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3,799,850

ELECTROLYTIC PROCESS OF EXTRACTING METALLIC ZINC

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4 Claims

ABSTRACT OF THE DISCLOSURE

A method for obtaining zinc from its sulfuric acid solutions by an electrolytic process in which the current flow between the electrodes is reversed for from 0.3 to 1.2% of the electrical current cycle and the frequency of changing the sign of the electrodes is from 2.0 to 6.0 times a minute.

This application is a continuation-in-part of application Ser. No. 796,605, filed Feb. 4, 1969, and now abandoned.

The processes of electrodeposition of zinc to plate a metal base and electrolytic extraction of zinc in applying the relatively simple method of electrolysis, commonly come under the heading of electrodeposition of zinc. These processes find their foundation in the changes which take place when electric current is applied by means of suitable electrodes immersed in solutions of zinc salt. The salt is appreciably ionized, the zinc ions migrating to the cathode and being deposited there, while at the anode, made of an appropriate metal, the salt is reformed by the anode metal, passing into the ionic form. If an insoluble anode is used, secondary reactions take place which lead to a progressive depletion of the metal content of the solution and the need, therefore, for other means of maintaining the metal ion concentration. Under the usual conditions of deposition, the ionic migration of the zinc ions is extraordinarily slow. In any case, the transport number of the zinc ions is only a fraction of the total current which is responsible for deposition; hence there is a need for some type of movement in practical deposition.

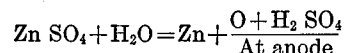
The deposition of zinc follows known laws. The ampere-hour is thus associated with definite amounts of zinc which cannot be exceeded and may not be attained through failure to reach the quantitative conditions, i.e. that the quantities of substances liberated in electrolysis are (1) proportional to the coulombs passed per second, including, there, the conditions of current and time, and (2) the chemical equivalents of those substances. Theoretically, the quantities of zinc deposited by the ampere-hours are 1.22 gr. In practical deposition this quantitative value is not attained. The physical character of the deposit is far more important than its theoretical quantity. Many circumstances operate to depreciate these physical properties.

In general, the depositing solution should (1) be of high metal content, (2) have good electrical conducting power, (3) be stable in contact with the metal on which deposited, (4) be stable against atmospheric conditions, (5) have constant metal content during the process, (6) yield compact deposits, and (7) possess the power of "throwing." Substances which usually assume the colloidal form, the so-called "addition agents," migrate towards the cathode and are there deposited in minute quantities, to induce fine crystalline structure.

In the zinc extraction process insoluble anodes are used, so that definite chemical changes occur, resulting in the decomposition of one or more substances involving larger

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energy consumption. With electrolytic zinc extraction the reaction is:



This reaction theoretically requires about 2.3 volts. The average figure in practice is 3.5 volts, with a "current efficiency" of 90%, giving rise to an energy consumption of 3,240 kwh. per ton.

The extensive application of zinc as an anodic protective coating for iron and steel led to the process being first known as "electroalgalvanizing." In fact this is a typical case of an electroplating-process used in the art.

It was recognized, however, that the inherent nature of electroplating baths necessitates limitation of current densities within a certain specified range to secure acceptable metal deposits. If the cathode current density exceeds the specified maximum commonly designated in good practice, the resultant is a so-called "burnt" deposit which is generally dark, flaky, loosely adherent and not acceptable. Excessive cathode polarization at high current densities is a well known phenomenon and the limitation of current density to a narrow range necessary for obtaining a proper character of the plated surface has prevented thicker coatings being applied within periods of time assigned to plating cycles. It should be noted that if the cathode current density could be increased considerably, double for example, without detrimental effect upon the constituency of the plated surface, the time involved would be halved for the same thickness of deposit, or the thickness doubled when continuing the plating for the same time as before. In other words, production or coating would be doubled by doubling the current, but unfortunately the plating current has been found limited to a definite permissible maximum beyond which the resultant deposit is of inferior and unacceptable character, metallurgically and otherwise.

Canadian Pat. No. 446,112 to Buonincontri et al. attempts to overcome the above-noted limiting factors to an extent that will materially increase production with plated surfaces as acceptable or more so than accomplished in practice and more specifically to decrease, for a given thickness and character of deposit, the time involved in producing the result desired. Such patent discloses a method of electrodeposition comprising applying a D.-C. source of current to a piece of work in an electrolytic bath, and superposing a pulsing current on the applied D.-C. current and with the work constantly constituting the cathode for both currents. It will be noted that since the pulsed current is superposed on the D.-C. plating current, the total effective plating current represents the average driving current. The electrodeposition disclosed is typical for noble metals, e.g. silver.

In electrodepositing metals by using direct current alone in the conventional manner or by increasing the current above the maximum allowable density by superimposing thereon a further direct current, unusually great care is required as thicker deposits of electroplated metal are produced, since they tend to become progressively rougher and the quality rapidly deteriorates. Thus, the object of the invention disclosed in U.S. Pat. No. 2,524,912 to Jernstedt is to provide for depositing on a base member a sound and homogeneous electroplate. The metal is electroplated by applying, consecutively and separately, first, a conventional direct current rendering the member cathodic to deposit an increment of metal from the electrolyte, followed by an alternating current alone at a much heavier current density for a brief interval to smooth out and otherwise improve the previously deposited thickness of increment of metal. Repetition of this cycle will build up the required electrodeposit. Plating times can be re-

duced to 25% to 50% of the time required with direct current alone. It is critical that the voltage and current density of the alternating current must be much higher than that of the direct-current portion of the cycle. The electrodeposition disclosed is typical for a metal from the group consisting of copper, silver and brass.

Zinc electrodeposits have been produced with highly desirable uniformity and brightness in applying the process disclosed in U.S. Pat. No. 2,575,712 to Jernstedt. Zinc from a liquid electroplating electrolyte having only zinc dissolved therein as the sole platable metal is plated on the base member when this is the cathode, the zinc being readily depleted from the base member and put into solution in the electrolyte when the base member is the anode. The electroplating process consists in first applying a direct current to the base member and thereafter discharging a condenser through the base member. The prime requirement is that the condenser discharge shall apply enough coulombs of current to deplete metal from the previous deposited zinc on the metal surface. As much as 25% or more of the plated zinc may be depleted with considerable benefit. The electric current to make the base member cathodic is applied with a current density varying from 50 to 150 amperes per square foot; during the discharge of the condenser charged to a potential of from 30 to 1000 volts, the current density reaches a value much greater than with the cathodic current. The coulombs available on discharge of the condenser are in the range from 0.003 coulombs to 10 coulombs per square foot.

The process of electrolytic extraction of zinc, which appears easy in theory, is difficult in practice. The zinc is deposited on aluminium cathodes by the application of direct current through insoluble lead anodes. Simultaneously, the electrolyte is decomposed to form oxygen at the anode and sulfuric acid at the cathode. The operation is affected by several factors, one of the most important being polarization caused by overvoltage. The potential required to deposit zinc on a metal surface in sulfuric acid is 2.35 volts, and the potential to deposit hydrogen under the same conditions is 2.4 volts. This difference of 0.05 volt is the narrow margin which spells success or failure of the commercial production of electrolytic zinc. Any controllable factor that will cause a lowering of the hydrogen overvoltage on zinc should be avoided. The electrode surface should be smooth, circulation must be adequate to provide plenty of zinc ions at each cathode surface, and the temperature in electrolyte should ideally be kept below 35° C. Close spacing of electrodes is desirable to minimize the voltage drop through the solution. The proximity is limited, however, by the tendency of zinc to deposit at localized points on the cathode rather than uniformly over the entire surface. Once such uneven deposition starts, it tends to become self-accelerating, since the resistance of the electrolyte is proportional to the distance between electrodes, and the building out of the so-called "tree" on the cathode reduces this resistance locally, causing current to concentrate along the path of least resistance and to deposit more zinc on the tree, finally resulting in a short circuit. To minimize treeing, a protective colloid is added to the electrolyte. In general, a current efficiency of over 90% can be expected, with lead content as low as 10 p.p.m. in the cathode deposit, if the electrolyte is sufficiently free of impurities, giving rise to an energy consumption of about 3,240 kwh. per ton of zinc. Deposition time is dependent with current densities applied.

The electrowinning or electrolytic extraction process as carried out today is generally considered to derive from Letrange's German Pat. of 1881. The zinc electrolysis step and the rest of the electrowinning procedure were conducted in the prior art in two different modes. According to the so-called "Standard" or Anaconda method, the plant operates with low current-density, low acid, circuits,

where current-density ranges from 20 to 40 amps./sq. ft. of cathode area below solution level. Acid strength of the electrolyte should not rise above 6%. According to the second mode, which is often called the Tainton process after its developer, the procedure is conducted with high current-density, high acid, circuits, in which current-density is normally above 100 amps./sq. ft. Acid strength may range between 22 and 28% H₂SO₄.

Many attempts have been made to increase the limiting maximum of current density effective on the cathode without detriment to the metallurgical or other required characteristics of the resulting plated zinc. In the specification of a prior Tainton U.S. Pat. No. 1,210,017 an electrolytic recovery process is described wherein the concentration of both zinc and acid in the solution contains a fairly high value, such as 140 grams of zinc per liter, and from 50-300 grams of free sulfuric acid per liter. The solution is electrolyzed with insoluble anodes, and with a current of high density between 50 and 300 amperes per square foot. In the same specification it was proposed to operate with a current density as high as 1000 amperes per square foot.

In both the above electrolytic extraction systems care must be taken not to allow the ratio of acid to zinc to become too high or the resolution rate becomes inordinate. Hence in the second described system the zinc content of the electrolyte must be kept much higher than in the first. The advantages accruing to the Tainton method of treatment are: ability of the strongly acid electrolyte to dissolve any zinc ferrite formed in roasting; the dissolving of more iron, hence better purification; production of three times as much zinc per unit of cathode area; improved filtration; and compactness. Balanced against these are: the disadvantages of corrosion of the zinc deposit by strong acid, an equal or greater capital investment per unit of capacity, and the cost of heating the solutions. With high current densities, stripping periods must be more frequent to prevent short-circuiting, because if electrodes are spaced further apart voltage drops rise proportionately. Stripping periods range from 8-72 hr., the shorter intervals being used in the high current-density methods.

Thus, the disadvantages of Tainton's process for the electrolytic extraction of metallic zinc (e.g. high acid concentration, forced circulation of the electrolytes, special arrangements in the bath, development of acid fogs over the bath, etc.) are perhaps the reasons why this mode of treatment is not widely used. The great majority of the prior art processes for extracting zinc by electrolysis were conducted in accordance with the "Standard" method. Newly built plants, however, as for example that of the American Smelting and Refining Co. at Corpus Christi, Tex., use current densities intermediate between these of both the hereinabove described processes, i.e. about 60 amp./sq. ft. With these current densities deposition time is normally 24 hours.

Every effort is made in the art to reduce to a minimum the deleterious impurities contained in the cathodically deposited zinc. In particular, such efforts are directed to reducing the lead content of the cathodic zinc, and the art is constantly seeking methods and means to control the lead contamination in the zinc deposited at the cathode. Thus, U.S. Pat. No. 2,863,810 to Henderson et al. discloses an improvement which comprises coating anodes for the process with a coating of manganese dioxide prior to their use in the zinc electrodeposition step. The current density used is 76.19 amperes per square foot, the voltage drop is 3.2 to 3.5 volts, and the electrolyte temperature is 36° to 38° C. The zinc deposited on the cathode was stripped every 16 hours. The electrolyte entering the tanks contains 191 grams per liter of sulfuric acid, 73.1 grams per liter of dissolved zinc, and 1.55 grams per liter Mn. All of the zinc produced had a lead content well below .003%.

It will be noted that the results obtained with the method of electroplating zinc disclosed in U.S. Pat. No. 2,576,998 to Main et al. were improved by agitation of the bath or by relative movement of the electrolyte and the cathode, as by moving it through the bath or rotating it. Thus, the turbulence of the solution adjacent to the cathode is maintained by projecting jets of the solution through the body thereof toward the cathode.

In the recovery of zinc by electrolysis according to the U.S. Pat. No. 1,322,071 to Stevens, a certain small proportion of glue is added either to the electrolyte before it passes into the cells or to the electrolyte in the cells, in order to minimize the deleterious effect of the impurities upon the deposition of the zinc.

Generally speaking, the electroplating process per se is characterized by cathodic processes of relatively short duration. On the contrary, the duration of the cathodic deposition of the zinc increases many times in the electro-winning processes. The commercial methods of electroplating zinc from sulfate acid baths are directed mainly to the provision of a coating which is sound, whitish in color and uniform in appearance and texture, regardless of the power consumption efficiency. On the contrary, the building out of a "tree" during the cathodic deposition of the zinc in the electro-winning process is not critical unless resulting in a short circuit. The arrangement of the electrodes helps to reduce cathode current density, and therefore the power consumption efficiency, close spacing of electrodes being desirable to minimize the voltage drop through the solution. The amount of impurities is critical in both cases, a strongly acid electrolyte means better purification and hence improved current efficiency; however, strong acid causes corrosion of the zinc deposit. In general, electroplating and electro-winning are considered analogous arts and similar theoretical considerations are involved.

In its broadest aspect, the present invention has as an object thereof the overcoming of the above-mentioned limiting factors to an extent that will materially increase production of electrolytic zinc as acceptable in quality as that produced in prior practice.

More specifically, an object of the invention is to decrease, for a given thickness and character of zinc deposit, the time involved in producing the result desired.

A further object of this invention is to provide for applying zinc to an insoluble electrode employing direct current in combination with the same direct current with its polarity reversed at predetermined intervals.

The electrodeposition process of the present invention consists in first applying a direct current to the first of the electrodes to render this electrode cathodic whereby zinc is deposited thereon, thereafter reversing the polarity of the direct current applied to the first of the electrodes to render this electrode anodic during a predetermined interval, and repeating the cycle until a predetermined thickness of deposited zinc has been produced. Unusual and unexpected results have been obtained by reversing the polarity of the direct current through the electrodes in the cycle. High current densities can be used without disturbing the metallurgical characteristics of the zinc deposit, thereby increasing the effective rate of deposition.

The electrodes are supplied with current flowing from a direct current source. A suitable switching means is interposed in the circuit to reverse the flow of current to the electrodes. The electrode on which zinc is deposited is an aluminium or an aluminium alloy electrode as commonly used in the art. The other electrode is an insoluble one comprised of graphite, lead or another metal with a coating as used in the art. At first the direct current is applied to the electrode on which zinc is deposited, in a manner to render this electrode cathodic, at a determined current density, so that deposition occurs during a certain time interval. This time interval may vary from about 10 to 30 seconds. In actual practice, it has been found

that the current density used may be considerably higher than the current density which is employed for any given electrolyte using continuous direct current. Thus when zinc deposition is carried out conventionally with continuous direct current, the current densities are ordinarily from 60-70, and in some cases up to 100 amperes per square foot. According to the present invention, on the other hand, the current density may vary from 60 to 300 amperes per square foot without undesirable results. It will be noted that the direct current during this period is constant.

After the above-described initial period of from 10 to 30 seconds, the switching means is actuated to reverse the polarity of the direct current supplied to the electrode on which zinc is deposited, in such manner as to render this electrode anodic, at the same current density as first employed. In fact, the current density drops to the value of zero, and immediately thereafter it reaches a value not greater than with the cathodic current firstly applied. The electrode remains anodic during a predetermined interval. Such interval may vary from about 0.06 to 0.24 second. During this interval the direct current remains constant. Thereafter, the current cycle is repeated. In other words, the electrodeposition process is conducted by applying reversed direct current flow at a duration of 0.3 to 1.2% of the whole cycle of flow of the electric current, and the frequency of changing the polarity or sign of the electrodes is 2.0 to 6.0 times a minute.

The exact nature of the reaction that takes place during the reversed-current portion of the cycle is not known. It is believed that the reversed current, due to its parameters, reacts during the anodic portions of the cycle to cause a de-polarization of the cathodic electrode. Before electrolysis starts, the single potentials of the electrodes are alike, having a value that depends upon the zinc-ion concentration of the electrolyte. As electrolysis proceeds, it will be observed that the potential of the anode becomes more positive and that of the cathode more negative than the initial, or equilibrium, potential. The change in potential of an electrode as a result of electrolysis is known as the "polarization" of that electrode. One obvious explanation of such a change in potential is the change in concentration that occurs near an electrode as a result of electrolysis. In the case considered, zinc is deposited at the cathode, and the adjacent solution tends to become less concentrated in zinc sulfate and zinc ions. The polarization at the electrode that is caused by the changes in local concentration of metal salts and ions is known as "concentration polarization." Certain processes such as diffusion, ion migration, and convection (commonly though vigorous agitation) tend to equalize the concentration at the electrodes and in the bath but never produce entirely uniform concentrations. Thus, the change in potential of the cathodic electrode as a result of the reversal of polarity provides an equilibrium potential and corresponds to a change in concentration of the film of solution at the electrode surface. Consequently, the reversal of polarity equalizes the concentration at the electrodes and in the bath, i.e. uniform concentrations are produced.

One obvious advantage in operating with uniform concentrations is the achievement of a more uniform electrocrystallization of the zinc; consequently a more fine crystalline and close-packed structure could be expected.

Generally, an increase in electrolyte concentration produces a decrease in zeta-potential of the electrical double layer which exists in the neighborhood of the charged electrode surface, and ions of high charge of opposite sign to that of the electrode can completely reverse the sign of the zeta-potential. Consequently, the electrokinetic phenomena associated with the movement of the ions, being related to one another through the zeta-potential, are affected by the value and the sign of this potential. Excessive cathode polarization at high current densities is a phenomenon well known in practice. Such a change

in potential corresponds to the change in concentration, and consequently, affects the movement of the ions. As stated above, the reversal of polarity provides an equilibrium potential and tends to equalize the zeta-potentials of both charged electrode surfaces.

Another obvious advantage in operating with equalized zeta-potentials is the lack of a so-called "burnt" deposit which is generally dark, flaky, loosely adherent, and not acceptable.

The tendency of zinc to deposit at localized points on the cathode is the cause of building out of a "tree." This is a tree-like crystal formation. The crystallization starts at a nucleus and proceeds more rapidly in certain axial directions. From these primary branches secondary branches are formed at periodic intervals, and these in turn produce further branches. In this way a skeleton crystal or dendrite is formed. A structure of the dendritic mode of growth is known as a "cored structure." When the anodic direct current is applied, a dissolution of the deposited zinc starts, and the primary branches and nuclei of the dendrites are dissolved to a greater extent than the other spots of the deposited zinc surfaces, since they extend higher from the surface thereon.

It has been observed that after the anodic period of the cycle in accordance with the present invention, the entire deposited zinc is rendered smoother than it was previous to this period. Also, any zinc dissolved now from the anodic rendered electrode is driven into the solution immediately adjacent the electrode, so that a relatively great concentration of zinc ions is present when deposition is resumed during the next interval of direct cathodic current.

Furthermore, the electrical power consumed to form the zinc crystal grating is released during the anodic period, the resistance between the electrodes drops, and therefore the potential in the bath decreases at about that time. The decomposition voltage of water is attained, and hydrogen is liberated at the anodic electrode.

The atomic state of the hydrogen liberated causes the active depolarization of that electrode. The oxygen which was liberated during the former cathodic period of the current cycle is reduced by the hydrogen, so that autocatalytic decomposition and destruction of the insoluble anode is avoided. Furthermore, the atomic state of the hydrogen present causes the reduction of the manganese ions of higher valency present in the electrolyte. In fact, the seven valency oxides of the manganese, produced at the anode because of its oxidizing effect, are strong oxidants and affect the current efficiency. These are, however, unstable and are oxidized to manganese oxides with a lower valency, e.g. permanganates, when reversal of polarity occurs. The permanganates react slowly with more manganese sulfate to precipitate hydrated manganese dioxide. The precipitate adheres to the anode until it builds up sufficiently to fall to the bottom of the tank.

It should be emphasized that the upper limit of time during which the electrode is rendered anodic and the above-noted beneficial processes take place, is quite critical. It has been observed that employing a current cycle anodic period greater than 1.2% of the whole cycle of the electric current is not effective for its intended purposes. In fact, an intensive reduction occurs, and the lead dioxide layer on the electrode is depleted and enters in the solution. Lead is objectionable primarily because it affects cathode metal purity. The lead dioxide is favorable to form dendrites on the cathode and has an oxidizing effect thereon. Furthermore, the specific weight and the electric resistance of the solution are increased.

It is preferable to arrange the zinc electrolysis step so that the concentrations of both zinc and sulfuric acid in the electrolyte fed into the electrolytic tank contain about 100-200 grams per liter of sulfuric acid and about 40-70 grams per liter of dissolved zinc.

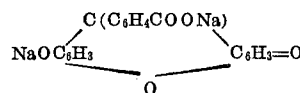
It may be noted in this connection that one of the main difficulties in the prior art arose with the accumulation of

acid in the solution when relatively high values of sulfuric acid were present in the electrolyte fed into the tank. The current efficiency fell off rapidly as the acid content rose. With the current cycle in accordance with the invention and the above-noted concentrations, however, no decrease in the current efficiency was observed.

At the zinc sulfate concentrations typical of those used in the present invention, the hydrogen over-voltage should be observed in any case. Because of this, the process could be conducted on the condition that there are no harmful impurities introduced with the electrolyte. The elements especially harmful in this manner are germanium, antimony, tellurium, cobalt, and arsenic, in decreasing order. The other impurities, such as lead, manganese, copper, iron, chlorine, etc., are tolerated up to the concentrations encountered heretofore in good practice.

The process of the present invention may often be carried out without the addition of any surface-active agent. However, such an agent may be added if desired. It is generally recognized in the electrodeposition of zinc that a certain small proportion of bone glue could be used advantageously. In practicing the method of the invention, 50-100 mg./l. of bone glue were added to the electrolyte with good results.

It has been discovered, however, as a part of the present invention, that when certain small amounts of uranine



(molecular weight 336) are present in the solution, very high cathode voltage values are obtained.

Therefore, a series of tests were carried out using 10-100 mg./l. of bone glue and 15-70 mg./l. of uranine, respectively. The kinetics of the cathode process were followed by changing the cathode voltage value in relation to the current densities applied. The results obtained have shown that the lowest voltage values are observed at all current densities when neither uranine or bone glue was present in the solution. The cathode voltage value varies in linear relation to the logarithm of the current density, i.e. the process as conducted conforms with theory for the delayed discharge of the ions. In raising the concentration of uranine or bone glue, respectively, the cathode voltage values also rose. It was proved, however, that when uranine was used higher voltage values were attained as when bone glue was employed, and it should be noted that this is well in accordance with the rule of Traube, which states that "the cathode polarization increases with the complexity of the molecule of the substance adsorbed on the cathode." The relation is most expressive at high current densities, since organic and inorganic cations or particles are intensively directed to the negative pole. The results have shown, furthermore, that the highest current efficiencies were obtained when 15-35 mg./l. of uranine were added to the solution.

It has been also found that the current efficiency rapidly decreases (60-65%) when about 60-70 mg./l. of uranine were added. It is clear, therefore, that an optimal value of the uranine concentration exists, and that when uranine is added in amounts over this optimum value a decrease in current efficiency occurs.

In using 15.35 mg./l., preferably 20-30 mg./l., of uranine under the set of conditions in accordance with the invention, the electrodeposited zinc surface is smooth and bright, the cathode surface is remarkably wetted by the electrolyte, and the bubbles of hydrogen are more easily removed therefrom, so that the gas-filling of the solution is diminished. Furthermore, the uranine gives rise to a steady foam on the free surface of the electrolyte, thus considerably decreasing the sulfuric acid mist over the bath. On the other hand, the time period for the normal extraction is shortened, and the cathodic zinc is more

brittle. In all probability this is due to the sorption of the uranine particles into the zinc electrodeposit.

By comparison, zinc deposited in using 60–70 mg./l. of uranine results in rapidly decreased current efficiency. A smooth, but dull (burned) and very brittle electrodeposit is obtained on the cathode.

Under the electrolysis conditions according to the invention, when the process is conducted at higher current densities and relatively higher acidity, the temperature of the electrolyte rises considerably. Increased temperature of the electrolyte causes a drop of the hydrogen overvoltage, and shifts the influence of other factors to unfavorable values. Thus, under these conditions the temperature of the electrolyte is maintained at about 30–50° C.

Generally, the zinc electrolysis step is conducted in the conventional manner. Thus, the spent electrolyte may be recycled to the leaching step, and the refortified and purified liquor may be returned to the zinc electrolysis step. Conventionally, the latter step is conducted in accordance with the so-called "circulating" procedure. The circulation of the solutions is effected by supplying fresh solution through several inlet pipes disposed at intervals on the long or the short side walls of the electrolytic cells. These pipes are at a certain distance from the bottom of the cell, and substantially at the same level as the lower end sides of the anodes. The solution flows upwardly and is discharged from the cell through a longitudinal passage disposed in the opposite side wall as regards to the inlets. The slime remains at the relatively calm zone at the bottom, and the impurities are easily carried away by the flowing solution. The "transverse" and "longitudinal" circulation may also be called "channel" circulation. Channel circulation denotes the movement of the solution parallel to the electrode surfaces and perpendicularly to the direction of the distribution of the electric force lines of the ions.

In prior common electrowinning practice the optimal flow rate of the electrolyte within the bath is from about 10 to 50 l./min., depending upon the current density, in tanks having a size of about 2 to 3 m.³. The use of such a flow rate is not recommended in the practice of the present invention, since the process efficiency is decreased thereby despite the use of current reversal. Because of this, in the practice of the present invention, the fresh solution is preferably supplied in the bath with a flow rate which is three times greater than the flow rate required for the complete replacement of the metal in the solution, i.e. three times greater than that theoretically technologically necessary.

To be more precise, the flow rate in 2–3 m.³ tanks required for the complete replacement of the metal in the solution, i.e. that technologically necessary, being also in relationship with the current density, is:

50 amps/sq. ft. (current density)—40 to 60 ml./ah.
 100 amps/sq. ft. (current density)—80 to 140 ml./ah.
 150 amps/sq. ft. (current density)—100 to 200 ml./ah.
 200 amps/sq. ft. (current density)—150 to 300 ml./ah.
 300 amps/sq. ft. (current density)—200 to 400 ml./ah.

As stated the use of such a flow rate is not recommended in the conditions of the present invention. In fact, the recommended flow rate is two to three times greater than the technologically necessary, i.e. the above values should be accordingly raised.

Consequently, the range is from 80 ml./ah. to 1200 ml./ah., depending upon the current density. The preferred values are as follows: 125 ml./ah.; 275 ml./ah.; 375 ml./ah.; 450 ml./ah.; and 750 ml./ah. for the respective current densities of 50, 100, 150, 200 and 300 amps/sq. ft.

This mode of circulation, and this flow rate of the electrolytic, along with the current reversal, have the advantage of decreasing the limitations due to the diffusion

effects and of diminishing the concentration of the impurities in the solution as well as in the electrodes.

There is considerable variation possible in the matter of size, material and design of the tanks, each containing a plurality of anodes and cathodes. Preferably, the anodes are placed in the tank together with the cathodes, so as to be disposed therein with their surfaces parallel to each other and with a cathode on each side of an anode and aligned therewith with the former spaced 20 to 30 mm. from the latter.

Any suitable cathodes and anodes may be used in this invention. However, sheet aluminium or its alloys with titanium, silicon, chromium, and others are preferred for the cathodes. The sheet form is also preferred for the anodes. Insoluble lead anodes containing silver, cobalt, antimony, tellurium, palladium, and silicon could be used. The anodes could be rolled or cast. Anodes made of an appropriate graphite, or platinized titanium, or lead anodes coated with manganese dioxide could also be used. However, sheet lead anodes containing 1% silver, cobalt and antimony are preferred.

The following examples will further illustrate the present invention. It should be understood, however, that the examples are given for purposes of illustration and that the invention in its broader aspects is not limited thereto.

EXAMPLE 1

30 sheet lead anodes containing 1% silver, 0.024% cobalt and 0.26% antimony were placed in an electrolyte tank together with 31 pure aluminium sheet cathodes, with a spacing of 25 mm. between the anodes and cathodes. The tank contained a zinc sulfate electrolyte containing 60 grams per liter zinc and 150 grams per liter sulfuric acid. 25 mg./l. of uranine were added to the solution. The electrolyte temperature was 40° C. and the electrolyte was circulated through the tank during the electrolysis with a flow rate of 375 ml./ah., which was three times greater than that technologically necessary. A bidirectional electrical current to provide a voltage drop of 3.4 volts between the electrodes and to impress a current density of 150 amperes per square foot was passed through the aluminium sheets and the electrolyte so as to render the former cathodic for a period of time of 15 sec. to electrodeposit zinc thereupon, and then with reversed current flow through the aluminium sheets and the electrolyte to render the former anodic for a shorter period of time of 0.12 sec. The bidirectional electrical current cycle was repeated for 20 hours. Then the bank of cathodes in the tank was removed, the zinc was stripped therefrom, and the cathodes were reinserted in the tank. Inspection of the electrodeposited zinc surfaces has shown that these are smooth and bright. The zinc produced was of high purity of 99.99% Zn. The current efficiency was 91%, and the energy consumption was 3700 kwh. per ton of zinc produced.

EXAMPLE 2

The process was carried out with the above anodes and cathodes, but with a zinc sulfate electrolyte containing 50 gr./l. zinc and 130 gr./l. sulfuric acid and with an electrolyte flow rate of 150 ml./ah. The electrolyte temperature was 33° C. and 20 mg./l. of uranine were added to the solution. The bidirectional electric current had a current density of 60 amperes per square foot; the current passed first as a cathodic current through the aluminium sheets for a period of time of 20 sec. and then passed as a reversed current flow for 0.12 sec. The zinc was stripped after 48 hours. The zinc surfaces were smooth and bright. The production was of a high purity of 99.99% Zn. The current efficiency was 93% and the energy consumption was 3250 kwh. per ton of zinc.

EXAMPLE 3

The process was carried out with the above anodes and cathodes but with a zinc sulfate electrolyte containing

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70 gr./l. zinc and 200 gr./l. sulfuric acid and with an electrolyte flow rate of 750 ml./ah. The electrolyte temperature was 45° C., and 30 mg./l. of uranine was added to the solution. The bidirectional electric current used was impressed a current density of 300 amperes per square foot, and passed first as a cathodic current through the aluminium sheets for a period of time of 15 sec. and then as a reversed current flow for 0.18 sec. The zinc was stripped after 12 hours and the zinc surfaces were smooth and bright. The production was of a purity of 99.95% Zn. The current efficiency was 99% and the energy consumption was 4400 kwh. per ton zinc.

The invention is illustrated and described with a reference to a plurality of preferred embodiments thereof and it is to be understood that it is in no way limited to said plurality of embodiments but is capable of numerous modifications according to the appended claims.

What is claimed is:

1. A method for the electroextraction of zinc at high current density comprising preparing an electrolyte comprising sulfuric acid and zinc, and applying reversed current flow from a single source at a duration of 0.3 to 1.2% of the whole cycle of the electric current, the frequency of changing the sign of the electrodes being 3.0 to 6.0 times a minute, and the current density employed being in the range of 60-300 a./ft.² of electrode area and being the same in both directions of current flow.

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2. The method for the electrolytic preparation of zinc according to claim 1, comprising providing a transverse and a longitudinal circulation of the solution from below upwards.

3. The method for the electrodeposition of zinc according to claim 1, wherein the electrolyte comprises 100 to 200 g./l. sulfuric acid, and 40 to 70 g./l. zinc.

4. The method for the electrodeposition of zinc according to claim 1, wherein the electrodeposition process is carried out with the temperature of the electrolyte at about 30° C. to 50° C.

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