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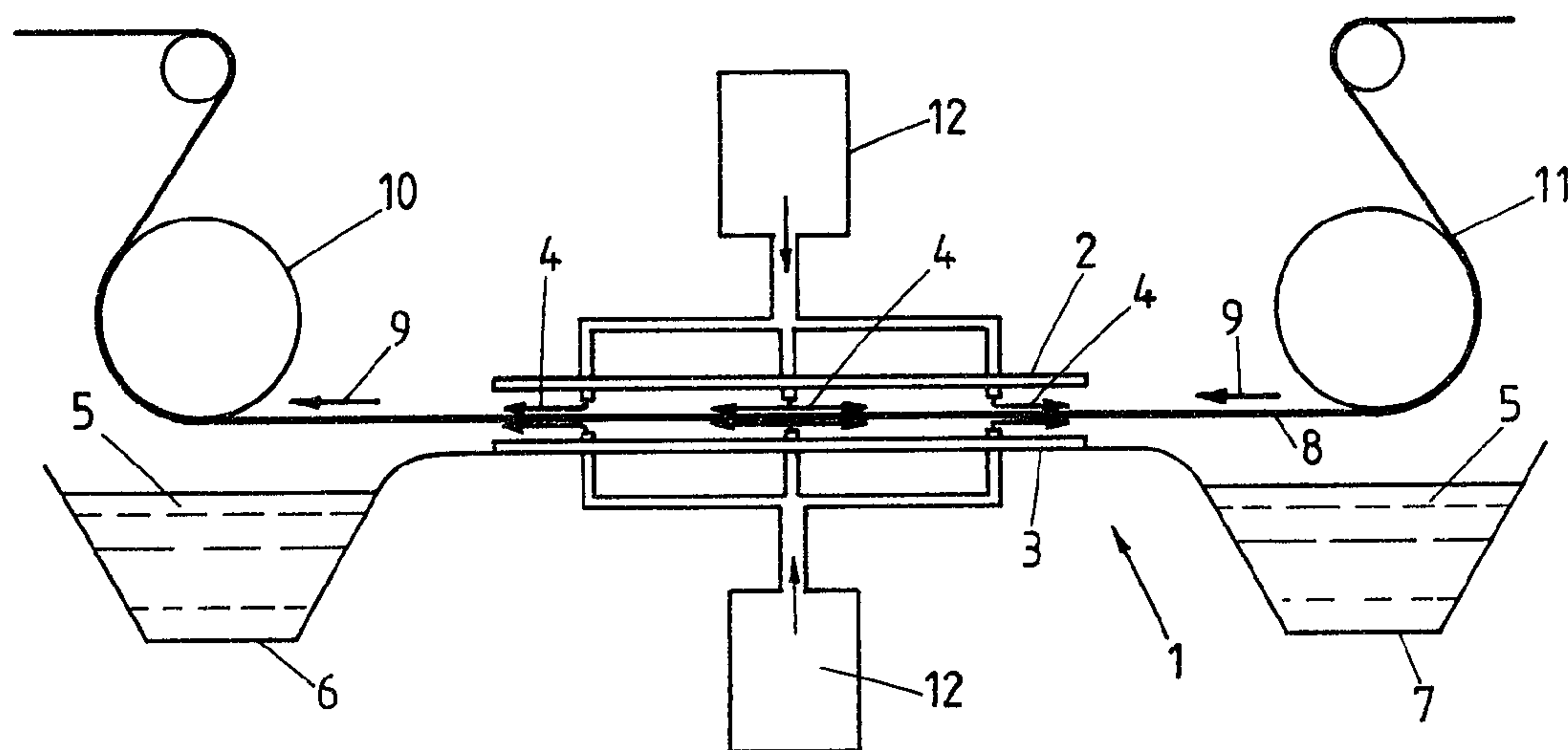
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(54) **PROCEDE D'ELECTRODEPOSITION D'UN ALLIAGE DE
NICKEL ET DE COBALT ET SOLUTION D'ELECTROLYTE
UTILISEE A CETTE FIN**

(54) **PROCESS FOR ELECTRODEPOSITING A METALLIC
COATING OF A NICKEL-COBALT ALLOY ON AN OBJECT
AND ELECTROLYTE SOLUTION USED THEREIN**



(57) A process for electrodepositing a metallic coating, mainly composed of a nickel-cobalt alloy, on a surface of an object, in particular a strip-iron, by means of an electrolysis bath wherein at least one insoluble anode is arranged in a substantially chloride-free electrolyte solution which comprises at least nickel sulfate, cobalt sulfate, boric acid and sulfuric acid, according to which process at least said surface is immersed in the electrolyte solution and an electric tension of such a value is applied between said anode and the object acting as cathode that near said surface, a current density of at least 30 A/dm^2 is realized.

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ABSTRACT

"Process for electrodepositing a metallic coating of a nickel-cobalt alloy on an object and electrolyte solution used therein"

5 A process for electrodepositing a metallic coating, mainly composed of a nickel-cobalt alloy, on a surface of an object, in particular a strip-iron, by means of an electrolysis bath wherein at least one insoluble anode is arranged in a substantially chloride-free electrolyte solution which comprises at least nickel sulfate, cobalt sulfate, boric acid and sulfuric acid, according to which process at least said surface is immersed in the electrolyte solution and an electric tension of such a value is applied between said anode and the object acting as cathode that near said surface, a current density of at least 30 A/dm² is realized.

"Process for electrodepositing a metallic coating of a nickel-cobalt alloy on an object and electrolyte solution used therein"

The present invention relates to a process for electrodepositing a metallic coating, mainly composed of a nickel-cobalt alloy, on a surface of an object, in particular in strip-iron, by means of an electrolysis bath wherein at least one anode is arranged in a substantially chloride-free electrolyte solution which comprises at least nickel sulfate, cobalt sulfate and boric acid, according to which process at least said surface is immersed in the electrolyte solution and an electric tension is applied between said anode and the object acting as cathode.

Such a process is disclosed in the article "les bains de nickel-cobalt brillants" (the bright nickel-cobalt baths) published in the periodical "Galvano" n° 401 of June 1970, pages 487-491. This article describes some examples of electrolysis baths for depositing simultaneously nickel and cobalt. The electrolysis is carried out at low current densities, of 10 A/dm² at the most, and for depositing nickel and cobalt, use is made of a soluble anode. In this article, only the SCHEER bath comprises a solution containing nickel sulfate, cobalt sulfate and boric acid. This SCHEER bath comprises 110 g/l nickel sulfate, 390 g/l cobalt sulfate, 25 g/l boric acid and, moreover, 7.5 mg/l potassium sulphocyanide. The electrolysis is realized at a temperature comprised between 60 and 80°C and with a current density of 10 A/dm².

A problem which arises when using the SCHEER bath is that nickel is deposited easier than cobalt resulting in a low cobalt content of the nickel-cobalt alloy deposited on the surface. Therefore, in order to solve this problem, an electrolyte solution is required comprising a relatively high cobalt concentration so as to be sure that an appropriate cobalt content is obtained in the deposited

coating. However, this solution is not economical and has a small efficiency.

5 An object of the invention is to provide a process by which the cobalt is deposited in a satisfactory manner without hampering the nickel deposition and without requiring high cobalt concentrations in the electrolyte solution.

10 To this end, a process according to the invention is characterized in that the electrolysis is realized in the electrolyte solution to which sulfuric acid has been added, and in that the tension, which is applied between the cathode and the anode, which is a substantially insoluble anode, is of such a value that near said surface, a current density of at least 30 A/dm² is realized. It has been found that by using a high current density in the bath described in the preamble, a simultaneous nickel-cobalt deposit of a good quality is obtained.
15 By using a current density of at least 30 A/dm², the deposition process goes on in a quicker and more efficient way. A surprising effect of applying a higher current density is that the cobalt is deposited easier so that even a small cobalt content in the electrolyte solution ensures already the presence of cobalt over the whole deposited coating.
20 The higher current density requires the use of an insoluble anode. Sulfuric acid is added to the electrolyte to increase the conductivity of the bath.

In a preferred embodiment of the process according to the invention, the applied electric tension is of such a value that
25 said current density is comprised between 50 and 300 A/dm² and in particular between 240 and 250 A/dm². It was found that the best quality of the deposit was obtained with a current density between 240 and 250 A/dm². Indeed, at these current densities a homogenous coating was obtained.

30 Preferably, a solution having a sodium sulfate concentration of upto the solubility limit is used as electrolyte solution. This maximum value is imposed by the solubility of the sodium sulfate in the bath. Above this value, a negative effect on the appearance of the deposit is obtained.

35 Preferably, a solution having a boric acid concentration

of about 30 to 60 g/l and preferably of about 50 g/l and a sulfuric acid concentration of about 5 to 15 g/l and more particularly of about 10 g/l is used as electrolyte solution. A sulfuric acid content of 10 g/l influences very advantageously the conductivity without having, however,
5 a negative effect on the Faraday efficiency.

A preferred embodiment of a process according to the invention is characterized in that the electrolysis is realized at a temperature comprised between 50 and 80°C and preferably at a temperature of about 70°C. In this temperature range, the object
10 is not subjected to high thermal constraints.

Preferably, said object surface and said anode are disposed substantially in parallel relationship to one another and the electrolyte solution is injected between said surface and the anode. This allows to obtain good agitation conditions of the electrolyte in
15 the cell.

Other particularities and advantages of the invention will become apparent from the following description of a process for electrodepositing nickel-cobalt alloys according to the invention. This description is only given by way of example and does not limit
20 the scope of the invention. The invention is illustrated by means of the annexed drawings.

The sole figure shows a schematical sectional view of an electrolysis cell for applying a process according to the invention.

The invention relates to a process for electrodepositing
25 a metallic coating, mainly composed of a nickel-cobalt alloy, on a surface of an object, in particular on a strip-iron or a sheet-iron. This electrolysis is carried out for example by means of an electrolysis cell 1 which comprises, as schematically illustrated in the figure, two anodes 2 and 3, preferably plate-shaped anodes disposed horizontally
30 and substantially in parallel relationship to one another, between which an electrolyte solution 5 is injected according to arrows 4, at a speed in the range of 3 m/s by means of an injection device 12. The cell 1 also comprises chutes 6 and 7 for collecting the electrolyte solution 5 which can then be injected again between the two anodes 2 and
35 3 after being enriched. For enriching the solution, at least nickel

sulfate and cobalt sulfate are added in order to maintain the bath composition substantially constant.

The strip-iron 8 is guided between the two anodes 2 and 3, in a direction indicated by arrow 9, by means of rollers 10 and 11 which form an electric conductor. The strip-iron, which is in galvanic contact with rollers 10 and 11, forms thus a cathode. An electric tension is applied between the cathode, comprised of the strip-iron 8, and the anodes 2 and 3 by means of a direct current voltage source, which has not been represented in the figure, in such a manner that a predetermined current density is realized at both sides of the strip-iron 8. If necessary, this tension and consequently the current density may be different at each side of the strip-iron 8 resulting in a different amount of nickel-cobalt alloy being deposited on both sides of the strip-iron 8. The cell may also comprise only one anode which allows to deposit the nickel-cobalt alloy on only one side of the strip-iron.

The employed anodes 2 and 3 are substantially insoluble anodes which are for example comprised of a lead-silver anode or a titanium anode coated by a noble metal such as ruthenium or iridium. As such anodes do not provide any nickel or cobalt, the electrolyte solution must contain all the nickel and cobalt which has to be deposited. Moreover, this electrolyte solution may practically not contain chlorides, a.o. for preventing corrosion of the anodes.

The use of the process according to the invention allows to deposit a metallic coating of a superior quality on the strip-iron 8. To this end, use is made according to the invention of a chloride-free solution containing at least nickel sulfate, cobalt sulfate, boric acid and sulfuric acid and this in combination with a cathode current density of at least 30 A/dm². Comparative tests showed that due to this combination it is possible to realize after tempering high quality metallic deposits, by which are meant here a.o. uniform deposits having a fine grain structure.

It has been found, in contrast to the theories developed in the state of the art, that by applying a high cathode current density the cobalt is deposited easier so that the cobalt content in the nickel-

cobalt alloy is increased with respect of the coatings deposited by the known processes of co-depositing nickel and cobalt wherein a low cathode current density, comprised between 0 and 13 A/dm², is applied. According to the state of the art, it is known that in this range of low current densities, an increase of the current density reduces the cobalt content in the deposited nickel-cobalt alloy. However, it was found that by using substantially insoluble anodes and by applying a current density situated according to the invention between 30 and 300 A/dm², a higher cobalt content in the deposited alloy is obtained, with the cobalt content being higher the more the cathode current density increases.

In a preferred embodiment of the process according to the invention, a current density of between 50 and 300 A/dm² and preferably between 150 to 300 A/dm² is applied. A current density of at least 150 A/dm² offers the advantage that the cobalt is deposited so easy that obtaining a homogenous nickel-cobalt alloy does not involve any problems even with low cobalt contents in the electrolyte solution. By applying, for example, a cathode current density comprised between 240 and 250 A/dm² and an electrolyte solution containing 0.2 % cobalt sulfate, a deposited nickel-cobalt alloy coating can be obtained having a cobalt content of about 2 %. In order to allow such high current densities, the used electrolyte solution has to meet certain conditions such as, for example, with respect to the conductivity. A specific composition of the electrolysis bath is also necessary in combination with these high current densities, for realizing high quality deposits.

In this way, in a preferred embodiment of the invention, an electrolyte solution containing between about 30 and 60 g/l and preferably 50 g/l boric acid and about 5 to 15 g/l and preferably 10 g/l sulfuric acid is used. By using the combination of boric and sulfuric acid, it is possible to combine a good conductivity with a good Faraday efficiency. Indeed, the used sulfuric acid has an advantageous influence on the conductivity but a negative effect on the Faraday efficiency, whereas the boric acid has an advantageous influence on the Faraday efficiency but reduces slightly the conductivity.

The Faraday efficiency is, moreover, also influenced

by the temperature of the electrolyte solution, which is comprised between 50 and 80°C, and is preferably substantially equal to 70°C during the electrolysis. An increase of this temperature has an advantageous effect on the efficiency but is limited as a consequence of the technical constraints of the materials. Agitating the electrolyte solution by injecting it between the two anodes increases also the Faraday efficiency. Moreover, sodium sulfate may be added to the electrolyte solution, more precisely an amount of upto the solubility limit of sodium sulfate. By adding sodium sulfate, the conductivity of the electrolyte solution increases also. However, the added amount of sodium sulfate may not be too large since this has a negative effect on the appearance of the deposit.

The electrolyte solution used in a preferred embodiment contains about 200 to 270 g/l nickel sulfate, preferably 222 to 242 g/l and an amount of about 232 g/l nickel sulfate is particularly preferred. This solution contains, moreover, cobalt sulfate starting from the lowest contents of about 0.1 % of the electrolyte solution. It was found that due to such a specific electrolyte solution, with a relatively low nickel sulfate content, in combination with the described high current densities, high quality deposits can be obtained. An additional advantage of higher current densities is that the deposition proceeds at higher speeds.

As to the quality of the metallic deposits obtained by applying the process according to the invention, it was found experimentally that due to the high current density, very fine-grained uniform metal deposits are obtained. Due to the fine grain structure, the deposits are brilliant and very resistant to corrosion considering the high density of the coating. As a consequence of the uniform growth of the coating during the electrolysis, a homogenous layer having a substantially uniform thickness is deposited. Consequently, the smallest thicknesses, i.e. possibly even smaller than 0.5 microns, are already sufficient to provide the deposited metallic coating with good anti-corrosion properties. In this way, a considerable amount of metal to be deposited may be saved by using the process according to the invention. This process causes further an increase of the electrical

performance of the metallic deposit. The presence of cobalt in the deposited coating has a positive influence on the corrosion resistance and on the hardness of this deposit without reducing the stamping possibilities. Moreover, the cobalt increases the melt temperature of the nickel-cobalt alloy which reduces considerably the problem of sticking together when hardening rolls of strip-iron.

It will be clear the the hereabove described embodiments of the process according to the invention may be modified in many ways without leaving the scope of the present invention.

In this way, the metallic coating may not only be deposited on a strip-steel but also on other objects, possibly of another material, such as, for example, materials previously coated with copper. It is also possible to add other materials to the electrolyte solution, which have also an effect on the deposited metallic coating. An example of these materials are the brighteners.

1. A process for electrodepositing a metallic coating comprising a nickel-cobalt alloy onto the surface of a cathode by means of an electrolysis bath, said electrolysis bath comprising
a chloride free electrolyte solution further comprising nickel
5 sulphate, cobalt sulphate, and boric acid;
at least one insoluble anode; and
the surface of said cathode to be coated is immersed in the electrolyte solution, wherein,
upon the addition of sulphuric acid to the electrolyte solution, a
10 voltage is applied between said at least one insoluble anode and the cathode such that a current is induced to flow within the electrolyte solution to produce a current density of at least 30 A/dm^2 at the surface of the cathode.
- 15 2. A process according to claim 1, wherein the cathode is a strip of iron.
3. A process according to claim 1, wherein the current density is within the range 50 to 300 A/dm^2 .
- 20 4. A process according to claim 3, wherein the current density is within the range 150 to 300 A/dm^2 .
5. A process according to claim 4, wherein the current
25 density is within the range 240 to 250 A/dm^2 .
6. A process according to claim 1, wherein the electrolyte solution further comprises sodium sulphate dissolved therein at a

concentration up to the solubility limit.

7. A process according to claim 1, wherein the concentration of nickel sulphate in the electrolyte solution is within the range 200 to 270 g/L.

8. A process according to claim 7, wherein the concentration of nickel sulphate in the electrolyte solution is within the range 222 to 242 g/L.

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9. A process according to claim 8, wherein the concentration of nickel sulphate in the electrolyte solution is 232 g/L.

10. A process according to claim 1, wherein the concentration of boric acid in the electrolyte solution is within the range 30 to 60 g/L.

11. A process according to claim 10, wherein the concentration of boric acid in the electrolyte solution is 50 g/L.

12. A process according to claim 1, wherein the concentration of sulphuric acid in the electrolyte solution is within the range 5 to 15 g/L.

13. A process according to claim 12, wherein the concentration of sulphuric acid in the electrolyte solution is 10 g/L.

14. A process according to claim 1, wherein the temperature of the electrolysis solution is within the range 50 to 80°C.

15. A process according to claim 14, wherein the temperature of the electrolysis solution is 70°C.

16. A process according to claim 1, wherein said at least one insoluble anode includes at least one lead-silver anode.

17. A process according to claim 1, wherein said at least one insoluble anode includes at least one titanium anode coated with a noble metal.

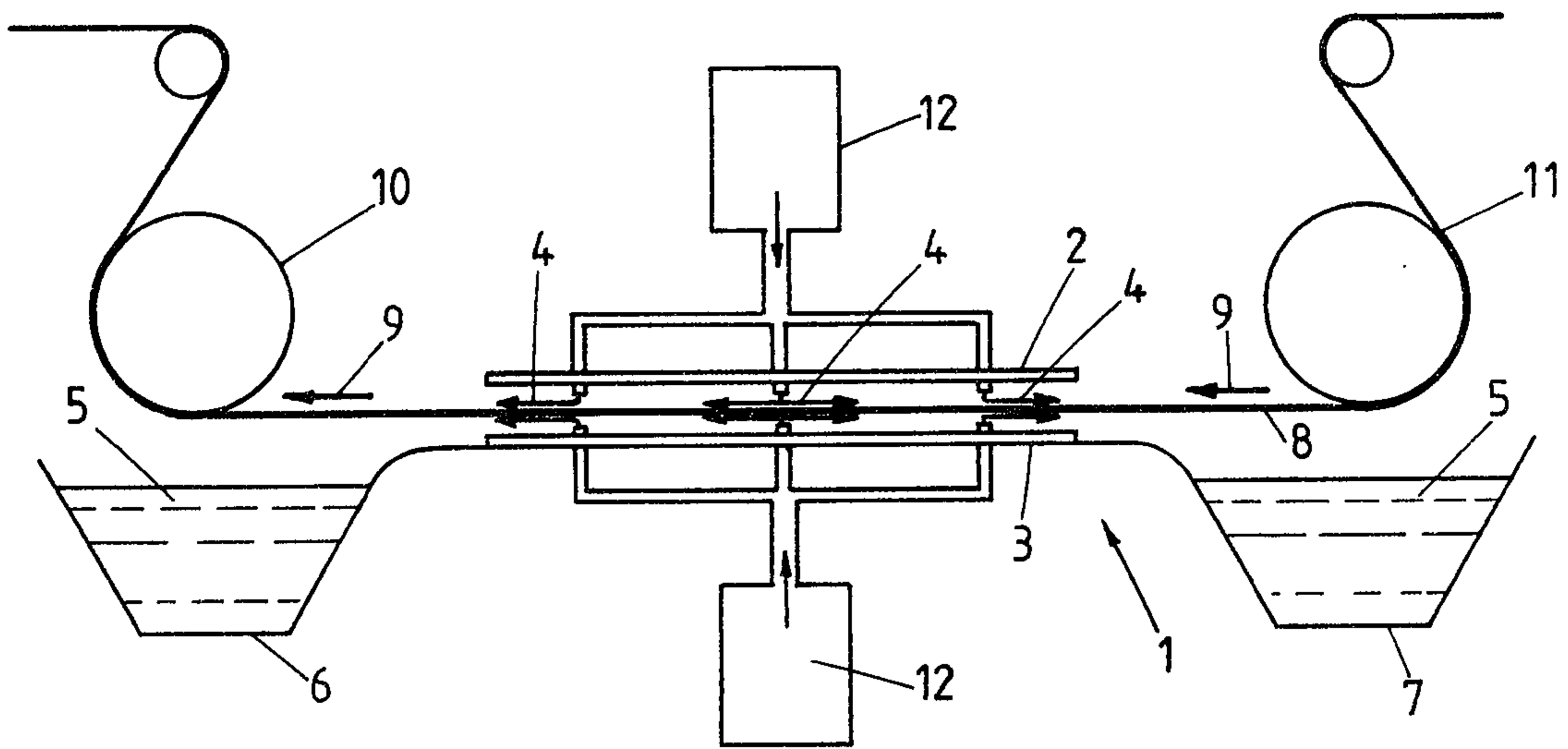
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18. A process according to claim 1, wherein the cathode and said at least one insoluble anode are substantially disposed in a parallel relationship to one another and the electrolyte is injected in between the cathode and said at least one insoluble anode.

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19. The use of an electrolyte in a process according to any one of claims 1 to 18, said electrolyte solution being chloride free and comprising nickel sulphate, cobalt sulphate and boric acid, wherein the electrolyte solution further comprises sulphuric acid.

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