodic reversal of the current in each and every electrode of a cell, through the appropriate design of the aforementioned bars and the proposed switches that make up the invention. This has been experimentally validated in our laboratory:

In this electrowinning system, by activating the switches (7) to the bars (1) and (4) and (5), and through these bars and the hanger bars, we are applying the electrical bridge to each electrode or pairs of anode (3) and cathode (2). For example, using $8 + 8 = 16$ switches per cell would be an acceptable compromise between simplification through grouping and the current path on the transport bars for reverse current and the switches. The path of the discharge or reverse currents (12) must be limited, given that in a single cell operating at 600 A/m^2 , with electrodes covering one square meter and 63 cathodes, applying a reverse current amplitude double that of the direct current results in a discharge $63 \times 1200 = 75600$ amperes. If these currents had to travel many meters along the bar, it would require a large section in said bar, which in practice is not

achievable or reasonably available.

[0068] It may be surprising that simply establishing an electrical bridge between an anode (3) and a cathode (2) produces a significant reverse current (12) of more than 600 A/m^2 . We include the discovery of this fact, obtained experimentally, to explain that the current is generated by the energy stored in the plates and behaves like the voltage generated by a battery.

[0069] The small-scale experimental replication of the invention in the laboratory and the performance of dozens of tests confirm the most optimistic reports about the immediate benefits of periodic current reversal when executed with the described switching design, as shown in Figures 4 and 5. The quality of the copper deposited is, at high densities, double or triple the nominal value with the described process, or pulsing, and is equal to or better than the copper deposited at low currents without pulsing.

[0070] The small-scale replication of the invention in our laboratory and the performance of dozens of tests confirm the most optimistic estimates regarding the immediate benefits of periodic current reversal when operating with the switching design described above. The resistance of the micro cell operating at low load, at about 200 A/m^2 , is in the order of $0.96 \text{ m}\Omega$ per m^2 . If the current density is increased to 900 A/m^2 , which is 4.5 times higher, but applying the described periodic current reversal procedure, also known as pulsing, with the invention, the passivation or polarization of the anode (3) does not occur. Instead, the resistance of our micro cell decreases to $0.77 \text{ m}\Omega$ per m^2 . The copper plate produced at this high current density for about 14 hours with pulsing has a perfectly acceptable grain. The application of 900 A/m^2 to the same cell under the same conditions without pulsing results in an anode (3) to cathode (2) resistance of about $1.85 \text{ m}\Omega$ per m^2 within a few hours, an increase that shows the inevitable passivation of the anode (3).

[0071] Persons skilled in the art will easily understand that the characteristics of different embodiments can be combined with characteristics of other possible embodiments whenever such a combination is technically possible.

[0072] All the information referring to examples or modes of embodiment, form part of the description of the invention.

Claims

1. - Electrowinning system with interconnectable inter-cell bars, **characterised in that** it comprises

- at least three cells connected in series between the positive (10) and negative (11) poles of a rectifier, each cell comprising a plurality of anodes (3) and cathodes (2) supported on their respective hangers, with the first cell connected

- to the positive pole of the rectifier,
- a set of at least two electrical connection bars arranged parallel to each other between each cell and the next, comprising a main bar (1) and at least one side bar, which can be an upper side bar (4), a lower side bar (5), or both,
 - a plurality of high-current electrical switches (7), which can be remotely activated and deactivated via communication means, electrically connected between the main bar (1) and the side bar(s) (4, 5) and evenly distributed along the electrical connection bars (1, 4, 5), and
 - at least one control equipment (13) equipped with means of communication with the electrical switches (7),
 - each main bar (1) serving as both mechanical support and electrical connection for one end of all the cathode hangers (2) of the preceding cell in the series and also as a mechanical support and electrical connection for one end of the anode hangers (3) of the next cell.
 - each upper side bar (4), if any, serving as both a mechanical support and electrical connection of all the anodes (3) of the preceding cell, and
 - each lower side bar (5), if any, serving as both a mechanical support and electrical connection of all the cathodes (2) of the next cell.
2. - Electrowinning system with interconnectable inter-cell bars, according to the preceding claim, **characterized in that** it comprises a main bar (1) and an upper side bar (4) located on the main bar (1).
 3. - Electrowinning system with interconnectable inter-cell bars, according to any of the preceding claims, **characterized in that** it comprises a main bar (1) and a lower side bar (5) located under the main bar (1).
 4. - Electrowinning system with interconnectable inter-cell bars, according to any of the preceding claims, **characterized in that** it comprises a main bar (1), an upper side bar (4) and a lower side bar (5), in this case the main bar (1) being located between the upper side bar (4) and the lower side bar (5).
 5. - Electrowinning system with interconnectable inter-cell bars, according to any of the preceding claims, **characterized in that** the means of communication between the control equipment (13) and the electrical switches (7) are chosen from the group formed by wired or wireless.
 6. - Electrowinning system with interconnectable inter-cell bars, according to any of the preceding claims, **characterized in that** the electrical switches (7) are associated with a printed circuit board equipped with a microcontroller with communication capacity by means of digital communication protocols with the control equipment (13).
 7. - Electrowinning system with interconnectable inter-cell bars, according to any of the preceding claims, **characterized in that** the printed circuit boards associated with the electrical switches (7) have current sensors.
 8. - Electrowinning system with interconnectable inter-cell bars, according to any of the preceding claims, **characterized in that** the first cell connected directly to the positive pole (10), and the last cell connected directly to the negative pole (11), are semi-sacrifice cells without current reversal.
 9. - Electrowinning system with interconnectable inter-cell bars, according to any of claims 1 to 7, **characterized in that** the first cell directly connected to the positive pole (10), and the last cell directly connected to the negative pole (11), are power resistances, with a resistive value similar to that of the cells.
 10. - Method of reversing current of an electrowinning system with interconnectable intercell bars, according to any of the preceding claims, **characterized in that**
 - E1 being the state wherein the electrical switches (7) associated with a cell are activated, and therefore in electrical conduction,
 - T1 being the configurable time in the control equipment wherein the electrical switches are in E1 state in each cycle,
 - E0 being the state wherein the electrical switches (7) associated with a cell are deactivated, and therefore without electrical conduction,
 - T0 being the configurable time in the control equipment wherein the electrical switches (7) are in E0 state in each cycle,
 - NC being the number of cells that make up the series circuit between the positive and negative poles,
 - NCP being the number of cells per package, calculated as $NCP = (T0 + T1) / T1$, always rounding the decimals of T0 and T1 so that it results in an integer, and
 - i being the cell index in each package, which will start with i=1,

the following sequence is carried out simultaneously in each of the cell packages:

 - in a first step, the electrical switches (7) associated with cell i are set to the E1 state (closed), while the electrical switches associated with all

other cells in the package remain in the E0 state (open),

- in a second step, time T1 is allowed to elapse,

- in a third step, the electrical switches (7) associated with cell i of the package are set to the E0 state, 5

- the value of i is incremented by 1 ($i=i+1$) and the previous steps are repeated sequentially for the following cells, from 1 to NCP, simultaneously in each package, if there are several packages. 10

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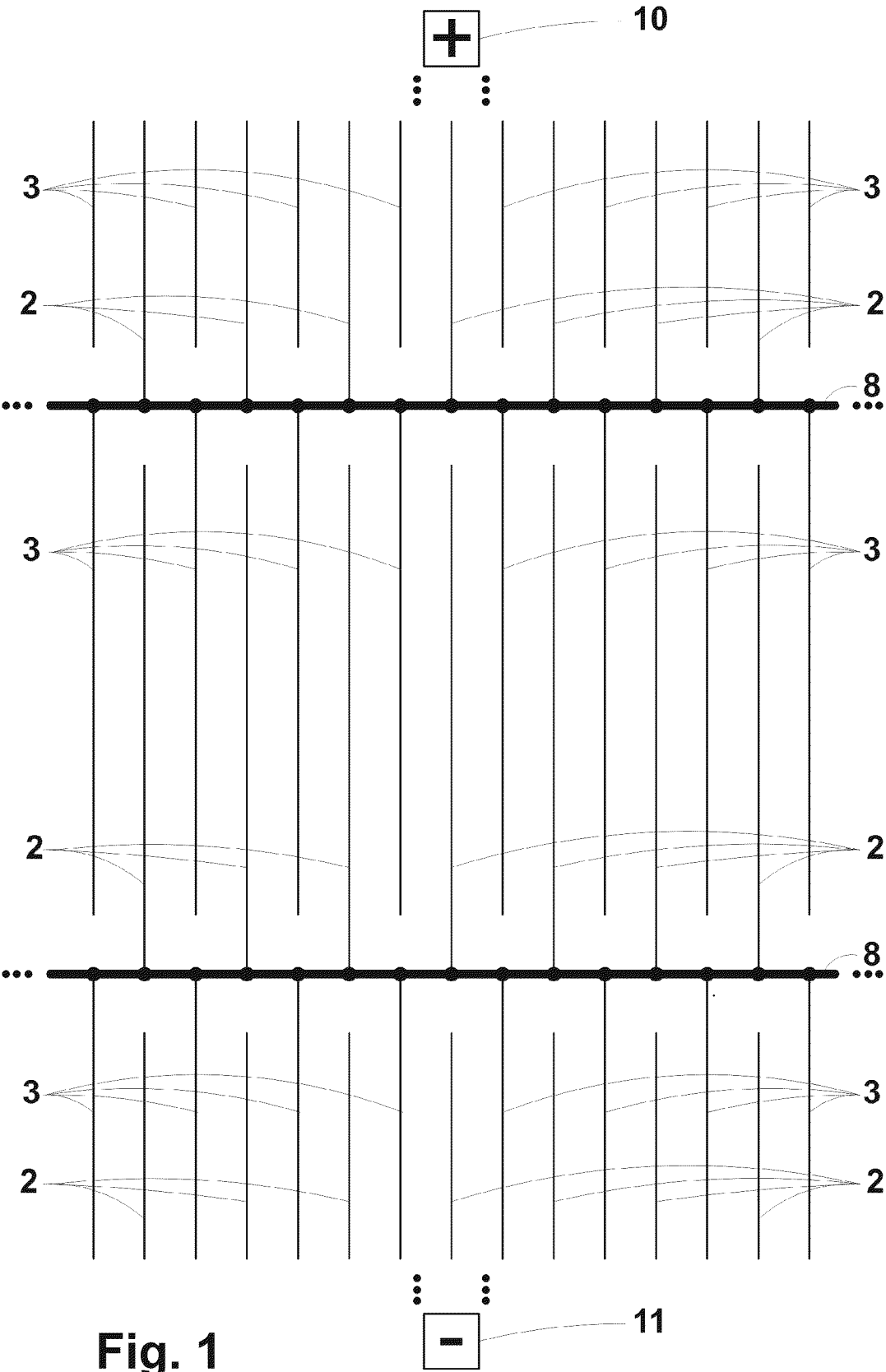
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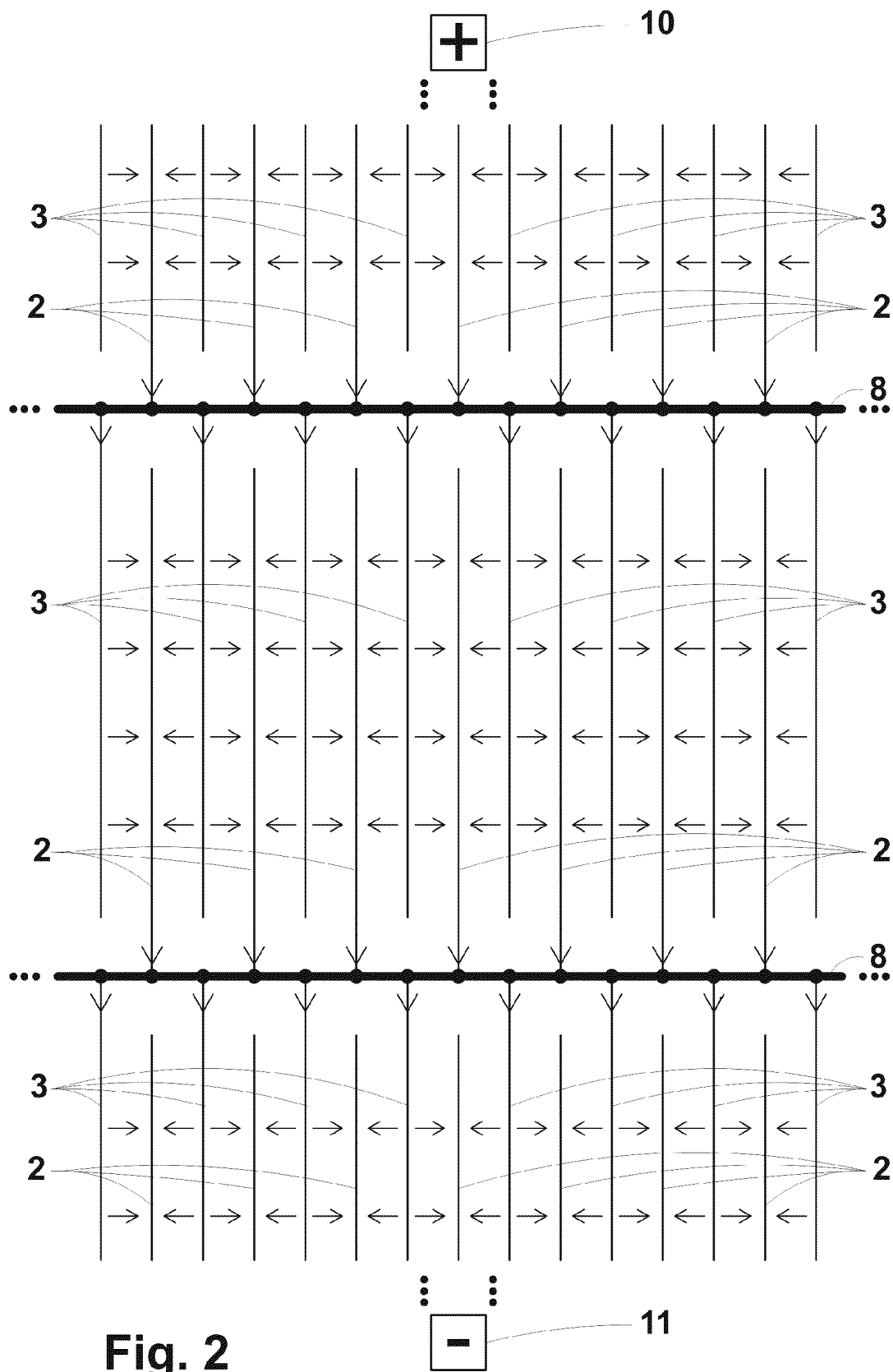
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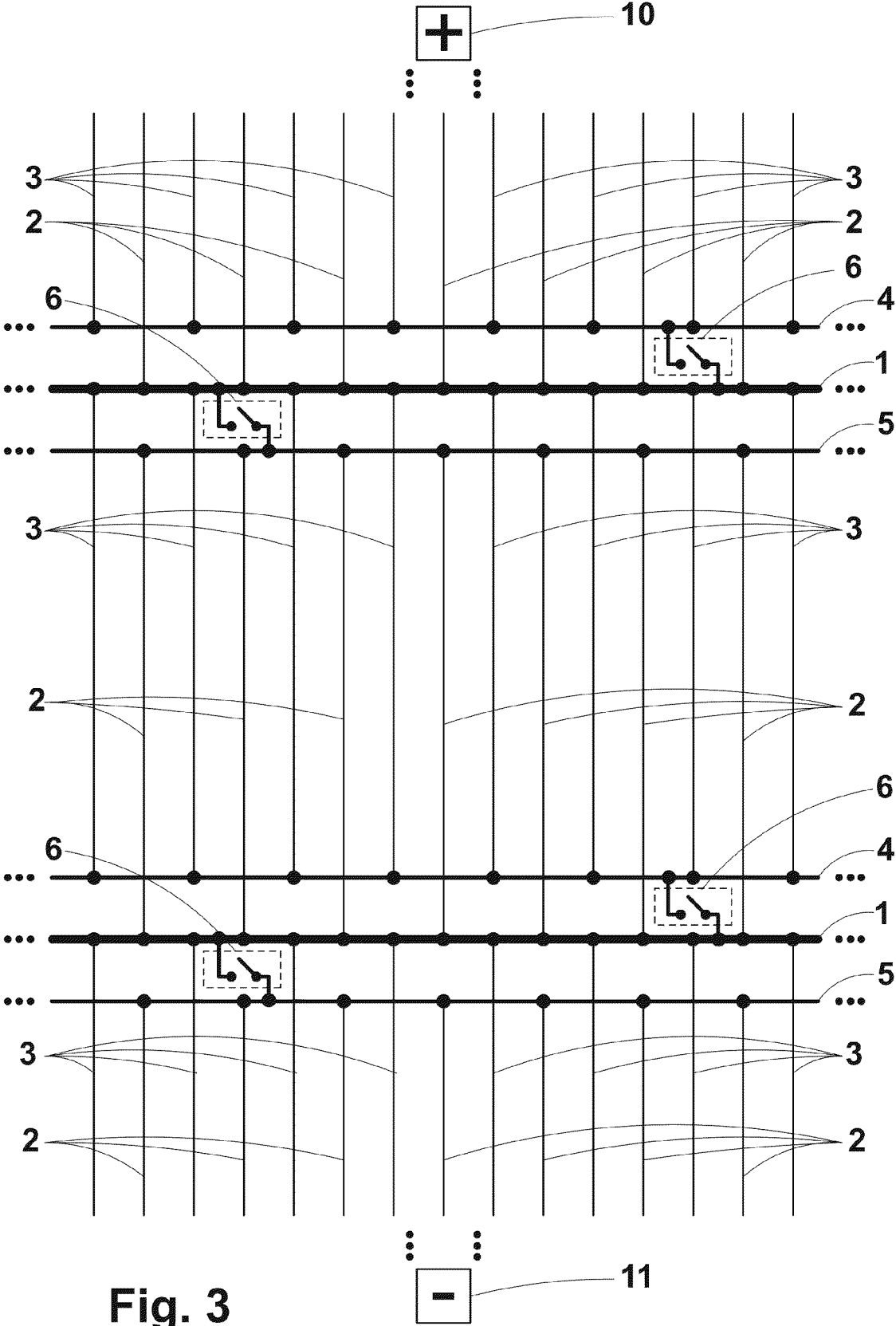


Fig. 3

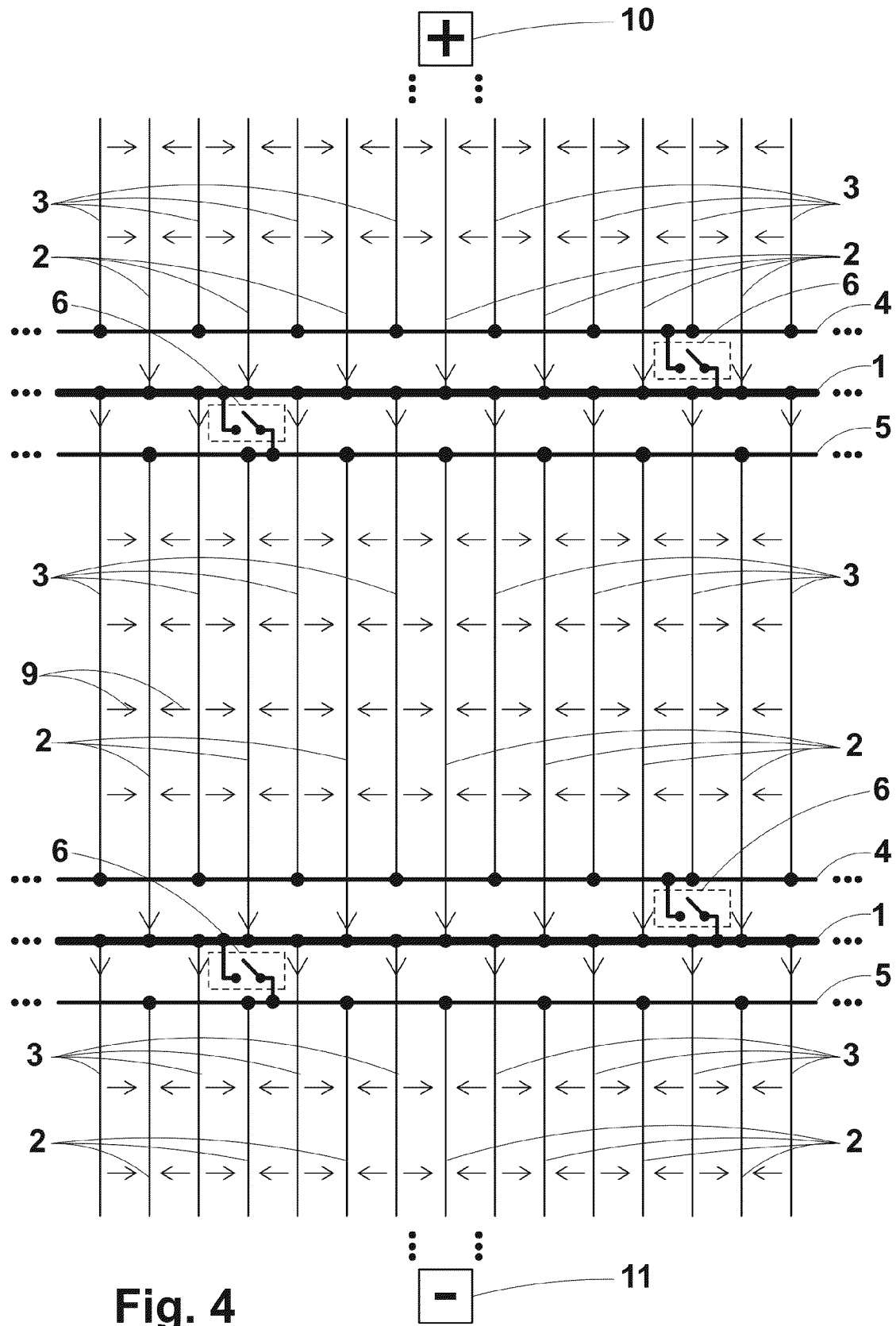


Fig. 4

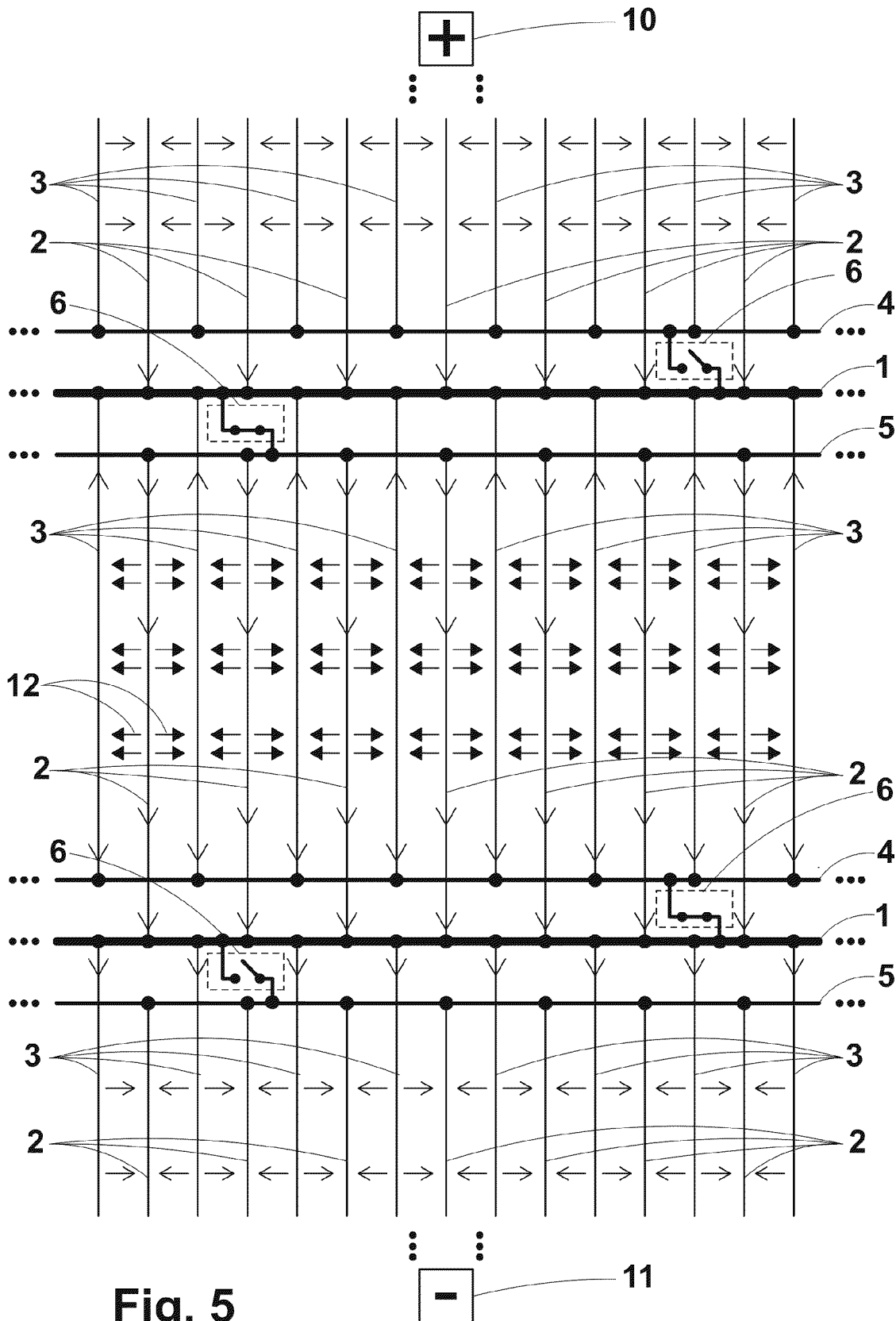


Fig. 5

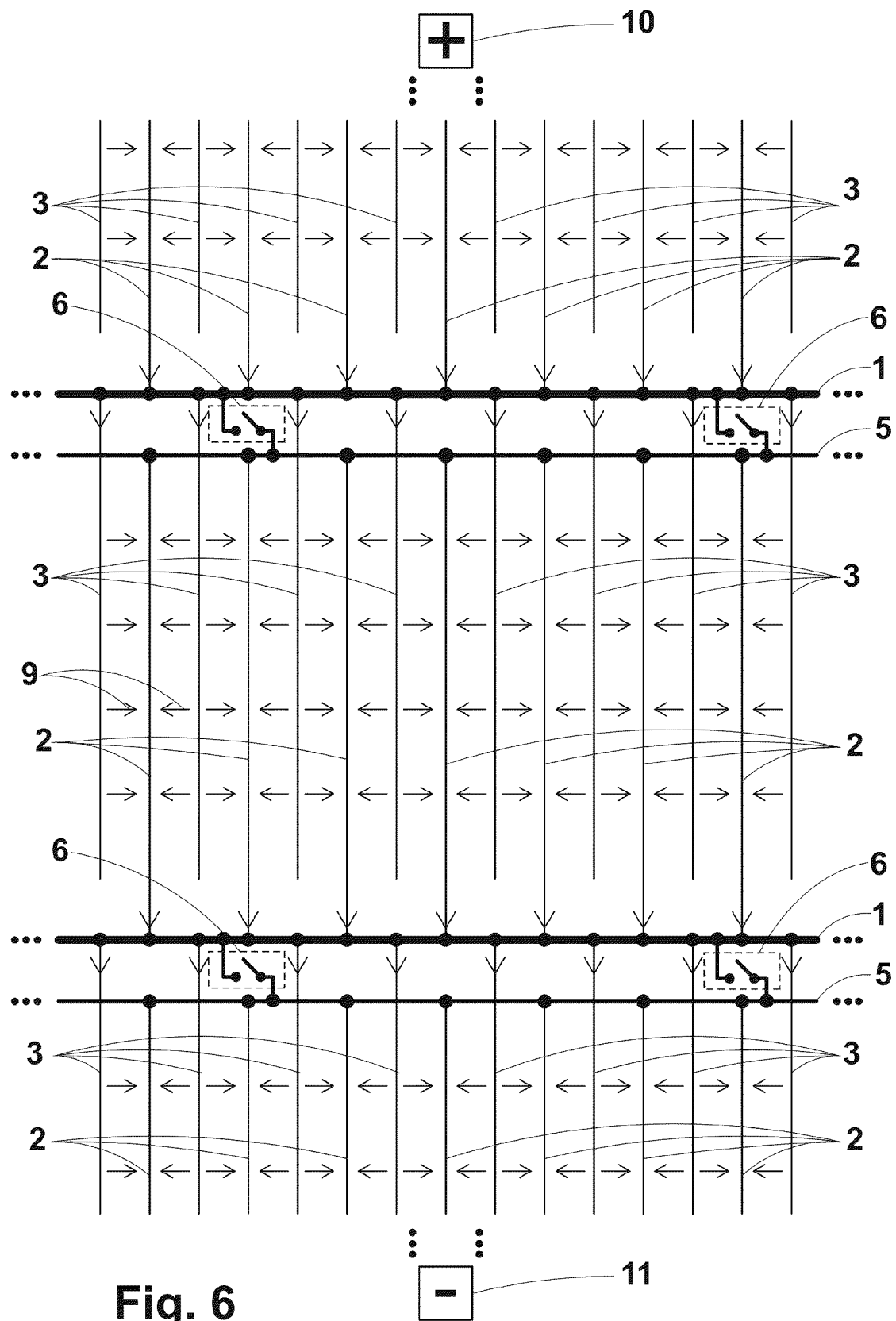


Fig. 6

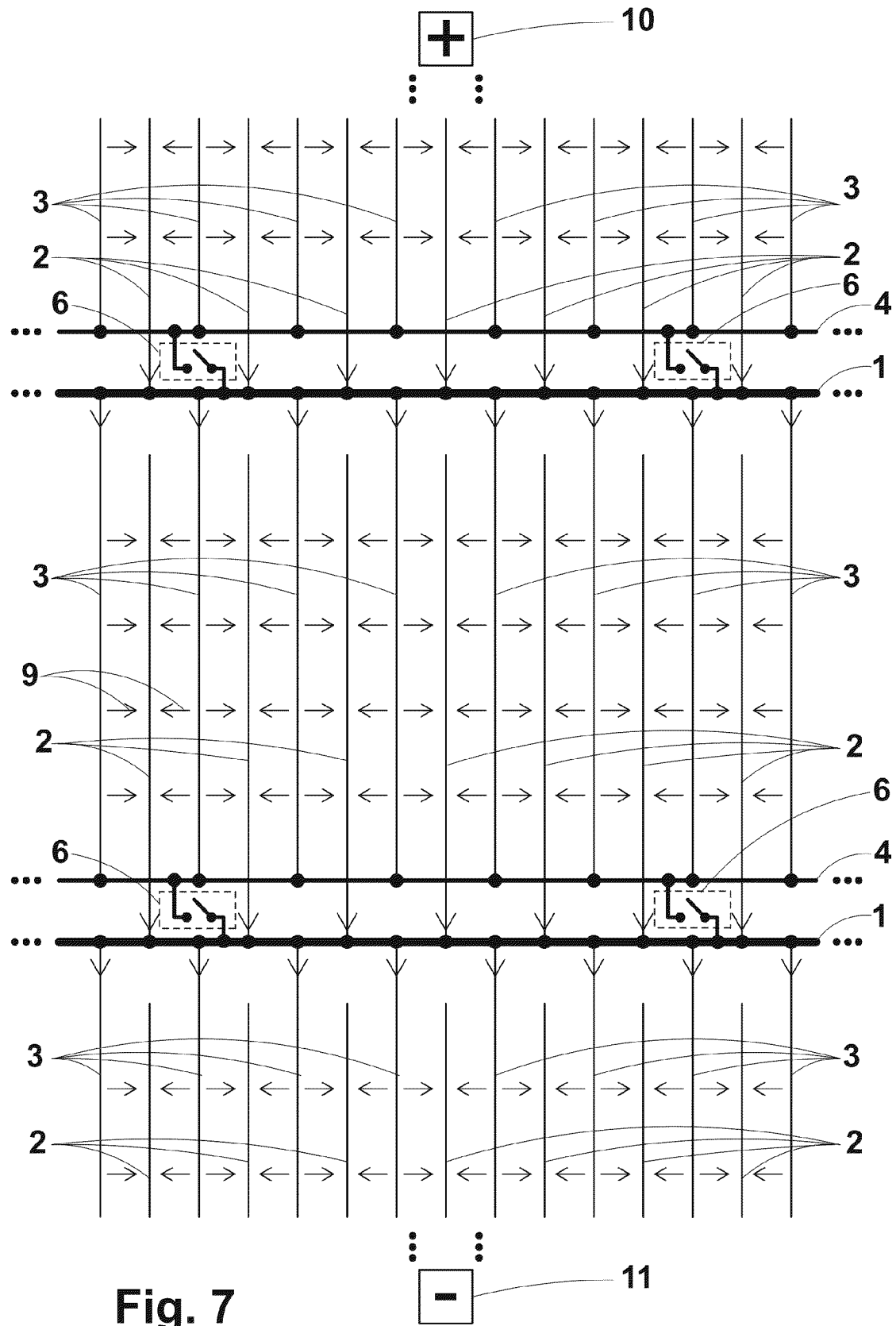


Fig. 7

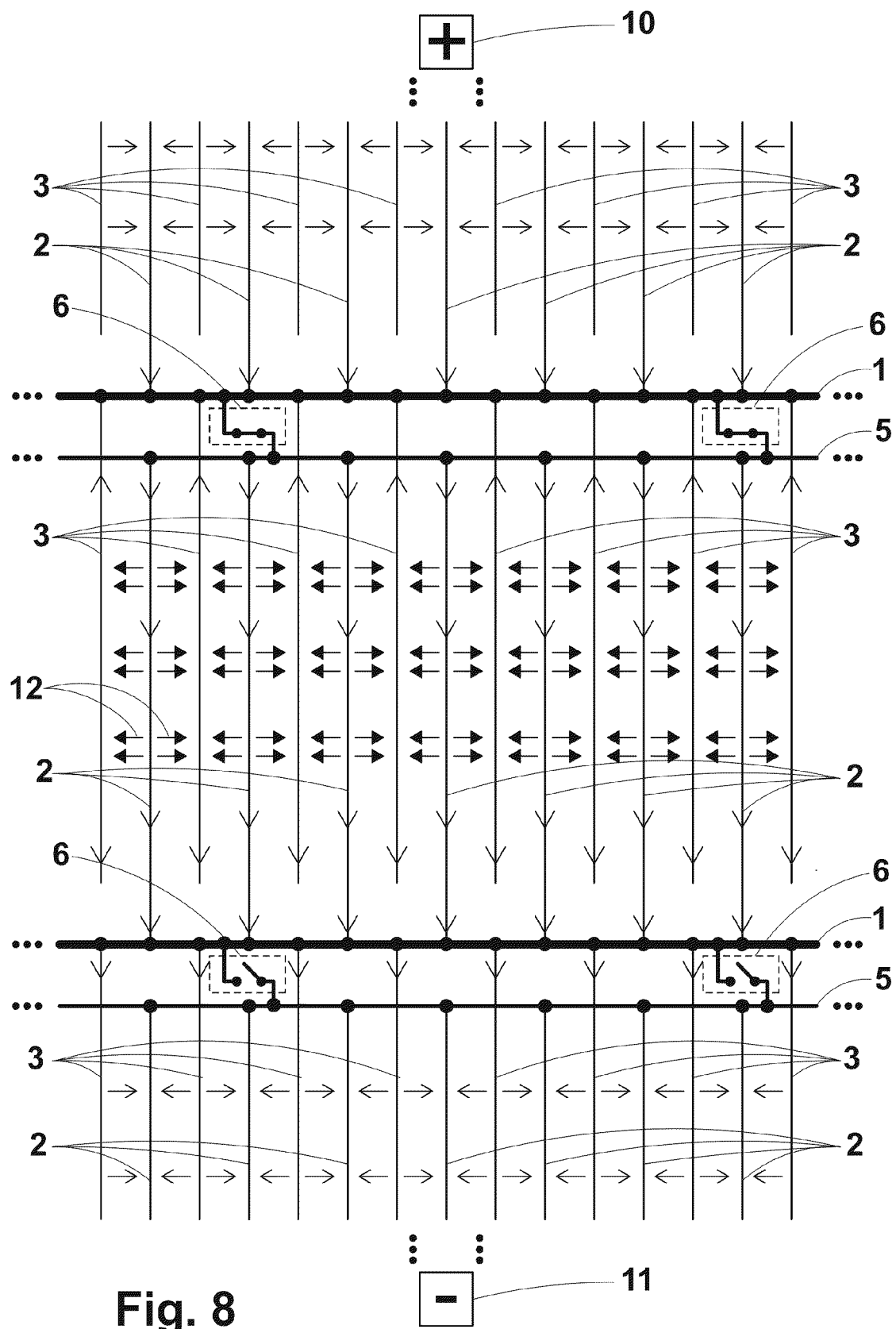


Fig. 8

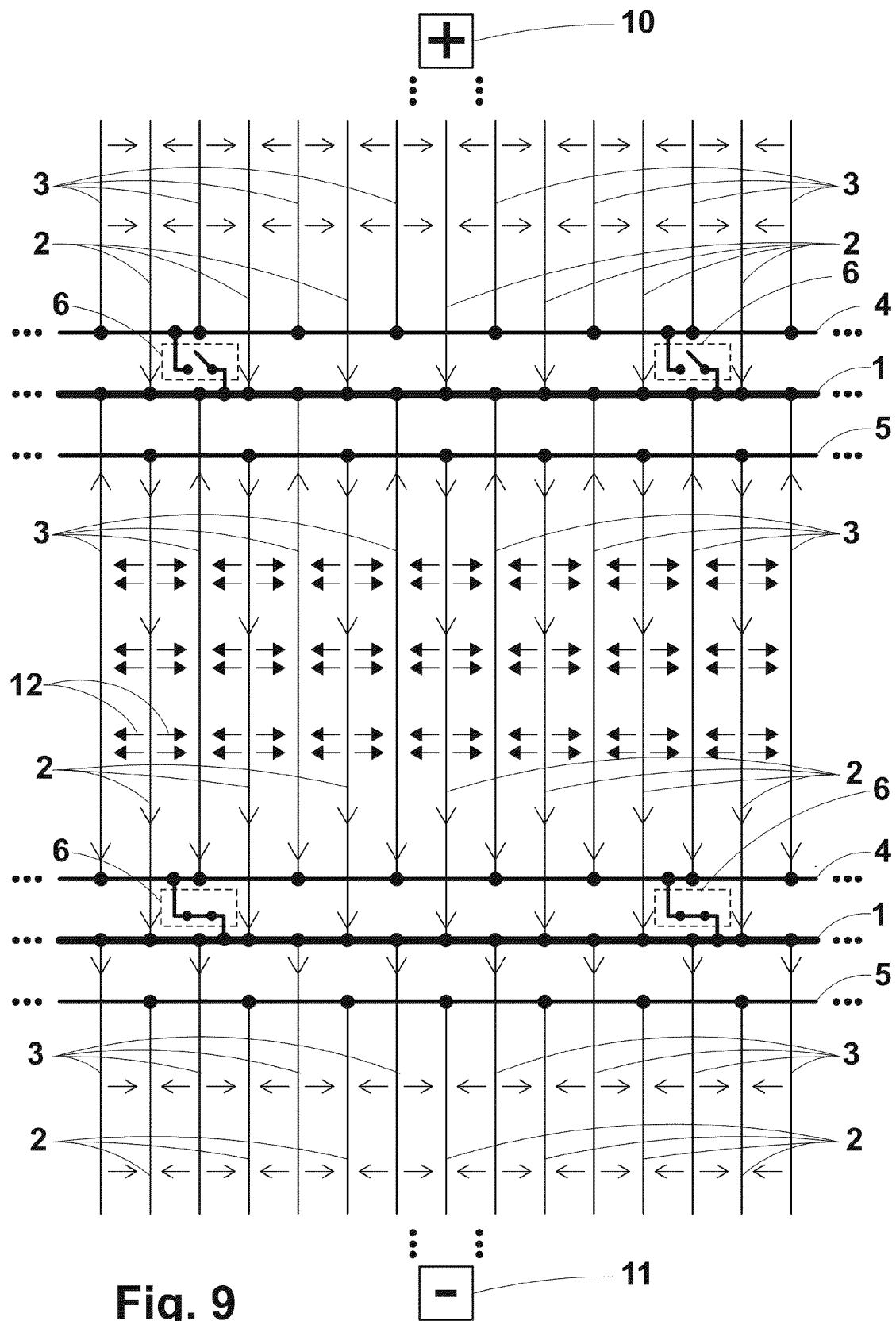


Fig. 9

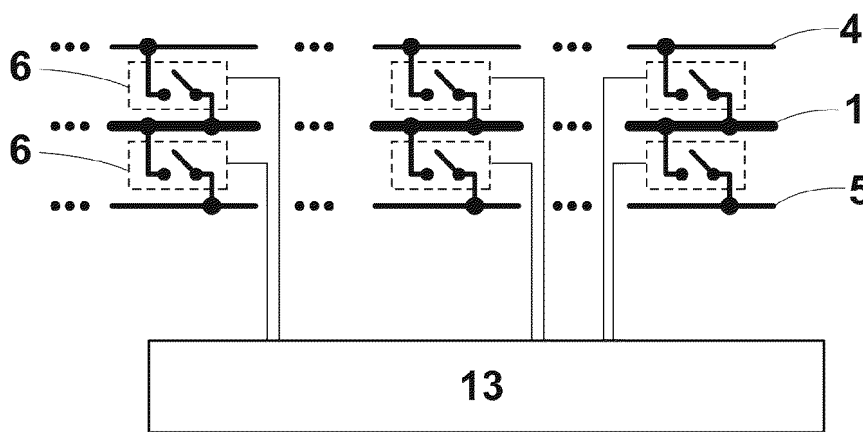


Fig. 10

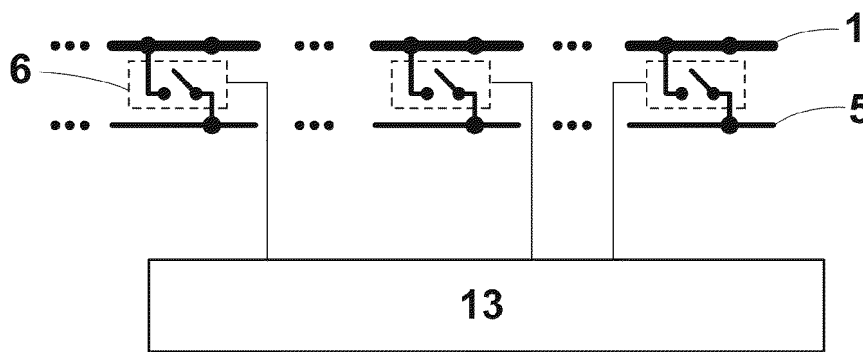


Fig. 11

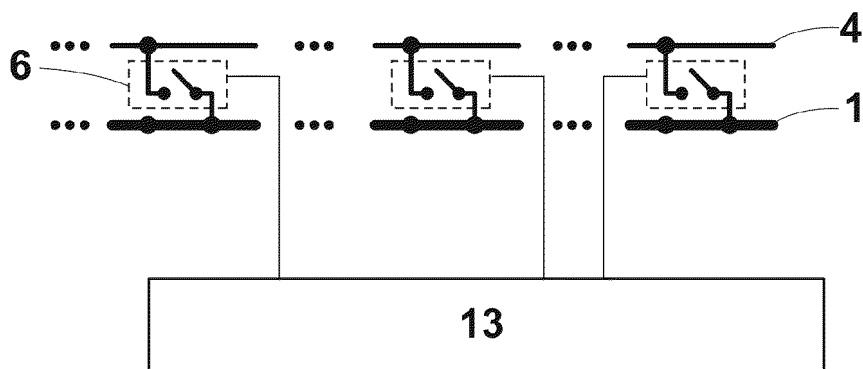


Fig. 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/ES2023/070170

A. CLASSIFICATION OF SUBJECT MATTER

C25C3/20 (2006.01)

C25C7/06 (2006.01)

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)
C25C

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 practicable, search terms used)

EPODOC, INVENE, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ES 2818224 A1 (PRADO PUEO FELIX) 09/04/2021, figures 3-6	1-10
A	US 4140596 A (WOBKING HANS) 20/02/1979, abstract.	1-10
A	WO 2013037899 A1 (INDUSTRIE DE NORA SPA; PRADO FELIX) 21/03/2013, the whole document.	1-10

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

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"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

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Date of the actual completion of the international search
27/06/2023

Date of mailing of the international search report
(29/06/2023)

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/ES2023/070170

Information on patent family members

Patent document cited in the search report	Publication date	Patent family member(s)	Publication date
ES2818224 A1	09.04.2021	CL2021002975 A1 PE20220921 A1 WO2021069774 A1 EP4043617 A1	17.06.2022 30.05.2022 15.04.2021 17.08.2022
US4140596 A	20.02.1979	SE7612329L L GB1520058 A FI810001L L FI763210 A ES453418 A1 DE2650589 A1 DE2650589 C2 BE848317 A ATA973275 A AT342877B B	23.06.1977 02.08.1978 02.01.1981 23.06.1977 16.12.1977 30.06.1977 13.11.1986 16.03.1977 15.08.1977 25.04.1978
WO2013037899 A1	21.03.2013	NO2756115T T3 PL2756115T T3 ES2657057T T3 ZA201401254 B BR112014005340 A2 BR112014005340 B1 MX2014003000 A MX339955 B CL2014000615 A1 PE20141027 A1 JP2014527125 A JP6081462B B2 US2014209455 A1 US9255338 B2 EA201490335 A1 EA029460 B1 KR20140061414 A KR101930702B B1 CN103797161 A CN103797161B B CA2845675 A1 CA2845675 C AU2012307358 A1 AU2012307358B B2 TW201314996 A TWI544675B B EP2756115 A1 EP2756115 B1 ITMI20111668 A1	07.04.2018 30.04.2018 01.03.2018 28.10.2015 28.03.2017 01.12.2020 12.09.2014 20.06.2016 12.09.2014 21.09.2014 09.10.2014 15.02.2017 31.07.2014 09.02.2016 30.06.2014 30.03.2018 21.05.2014 19.12.2018 14.05.2014 02.11.2016 21.03.2013 10.09.2019 27.02.2014 11.05.2017 01.04.2013 01.08.2016 23.07.2014 08.11.2017 17.03.2013

Form PCT/ISA/210 (patent family annex) (July 2022)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2015079072 A [0015]
- US 4140596 A [0017]
- WO 2015056121 A [0020]
- WO 2015075634 A [0020]