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ELECTROGALVANIZING PROCESS

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This invention relates to new and useful improvements in electrogalvanizing processes.

Commercial electrogalvanizing as practiced at the present time is carried out either in sulfuric acid or cyanide solutions. When heavy coatings are required on wire, strip or similar products the work is done exclusively with sulfuric acid solutions. In one type of process for depositing heavy coatings the zinc is derived from anodes of relatively pure zinc. In another type, insoluble anodes are employed with electrolytes prepared by dissolving zinc metal or ore of lower purity in sulfuric acid and purifying the solution. The spent electrolyte is used to dissolve more zinc metal or ore, the solution thus obtained being repurified and used again as an electrolyte. Since sulfuric acid is effective to leach zinc from comparatively cheap zinc-bearing materials, this process offers a means of utilizing some of the less expensive forms of zinc for electrogalvanizing without first isolating the pure metal in the form of anodes, but it requires that numerous impurities be excluded from the electrolyte before a satisfactory deposit can be obtained and hence is not commercially feasible for the use of some raw materials.

Proposals have been made for the production of electrolytic zinc from roasted ores and like materials by dissolving such materials in solutions of ammonia and ammonium carbonate, or of ammonia and ammonium sulfate, instead of the usual sulfuric acid electrolyte. Such solutions readily dissolve zinc oxide and other zinc-bearing materials, except the metal, and can be purified by simple and inexpensive means. So far as we have been able to discover, however, no one has succeeded in obtaining smooth, adherent and ductile deposits suitable for plating from such solutions under practical operating conditions. In laboratory experiments reported in the literature, current densities in excess of about 40 amperes per square foot were found to result in porous, unsatisfactory deposits. To make an electrogalvanizing process commercially attractive current densities of at least 500 and preferably 1000 amperes per square foot or more are desirable. Furthermore, in these experiments various addition agents such as gum arabic and gelatin were used in the electrolyte in order to obtain satisfactory deposits even at very low current densities.

An object of our invention is to provide a new and improved electrogalvanizing process which meets the commercial requirements for electrogalvanizing on wire or strip and produces rela-

tively thick zinc coatings of high quality due to their smoothness, ductility and strong adherence to the base metal.

Another object of our invention is to provide an electrogalvanizing process in which various zinc-bearing materials, including materials which are low in price because of their chlorine content, may be utilized economically as the source of the zinc. In known commercial electrogalvanizing processes even small amounts of chlorine are objectionable. Since zinc chloride is volatile at elevated temperatures, zinc-bearing materials which contain much chlorine cannot be treated effectively by ordinary metallurgical practices. The result is that if materials containing chlorine are to be used as a source of zinc they must first be subjected to weathering and roasting or other treatments which remove all but a trace of the chlorine. These special treatments, apart from their expense, cause the loss of considerable zinc.

Another object of our invention is to provide an improved electrogalvanizing process which enables the production of high quality galvanized stock from solutions of low grade zinc-bearing materials without requiring complicated or expensive purification of the solutions or the use of colloidal addition agents.

Another object of the invention is to establish operating conditions under which relatively heavy, smooth, adherent electrolytic coatings of high purity zinc may be produced from ammoniacal zinc solutions.

Still another object of our invention is to provide an improved electrogalvanizing process employing a novel ammoniacal zinc electrolyte.

Further objects and advantages of the invention will appear from the ensuing part of this specification, which includes a detailed description of illustrative embodiments of our improved electrogalvanizing process.

We have found that the present commercial electrogalvanizing process, in which a substantially pure sulfuric acid electrolyte is essential, can be substituted to advantage by a new process employing an ammoniacal solution of a complex zinc ammonium salt and high current densities for electrolysis, with special control over the concentrations of zinc and ammonia in the solution and the movement of the solution with respect to the work during the plating operation. Contrary to prior expectations, excellent galvanized stock of a quality comparable to the best commercial product now on the market may be produced by our process, and the process possesses

economic advantages which make it distinctly superior to known practices in many respects.

The electrolyte used in this process is a solution of a complex zinc tetrammine salt containing four atoms of ammonia and one atom of zinc in the molecule. Any of the ordinary zinc compounds is suitable as a source of zinc. The electrolyte may be prepared, for example, by leaching oxidized zinc compounds with a solution containing ammonia and an ammonium salt, such as ammonium chloride, ammonium sulfate or ammonium carbonate, in proportions selected to form the complex zinc tetrammine salt and furnish a considerable excess of free ammonia.

An important feature of our invention consists in the provision of a process utilizing ammoniacal solutions containing chloride as the electrolyte. We have found that even better zinc coatings may be obtained from such solutions than from corresponding solutions containing ammonia and other ammonium salts. In addition to the provision of a distinctly new type of electrolyte for electrogalvanizing, this discovery is especially important because it makes it possible to use zinc-bearing raw materials which contain chlorine as the source of zinc, without preliminary treatment to eliminate chlorine. One such material is sal skimmings, which is a by-product of hot galvanizing and is the cheapest form in which zinc can be purchased at the present time. Although variable in composition, sal skimmings generally contain from 40 to 50% zinc, up to 35% chlorine, less than 2% iron and the balance oxygen and dirt. The use of sal skimmings and similar materials as a source of zinc for electrogalvanizing effects a substantial reduction in the cost of the zinc-coated product.

In plating from these ammoniacal zinc solutions current densities of from 500 to 1000 amperes per square foot of cathode surface or greater are used for optimum performance. Galvanized wire possessing a relatively thick and uniformly smooth, adherent and ductile coating of zinc may be obtained from such solutions under properly controlled conditions at current densities of approximately 1000 amperes per square foot, and coatings of like quality are produced on objects of greater surface area wherever similar current densities are locally effective. Depending upon the uniformity of current distribution and the "edge effects" encountered adjacent the work being plated, average current densities considerably lower or higher than the preferred values may be used, as will be understood by persons skilled in the art. At the high current densities we employ, large tonnages of excellent galvanized stock can be obtained with a relatively small plant investment.

Another advantageous feature of our process is that the ammoniacal zinc solutions used as the electrolyte are much less sensitive to impurities than the sulfuric acid solutions heretofore employed in the art. Good coatings of zinc may be obtained from an ammoniacal solution prepared simply by leaching treated and milled zinc ash, with no purification whatever except to oxidize and remove the iron. A solution of this type may contain enough copper to give it a blue color, and may also contain cadmium and other impurities. A sulfuric acid solution made from the same raw material would require thorough removal of these impurities before equally satisfactory results could be obtained.

In the practice of the process the ammoniacal

zinc solution should be prepared with a high zinc content and an excess of free ammonia, and vigorous agitation of the solution should take place during electrolysis.

For satisfactory operations the zinc content of the solution should not be allowed to fall much below 100 grams per litre, and in no event below 80 grams per litre, since there is a tendency for the zinc coating to become spongy, instead of smooth and compact, at lower zinc concentrations and also an increased tendency toward tree formation at any point where the current density is even momentarily higher than the average. Best results are obtained when the zinc content is kept as high as 110 to 150 grams per litre. Zinc concentrations of the order specified can be maintained continuously by using solution from which zinc has been partially removed for leaching fresh zinc-bearing material.

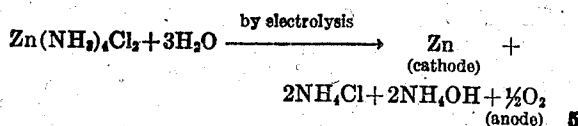
When the solution contains little or no excess free ammonia the coatings are usually rough. On increasing the free ammonia content the coatings become smoother. With enough free ammonia they are so smooth that they have a silky feel when the finger is run over them. The free ammonia content should not be allowed to drop below about 8 grams per litre for good results. Increasing the ammonia content beyond this point does no harm and indeed may be slightly beneficial as far as the coating is concerned. The only objection to maintaining a larger excess of free ammonia than is necessary comes from the fact that with more free ammonia the tendency of the solutions to lose ammonia is increased.

Suitable relative motion between the solution and the work during electrolysis can be effected by agitation, either with the use of special agitating means or by movement of the work being plated. The only essential is that relative motion between the work and the solution be maintained at sufficient vigor to produce turbulent or eddy motion in the solution adjacent the work. In electrogalvanizing wire, for example, the wire may be drawn through the solution rapidly enough to maintain the conditions necessary for good deposits. The critical speed of the work, at which turbulent flow of the solution is obtained, is determined by the value of the Reynolds modulus. The critical speed is fixed by the density of the solution, the viscosity, and the diameter of the wire. In some cases, it may be necessary to depend partly, and in others entirely, on agitation by means other than movement of the work, as will be understood fully by persons skilled in the art.

These three factors, zinc content, free ammonia content and agitation, are interrelated to a considerable degree. Thus, increasing the zinc content allows less vigorous agitation, for example, a slower rate of movement if the work is being moved. Conversely, when the zinc content of the solution is relatively low more vigorous relative motion between the work and the solution is necessary to obtain a coating of highest quality. The amount of free ammonia bears somewhat the same relation to the degree of agitation as the zinc content.

In carrying out this process the selected zinc-bearing raw material, for example raw zinc ash, treated and milled zinc ash, zinc oxide or sal skimmings, is first leached with a solution of ammonia and an ammonium salt in order to dissolve the zinc. The reaction which takes place in our preferred embodiment, using a solution of ammonia and ammonium chloride and assuming

zinc oxide to be the material dissolved, is believed to be essentially as follows:



As pointed out above, the electrolyte thus obtained is prepared with at least 8 grams, or approximately $\frac{1}{2}$ mol, per litre or more of excess free ammonia and is preferably made of sufficient concentration to contain more than 100 grams of zinc per litre of electrolyte. In speaking of excess or free ammonia we mean the amount of ammonia present in excess of that required to form a zinc tetrammine salt and to combine with acid radicals present in the solution. Various complex salts of zinc and ammonia may be present, but we find it convenient to assume the presence of the tetrammine salt and to consider ammonia in excess of 4 moles per mole of zinc as uncombined with zinc. In addition to the excess of free ammonia we prefer to employ an excess of an ammonium salt such as ammonium chloride or ammonium sulphate, since we find that this practice improves the conductivity of the solution and reduces energy consumption during electrolysis. A considerable excess of such ammonium salt has no deleterious effect on the quality of the zinc coating.

In several embodiments of our process, wherein sal skimmings or raw zinc ash are used as the source of zinc, substantial purification of the electrolyte occurs automatically due to the fact that considerable metallic zinc is always present in sal skimmings and usually in raw zinc ash. When treated and milled zinc ash or other zinc-bearing raw materials including very little or no metallic zinc are used as the source of zinc, it may be desirable to precipitate certain impurities by adding zinc dust or scrap zinc to the solution or by treating it with hydrogen sulfide. It is generally desirable to remove the traces of iron which may be present in the solution by oxidation, for example with hydrogen peroxide. A small addition of oxidizing agent suffices to oxidize the little iron that is present when the usual raw material is employed.

Any preliminary purification of the electrolyte which may be found desirable, or in fact any operation with this solution, is preferably carried out in closed vessels in order to avoid ammonia losses. The electrolyte thus prepared is then filtered thoroughly to remove suspended matter and led to an electrolytic cell, where the electrogalvanizing takes place.

The anodes employed in electrolyzing consist of insoluble materials; the cathode is the work being galvanized, as in present commercial practice. When the electrolyte is an ammoniacal zinc solution which does not contain chloride, anodes of iron, and preferably of 18:8 stainless steel, may be used. When the electrolyte contains chloride we prefer gas carbon or graphite anodes, since ferrous anodes are attacked under these conditions.

During the electrolysis a high cathode density is used, preferably as high as 500 to 1000 amperes per square foot, although the value of the process is not restricted to such preferred current densities but extends also to other commercial operations using high current densities. In galvanizing wire, the wire may be moved through the solution at a rate sufficient to maintain proper agitation, as explained above. The reaction occurring in the electrolyzing cell, using a chloride electrolyte, is substantially as follows:

This reaction is typical of what occurs where solutions of ammonia and other ammonium salts such as ammonium sulfate and ammonium carbonate are employed as the electrolyte.

It will be observed that oxygen passes off at the anodes. To permit the escape of this oxygen and at the same time to avoid substantial loss of ammonia, the electrolysis preferably is carried out in a closed but vented vessel. In addition, when operating the process continuously it is desirable that the solution in the electrolyte cell be filtered continuously in order to exclude accumulating solids which otherwise may be carried into the deposit and cause it to become rough.

The current efficiency in electrogalvanizing according to this process is so high that hardly any hydrogen evolution is perceptible at the cathode. When the conditions are not at the optimum, as for example when the zinc content is lower than desired or the agitation is insufficient, more hydrogen is formed. Under these conditions bubbles of hydrogen may sometimes adhere to the cathode surface and cause a spongy deposit. We have found it helpful in such circumstances to add a small quantity of a surface tension depressant to the solution. As little as 10 to 20 milligrams per litre of sodium lauryl sulfate reduces the size of the bubbles considerably and reduces the tendency of the bubbles to adhere, thus permitting better deposits to be obtained.

The temperature of the solution while galvanizing is not critical, but it is desirable to avoid high temperatures in order to minimize ammonia losses. At the high current densities used in this work, the solution tends to increase in temperature; hence provision should be made for cooling the solution, as by the use of cooling means within the electrolytic cell or by circulating the solution through suitable cooling apparatus. Temperatures of about 30° C. have been found to give very good results.

After the zinc has been partially removed from the ammoniacal zinc solution and the conditions for obtaining a good deposit become more exacting, the solution is preferably enriched by using it to leach fresh zinc-bearing material. A suitable procedure for continuous operation of the process is to circulate the solution continuously back and forth between the electrolytic cell and the leaching tanks so as to keep the electrolyte reasonably uniform in composition during electrolysis. Continuous counter-current leaching is desirable to insure efficient extraction of zinc and to maintain a high zinc content in the solution.

The importance and advantages of our process will be further understood by persons skilled in the art from the following description of illustrative embodiments.

Example I

Commercial sal skimmings were used as a raw material for the production of high grade electrogalvanized stock. The sal skimmings were leached with a solution of ammonia and ammonium chloride until an electrolyte showing approximately the following composition was obtained:

	Grams per litre
Zinc.....	104
Chloride.....	159
Total ammonia.....	164.2
5 Including:	
Ammonia combined as zinc tetra-	
mine salt.....	about 108
Ammonia combined as ammonium	
chloride.....	about 22
10 Free ammonia.....	about 34

A small amount of oxidizing agent, hydrogen peroxide, was added to the solution to oxidize the small amount of iron therein, resulting in a precipitate which was filtered off before introducing the solution into the electrolytic cell. Without further purification, the solution was used to electrogalvanize 12 gauge steel wire, employing graphite anodes and a cathode current density of 1000 amperes per square foot. The wire was made to travel through the bath at a linear speed of at least 120 feet per minute, no further agitation being essential. It issued from the cell with a smooth, adherent and ductile coating of zinc, which was attractive in appearance and consisted of 1 ounce or more of zinc per square foot. The galvanized product was bent and worked without evidence of loosening or rupturing the coating.

30 Example II

Raw zinc ash was leached with a solution of ammonia and ammonium chloride until a solution showing the following composition was obtained:

	Grams per litre
Zinc.....	91.6
Chloride.....	159.5
Total ammonia.....	159.9
40 Including:	
Ammonia combined as zinc tetramine	
salt.....	95.3
Ammonia combined as ammonium	
chloride.....	28.9
45 Free ammonia.....	35.7

The solution was oxidized to remove iron, filtered and electrolysed substantially as in Example I.

Example III

50 A solution having the composition indicated below was obtained by leaching zinc ash with a solution of ammonia and ammonium sulfate:

	Grams per litre
Zinc.....	101
Sulfate.....	228
Total ammonia.....	146.4
Including:	
Ammonia combined as zinc tetramine	
salt.....	105.4
60 Ammonia combined as ammonium	
sulfate.....	28.2
Free ammonia.....	12.8

65 After preliminary purification and filtration this solution also was used for electrogalvanizing wire at high cathode current densities, substantially as in Example I.

When employing sal skimmings as a source of zinc in the practice of our process, the solution in the electrolytic cell preferably is continuously withdrawn therefrom, passed to the leaching tank, enriched with zinc by flowing it in counter-current relation to more sal skimmings, treated again with an oxidizing agent, filtered, and re-
75 introduced into the cell. In addition, chloride is

continuously extracted from the solution, since chloride otherwise would keep building up to an objectionable extent by accretions from the sal skimmings. This can be done economically by treating part of the spent solution from the electrolytic cell with lime and heating. The ammonia in the solution comes off in the vapor and is recovered either by passing it through a scrubbing tower countercurrent to cold water or by passing it directly back to, and absorbing it in, the leaching solutions. The zinc contained in the spent cell solution is precipitated by the lime treatment and can be redissolved in the leaching operation. No special care is necessary to obtain the zinc precipitate free from chloride or calcium. 15

As an alternative method of operation, most of the zinc-bearing raw material can be substantially free of chloride, only enough sal skimmings being used to furnish the chloride lost in the cycle. The amount of chloride in the raw material and consequently the amount of solution treated for elimination of chloride when operating continuously are purely economic questions, depending on the cost of zinc in the form of sal skimmings and its cost in the form of chlorine-free oxidized materials. 25

While we do not wish to be bound by any theory as to the mechanism of our process, a working hypothesis has been developed which may explain the significance of maintaining an excess of free ammonia and agitating the solution during electrolysis: Only the main part of the current is effective in depositing zinc. The balance tends to liberate hydrogen and produce an equivalent amount of alkali at the cathode. During electrolysis at the high current densities employed, even though the current efficiency for zinc deposition is very high, the solution immediately adjacent the cathode becomes much more alkaline than the bulk of the solution. As a result, there is a tendency to form insoluble basic zinc compounds, which tend to be carried into the deposit and to cause it to become rough. 40

The presence of sufficient free ammonia is believed to keep these compounds in solution, thereby preventing interference with the orderly growth of the crystal lattice of the coating. 45

The apparently critical effect of relative motion between the work and the solution is believed to be related to the above phenomena. When wire is moved through the solution, it drags along with it a film of solution, the thickness of which depends on the speed of the wire. The wire being cathodic, the zinc content of the film tends to become depleted, and the alkalinity tends to become excessive, so that conditions unfavorable to the production of a good electrodeposit are soon established unless zinc and free ammonia reach the film rapidly enough by diffusion from the main body of the solution. The thickness of the film across which diffusion must take place is therefore an important factor in determining whether the coating will be smooth and compact or rough and non-adherent. The faster the wire moves, the thinner the cathode film will be and the better the coating. The greatest change is produced when the motion of the wire is increased to such a speed that the motion of the adjoining layer of solution changes from straight line to turbulent flow. This is the critical speed, determined by the value of the Reynolds modulus. 50 55 60 65 70

In the foregoing specification we have described our improved electrogalvanizing process and illustrative embodiments thereof in considerable detail and have presented an hypothesis 75

which may explain its operation. This description has been given by way of explanation and illustration only, since we are aware that numerous changes in the materials and in the conditions and mode of operation may be made by persons skilled in the art without departing from the principles of the invention. We therefore desire that the invention be accorded a scope consistent with the spirit of the specification as limited only by the requirements of the claims.

We claim:

1. The process of producing smooth electrogalvanized products which comprises passing a current at high cathode current density through a concentrated ammoniacal zinc solution in which the work being plated is immersed as the cathode, said solution containing ammonia substantially in excess of the amount required to form zinc tetramine compound with all of the zinc in solution.

2. The process of producing smooth electrogalvanized products which comprises subjecting the work to be plated to a current having a density of at least 500-1000 amperes per square foot in a concentrated ammoniacal zinc solution, said solution containing ammonia substantially in excess of the amount required to form zinc tetramine compound with all of the zinc in solution.

3. The process of producing smooth electrogalvanized products which comprises passing a current at high cathode current density through a solution of zinc tetramine salt containing more than 80 grams of zinc per litre and a substantial excess of ammonia, in which the work being plated is immersed as the cathode, and maintaining relative motion between the work and said solution during electrolysis.

4. The process of producing smooth electrogalvanized products which comprises passing a current at high cathode current density through a solution of a zinc tetramine salt containing more than 80 grams of zinc per litre and at least 8 grams per litre of excess ammonia, in which the work being plated is immersed as the cathode.

5. The process of producing smooth electrogalvanized products which comprises subjecting the work to be plated to a cathodic current of high density in a solution of a zinc tetramine salt containing more than 80 grams of zinc per litre and at least 8 grams per litre of excess ammonia, and maintaining relative motion between the work and said solution during electrolysis.

6. The process of producing smooth electrogalvanized products which comprises subjecting the work to be plated to a cathodic current of high density in a solution of a zinc tetramine salt containing more than 80 grams of zinc per litre and at least 8 grams per litre of excess ammonia, and maintaining turbulent flow in the solution adjacent the work during electrolysis.

7. The process of claim 6 in which the work to be plated is passed through the solution at a rate sufficient to maintain turbulent flow of solution adjacent thereto.

8. The process of producing smooth electrogalvanized products which comprises dissolving zinc from zinc-bearing raw material in a solution of ammonia and an inorganic ammonium salt to produce an electrolyte containing more than 100 grams of zinc per litre in the form of a zinc tetramine salt and an excess of ammonia and depositing metallic zinc onto work immersed in the electrolyte, by passing current of high cathode current density through the electrolyte while

maintaining relative motion between the same and said work.

9. The process of producing smooth electrogalvanized products which comprises dissolving zinc from zinc-bearing raw material in a solution of ammonia and an inorganic ammonium salt to produce an electrolyte containing more than 100 grams of zinc per litre in the form of a zinc tetramine salt and an excess of ammonia, treating the electrolyte to precipitate iron therein, filtering the same to remove suspended matter, and depositing metallic zinc onto work immersed in the electrolyte by passing current of high cathode current density through the electrolyte while maintaining relative motion between the same and said work.

10. The process of electrogalvanizing which comprises dissolving zinc from zinc-bearing raw material in a solution of ammonia and an inorganic ammonium salt to produce an electrolyte containing more than 80 grams of zinc per litre in the form of a zinc tetramine salt and an excess of ammonia, depositing metallic zinc onto work immersed in the electrolyte by passing current of high cathode current density through the electrolyte while maintaining relative motion between the same and said work, dissolving additional zinc in electrolyte from which zinc has been deposited and depositing additional zinc therefrom onto work to be plated as aforesaid.

11. In a process of producing smooth electrogalvanized products, the step which comprises electrolyzing an ammoniacal zinc solution containing chloride and ammonia in amounts sufficient to form zinc tetramine chloride with the zinc, said solution also containing a substantial excess of ammonia.

12. The process of producing smooth electrogalvanized products which comprises dissolving zinc from sal skimmings in a solution of ammonia and ammonium chloride to produce an electrolyte containing more than 80 grams per litre of zinc in the form of a zinc tetramine salt and an excess of ammonia, and depositing metallic zinc onto work immersed in the electrolyte by passing current of high cathode current density through the electrolyte while maintaining relative motion between the same and said work.

13. The process of producing smooth electrogalvanized products which comprises dissolving zinc from sal skimmings in a solution of ammonia and ammonium chloride to produce an electrolyte containing more than 100 grams per litre of zinc in the form of a zinc tetramine salt and an excess of ammonia, depositing metallic zinc onto work immersed in the electrolyte by passing current of high cathode current density through the electrolyte while maintaining relative motion between the same and said work, leaching sal skimmings with electrolyte from which zinc has been deposited to increase the zinc content thereof and thereafter depositing more metallic zinc therefrom as aforesaid, and extracting chloride from said electrolyte to prevent objectionable accumulation of chloride by accretion from the sal skimmings.

14. The process of producing smooth electrogalvanized products which comprises dissolving zinc from low grade zinc-bearing raw material by leaching the same with a solution of ammonium and ammonium chloride to produce an electrolyte containing more than 80 grams per litre of zinc in the form of a zinc tetramine salt and at least 8 grams per litre of excess ammonia, treating the electrolyte with metallic zinc, treat-

ing the electrolyte to remove iron, filtering the treated electrolyte, and thereafter depositing zinc onto work immersed in the electrolyte by passing current through the electrolyte while maintaining relative motion between the same and said work sufficient to cause turbulent flow in the electrolyte adjacent the work.

15. The process of producing smooth electro-galvanized products wire which comprises passing wire at a speed of at least 120 feet per minute through a solution of a zinc tetrammine salt containing at least 100 grams of zinc and at least 8 grams of excess ammonia per litre, and passing current at a density at least of the order of 500 to 1000 amperes per square foot of cathode surface through said solution and wire.

16. An electrolyte for electrolysis containing in aqueous solution more than 80 grams of zinc per litre, acid radicals from the group consisting of chloride, sulphate and carbonate radicals in excess of the amount required to form zinc tetrammine compound with all of said zinc, and ammonia in excess of the amount required to form said zinc tetrammine compound and to form ammonium compound with the excess of said acid radicals.

17. An electrolyte for electrolysis comprising a concentrated solution of a zinc tetrammine compound, said solution containing at least 8 grams per litre of excess ammonia.

18. An electrolyte for electrolysis comprising an aqueous ammoniacal zinc solution containing at least 100 grams of zinc per litre, ammonia and acid radicals from the group consisting of chloride, sulphate and carbonate radicals in amounts at least sufficient to form zinc tetrammine compound with all of said zinc, and at least 8 grams per litre of excess ammonia.

19. An electrolyte for electrolysis comprising an aqueous ammoniacal zinc solution containing ammonia and chloride in amounts at least sufficient to form zinc tetrammine chloride with all of the zinc, said solution containing at least 8 grams of excess ammonia per litre.

20. An electrolyte for electrolysis containing in aqueous solution more than 80 grams of zinc per litre, chloride in excess of the amount required to form zinc tetrammine chloride with all of said zinc, and ammonia in excess of the amount required to form said zinc tetrammine chloride and to react with the excess of said chloride.

21. An electrolyte for electrolysis comprising an aqueous solution containing more than 100 grams of zinc per litre, more than 108 grams of chloride per litre and ammonia in excess of the amount required to form zinc tetrammine chloride with all of the zinc and ammonium chloride with any chloride that does not enter into the zinc tetrammine chloride.

22. The process which comprises electrolyzing at high cathode current density an ammoniacal zinc solution containing more than 80 grams of zinc per litre, acid radicals from the group consisting of chloride, sulphate and carbonate radicals substantially in excess of the amount required to form zinc tetrammine compound with all of said zinc and ammonia substantially in excess of the amounts required to form said zinc tetrammine compound and to form ammonium compound with the excess of said acid radicals, and maintaining turbulent flow in said solution adjacent the cathode during the electrolysis.

23. The process which comprises electrolyzing at a cathode current density of at least 500 to 1000 amperes per square foot, an ammoniacal zinc chloride solution containing more than 80 grams of zinc per litre, chloride radicals substantially in excess of the amount required to form zinc tetrammine chloride with all of said zinc and ammonia substantially in excess of the amounts required to form said zinc tetrammine chloride and to form ammonium chloride with the excess of said chloride radicals, and maintaining turbulent flow in said solution adjacent the cathode during the electrolysis.

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