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(54) PROCESS FOR CLEANING GALVANIC BATHS TO PLATE METALS

VERFAHREN ZUM REINIGEN VON GALVANISCHEN BÄDERN ZUR ABSCHEIDUNG VON METALLEN

PROCÉDÉ POUR NETTOYER DES BAINS GALVANIQUES POUR LE PLACAGE DE MÉTAUX

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Description

Nature of the invention

[0001] The invention concerns a process for cleaning galvanic baths to plate metals, in particular alkaline zinc-nickel alloy baths, using ion exchangers in order to prolong the lifetime of electrolytes and remove any undesirable decomposition products.

Background of the invention

[0002] Zinc-nickel coatings are used in all applications that require high quality surface protection when subject to corrosion, The conventional field of application is the automobile manufacture for components that are used in the engine bay, on braking systems and in the landing gear bay. For this reason, alkaline zinc-nickel electrolytes have been used more recently as published in US 4,889,602, and US 6,755,960 which for example have the following electrolyte composition:

Table 1: Electrolyte deposit of a zinc-nickel electrolyte

Zinc oxide	ZnO	11.3 g/l
Nickel sulphate hexahydrate	$NiSC_4*6H_2O$	4.1 g/l
Sodium hydroxide	NaOH	120 g/l
Polyethyleneamine (complexing agent)	eg. $(C_2H_5N)_n$	5.1 g/l

[0003] The amines in the electrolyte act as complexing agents for the nickel ions. Complexing agents are constituents of numerous galvanic and chemical processes which are used in the separation of metals. The zinc-nickel electrolyte is usually driven by insoluble nickel anodes. The zinc content is kept constant by adding a suitable zinc ion source and the nickel content is kept constant by adding a source of nickel ions. The colour of the zinc-nickel electrolyte however changes from blue-purple to brown after a certain time of operation.

[0004] After a certain time of operation, nitriles (so-called organically bonded cyanide which can contain nitriles as well as isonitriles) and cyanide ions are formed in the zinc-nickel electrolytes through anodic oxidation from the amine-containing complexing agents. The problem of cyanide pollution requires the continuous replacement of the electrolytes and a special waste water treatment which in turn significantly affects the operating costs of the electrolyte. After several days, or weeks, there is a noticeable increase in the discolouration and a separation into two phases. The top phase is dark brown. This phase causes considerable problems when the work pieces are coated, for instance the uneven distribution of the coating thickness or blistering. The continuous removal or skimming of this second brown phase is therefore absolutely essential. This operation requires a considerable amount of time and money. The formation of the second phase is traced back to the concept that the amines in an alkaline solution on the nickel anodes are transformed to nitriles (organically bonded cyanides). This however means that because of the decomposition of the amines, new complexing agents have to keep being added which in turn increases the process costs.

[0005] Several processes are described in the prior art to reduce the concentration of cyanides.

[0006] The activated carbon cleaning process is a common process that is used in electroplating to remove organic impurities in nickel electrolytes. The quantities of activated carbon used are determined in preliminary tests. The quantities most frequently used for activated carbon cleaning are 2 - 5 g/l. The activated carbon is added at a temperature of between 50 - 60°C. Once added, the electrolyte is stirred intensively. After approximately half an hour, the absorbable substances are absorbed by the activated carbon and are filtered out. The disadvantage of this process, however, is that all organic constituents are thereby removed from the electrolytes. For zinc-nickel electrolytes this would mean that not only the decomposition products, but also all other organic constituents such as for example brighteners and complexing agents, are removed.

[0007] The publication EP 1 344 850 A1 features a device to reduce the build-up of cyanide by separating the anode from the alkaline electrolyte using an ion exchanger membrane. This separation prevents a reaction of the amines on the nickel anodes and therefore also any undesirable side-reactions. The occurring side-reactions, problems of disposal, formation of a second phase and the adverse impact on the quality of the plated zinc-nickel layer, are thereby also avoided. It is therefore no longer necessary to replace the bath and spend lots of time and money on skimming the second phase which has formed. The zinc-nickel electrolyte acts as a catholyte. The medium in the anode compartment which is separated using the aforementioned ion exchanger membrane, is known as the anolyte whereby in this case either sulphuric acid or phosphoric acid can be used. The disadvantage of this process is the use of a costly and highmaintenance ion exchanger membrane, which can also not be used for all common metallization baths.

[0008] The publication EP 0 601 504 B1 describes the cleaning of galvanic baths for the separation of metals using polymer absorber resins. Similar to the activated carbon treatment, the disadvantage is that not only the decomposition products, but also all other organic constituents such as for example brighteners and complexing agents, are removed.

[0009] Description of the drawings:

Figure 1:	Ion exchanger regeneration unit
Figure 2:	Hull cell set-up
Figure 3:	Procedure and regeneration effect using a combination of an ion exchanger and the freezing out of sodium carbonate
Figure 4:	Comparison of the layer thickness distribution of different zinc-nickel electrolytes

Description of the invention

[0010] The aim of this invention is to selectively remove the cyanide and nitriles that have formed during the metallization process, from the electrolytes. Surprisingly, by using ion exchange resins which are able to bind cyanide ions, it was possible to remove not only the cyanide ions but also the nitriles from the bath. The use of ion exchange resins for this specific purpose is unknown in prior art.

[0011] In alkaline zinc-nickel electrolytes with amine-containing complexing agents (eg. polyethyleneamine), a nitrile compound is formed during the operation. The disadvantage of the decomposition product is that as the lifetime of the electrolyte is extended or as the decomposition product increases, an oily and waxy second phase is formed. The formation of the decomposition product is responsible for the loss of expensive complexing agents and the formation of highly toxic cyanide. From the amine-containing complexing agents, nitriles (R-CN, this always includes isonitriles, R-NC) are formed, initially in the oxidative reaction at the anode, which then react further to form cyanide ions (CN^-).

[0012] These problems lead to reduced efficiency and loss of quality of the plated layer. Here the efficiency is the percentage part of the total current introduced to plate a defined amount of metal. To counteract the reduced efficiency, the current density is usually increased, which however in turn accelerates the decomposition rate of the complexing agent to the nitrile (R-CN) and cyanide. Tests have shown that the second phase contains large quantities of cyanide, metal and sodium carbonate (Na_2CO_3). It can therefore be assumed that these decomposition products are influenced by the nitrile or that they exist together as the concentration continues to increase and form a second phase. From a procedural point of view, it is difficult to separate the second phase since the liquid in the bath is constantly moving. Furthermore this also means a constant loss of complexed metal ions and other precious additives which are also in this phase. It is therefore an object of the present invention to selectively remove the cyanide and organically bonded cyanide (nitrile) from the electrolyte.

[0013] The reduction in organically bonded cyanide would be noticeable in the change in content of the total organic carbon found in the process solution. This could, however, also mean that other vital organic constituents, such as brighteners or organic complexing agents are lost in the electrolyte. If it was the case that brighteners are removed from the electrolyte, this would considerably affect the optical quality of the plated layer. A reduction in the content of cyanide and nitrile compounds would subsequently increase the efficiency.

[0014] According to the present invention, the cyanide and organically bonded cyanide is to be removed using an ion exchange resin.

[0015] Ion exchange resins are used to remove toxic substances or interfering anions or cations from waste water. The advantage of this process is that it does not require a precipitation or chemical destruction since the interfering substances can be removed from the waste water without being changed. Ion exchange resins are high-molecular organic substances. The rigid and insoluble frame has easily interchangeable counterions on it. These are easily movable and interchangeable counterions, usually hydrogen ions or hydroxyl ions. The regeneration of galvanic process baths is therefore a suitable process to extend the lifetime of electrolytes by removing interfering cations or anions. The batch operation is a process for the ion exchange. The ion exchanger resins come into contact with the electrolyte solution in a receptacle. The process is finished as soon as there is an exchange equilibrium between the counterions from the exchanger and similarly charged ions from the electrolyte solution. If additional ions have to be removed from the electrolyte using the ion exchanger resins, then new resins have to be added. The resins are filtered out once the equilibrium is established.

[0016] The column process is the process most commonly used in the laboratory. Here, the ion exchanger resin is packed into a column. All necessary operations are then performed in the pack which has been created. Two different work techniques are distinguished, namely working with a decreasing and increasing liquid layer. With the decreasing liquid layer, the electrolyte flows through the column from the top down and with the increasing liquid layer from the bottom up. Filling the column is a straightforward operation. The resin in its current form is first of all transferred to a beaker containing distilled water to swell the resins. This operation is necessary to prevent the column from shattering and to avoid the column from being to densely packed as the resins swell. Two hours is usually sufficient for the resins to swell. The resin is then sludged in the column whilst making sure that the resin which is already layered, is covered with water at all times. This is necessary in order to prevent any effects from air bubbles. Any excess water is constantly removed from the column. Finally, once the resin has been filled, a piece of cotton wadding is placed across the top of the pack. The following sub-processes should be carried out during the operating cycle of a ion exchanger column:

1. Load (ion exchange)
2. Wash exchanger pack
3. Regenerate
4. Wash exchanger pack

[0017] Washing between operations is necessary to remove any residues of reagents in the ion exchanger column. During the regeneration process, the exchanger pack is transformed to its original state (non-loaded state). If the ion that was exchanged during the ion exchange is to be recovered again, it is removed hy the ion exchanger by eluting with a suitable liquid. According to the invention, the process solution flows through the ion exchanger resins, whereby the cyanides are taken up on the anchor groups through interactions and the hydroxide anions are released on the electrolytes. Surprisingly, nitrile compounds can also be removed in this way.

[0018] Each ion exchanger resin that is capable of binding cyanide ions, can be used within the framework of the present invention. Suitable ion exchange resins to bind cyanide ions are for example described in Ludwig Hartinger: Handbuch der Abwasser- und Recyclingtechnik, 2nd ed. 1991 on pages 352 - 361. According to paragraph 5.2.3.3.4 and Table 5-1 anions like cyanide can be exchanged utilizing strongly alkaline anion exchange resins. Such resins comprise resins made from polyacrylamide possessing quarternary ammonium groups. Such resin material is commercially available and for example described in Table 13 (page 89) of: Robert Kunin, Ion Exchange Resins, reprint 1985. Quarternary strong base resins suitable comprise Amberlite IRA-400 (Rohm & Haas Co.), Amberlite IRA-401 (Rohm & Haas Co.), Amberlite IRA-410 (Rohm & Haas Co.), Dowex 1 (Nalcite SBR) (Dow Chemical Co.), Dowex 2 (Nalcite SAR) (Dow Chemical Co.).

[0019] All such resins are also capable of binding nitriles.

[0020] By way of example, tests were carried out using the ion exchanger resins Lewatit MonoPlus M600 and MonoPlus M500 produced by Lanxess Deutschland GmbH. These resins are extremely alkaline anion exchangers which as a functional group, have quaternary amines. The matrix is a cross-linked polystyrene. The bulk density is 680 g/l, the effective grain size is 0.62 mm.

[0021] A device used to carry out the process according to the present invention comprises a receptacle (1) to take a zinc or zinc alloy bath, a connected pump system (2), which is connected to the ion exchanger device (4) to take the zinc or zinc alloy bath, which has an ion exchanger (5) and a collection device (7) for the zinc or zinc alloy bath conveyed through the ion exchanger resin (5), which can be identical to the receptacle (1).

[0022] Figure 1 shows the column process with an increased liquid layer according to one embodiment of the present invention. In the bottom part of the column (4) is a glass, ceramic or plastic frit, or a spray register or spray pole or sieve (6) through which the process solution can flow evenly through the ion exchanger resin (5). The ion exchanger resin (5) is embedded in the column. At the top end of the column, there is a glass, ceramic or plastic frit or a sieve (3). This is to prevent the resins from moving upwards and to ensure that only the process solution gets through. In the collection receptacle (1) which is used for the galvanic bath for the separation of metals, is the contaminated process solution which is conveyed through the column using a hose pump (2). Once the process solution has passed through the column, it is collected in a receptacle (7) which can be identical to receptacle (1). The device used for the metallization process comprises, as shown in figures 1 and 3, a receptacle (1) to take a zinc or zinc alloy bath, a connected pump system (2), which is connected to the ion exchanger device (4) to take the zinc or zinc alloy bath, which contains ion exchanger resin (5) and a collection device (7) for the zinc or zinc alloy bath passing through the ion exchanger resin (5), which can be identical to receptacle (1).

[0023] The ion exchanger resin (5) in the ion exchanger device (4) can be on a spray register, spray pole or sieve.

[0024] The receptacle (1) is generally equivalent to the galvanic zinc or zinc alloy bath and consists of at least an anode, a cathode (the substrate to be coated) and a voltage source.

[0025] In addition, there can also be — as shown in Figure 3 — a freezing device (8) between the receptacle (1) and the ion exchanger device (4) to cool the solution and separate a sodium carbonate solid. The freezing device (8) includes a cooling unit (9) to cool the solution to a temperature that is preferably below 10°C, more preferably between 2 - 5°C and an outlet (10) to separate the crystallised sodium carbonate.

[0026] There can also be a receptacle (11) between the freezing device (8) and the ion exchanger (4) to take the zinc or zinc alloy bath that has been cleaned from carbonates.

[0027] It was not possible to regenerate the resins Lewatit MonoPlus M600 and M500 using a sodium hydroxide solution. A stronger anion is needed to exchange the bonded cyanide anions. Strong acids such as for example hydrochloric acid (HCl) cannot be used as this would immediately form toxic hydrogen cyanide. During the regeneration test of the resins, sodium chloride was used to separate the cyanide from the resins and transform the resins back to the chloride form. The regeneration solution with sodium chloride was moved into the very alkaline range (pH value > 10) with a 0.5 % by weight sodium hydroxide, since cyanides can quickly decompose below this pH value and form toxic hydrogen cyanide. The regeneration tests were examined using three different concentrations of sodium chloride (6, 12 and 18 % by weight, Tables 2 - 7). The regeneration operation was realised at a linear speed of 5 m/h. One litre of sodium chloride solution was used for the regeneration and conveyed through the ion exchanger pack. Four portions of sample fractions having a volume of 250 ml each were taken and the content of different electrolyte parameters was analysed, compared and assessed. Data from the analysis was used to calculate the amount of cyanide which had bonded to the resin and was able to be eluted through the regeneration process. Referring to Table 2: a total volume of 1 l of regeneration solution with 6 % in weight of NaCl was used to elute the cyanide (including organic nitrile) from the column containing Lewatit MonoPlus M600. Sample 1 is an analysis of the first 250 ml of regeneration solution used to elute the cyanide from the column, Sample 2 the second portion of 250 ml, Sample 3 the third portion of 250 ml and Sample 4 the fourth portion of 250 ml, giving 1 l of total eluent. The amount of total cyanide in 1 l eluent is 1.525 mg. The same was performed for the other regeneration cycles according to Tables 3 - 7.

[0028] The results show that it is beneficial to use solutions with a high chloride ion content to regenerate the columns.

Table 2: Lewatit MonoPlus M600 - Determination of the eluted quantity of cyanide, regeneration with 6 % in weight of NaCl solution

Lewatit MonoPlus M600 Regeneration	Cyanide concentration	Quantity of cyanide in 250 ml sample volume
	[mg/l]	[mg/sample volume]
Sample 1	1.8	0.450
Sample 2	1.5	0.375
Sample 3	1.5	0.375
Sample 4	1.3	0.325
From 100 ml resin, eluted quantity of cyanide ->		1.525

Table 3: Lewatit MonoPlus M500 - Determination of the eluted quantity of cyanide, regeneration with 6 % in weight of NaCl solution

Lewatit MonoPlus M500 Regeneration	Cyanide concentration	Quantity of cyanide in 250 ml sample volume
	[mg/l]	[mg/sample volume]
Sample 1	3.6	0.900
Sample 2	3.7	0.925
Sample 3	2.9	0.725
Sample 4	2.2	0.550
From 100 ml resin, eluted quantity of cyanide ->		3.100

Table 4: Lewatit MonoPlus M600 - Determination of the eluted quantity of cyanide, regeneration with 12 % in weight of NaCl solution

Lewatit MonoPlus M600 Regeneration	Cyanide concentration	Quantity of cyanide in 250 ml sample volume
	[mg/l]	[mg/sample volume]
Sample 1	7	1.750
Sample 2	6.5	1.625

(continued)

Lewatit MonoPlus M600 Regeneration	Cyanide concentration	Quantity of cyanide in 250 ml sample volume
	[mg/l]	[mg/sample volume]
Sample 3	6.5	1.625
Sample 4	6.5	1.625
From 100 ml resin, eluted quantity of cyanide ->		6.626

Table 5: Lewatit MonoPlus M500 - Determination of the eluted quantity of cyanide, regeneration with 12 % in weight of NaCl solution

Lewatit MonoPlus M500 Regeneration	Cyanide concentration	Quantity of cyanide in 250 ml sample volume
	[mg/l]	[mg/sample volume]
Sample 1	18.0	4.500
Sample 2	8.5	2.125
Sample 3	8.5	2.125
Sample 4	6.2	1.550
From 100 ml resin, eluted quantity of cyanide ->		10.300

Table 6: Lewatit MonoPlus M600 - Determination of the eluted quantity of cyanide, regeneration with 18 % in weight of NaCl solution

Lewatit MonoPlus M600 Regeneration	Cyanide concentration	Quantity of cyanide in 250 ml sample volume
	[mg/l]	[mg/sample volume]
Sample 1	35	8.75
Sample 2	41	10.25
Sample 3	44	11.00
Sample 4	45	11.25
From 100 ml resin, eluted quantity of cyanide ->		41.25

Table 7: Lewatit MonoPlus M500 - Determination of the eluted quantity of cyanide, regeneration with 18 % in weight of NaCl solution

Lewatit MonoPlus M 500 Regeneration	Cyanide concentration	Quantity of cyanide in 250 ml sample volume
	[mg/l]	[mg/sample volume]
Sample 1	17	4.25
Sample 2	18	4.50
Sample 3	17	4.25
Sample 4	17	4.25
From 100 ml resin, eluted quantity of cyanide ->		17.25

[0029] Tests where the temperature was increased (flow temperature in the beaker 55°C, average temperature in the ion exchanger column 35°C) have shown that achieving the correct temperature significantly reduced the regeneration medium requirement. The solution used had a sodium chloride ion concentration of 18 % in weight.

Table 7b): Lewatit MonoPlus M600 - Determination of the eluted quantity of cyanide, regeneration with 18 % in weight of NaCl solution

Volume flow rate	Temperature	Concentration (NaCl + NaOH)	Elution capacity	Volume regeneration solution
[BV/h]	[°C]	[%]	[mg cyanide / per litre regeneration solution]	[BV]**
33	RT	18+5	42	238
2.5	RT	18+5	119	84
2.5	55°C first runnings, 35°C in the column	18+5	310	33
2.5	55°C first runnings, 35°C in the column	18+5	312	32
2.5	55°C first runnings, 35°C in the column	18+5	286	35
[BV/h] = bed volume per hour [BV] = bed volume				

[0030] The aged electrolyte which is to be regenerated, should if possible be as close as possible to the original state (new batch). New batches of alkaline zinc-nickel electrolytes usually have an efficiency of 70 % for a current density of 1 A/dm^2. In electroplating, in order to assess the regeneration effect, the Hull cell test can be used and there is the option to determine the efficiency of the electrolyte using Faraday's law. Based on the layer thickness distribution of the electrolyte, it is possible to assess how good the regeneration effect is using an ion exchange resin. The Hull cell is used to determine the effects of the bath parameters (eg. temperature, pH value, electrolyte composition, lack of or surplus of additives, cleanliness, impurities from foreign metals) on the property of the plated layer depending on the current density.

[0031] Since in a Hull cell the cathode is diagonal to the anode (see Figure 2), there is a distribution of current densities on the cathode. This makes it possible to examine the effect of the current density in a single experiment. Understandably the current density is higher at the edge nearest the anode than at the edge away from the anode (Figure 2). The quality of coated surfaces, ie. the composition, thickness, evenness and other properties, therefore primarily depend on the composition of the electrolyte and the plating conditions. The key quality factors are the composition of the electrolyte and the current parameters which must be monitored to assure a high quality coating. The composition of the electrolyte plays a significant role in this instance. Each individual additive in the electrolyte influences the properties of the electrolyte and the plated layer. In order to obtain the desired layer quality, the concentration of the electrolyte constituents must be within certain limits. The majority of electrolytes contain, in addition to the inorganic constituents, additional organic-type additives. These organic constituents are designed to influence the properties of the layer that is to be plated. This includes for instance brightening, levelling, hardness, ductility and throwing power ability. The Hull cell test was carried out to examine the appearance of the plated layer and the zinc-nickel composition. Tests were carried out with the Hull cell on a new, on an aged and on an electrolyte that had been regenerated using ion exchange resins. This test is designed to give an indication as to how effective it is to come close to the original state (new batch). The Hull cell can be used to establish how losses during the ion exchange process affect the plating rate. The additives however only work effectively if they are used in a certain concentration and composition.

[0032] Qualitatively, by visually assessing the brightness of the coated plates, it can be said that the reduction in the TOC (Total Organic Carbon) content, as shown in Tables 8 and 9, is due to the reduction of the nitrile concentration and that of the amine-containing complexing agents.

[0033] The ion exchange process can preferably be carried out in conjunction with the freezing out of sodium carbonate to further increase the efficiency of the process and match the plating performance of a non-aged electrolyte. The electrolyte solution can be conveyed through a cooling device either before or after treatment in the ion exchange resin column (see Figure 3). During cooling, a sodium carbonate phase which can be separated, is formed. The old electrolyte is preferably treated in the freezer unit first and then in the ion exchange resin unit.

Operational examples

[0034] Tests were carried out on an electrolyte to plate zinc-nickel alloys in accordance with Table 1.

[0035] For this test, 100 ml of resin was swelled in fully desalinated water for two hours and then sludged into the column. Prior to the loading process, the Lewatit MonoPlus M600 was regenerated using a 2 % by weight sodium hydroxide solution to transform the resins to the OH- form. For the Lewatit MonoPlus M500, this was done using a 3 % by weight sodium hydroxide solution. The loading process is realised according to the values indicated by the manufacturer. In practice, it is customary to indicate the loading process in bed volume per hour (BV/h). This value in turn refers to the embedded quantity of resin which is embedded in the column. Loading generally takes place at 10 BV/h. Based on our quantity of resin used (100 ml), the volume flow rate is 1000 ml/h. This represents a rate of 1.51 m/h and is within the value range specified by the manufacturer. Before the tests were carried out, a reference sample was taken from the zinc-nickel electrolyte which was to be regenerated (Sample 0 in the tables corresponds to an aged electrolyte). In the preliminary test which was carried out to examine the selectivity of the ion exchanger resins, 1000 ml of alkaline zinc-nickel electrolytes were conveyed through the ion exchanger column, where 250 ml of sample fractions were taken every fifteen minutes (Samples 1 - 4 in Tables 8 and 9).

[0036] The content of the different constituents was then examined in the sample fractions and compared with one another. The metal content, sodium hydroxide content, sodium carbonate content, sodium sulphate content, content of the complexing agents, TOC content and the total cyanide content of the samples was examined. Tables 8 and 9 show the test results.

Table 8: Test results of the loading process for Lewatit MonoPlus M600 (aged electrolyte)

Lewatit MonoPlus M600			Sample 0	Sample 1	Sample 2	Sample 3	Sample 4
			Time	Time	Time	Time	Time
			[min]	[min]	[min]	[min]	[min]
			0	0-15	15-30	30-45	45-60
Zinc	Zn	[g/l]	12.4	11.9	12.0	12.1	12.0
Nickel	Ni	[g/l]	1.5	1.5	1.5	1.5	1.5
Sodium hydroxide	NaOH	[g/l]	94.5	78.9	94.7	95.5	94.1
Sodium carbonate	Na_2CO_3	[g/l]	56.6	58.8	59.2	57.8	58.3
Sodium sulphate	Na_2SO_4	[g/l]	4.50	4.73	4.77	4.51	4.70
Complexing agent	-	[ml/l]	140	132	135	138	135
Total cyanide	CN-	[mg/l]	92.0	5.2	5.1	5.2	4.8
TOC	-	[g/l]	45.8	40.0	44.2	44.0	44.0

Table 9: Test results of the loading process for Lewatit MonoPlus M500

Lewatit MonoPlus M500			Sample 0	Sample 1	Sample 2	Sample 3	Sample 4
			Time	Time	Time	Time	Time
			[min]	[min]	[min]	[min]	[min]
			0	0-15	15-30	30-45	45-60
Zinc	Zn	[g/l]	11.5	7.7	11.4	11.7	11.5
Nickel	Ni	[g/l]	1.4	1.4	1.4	1.5	1.4
Sodium hydroxide	NaOH	[g/l]	147	140	148	146	149
Sodium carbonate	Na_2CO_3	[g/l]	72.1	60.4	71.6	71.2	72.8
Sodium sulphate	Na_2SO_4	[g/l]	7.69	5.48	7.59	7.52	8.19
Complexing agent	-	[ml/l]	137	97	128	132	131
Total cyanide	CN-	[mg/l]	75.0	17.0	7.5	7.6	7.7

(continued)

Lewatit MonoPlus M500			Sample 0	Sample 1	Sample 2	Sample 3	Sample 4
			Time	Time	Time	Time	Time
			[min]	[min]	[min]	[min]	[min]
			0	0-15	15-30	30-45	45-60
TOC	-	[g/l]	42.9	25.9	40.8	41.6	42.2

[0037] The values in Tables 8 and 9 show that the metal content concentrations are virtually constant and do not change significantly. The nickel concentration remains unchanged and does not fluctuate. The sodium hydroxide concentration slightly drops at first. The reason for this is that the resins could not be fully transformed to the OH- form during the regeneration process. The resins therefore were still able to absorb the hydroxide ions. The sodium hydroxide concentration, however, takes on the same order of magnitude again as that of Sample 0 and remains virtually the same. The content of sodium carbonate and sodium sulphate remain virtually unchanged.

[0038] There is a clear reduction in cyanide and a lower yet significant reduction in the TOC.

[0039] The test shows that the resin Lewatit MonoPlus M600 retains the interfering cyanide from the process solution. The test also shows that the resin's absorption capacity has by no means been reached and that the cyanide content dropped even after 60 minutes. In comparison to the Lewatit MonoPlus M500 it is clear that the cyanide concentration is initially accompanied by a reduction in the concentration of zinc, sodium hydroxide, sodium carbonate, sodium sulphate and the complexing agent in the first fraction (Sample 1). The nickel concentration remains virtually constant throughout the whole test period.

[0040] The Hull cell tests were carried out to examine the appearance of the plated layer and the zinc-nickel composition. Tests were carried out with the Hull cell on a new, on an aged and on an electrolyte that had been regenerated using ion exchangers. This test is designed to give an indication as to how important it is to come close to the original state (non aged electrolyte). The Hull cell can be used to establish how losses during the ion exchange process effect the plating rate.

[0041] The Hull cell was filled with 250 ml of electrolyte as per Table 1. A nickel anode was used as the anode. Once the Hull cell plate had been cleaned, a 1-ampere current was applied. The coating time was fifteen minutes.

[0042] The low current density range (see Fig. 2) shows an even and bright plating result. The electrolyte which was treated using the ion exchanger resin Lewatit MonoPlus M600, revealed an even and bright surface across the whole current density spectrum. The assessment of the surface should be classed as bright. It can therefore be confirmed that the ion exchange process which is used to remove cyanide from the alkaline zinc-nickel electrolyte, significantly improves the appearance of the plated layer. More importantly however is the finding that the appearance was not in any way worsened, which indicated that no organic additives, which are responsible for the appearance of the depsit, were removed from the plating bath by the ion exchange process.

[0043] This also leads to the conclusion that the reduction of the TOC content is due to the reduction of the organic complexing agent and the organically bonded cyanide (nitrile). The same result was obtained using an electrolyte which was treated with the Lewatit MonoPlus M500 ion exchanger resin.

[0044] The high and low current density ranges shown in Figure 2 act as measuring points for determining a layer thickness and the alloy composition of the zinc-nickel layer. After the coating process in the Hull cell, the layer thicknesses were measured using an X-ray fluorescence measurement device at the two measuring points A (high current density range) and B (low current density range). Five measurements were taken at each measuring point. In electroplating, the X-ray fluorescence analysis is a standard method used for a quick and non-destructive determination of layer thicknesses. By using this measurement method, it was possible to ascertain the layer thickness and the amount of nickel and zinc. Based on the layer thickness distribution, it was then possible to draw a conclusion concerning the effect of the ion exchange process on the electrolyte parameters. The base or reference value which is to be obtained using the regeneration process, is the layer thickness distribution of the newly included electrolyte [Table 10].

[0045] A comparison of the layer thickness distribution for a new and an aged electrolyte [Table 11] also shows how quickly the efficiency level and thereby also the separation rate of the electrolyte drops as the lifetime increases. In order to retain the same matrix relating to the batch, it is necessary to replenish the quantities of metal ions for the old electrolyte as per Table 11 as well as those lost through the ion exchange process. The initial concentration (Sample 0) is needed for this.

Table 10: Composition of the layer - new electrolyte

Layer thickness distribution of the new electrolyte	Measuring point A			Measuring point B		
	Layer thickness	Nickel part	Zinc part	Layer thickness	Nickel part	Zinc part
	[μm]	[%]	[%]	[μm]	[%]	[%]
1	5.15	13.9	86.1	1.76	13.7	86.3
2	5.22	13.8	86.2	1.77	14.2	85.8
3	5.14	14.5	85.5	1.78	13.9	86.1
4	5.10	14.2	85.8	1.87	14.5	85.5
5	5.18	13.9	86.1	1.80	13.7	86.3
Mean value	5.16	14.1	85.9	1.80	14.0	86.0

Table 11: Composition of the layer - aged electrolyte

Layer thickness distribution of the aged electrolyte	Measuring point A			Measuring point B		
	Layer thickness	Nickel part	Zinc part	Layer thickness	Nickel part	Zinc part
	[μm]	[%]	[%]	[μm]	[%]	[%]
1	3.13	14.2	84.7	1.27	15.4	84.6
2	3.14	14.5	85.5	1.25	15.0	85.0
3	3.13	15.1	84.9	1.26	14.2	85.8
4	3.16	14.5	85.5	1.26	14.5	85.5
5	3.13	14.3	85.7	1.25	14.2	85.8
Mean value	3.14	14.5	85.3	1.26	14.7	85.3

[0046] After the regeneration and replenishment ot the aged electrolyte [Tables 12 and 13], the Hull cell test shows that the plated layer thickness at measuring points A and B is considerably higher and is closer to the non aged electrolyte, in comparison to the aged electrolyte [Table 11]. The result also shows that the nickel and zinc composition has not changed in the layer. It can therefore be said that removing the cyanide and organically bonded cyanide accelerates the separation rate of the alkaline zinc-nickel electrolyte and that the bath quality is significantly increased in comparison to the aged plating bath by using an ion exchanger system.

Table 12: Layer thickness at the measuring point / electrolyte regenerated with Lewatit MonoPlus M600 and missing quantities supplemented

Layer thickness distribution Electrolyte regenerated and supplemented Lewatit MonoPlus M600	Measuring point A			Measuring point B		
	Layer thickness	Nickel part	Zinc part	Layer thickness	Nickel part	Zinc part
	[μm]	[%]	[%]	[μm]	[%]	[%]
1	3.60	14.0	86.0	1.30	13.5	86.5
2	3.59	14.8	85.2	1.33	14.0	86.0
3	3.66	14.9	85.1	1.39	14.5	85.5
4	3.65	14.7	85.3	1.38	14.0	86.0
5	3.63	13.6	86.4	1.39	14.3	85.7
Mean value	3.63	14.4	85.6	1.36	14.1	85.9

Table 13: Layer thickness at the measuring point / electrolyte regenerated with Lewatit MonoPlus M500 and missing quantities supplemented

Layer thickness distribution Electrolyte regenerated and & supplemented Lewatit MonoPlus M600	Measuring point A			Measuring point B		
	Layer thickness	Nickel part	Zinc part	Layer thickness	Nickel part	Zinc part
	[μm]	[%]	[%]	[μm]	[%]	[%]
1	3.75	14.7	85.3	1.41	14.3	85.7
2	3.69	14.5	85.5	1.35	14.3	85.7
3	3.69	14.5	85.5	1.39	14.9	85.1
4	3.70	14.3	85.7	1.38	14.5	85.5
5	3.71	14.4	85.6	1.40	14.4	85.6
Mean value	3.71	14.5	85.5	1.39	14.5	85.5

[0047] The efficiency of the electrolyte can be increased further by freezing out the sodium carbonate. A comparison of the layer thicknesses in the aged electrolyte with the lower concentration of sodium carbonate [Table 14] after the freezing out process and the aged electrolyte with the higher concentration of sodium carbonate [Table 11] where there was no freezing out, shows that the decrease in the sodium carbonate concentration at the least affects the separation rate. There was no evidence that the metal composition was affected. An examination of the efficiency of the electrolyte once the sodium carbonate had been frozen out revealed a 7 % increase in the efficiency of the electrolyte. A regeneration of the zinc-nickel electrolyte by freezing out the sodium carbonate and removing the cyanide and nitrile using the ion exchanger is particularly advantageous.

Table 14: Layer thickness distribution - electrolyte - sodium carbonate frozen out.

Layer thickness distribution Electrolyte Na_2CO_3 removed by means of freezing out	Measuring point A			Measuring point B		
	Layer thickness	Nickel part	Zinc part	Layer thickness	Nickel part	Zinc part
	[μm]	[%]	[%]	[μm]	[%]	[%]
1	3.22	13.8	86.2	1.23	13.8	86.2
2	3.22	14.1	85.9	1.25	14.6	85.4
3	3.22	13.8	86.2	1.24	14.6	85.4
4	3.25	14.0	86.0	1.25	13.7	86.3
5	3.22	14.5	85.5	1.24	14.9	85.1
Mean value	3.23	14.0	86.0	1.24	14.3	85.7

[0048] Using macro throwing power measurments, it was also possible to assess how effectively the ion exchange process can bring the aged electrolyte to the original state (non aged electrolyte). 250 ml of electrolyte were again filled into the Hull cell as per Table 1. The Hull cell plate was galvanised for 15 minutes. In order to be able to assess the throwing power and the regeneration effect as a result of the ion exchanger and the freezing out process, the throwing power abilities of various electrolytes were assessed. To do so, the Hull cell plate which was to be coated and was 30 mm from the lower edge of the plate, was measured at intervals of a centimetre. The measuring points were indicated by crosses on the coated plate. The measurement was taken using the X-ray fluorescence measurement process. From the layer thickness distribution of the plates it was possible to determine the effects of the regeneration process on the electrolyte. The measured layer thicknesses were applied across the length of the plate [Figure 4]. It shows that after 15 minutes of metallization, across the whole length of the Hull cell plate, the electrolytes which were regenerated with Lewatit MonoPlus500 and Lewatit MonoPlus600 created a layer thickness which was significantly higher than could be achieved using the aged bath.

Claims

1. Process used to deposit functional layers of zinc or zinc alloys from alkaline zinc or zinc alloy plating baths which contain nitrogenous organic additives, a soluble zinc salt and optionally other metal salts selected from the group consisting of Fe, Ni, Co and Sn salts, comprising the following steps:

    (i) providing a zinc or zinc alloy bath containing the above mentioned components;
    (ii) electrolytically depositing a zinc or zinc alloy layer on a substrate that is to be coated according to known processes;
    (iii) removing at least a part of the zinc or zinc alloy bath and conveyancing the part that has been removed and which contains cyanide ions and nitriles that have been formed during the deposition according to step (ii) through a device that includes an ion exchange resin which is designed specifically for separating cyanide ions;
    (iv) returning the conveyed part to the zinc or zinc alloy bath, and

    the ion exchange resin is regenerated through contact with a sodium chloride solution and then by means of conditioning using sodium hydroxide.

2. Process according to one of the abovementioned claims, **characterised in that** the following procedural step is also scheduled: (v) Supplementing of used components from the zinc or zinc alloy bath.

3. Process according to one of the abovementioned claims, **characterised in that** the removal of the part of the zinc or zinc alloy bath and its return is a continuous or discontinuous process.

4. Process according to one of the abovementioned claims, **characterised in that** the zinc or zinc alloy bath contains organic additives selected from brighteners, surface-active agents and nitrogenous complexing agents.

5. Process according to one of the abovementioned claims, **characterised in that** the nitrogenous complexing agents are selected from the group comprising polyalkyleneamines.

6. Process according to one of the abovementioned claims, **characterised in that** it is a galvanic bath which is used to plate zinc-nickel alloys.

7. Process according to one of the abovementioned claims, **characterised in that** the ion exchange resin is selected from the group consisting of strongly alkaline anion exchange resins.

8. Process according to one of the abovementioned claims, **characterised in that** the ion exchange resin is selected from the group consisting of ion exchange resins having as a functional group quarternary amines.

9. Process according to claim 1, **characterised in that** the sodium chloride solution presents a sodium chloride concentration of 5 - 35 % by weight.

10. Process according to either claim 1 or 9, **characterised in that** the temperature of the sodium chloride solution is 10 - 70°C during regeneration on the ion exchanger column.

11. Process according to one of the abovementioned claims, **characterised in that** the process includes the additional step iii b) cooling of the zinc or zinc alloy bath for the separation of sodium carbonate at a temperature which is below 10°C.

Patentansprüche

1. Verfahren zur Abscheidung funktionaler Schichten von Zink- oder Zinklegierungen aus alkalischen Zink- oder Zinklegierungsbädern, die stickstoffhaltige organische Zusätze, ein lösliches Zinksalz und gegebenenfalls weitere Metallsalze enthalten, welche ausgewählt sind aus der Gruppe enthaltend Fe-, Ni-, Co- und Sn-Salze, umfassend die folgenden Stufen:

    (i) Bereitstellen eines Zink- oder Zinklegierungsbades enthaltend die vorgenannten Komponenten;
    (ii) elektrolytisches Abscheiden einer Zink- oder Zinklegierungsschicht auf dem zu beschichtenden Werkstück

nach an sich bekannten Verfahren;
(iii) Entnahme wenigstens eines Teils des Zink- oder Zinklegierungsbades und Durchführen des entnommenen Teils, das Cyanidionen und Nitrile enthält, die während der Abscheidung nach Schritt (ii) entstanden sind, durch eine Einrichtung umfassend einen Ionenaustauscherharz geeignet zur Abtrennung von Cyanidionen;
(iv) Rückführen des durchgeleiteten Teils in das Zink- oder Zinklegierungsbad, und

der Ionenaustauscher wird regeneriert durch in-Kontakt-Bringen zunächst mit einer Natriumchlorid-Lösung und anschließender Konditionierung mit Natriumhydroxid.

2. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** zusätzlich folgender Verfahrensschritt vorgesehen ist: (v) Ergänzen verbrauchter Komponenten des Zink- oder Zinklegierungsbades

3. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** die Entnahme des Teils des Zink- oder Zinklegierungsbades und das Rückführen kontinuierlich oder diskontinuierlich erfolgt.

4. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** das Zink- oder Zinklegierungsbad organische Zusätze ausgewählt aus Glanzmitteln, Netzmitteln und stickstoffhaltigen Komplexbildnern enthält.

5. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** die stickstoffhaltigen Komplexbildner ausgewählt sind aus der Gruppe enthaltend Polyalkylenamine.

6. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** es sich um ein galvanisches Bad zur Abscheidung von Zink-Nickel-Legierungen handelt.

7. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** das Ionenaustauscherharz ausgewählt ist aus der Gruppe bestehend aus stark basischen Anionentauscherharzen.

8. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** das Ionenaustauscherharz ausgewählt ist aus der Gruppe bestehend aus Ionentauscherharzen, die als funktonale Gruppe quarternäre Ammoniumgruppen enthalten.

9. Verfahren nach Anspruch 1 **dadurch gekennzeichnet, dass** die Natriumchlorid-Lösung eine Konzentration an Natriumchlorid von 5 - 35 Gew.% aufweist.

10. Verfahren nach einem der Ansprüche 1 oder 9 **dadurch gekennzeichnet, dass** die Temperatur der Natriumchlorid-Lösung während der Regenerierung auf der Ionenaustauschersäule 10 - 70°C beträgt.

11. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** das Verfahren den zusätzlichen Schritt umfasst iii b) Herunterkühlen des Zink- oder Zinklegierungsbades zur Abtrennung von Natriumcarbonat auf eine Temperatur kleiner als 10°C.

Revendications

1. Procédé utilisé pour déposer des couches fonctionnelles de zinc ou d'alliages de zinc à partir de bains de placage alcalins de zinc ou d'alliage de zinc qui contiennent des additifs organiques azotés, un sel de zinc soluble et, optionnellement, d'autres sels métalliques, qui sont choisis dans le groupe composé de sels de Fe, Ni, Co et Sn, comprenant les étapes suivantes :

(i) obtenir un bain de zinc ou d'alliage de zinc contenant les composants susmentionnés ;
(ii) déposer par voie électrolytique une couche de zinc ou d'alliage de zinc sur un substrat devant être recouvert selon des procédés connus ;
(iii) prélever au moins une partie du bain de zinc ou d'alliage de zinc et conduire la partie qui a été prélevée et qui contient des ions cyanure et des nitriles qui ont été formés pendant le dépôt conformément à l'étape (ii) à travers un dispositif qui comprend une résine échangeuse d'ions qui est conçue spécifiquement pour séparer les ions cyanure ;
(iv) renvoyer la partie conduite au bain de zinc ou d'alliage de zinc, et

la résine échangeuse d'ions est régénérée par contact avec une solution de chlorure de sodium puis par conditionnement à l'hydroxyde de sodium.

2. Procédé selon l'une des revendications précédentes **caractérisé en ce que** l'étape procédurale suivante est également prévue : (v) faire l'appoint des composants utilisés dans le bain de zinc ou d'alliage de zinc.

3. Procédé selon l'une des revendications précédentes **caractérisé en ce que** le prélèvement de la partie du bain de zinc ou d'alliage de zinc et son renvoi sont un procédé continu ou discontinu.

4. Procédé selon l'une des revendications précédentes **caractérisé en ce que** le bain de zinc ou d'alliage de zinc contient des additifs organiques choisis parmi les agents de blanchiment, les tensioactifs et les complexants azotés.

5. Procédé selon l'une des revendications précédentes **caractérisé en ce que** les complexants azotés sont choisis dans le groupe comprenant des polyalkylène-amines.

6. Procédé selon l'une des revendications précédentes **caractérisé en ce que** c'est un bain galvanique qui est utilisé pour plaquer les alliages zinc-nickel.

7. Procédé selon l'une des revendications précédentes **caractérisé en ce que** la résine échangeuse d'ions est choisie dans le groupe composé de résines échangeuses d'anions fortement alcalines.

8. Procédé selon l'une des revendications précédentes **caractérisé en ce que** la résine échangeuse d'ions est choisie dans le groupe composé de résines échangeuses d'ions ayant les amines quaternaires comme groupe fonctionnel.

9. Procédé selon la revendication 1, **caractérisé en ce que** la solution de chlorure de sodium présente une concentration en chlorure de sodium de 5 - 35 % en poids.

10. Procédé selon l'une ou l'autre des revendications 1 et 9, **caractérisé en ce que** la température de la solution de chlorure de sodium est de 10 - 70 °C pendant la régénération sur la colonne échangeuse d'ions.

11. Procédé selon l'une des revendications précédentes **caractérisé en ce que** le processus comprend l'étape supplémentaire iii b) refroidir le bain de zinc ou d'alliage de zinc pour la séparation du carbonate de sodium à une température inférieure à 10 °C.

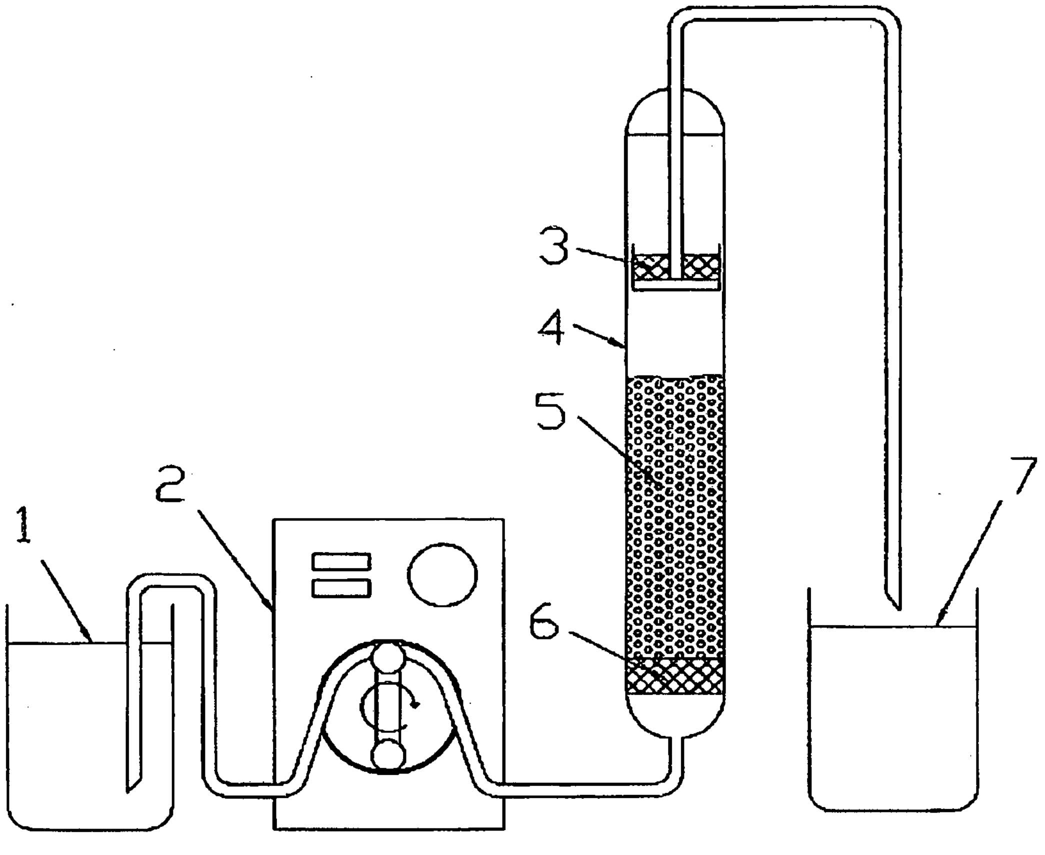

Figure 1

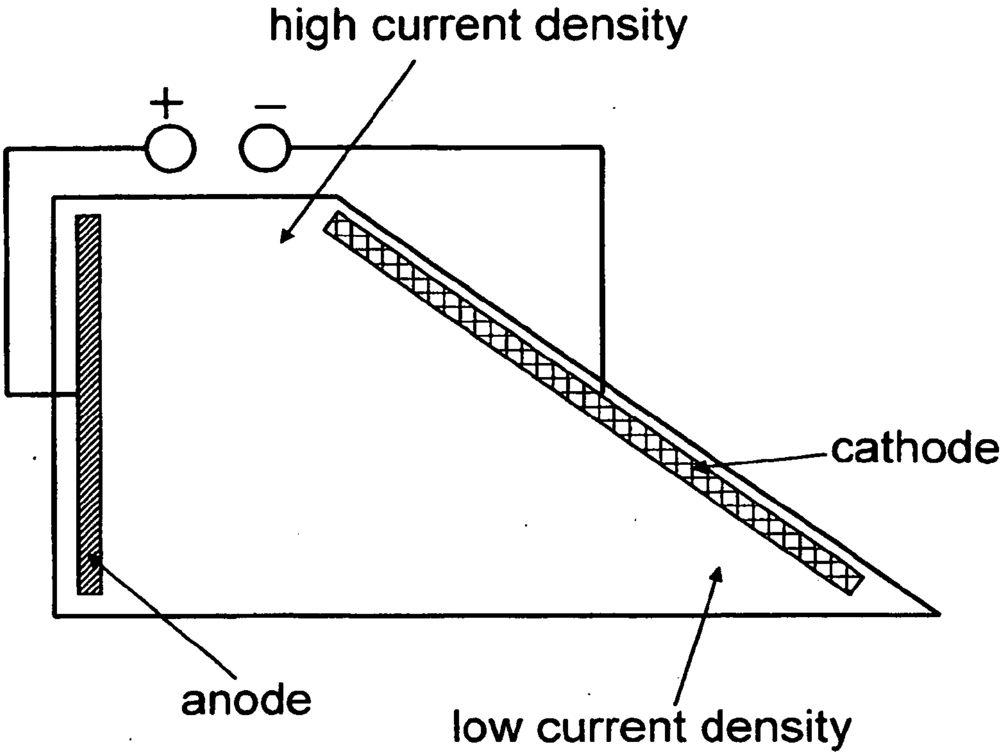

Figure 2

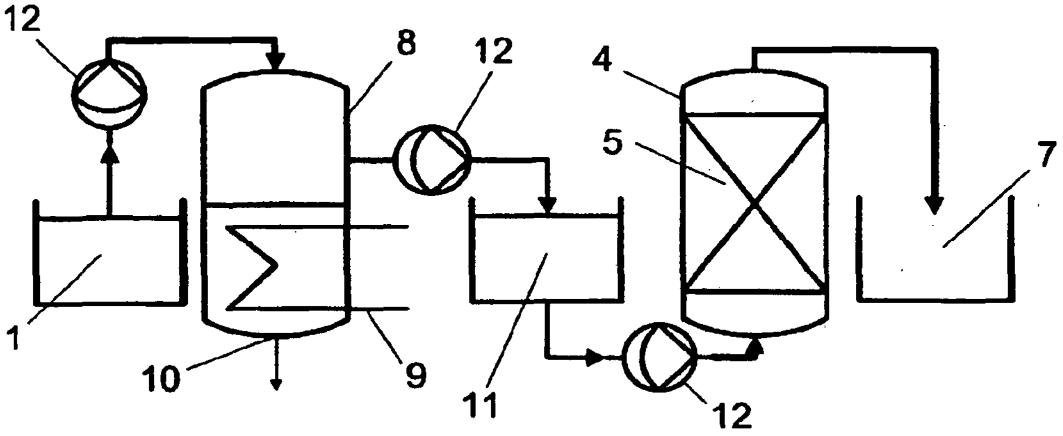

Figure 3

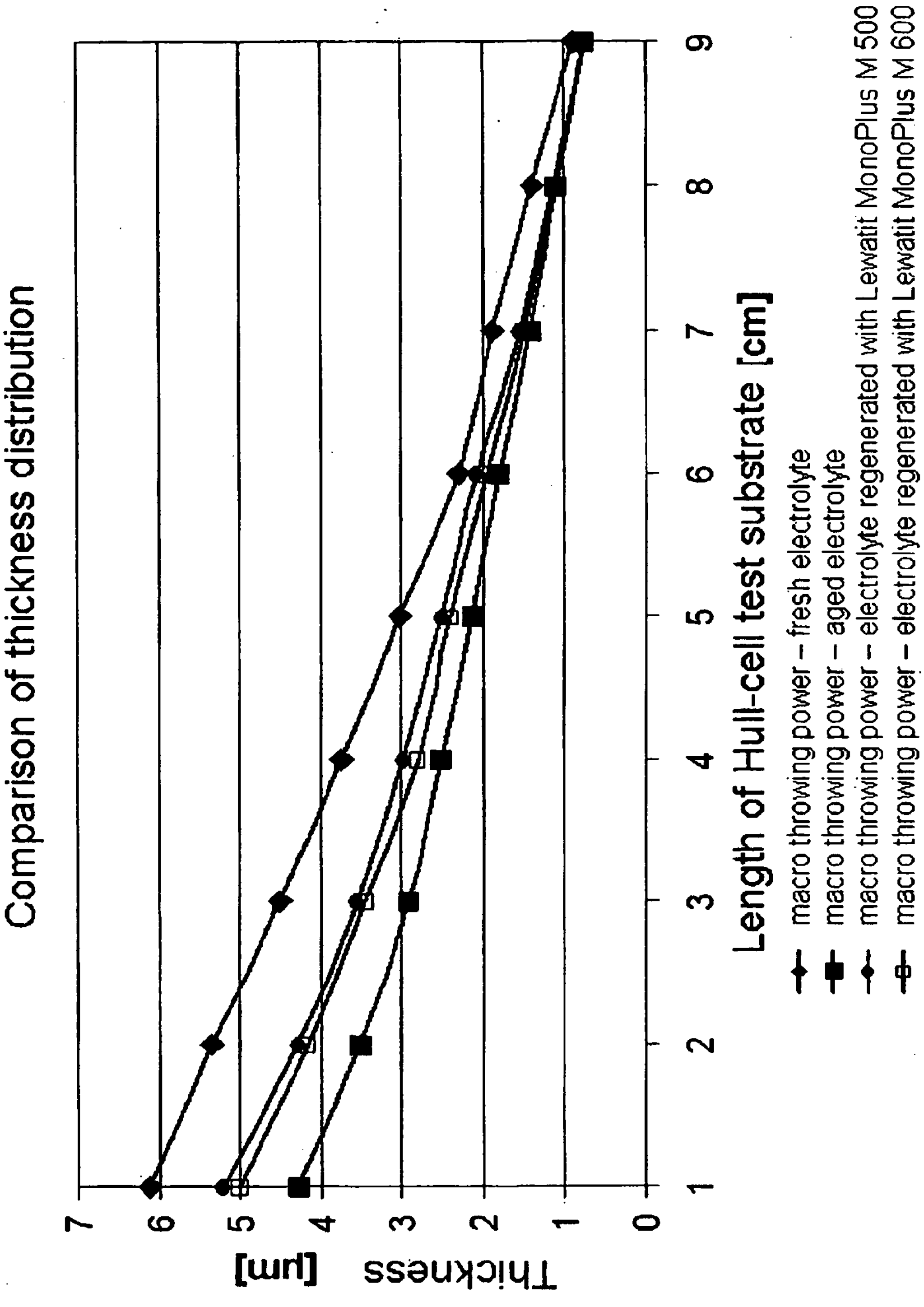
Comparison of thickness distribution
Thickness [µm]
0
1
2
3
4
5
6
7
Length of Hull-cell test substrate [cm]
1
2
3
4
5
6
7
8
9
macro throwing power – fresh electrolyte
macro throwing power – aged electrolyte
macro throwing power – electrolyte regenerated with Lewatit MonoPlus M 500
macro throwing power – electrolyte regenerated with Lewatit MonoPlus M 600

Figure 4

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 4889602 A **[0002]**
- US 6755960 B **[0002]**
- EP 1344850 A1 **[0007]**
- EP 0601504 B1 **[0008]**

Non-patent literature cited in the description

- **LUDWIG HARTINGER.** Handbuch der Abwasser- und Recyclingtechnik. 1991, 352-361 **[0018]**