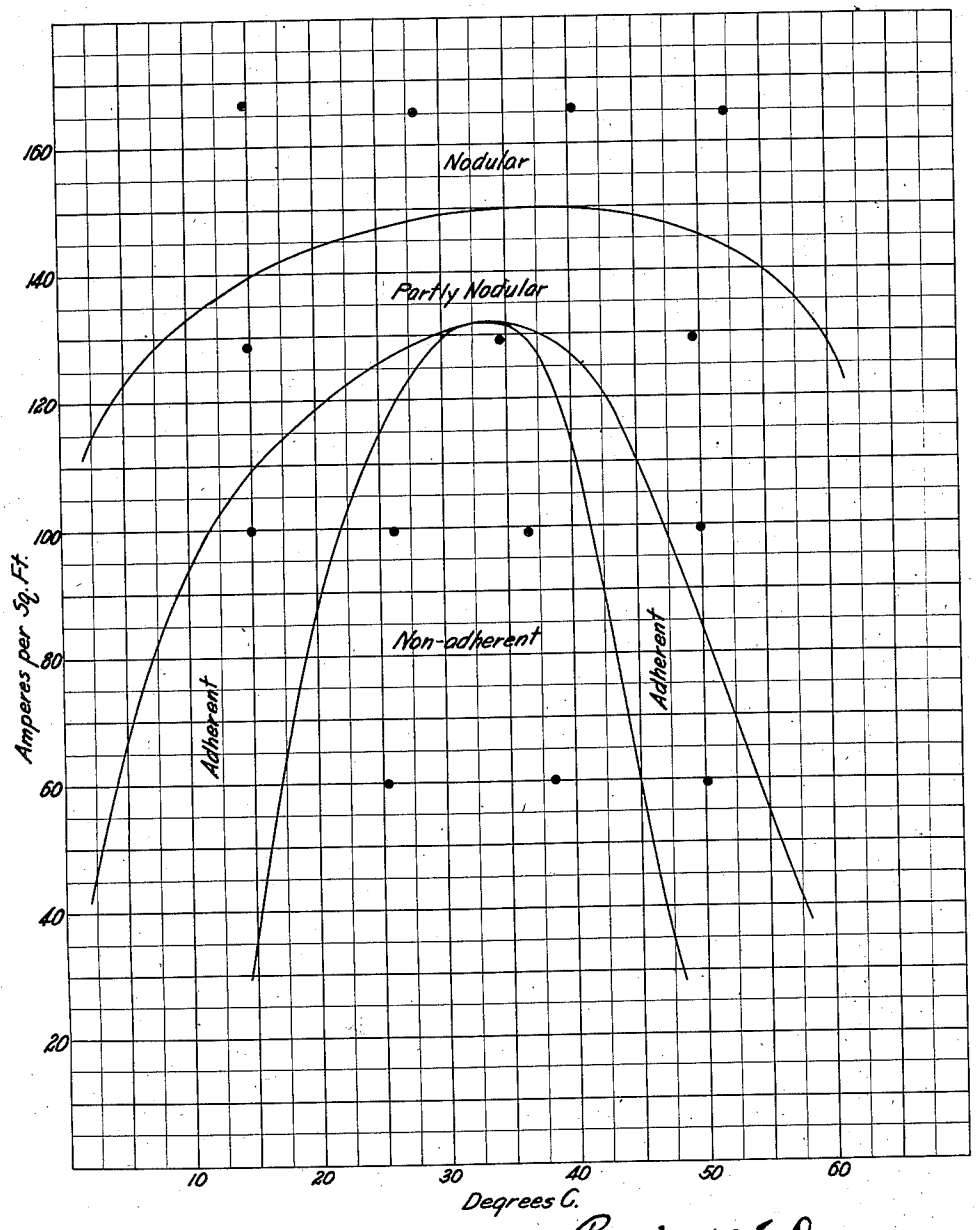
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ELECTRODEPOSITING MANGANESE

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ELECTRODEPOSITING MANGANESE

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This invention relates to the electrodeposition of manganese. It relates especially to processes for producing electrolytic manganese from pure manganous oxide or manganous carbonate. The invention has for its principal object the deposition of manganese from solutions of manganese salts containing pure manganous carbonate or oxide or other acid-soluble oxidic compound of manganese yielding a pure manganous salt by reaction with dilute acid in a state of suspension in such solutions. It also has for its aim the production of electrolytic manganese in a single compartment cell.

In the heretofore practiced art of electrodepositing manganese, it has been the practice to use a diaphragm cell. The reason for this practice will be clear from a consideration of the necessary conditions for depositing manganese. Since manganese is less noble than hydrogen, it can only be deposited from solutions of low hydrogen ion concentration, that is, from alkaline solutions. In the electrolysis of manganese solutions, the electrolyte immediately adjacent to the cathode becomes alkaline, and the electrolyte adjacent to the anode becomes acid. The overall effect, however, in electrodepositing manganese, is to free one equivalent of acid for each equivalent of manganese. The necessary alkalinity at the cathode can accordingly be maintained only by preventing complete diffusion of the acid, formed at the anode, into the cathode area. This has been accomplished in the known art by the interposition of a diaphragm between anode and cathode. Under these conditions, the alkalinity at the anode may be allowed to rise to almost any desired point. Since manganese salts are precipitated at a pH near 7, ammonium salts are usually added to prevent this precipitation.

It has also been proposed to prevent the diffusion of the acid, formed at the anode, to the cathode area by a rapid flow of solution through the cell, and also by the addition of ammonia to the cell. It will be obvious that these expedients are not practical because, in the first instance, only a very little manganese can be removed from a given volume of solution, and replenishment and readjustment of pH to the original condition becomes uneconomical. In the second instance, the accumulation of ammonium salts in the circuit eventually interferes with the process.

I have found that the diffusion of the acid formed at the anode may be conveniently controlled by the presence in the anode area of suspended particulate manganous oxide or manganous carbonate, or other oxidic compound of manganese yielding a pure manganous salt by reaction with dilute acid. These compounds not only serve to control acid diffusion but at the same time they replenish the manganese content of the electrolyte. If these compounds are pure, they do not interfere with the deposition of manganese. I have further found that the presence of these solid compounds, suspended in the electrolyte, does not in any way disturb the deposition of manganese; consequently, they may be suspended in the electrolyte which flows over the cathode. The evolution of hydrogen, which always accompanies the deposition of manganese, prevents the inclusion of any of the suspended solids in the cathode deposit.

It will be clear that these discoveries concerning the behavior of a suspension, in the electrolyte, of particulate acid-soluble oxidic compounds of divalent manganese, more particularly pure manganous oxide or manganous carbonate, lead to many important improvements in the process of electrodepositing manganese.

The pure manganous oxide and manganous carbonate of my invention may be prepared in many ways known in the art. I prefer to make manganous carbonate in accordance with my invention described in U. S. Patent No. 2,608,463. Pure carbonate may be converted to oxide, in whole or in part, by heating, and the use of partially decomposed carbonate is within the scope of my invention, as is also the use of manganous hydroxide, hydrated manganous oxide, or any other oxidic manganese compound which yields a pure manganous salt by reaction with dilute acid.

Perhaps the simplest embodiment of my invention is the suspension of pure manganous carbonate in the usual electrolyte for the preparation of electrolytic manganese, namely, a solution containing about 16 grams per liter of manganese as sulphate, 100 grams per liter of ammonium sulphate, and about .1 gram per liter of sulphite ion. If such a suspension is passed into a cell having a stainless steel cathode and a lead-silver anode, and the flow of solution adjusted so that it leaves the cell at a pH of about 4.5, deposition may be carried on continuously, and with the same efficiency as in a diaphragm cell. The amount of carbonate in the suspension may be conveniently adjusted so that the solution leaving the cell will, on agitation, become substantially clear at pH 6.0. Under these circumstances, the solution may, if desired, be purified by the addition of sulphide ion, in accordance with the known art, before preparing the suspension of manganese carbonate for reuse. It will be evident, from this simple example, how my invention may be used to obviate the necessity of using in the cell a diaphragm with all its attendant disadvantages.

My invention, however, goes beyond the mere elimination of the diaphragm from the usual electrolytic manganese cell. In an entirely general way my invention permits a wide control over the acidity developed at the anode. It likewise permits a more precise control over the alkalinity developed at the cathode. These features of my invention enable me to use electrolyte compositions, and conditions of deposition, not previously possible because of the inconsistency of anode and cathode conditions necessary without the practice of my invention.

An outstanding illustration of the practice of my invention, to accomplish the type of result just referred to, is the deposition of manganese from a suspension of pure manganous carbonate in an electrolyte comprising manganous chloride and ammonium chloride. In the known art, chloride electrolytes have been found to have many advantages, but their advantages have been overbalanced by the evolution of chlorine at the anode, and by the oxidation of the ammonium salts in the electrolyte at the anode. I have found that the presence of a suspension of manganese carbonate (or, manganous oxide) around the anode, whereby to increase the pH on the anode area to about 3.0, prevents the undesirable anode reactions mentioned. This may be accomplished by adding manganous carbonate or oxide to the anolyte compartment of a conventional cell, having a graphite anode. A more favorable result, however, may be obtained by simply passing the suspension at a pH of about 6.0 through a single compartment cell, and adjusting the rate of flow so that the exit pH is about 4.5.

The conditions just described cannot, of course, be established independently of other variables. The pH

gradient from anode to cathode, which is highly critical in any method of electrodepositing manganese, is a function of the rate of solution of the suspended particles of manganese carbonate (or its equivalent). This depends on the physical nature of the suspended carbonate, its total amount, the temperature of the electrolyte, and turbulence, which is in turn related to current density and the flow pattern of the electrolyte. All of these factors are in turn related to the primary plating conditions, solution flow, and current density. These primary factors determine the amount of acid per unit volume which must be neutralized by the carbonate in unit time.

In order to most fully explain my invention, as it applies to an electrolyte of ammonium chloride and manganese chloride, the following data are given. The preferred concentration of manganese in such an electrolyte is 12 grams per liter, but good results can be obtained with 6–18 grams per liter. The ammonium chloride concentration is preferably 125 grams per liter but good results are obtained with 100–150 grams per liter. The amount of manganese carbonate suspended in the electrolyte will depend on its physical nature, in a manner which will be discussed later.

I will first illustrate the relationship of current density to the nature of the electrodeposit, in a process where the entering electrolyte has a pH equal to 6.2 and the exit electrolyte has a pH equal to 4.5. Under these conditions the pH at the cathode is about 8.0, and at the anode 3.0. These are the preferred conditions at anode and cathode, respectively. In the experiments now to be described I have varied the flow rate of the electrolyte and the amount of carbonate in suspension so as to achieve these conditions, regardless of current density and temperature.

In the graph, Fig. 1, I have shown the relationship of current density and temperature to the type of electrodeposit obtained, and have indicated the combinations of temperature and current density, which give the best results for long time plating as required for electrowinning manganese.

It should be pointed out that the control of pH varies greatly with the physical nature of the carbonate. I prefer to use a coarse fully crystalline carbonate, since this dissolves slowly, and permits the control of the exit pH by flow rate with wide differences in the amount of suspended carbonate. If the carbonate is very fine, it becomes more difficult to control the exit pH.

Various features which enter into consideration in establishing and maintaining good plating conditions will now be mentioned.

The point at which the suspension is added to the body of electrolyte in the cell is important. If it is introduced directly adjacent the anode neutralization is too rapid and the pH at the cathode becomes unduly high for good plating. If the suspension is introduced directly adjacent the cathode the pH which would have to be established at the anode in order to give good cathode plating conditions is too low. The most favorable condition is to introduce the suspension approximately centrally between anode and cathode.

Other variables having an influence on the efficiency of plating are (*a*) the geometry of the cell and (*b*) the size of the hydrogen bubbles formed at the cathode. It is important that these factors be so controlled that turbulence is minimized. This is accomplished by having the depth of the cell in proper relation to the electrode spacing. If the depth is too great the hydrogen evolved near the bottom of the electrode will have a long path, with expanding bubbles, and will create too much turbulence. In general, it has been observed that in the carrying out of the invention minimization of turbulence is favorably influenced by making the cell shallower than conventional. The addition of wetting agents to the electrolyte, to decrease the size of the hydrogen bubbles, is also helpful in minimizing turbulence.

Control of turbulence can be accomplished, further, by the imposition of a suitable baffle or baffles between anode and cathode. These baffles are in no sense equivalent to the conventional diaphragm as their purpose is not to interfere with thermal convection or diffusion but rather to interfere with the setting up of gross eddy currents by the evolved hydrogen. These baffles can be perforated plastic plates or plastic screens and can be spaced between the electrodes. The size and number of openings (interstices) must be so selected as not to disturb the uniformity of the current flow between the electrodes.

In the discussion, supra, of the adherency of the manganese plate to the cathode it has been pointed out that at very high, or very low, temperatures the plate formed is unusually adherent to the cathode body. Advantage may be taken of this phenomenon in the preparation of adherently plated objects. This adherency is general to all metallic cathodes but is particularly important for such metals as titanium, zirconium, molybdenum, magnesium, aluminum, and alloys thereof, which have heretofore not been satisfactorily plated. Such adherent manganese platings, on the metals mentioned, can be used as undercoats for top platings of copper, nickel, or other desired electroplatable metal.

With the chloride electrolyte which I prefer, and which I have so far used to illustrate my invention, it is preferred to use a graphite anode. This anode may be in plate form; or, a multiplicity of rods may be used to decrease current density at the anode with relation to the cathode. This may be desirable where high cathode current densities are used, and if the same current density were used at the anode, chlorine might be formed. Various methods of sculpturing an anode plate may be used to increase surface and hence to lower the current density.

Other anodes than graphite may be used; for example, the porous titanium anode of U. S. Patent No. 2,608,531. I have found that with either graphite or porous titanium anodes the current density must not exceed about 100 amp. sq. ft. at pH=30, and about 150 amp. sq. ft. at pH=40.

The cathode may be stainless steel, but I prefer to use titanium in accordance with my previous invention, as disclosed in U. S. Patent No. 2,646,396.

While I have described my invention in terms of its preferred embodiment, using manganese carbonate and an electrolyte of manganese and ammonium chlorides, my invention may also be applied to other electrolytes, and to the use of manganous oxide and other acid-soluble oxidic compounds of manganese.

In selecting other electrolytes, consideration must be given to secondary anode reactions. We have seen that the secondary reaction at the graphite anode in a chloride electrolyte may be controlled by a proper selection of current density and pH.

In several electrolytes, the manganese is oxidized at the anode and this must be minimized by a suitable selection of anode. Thus, in the case of sulphate electrolytes, the anodes known in the art, such as lead-silver, may be used. I have found that when my invention is applied to sulphate electrolytes, the current densities which may be used are greater than those of the conventional diaphragm cell process and may be as high as or higher than 75 amp. sq. ft. The ability to use higher current densities with my process is one of its great advantages. The reason for this advantage of my process is to be found in the control of diffusion from anode to cathode. In the conventional process the upper limit of current density is established by the alkalinity at the cathode. This is controlled only by solution flow as diffusion of acid from the anode is effectively prevented by the diaphragm. In the process of my invention both flow and anode acidity may be controlled, and the upper limit of current density is set by the nature of the deposit.

Other electrolytes which may be used with my invention include: fluoborates, fluosilicates, sulphamates, alkyl-

sulphonates, alkylsulphates, acetates, and hydroxyacetates of manganese, and manganese salts of other acids forming soluble manganese compounds.

I have found that in all of these electrolytes, the best range of concentration of manganese is from 6 to 18 grams per liter, and the best concentration of ammonium salt is 100–140 grams per liter.

All of the above acids require the use of a graphite or porous titanium anode. The cathode may be stainless steel or titanium.

The addition agents which have been found useful in the heretofore known art of plating manganese may be advantageously used with my process. I have found that sulphites are a useful addition agent. I prefer that the suspension of manganese carbonate be in an electrolyte saturated with manganese sulphite. Any excess of manganese sulphite simply passes through the cell since it is less soluble at low pH. Manganese sulphite is more soluble at low temperatures, and when plating at low temperatures an excess of manganese sulphite suspended in the electrolyte is to be avoided to prevent sulphur entering the plate.

Sulphide ion may be used in my process as an addition agent much more effectively than in heretofore known processes, since it may be introduced as a suspension of manganese sulphide and is hence brought to the plating zone in highly effective form.

Since sulphide ion may be so effectively used in my process sulphite addition may be omitted.

Other addition agents may be added such as hydroxylamine salts, thiourea, thiocyanate, and dithionates.

Since my process uses pure manganese carbonate or manganous oxide for pH control and replenishment of the electrolyte, the problems of purification which beset the conventional process are not met. However, should impurities enter the cycle by inadvertence, their accumulation to damaging proportions may be readily prevented. The electrolyte if neutralized to pH 6.0 by manganese carbonate or oxide and filtered will be purified from iron, since the iron will have been oxidized to the ferric state at the anode. The electrolyte is then treated with NH_3 and CO_2 and a little H_2S to dissolve the manganese. Heavy metals will be precipitated as sulphides and may be removed by filtration.

The resulting solution of carbamates may be warmed to 70° C. and the magnesium and calcium which will have accumulated in the electrolyte will be precipitated as carbonates and may be removed by filtration. The resulting solution may be used to neutralize the exit electrolyte from the cell thus replenishing manganese and any ammonia lost from the system.

The solution will accumulate sulphate ion by oxidation of sulphide or sulphite. This may be removed by adding barium chloride and filtering the barium sulphate so precipitated.

Having described my invention in its general aspects, I will now illustrate it by specific examples.

Example 1

Type of cell	Diaphragm.
Electrolyte:	
Acid ion	Chloride.
Mn g./l.	12.
NH_4 salt g./l.	100 NH_4Cl.
Suspended solid:	
Chemical nature	$MnCO_3$.
Physical nature	5 microns.
Amount g./l.—	
In	10.
Out	5.
pH:	
In	6.0.
Out	4.5.
T° C.	30.

Example 1.—Continued

Additions	.2 g./1. sulphite ion.
Plating time	2400 amp. hrs./sq. ft. cathode.
Current density:	
Anode	125 amps. per sq. ft.
Cathode	50 amps. per sq. ft.
Deposit:	
Character	Smooth.
Efficiency	70%.
Adherence	Easily stripped.

Anode behavior: No measurable chlorine evolution at graphite anode.

Notes: Thick carbonate slurry added to anode compartment. Titanium cathode.

Example 2

Type of cell	Single compartment.
Electrolyte:	
Acid ion	Sulphate.
Mn g./l.	16.
NH_4 salt g./l.	140.
Suspended solid:	
Chemical nature	Manganese carbonate.
Physical nature	5 microns.
Amount g./l.—	
In	10.
Out	5.
pH:	
In	6.0.
Out	4.5.
T° C.	30.
Additions	Suspended $MnSO_3$.
Plating time	24 amp. hrs./sq. ft. cathode.
Current density:	
Anode	150 amps. per sq. ft.
Cathode	75 amps. per. sq. ft.
Deposit:	
Character	Smooth.
Efficiency	60%.
Adherence	Strippable.

Anode behavior: Lead-silver anode formed a small amount of adherent oxide.

Notes: Cathode stainless steel type 316.

Example 3

Type of cell	Single compartment.
Electrolyte:	
Acid ion	Chloride.
Mn g./l.	12.
NH_4 salt g./l.	125.
Suspended solid:	
Chemical nature	$MnCO_3$.
Physical nature	5 microns.
Amount g./l.—	
In	5.
Out	1.
pH:	
In	6.0.
Out	4.5.
T° C.	30.
Additions	Suspended $MnSO_3$.
Plating time	24 amp. hrs./sq. ft. cathode.
Current density:	
Anode	100.
Cathode	100.
Deposit:	
Character	Smooth.
Efficiency	70%.
Adherence	Strippable.

Anode behavior: 1% ammonia loss at graphite anode.

Notes: Flow rate 1 liter per minute per sq. ft. cathode. Cathode titanium.

Example 4

The conditions recited in Example 3 were repeated, except that the solid manganese carbonate was in a flocculant form, and was present in the ingoing electrolyte in the amount of 3 grams per liter. The outgoing electrolyte contained 1 gram per liter of the suspended flocculant carbonate. By maintaining a flow rate of 0.5 liter per minute the deposit secured was smooth and strippable, and the efficiency was 70%.

Example 5

In a further repetition of Example 3 all of the conditions of the latter example were observed except that the suspended (solid) manganese carbonate was in very fine (about 1 micron) crystalline form. It was found the amount of suspended solid had to be greatly reduced—2 g./l. in, and 0.1 g./l. out—in order to hold the pH of the outgoing electrolyte at 4.5. In this example a classifier was interposed in the circuit ahead of the cell. A good, strippable deposit was obtained.

Example 6

Type of cell ..... Single compartment.
Electrolyte:
- Acid ion ..... Fluoborate.
- Mn g./l ..... 12.
- NH_4 salt g./l ..... 125.

Suspended solid:
- Chemical nature ..... Manganese carbonate.
- Physical nature ..... 5 microns.
- Amount g./l.—
  - In ..... 10.
  - Out ..... 8.

pH:
- In ..... 6.0.
- Out ..... 4.5.

T° C ..... 30.
Additions ..... Suspension of .2 g./1 MnS.
Plating time ..... 2400 amp. hrs./sq. ft.
Current density:
- Anode ..... 60.
- Cathode ..... 60.

Deposit:
- Character ..... Smooth.
- Efficiency ..... 60%.
- Adherence ..... Strippable.

Anode behavior: No attack or oxidation on graphite anode.
Notes: Stainless steel cathode.

Example 7

The conditions were the same as in Example 3 except that the temperature was 50° C. The deposit was slightly nodular and very difficult to strip, and the efficiency was 55%.

Example 8

The conditions were identical with Example 3 except that the temperature was maintained at 10° C. The deposit was slightly nodular and was adherent and difficult to strip; the efficiency was 60%.

Example 9

Type of cell ..... Single compartment.
Electrolyte:
- Acid ion ..... Acetate.
- Mn g./l ..... 18.
- NH_4 salt g./l ..... 100 $NH_4C_2H_3O_2$.

Suspended solid:
- Chemical nature ..... MnO.
- Physical nature ..... Decomposed carbonate.
- Amount g./l.—
  - In ..... 2.
  - Out ..... 0.

Example 9.—Continued

pH:
- In ..... 5.0.
- Out ..... 3.0.

T° C ..... 30°.
Additions ..... Suspended sulphate.
Current density:
- Anode ..... 100.
- Cathode ..... 50.

Deposit:
- Character ..... Smooth.
- Efficiency ..... 60%.
- Adherence ..... Strippable.

Anode behavior ..... Graphite anode.

Example 10

The same conditions were observed, and the same results secured, as in Example 3. The acidity of the solution after leaving the cell was adjusted to pH=6.2 by stirring with manganese carbonate, and 0.1 g./l. H_2S and 0.1 g./filter aid were added. The solution was filtered. Ammonia was added to about 17 mol/liter, and CO_2 to about 4 mol/liter. The mixture was warmed to 70° C. for 30 minutes to precipitate $CaCO_3$ and $MgCO_3$. The precipitate was removed by filtration, and the filtrate was used to neutralize exit solution at pH=4.5 to pH=6.2 for re-use.

Example 11

The procedure in this example was the same as in Example 3. In carrying out the process cyclically, I add $BaCl_2$ to the exit solution to precipitate any sulphate formed. A small excess of $BaCl_2$ does no harm and may advantageously be maintained in the circuit so that any sulphate formed is precipitated. Precipitated sulphate must be periodically removed by acidifying to pH=5.0 with HCl to dissolve $MnCO_3$, and filtering.

The drawing shows an area wherein the electro-deposit is smooth and is strippable from the cathode, and further shows an area wherein the electro-deposit—while not nodular and quite smooth—is firmly adherent to the cathode. While this latter area is to be avoided when electrowinning manganese, it may be taken advantage of in case the desired result is electroplating with manganese. Examples 7 and 8 illustrate such electroplating situations where a titanium sheet is made the cathode. Similarly, firmly adherent electroplates of manganese on other base metals may be effected by purposefully maintaining the temperature of the electroplating operation at below 20° C. or above 40° C. and the current density at not substantially in excess of 100 amp. sq. ft.

I claim:

1. In a process for producing electrolytic manganese by electrolysis of an electrolyzable manganese-containing solution in an electrolytic cell having an anodic electrode and a cathodic electrode, the improvement which consists in having present in said electrolyzable manganese-containing solution, in contact with a surface of an electrode of the cell during the electrolysis operation, a suspended finely divided solid acid-soluble oxidic manganous compound in quantity sufficient to maintain the pH of the electrolyte at from about 3.0 to about 6.0.

2. The improved process defined in claim 1, characterized in that the suspended finely divided, solid, acid-soluble, oxidic manganous compound is selected from the group consisting of manganous carbonate and manganous oxide.

3. The process defined in claim 1, in which the electrolyte containing the suspended finely divided solid oxidic manganous compound is passed over the surfaces of the anode and of the cathode in a single compartment cell.

4. The process defined in claim 3, in which the electrolyte suspension is passed through the cell at such a rate that its initial content of suspended finely divided solid

oxidic manganous compound is not completely exhausted as it exits from the cell.

5. In the process of electrodepositing manganese by electrolyzing an electrolyzable solution of manganese and ammonium chlorides as the same is passed through an electrolytic cell provided with a cathode and a carbon anode, the step of minimizing decomposition of ammonium chloride adjacent the anode by maintaining in suspension in the electrolyte as the same flows through the anode space of the cell in contact with the anode surface a finely divided, solid, acid-soluble oxidic manganous compound in quantity sufficient to maintain the pH of the electrolyte adjacent the anode at above 3.0 and not more than 6.0 and operating at an anode current density below 150 amperes per square foot of anode surface.

6. Process of electrodepositing manganese by electrolyzing an electrolyzable solution of manganese and ammonium chlorides in an electrolytic cell provided with a cathode and a carbon anode, characterized in that the electrolyte during electrolysis thereof contains suspended therein a finely divided, solid, acid-soluble, oxidic manganous compound and is passed through the cell between the cathode and the anode at such a rate that its pH upon exiting from the cell is more than 3.0 and less than 6.0 when the anode current density is less than 150 amperes per square foot of anode surface.

7. Process of electrodepositing manganese as defined in claim 6, in which the pH of the electrolyte as it enters the cell is within the range 6.0–6.5 while its pH as it leaves the cell is within the range 4.0–6.0, and in which the temperature is maintained in the range 20°–40° C. and the current density is at least 40 amperes but not materially in excess of 130 amperes per square foot, the temperature and current density being correlated to yield a non-adherent and non-nodular plating.

8. Process of electrowinning manganese which comprises suspending a substantially pure and fully crystalline manganous carbonate in an electrolyte containing 6–18 grams per liter of manganese as chloride and 100–150 grams per liter of ammonium chloride and being saturated with manganous sulphite, adjusting the pH of the resulting electrolyzable suspension of manganese carbonate to 6.0–6.5 at 20–30° C., passing the electrolyzable suspension through an electrolytic cell having a carbon anode and a titanium cathode, and in contact with said anode and cathode, at such a rate that the electrolyzable suspension leaving the cell has a pH within the range 4.0–6.0 while passing a unidirectional electric current through the cell at a cathode current density of 40–125 amperes per square foot of cathode surface, and maintaining the temperature within the range 20–40° C.

9. Process of producing a firmly adherent electroplate of manganese on a conductive metal article which comprises making said metal article the cathode in a single compartment electrolytic cell, preparing an electrolyte suspension by suspending in an electrolyzable solution of manganese and ammonium salts a finely divided particulate acid-soluble manganous carbonate in quantity sufficient to maintain the pH of the electrolyte at from about 3.0 to about 6.0, passing the resulting electrolyte suspension through the cell between said cathode and a carbon anode, passing unidirectional current at a current density not substantially in excess of 100 amperes per square foot through the electrolyte suspension, so controlling the flow of the electrolyte suspension that it is partially neutralized and replenished in manganese by dissolution of the particulate manganous carbonate in said electrolyte as the same flows through the cell and in contact with the cathode, and maintaining the electrolyte suspension at a temperature within one of the ranges 10°–20° C. and 40°–50° C. and the current density at from 40 amperes to not materially in excess of 130 amperes per square foot, the temperature and current density being correlated to yield an adherent, non-nodular plating.

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