The present invention relates to the electrodeposition of manganese including the electro-winning of manganese from its ores, the electrodeposition of plates of manganese and the production of alloys of manganese, such as ferro-manganese and the like.

It has been shown that domestic manganese ores may be roasted and leached to yield manganese sulfide solutions suitable for electro-winning. This method has been applied on a pilot scale by the U. S. Bureau of Mines. However, the Bureau of Mines process suffers from a serious deficiency in that an amount of manganese is deposited at the anode as manganese dioxide which approximates ¼ or more of the weight of the metal deposited at the cathode. In other words, at least 20%, or so, of the manganese deposited is lost at the anode and must be recycled in order to approach acceptable standards of efficiency on an industrial scale for commercial purposes. The recovery of this manganese dioxide may entail removal of the dioxide from the electrolyte by filtration, re-roasting of the press cake, and re-leaching of the roasted press cake. It will be readily appreciated that these operations represent a considerable loss in material and energy. Furthermore, the manganese dioxide precipitate leaves the anode and settles to the bottom of the cell necessitating frequent cleaning of the cell in order to remove the precipitate. In addition unless the anode is separated from the cathode by a diaphragm, the precipitate prevents the deposition of pure metal at the cathode.

The work of Shelton and Royer of the U. S. Bureau of Mines has been reported in the Transactions of the Electrochemical Society in volume 74, pages 447-458. A small pilot plant was operated in accordance with Shelton and Royer’s process for a limited time. The process of Shelton et al. involves grinding manganese dioxide ores to a suitable size and then roasting the ores in a reducing atmosphere to convert the manganese to the bivalent stage of oxidation. The reduced ore is then leached with dilute sulfuric acid-ammonium sulfate solution and the leach solution purified. Iron and arsenic are removed from the solution by oxidizing the iron with hydrated manganese dioxide anode slimes. The iron, in precipitating, brings down with it the arsenic. Copper and zinc, if present, are removed as sulfides and nickel and cobalt precipitated as insoluble xanthates. The anodes are of “corrodine,” grade lead and duck diaphragms are used to separate the catholyte from the anolyte. During operation the solution fed to the cathode compartments is about neutral while the catholyte has a pH of about 9 to about 9.2. Due to the fact that a large amount of the manganese, at times as much as one half of the total, is deposited at the anode in the form of the dioxide. Shelton and Royer made provision to recover this manganese dioxide. A portion of it as mentioned heretofore, may be used to precipitate iron and arsenic but the remainder and by far the larger portion must be re-leached and leached again.

From the foregoing review of the many attempts made to utilize low grade manganese ores, it will be appreciated that no one, so far as we are aware, has provided a simple, efficacious, completely industrially acceptable process for electrowinning and the electropolating of manganese. It will be apparent that the greatest weakness of the process, which has found some favor in industry, is the large loss sustained due to the fact that manganese deposits at the anode as the dioxide and ether must be removed from the system as a total loss or considerable energy must be expended to recover the anodically oxidized manganese.

Shelton recognized the weakness in his original process discussed hereinbefore and proposed to overcome this deficiency by the Bureau of Mines process by adding to the electrolyte small quantities of sulfite ion. As pointed out by Shelton in U. S. Patent No. 2,119,560 the addition of small quantities of sulfite ion is intended to control the rate of formation of manganese oxides and hydrates on the anodes and in the electrolyte.

We have discovered that the considerable loss of manganese in known electrolytic processes can be reduced to a very small amount and under optimum conditions may be eliminated substantially entirely. We have also discovered that manganese sulfate solutions may be employed for the electrowinning of manganese from its ores, for the electrodoposition of protective layers and for the manufacture of manganese alloys or mixtures with other metals, such as ferro-manganese of any desirable grade. It is an object of the present invention to provide a process for recovering manganese from even low grade manganese ores by electrolysis on an efficient and commercial basis.

It is another object of the present invention to provide a means for recovering manganese from its ores, even of a low grade character, without the production of substantial amounts of anodic manganese dioxide.

It is a further object of the present invention to provide a means for producing alloys or mixtures of manganese with other metals having a desired manganese content.

The present invention likewise contemplates the provision of means for the deposition of surface films of manganese for protective and/or ornamental purposes.

It is also within the contemplation of the
present invention to provide alloys containing manganese including ferro-manganese having a commercially acceptable manganese content.

In addition it is within the purview of the present invention to provide novel anodes for use in the electrodeposition, including electro-winning, of manganese.

Other objects and advantages will become apparent from the following description:

Broadly stated, the commercial success of either electrolytic or electro-winning manganese metal is dependent upon the elimination of the factors during electrolysis that give rise to the formation of relatively insoluble oxides and other compounds of manganese. Such compounds not only contaminate the product but greatly reduce the efficiency of cell operation and as Edgar F. Smith in his well known book on Electroanalysis states "the electric current causes this metal (Mn), when in solution as chloride, nitrate or sulfate, to separate as the dioxide upon the anode. . . . A solution of the sulfate (MnSO4) is slightly acidulated with say 2 or 6 drops of sulfuric acid is preferable for electrolytic purposes." In other words, Smith recommends the manganese sulfate solution because it deposits manganese not as the metal but as the brown oxide, MnO2 at the anode in quantitative relationship to the manganese content of the electrolyte. Smith also cautions against the presence of tartaric, oxalic and lactic acids because they "retard the formation of manganese dioxide." On the other hand, Smith highly recommends the addition of formic acid to the manganese sulfate solution to ensure complete deposition of a "very adherent" deposit of manganese dioxide, MnO2. Acetic acid is likewise recommended to facilitate the precipitation of MnO2 at the anode. In other words, weak organic acids, such as oxalic, and tartaric decrease the formation of MnO2 whereas weak acids of the formic type increase the formation of MnO2. From the foregoing it is obvious that weak acids do not function primarily as buffers in the electrodeposition of manganese.

In general, we have found that by employing anodes having a critical composition the deposition of manganese dioxide at the anodes in manganese sulfate solutions can be reduced substantially or eliminated entirely. Lead anodes have been suggested as suitable for the electro-winning of manganese, but as those skilled in the art recognize, lead anodes even of such grade as Shelton and Royer advise, are not entirely acceptable for a completely satisfactory process. It has been found that lead anodes such as the prior investigators including Shelton and Royer advise probably initiate the oxidation of the manganese ion at the anode. The mechanism of this reaction is probably dependent upon the formation of lead peroxide at the electrodes which in turn catalyzes the oxidation of the manganese ion and the precipitation of manganese dioxide at the anode. Antimonial-lead anodes containing about 1% to about 16% antimony likewise interfere with efficient recovery of manganese probably for the same reason.

There are at least two possible reactions at the anode in a manganese deposition bath. First there is the discharge of hydroxyl ion and the liberation of gaseous oxygen in the nascent state in accordance with the equation

$$20H^- + \frac{1}{2}O_2 + H_2O + 2e^-$$

The second reaction is the formation of manganese dioxide.

$$Mn^{++} + 2H_2O = MnO_2 + 4H^++ 2e^-$$

The relative amounts of oxygen and MnO2 produced will depend upon the anode potential at which deposition of each is initiated, as well as upon the relative slopes of the anode-polarization curves. The foregoing statement assumes that no secondary electrolytic reactions or chemical reactions as such occur locally at the anode. In the event that this is true, should the potential for oxygen discharge be less than that required for the liberation of manganese dioxide, then only oxygen will be deposited. As the potential rises, as a result of current density increases, the voltage required for oxidation of manganese ion may be attained, and then the two reactions will occur simultaneously. We have found that anodes having a lower oxygen overvoltage than lead or antimonial lead may be employed in the electro-winning or electroplating of manganese. However, a reduction in the oxygen overvoltage is not the entire solution of the problem. Consequently, the novel results obtained by using the anodes of the present invention are not entirely dependent upon a reduction in the oxygen overvoltage. It would appear that the precipitation of manganese dioxide at the anode is dependent upon the formation of lead peroxide and a reaction between the lead peroxide and the manganous ion to precipitate manganese dioxide at the anode.

In accordance with the principles of the present invention, the formation of lead peroxide is inhibited by the addition to the lead anode of one or more elements or metals. These elements or metals appear to act as negative catalysts preventing the formation of lead peroxide or the oxidation of the manganous ion or both reactions at the anode. It has been found that in the novel anodes tin or cobalt or both act as an anti-catalyst or negative catalyst and inhibit the formation of lead peroxide. When electrodes constituted of lead and tin or lead, tin and cobalt are employed in the electrolysis of manganese solutions, little if any manganese dioxide is precipitated at the anode and substantially all of the manganese is recovered as a metallic deposit at the cathode.

For the purpose of giving those skilled in the art a better understanding of the improved process for the precipitation of metallic manganese substantially without the precipitation of manganese dioxide, the following description is provided. Lead anodes containing between about 10 to about 50% tin have proven effective in reducing the amount of manganese precipitated at the anode as manganese dioxide. It is to be observed, however that the loss of manganese as manganese dioxide is dependent to some extent, upon the anode current density. Thus, for example, with the prior art anodes, the anodic loss of manganese as manganese dioxide is between about 12 to about 16% for anodic current densities between about 5.4 amperes to about 15.1 amperes per square decimeter. When the anode contains about 10% tin, the anodic loss of manganese as manganese dioxide is reduced to about 10% for the same range of anodic current densities. However, at a current density of about 5.4 amperes per square decimeter, the loss of manganese at the anode amounts to approximately the same as that which occurs when prior art are lead anodes substantially free of tin are used.
An increase in the amount of tin incorporated in the anode to about 50% reduces the loss of manganese as manganese dioxide to about 0.5% at current densities up to about 15 amperes per square decimeter. This is clearly brought out in Table I.

**Table I**

| Anode | Per cent tin | Ratio Pb/Sn | Loss of Mn as MnO₂—
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5.4 amp./dm.</td>
<td>7.9 amp./dm.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>12.5</td>
</tr>
<tr>
<td>Lead</td>
<td>0</td>
<td>8.0</td>
<td>12.2</td>
</tr>
<tr>
<td>Alloy I</td>
<td>10</td>
<td>9/1</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>7/1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>5/1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* = amperes per square decimeter.

We have also found that the loss of manganese as manganese dioxide which occurs even when anodes containing as much as about 50% tin are employed can be still further reduced by the addition of cobalt to the lead-tin anode. The 12 to 16% loss of manganese as manganese dioxide which occurs with the use of a lead-tin alloy anode containing about 10% tin may be reduced to about 0.6 to about 1.4% by the addition of sufficient cobalt to provide an anode containing about 2.6% cobalt. The 0.5% to 2.5% loss of manganese as manganese dioxide which occurs when lead-tin anodes containing about 30% tin are employed can be reduced to about 0.2% or less by the addition of sufficient cobalt to provide a lead-tin-cobalt anode containing about 0.5% cobalt. Further improvements in overcoming the loss of manganese as manganese dioxide can be obtained by incorporating up to about 4.4% cobalt in a 50-50 lead-tin anode. Thus, while the use of a 50-50 lead-tin anode results in the loss of up to about 0.9%, the introduction of sufficient cobalt to provide a concentration of about 2.6% makes even this loss practically nil. Increasing the amount of cobalt in the 50-50 lead-tin anode to as much as 4.4% cobalt does not effect any noticeable further decrease in the loss of manganese as manganese dioxide. Those skilled in the art will readily appreciate the foregoing from an examination of Table II.

**Table II**

| Anode No. | Per cent cobalt | Ratio Pb/Sn | Loss of manganese as MnO₂—
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5.4 amp./dm.</td>
<td>7.9 amp./dm.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>12.2</td>
</tr>
<tr>
<td>1</td>
<td>0.0</td>
<td>9/1</td>
<td>12.5</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>9/1</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>9/1</td>
<td>0.6</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>1/1</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>1.2</td>
<td>1/1</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
<td>1/1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* = amperes per square decimeter.

Lead and tin are mutually soluble in the liquid state but only partially soluble in the solid state and form a simple eutectic at 183°C containing 62% tin. On the other hand, lead and cobalt are completely insoluble in both the liquid and the solid states. However, tin and cobalt are soluble in the liquid state, form very limited solid solutions and form two compounds. The compound richest in tin is CoSn, and an eutectic of tin and CoSn exists at 0.8% cobalt and 222°C. Lead-tin-cobalt and lead-tin-antimony-cobalt anodes may be prepared in many ways as those skilled in the art readily understand. Thus, for example, a quantity of cobalt chloride sufficient to provide the desired concentration of cobalt metal in the anode is introduced into a bath containing lead and tin or lead, tin and antimony in the proper proportions. The bath is then heated to about 500°C and stirred until the reaction ceases after which the anode is cast in any suitable manner. The novel anodes of the present invention may also be prepared from lead or lead and antimony and a tin-cobalt master alloy. The maximum cobalt content of the master alloy for easy dispersion in lead is about 8%. The master alloy is most easily prepared by melting the tin and cobalt in a first clay crucible with sodium chloride slag and heating to about 900°C to about 1000°C. The alloy for the anodes may be prepared by melting lead and adding the requisite amount of tin and cobalt-tin master alloy and stirring the mixture with a graphite rod. For satisfactory results, the melting point of the CoSn need not be reached, and the ingot melt actually consists of a solution of lead and tin containing dispersed particles of CoSn. Of course, higher temperatures may be employed if desirable. The anodes preferably are cast in horizontal graphite molds. Upon removal from the mold, surface unevenness is corrected in any suitable manner, for example, by filing or grinding and the anode "preformed" anodically in dilute ammonium sulfate solution in order to develop the proper anode film. When "preforming" our novel anodes, commercial lead may be employed as the cathode with satisfactory results during this treatment.

While lead-tin-cobalt anodes prepared as described hereinbefore have given satisfactory results, it is preferred to employ anodes of different type in which the cobalt-tin compound is present as a larger number of smaller particles and more uniformly distributed than has been obtained by preparing the anodes in the manner disclosed hereinbefore. The anodes may be homogenized and the CoSn distributed as smaller particles by precipitating the CoSn crystals from the melt at a low temperature rather than permitting the precipitation to occur at high temperatures. The lowest temperature at which the compound may be dissolved in tin is that of the eutectic, to wit: 220°C. Furthermore, since the eutectic freezes at constant temperature, the particle size of the CoSn is small. In order to prepare lead-tin-cobalt anodes having a more uniform distribution of the CoSn and having the CoSn present as smaller particles the metals are preferably melted at as low a temperature above the eutectic point as possible and cast with as rapid solidification as possible.

We have found that the precipitation of the CoSn in this manner results in an improvement in the characteristic of the anode. Thus, while 5 hours are required to satisfactorily preform anodes made from the 8% cobalt master alloy the preliminary oxidation of the more uniform anodes may be performed in about 1 to about 2 hours.

Although it has been found that antimonial lead alloys are not suitable for use as anodes due to the deposition of manganese at the anode, nevertheless it has been found that lead anodes
containing antimony in addition to cobalt and tin give results approaching the results obtained with homogenized lead–tin–cobalt anodes. Since it has been discovered that the alloying of antimony with lead alone increases the deposition of manganese dioxide markedly, the improvement secured with the quaternary alloy anodes is probably due to a more even distribution of the constituents. The addition of antimony in amounts up to about 10 or about 15% has given satisfactory results. For example, a quaternary alloy comprising about 75.5% lead, about 9.9% tin, about 6.9% cobalt and about 3.9% antimony has given satisfactory results. We have also found that composite anodes may likewise be employed with satisfactory results and a reduction in cost of the anodes. Such anodes may be made of a suitable core, for example, lead, and the desirable inhibited surface provided by dipping the core into a molten bath of the proper lead–tin–cobalt content. For chill-cast anodes it is preferred to use a composition containing about 30 to about 50% tin, about 0.3 to about 0.4% cobalt and the balance lead including common impurities. These chill-cast anodes may be made by dissolving the cobalt in molten tin at an elevated temperature, cooling to about 300 °C, and adding the requisite quantity of molten lead. The melt should then be mixed and cast in chilled molds.

The novel anodes of the present invention whether of unitary or composite structure also may be prepared by the conventional methods of powder metallurgy too well known to those skilled in the art to require detailed description herein. It will be appreciated by those skilled in the art as a result of the foregoing description of our invention that our novel anodes are formed with a film or skin of metallic compounds functioning as negative catalysts upon a core which may be constituted of the metals of the compounds of the anode. Thus, one form of our novel anodes embraces an anode having a whitish film, skin or coating of a tin compound probably a hydroxide (Sn(OH)₄) or a hydrated oxide while another type which has given very satisfactory results has a gray-green skin or coating of cobalt and tin compounds. It would appear that whatever be the composition of the oxide it is necessary that for anodes to function satisfactorily for our purpose the anode should have a film containing tin or cobalt or tin and cobalt compounds of the oxide or hydroxide or hydrated oxide type.

In the electrowinning of manganese, several metals are suitable for use as cathodes. Thus, for the production of ferro-manganese of desired manganese content, a ferrous strip, say mild steel, may be used as the cathode. Improved results may be obtained by employing as cathode high grade cast iron, preferably heat treated in a reducing atmosphere to embrittles the metal. After manganese has been deposited to the required thickness the composite sheet of ferro-manganese is readily broken up due to the brittle character of the core. Manganese is deposited upon the ferrous strip in sufficient thickness to provide an iron plus manganese content meeting the requirements of the trade. When desirable, and in order to reduce the losses of manganese due to volatilization in the manufacture of ferrous alloys, the composite iron manganese cathode can then be protected by a protective layer of suitable metal such as iron, chromium, nickel, etc. In addition, alloys similar to ferro-

manganese but containing copper, nickel, zinc, aluminum, chromium, etc., may be produced by depositing the manganese on a cathode strip of the other metals instead of a ferrous strip. Thus, in the production of manganese-copper-nickel alloys, a strip of a copper-nickel alloy such as that sold under the trademark Monel may be used as a cathode and manganese deposited in sufficient thickness to provide the requisite manganese content. When sufficient manganese has been deposited, the cathode is removed from the bath, freed of adherent electrolyte and melted under suitable conditions. In this way, for example, manganese-copper-nickel alloys containing about 14% to about 31% manganese, about 41% to about 81% copper and about 2% to about 16% nickel may be prepared. In a similar manner, manganese-copper-zinc alloys may also be prepared to contain, for example, about 29% manganese, about 65% zinc and about 15% copper. A master sheet for the preparation of manganese–aluminum alloys containing for example about 65% to about 75% aluminum and about 35% to about 25% manganese, may be manufactured by depositing manganese on aluminum sheets or an alloy containing about 81% to about 91% aluminum and about 1.1% to about 1.3% manganese and the balance principally aluminum may be manufactured by depositing manganese on a copper–aluminum plate of suitable composition.

It will be appreciated that in preparing ternary, quaternary and more complex alloys containing manganese a master ingot may be prepared from a sheet constituted of the principal constituent of the finished alloy. The sheet is then employed as a cathode and provided with an electrodeposited of manganese of sufficient thickness to provide the desired manganese content in the finished alloy. The plated sheet may then be melted and additional constituents of the finished alloy introduced into the bath. On the other hand, alloy sheets containing all the constituents of the final alloy in the proper proportions except manganese may be employed as cathodes and the desired amount of manganese deposited electrolytically after which the manganese plated sheet may be melted. Furthermore, a sheet constituted principally of the major constituent of the alloy may be provided with successive deposits of alloying metals including manganese and the composite sheet melted to form the finished alloy. A further embodiment of this feature of the present invention involves electrodepositing the desired amount of manganese on a cathode comprising principally the major constituent of the finished alloy for the production of complex alloys. The composite sheet may then be dipped into baths of molten metal constituted of the other constituents of the finished alloy.

We have found that in the electrowinning of manganese, the most satisfactory results are obtained with electrolyte containing about 100 to about 150 grams per liter MnSO₄.4H₂O and about 50 to about 200 grams per liter (NH₄)₂SO₄. While with an electrolyte containing about 100 grams of MnSO₄ and about 200 grams per liter of (OH)₂SO₄ operated at a current density of about 3.1 amperes per square decimeter and a bath temperature of about 25 °C, the use of conventional lead electrodes leads to a loss of manganese as manganese dioxide of about 16% to about 7.6% as the pH rises from about 2.3 to about 8.0, the use of our new lead–tin–cobalt
anode results in operation of the bath within the aforesaid range without any substantial loss of manganese at the anode. Table III clearly indicates the wide range over which a manganese-sulfate bath may be operated when employing anodes prepared in accordance with the principles of the present invention as compared with prior lead anodes.

Table III

<table>
<thead>
<tr>
<th>Anode constituent</th>
<th>Loss of manganese as MnO₂ (%)</th>
<th>At pH 1.2</th>
<th>At pH 4.2</th>
<th>At pH 5.0</th>
<th>At pH 6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>2.0</td>
<td>1.5</td>
<td>1.0</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Co₁₃Sn₁₃P₂</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

For the electroplating of thin deposits of manganese on brass, steel, copper, etc., for its protective and/or decorative value, it has been found that the neutral sulfate bath is the most convenient and reliable. In contrast with the electrowinning sulfate bath, we add not only ammonium sulfate to our novel electroplating bath but also glycerine. We prefer to add sufficient NH₄OH to the bath to provide a pH of about 7.0 to about 7.2. Satisfactory results have been obtained using electrolytes containing.

Table IV

<table>
<thead>
<tr>
<th>Bath constituent</th>
<th>Grams per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnSO₄·4H₂O</td>
<td>About 75 to about 200.</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>About 75 to about 200.</td>
</tr>
<tr>
<td>Glycerine</td>
<td>About 75 to about 75.</td>
</tr>
<tr>
<td>NH₄OH</td>
<td>100.</td>
</tr>
</tbody>
</table>

ufficient to provide a pH of about 7 to about 7.2.

Temperature: about 20°C to about 30°C. Cathode current density: about 4 to about 12 amperes per square decimeter. No diaphragm.

However, it is preferred to employ an electrolyte having the following composition:

Table V

<table>
<thead>
<tr>
<th>Bath constituent</th>
<th>Grams per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnSO₄·4H₂O</td>
<td>90.</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>90.</td>
</tr>
<tr>
<td>Glycerine</td>
<td>70-7.2.</td>
</tr>
</tbody>
</table>


It is preferred to maintain the pH by the addition of ammonium carbonate and to add freshly precipitated manganese hydroxide to replace the manganese plated at the cathode. To avoid contamination of the bath by flocks of this hydroxide we may use a porous cup submerged in the bath in conjunction therewith. That is, the manganese hydroxide is placed in a porous cup and the cup submerged in the electrolyte. Another procedure is to circulate the bath or an aliquot portion thereof over manganese hydroxide and back into the cell in order to maintain the pH of the bath within the preferred plating limits of about 6.5 to about 7.5.

After plating for a period of time, say about 2 to about 10 minutes, the cathode or work is removed and dipped into a dilute solution, say about 5% to about 15%, of sodium or potassium dichromate. When desirable, the dip may be omitted and a soft buff used to remove the thin film of basic manganese salts. Besides the bright plate, gun metal finishes are very readily obtained with the above bath.

While the anodes employed in the herein described baths may be any of the lead-tin-cobalt anodes hereinbefore mentioned, it is preferred to use lead-tin-cobalt anodes containing about 0.4% cobalt, about 40% tin, and the balance lead and conventional impurities.

It will be appreciated by those skilled in the art that the lead-tin and lead-tin-cobalt anodes of the present invention have a surface film or coating of a mixture of oxides of lead and tin or lead, tin and cobalt respectively after preforming in an ammonium sulfate bath. Consequently a further embodiment of the present invention provides anodes having a coating of or containing oxides of lead and tin, or lead, tin and cobalt or lead and cobalt.

Our new manganese dioxide inhibiting anodes give satisfactory results in the electrowinning of manganese. In conjunction with the new anodes an improved simplified process for the recovery of manganese even from low grade ores such as those of South Dakota has been developed. Low grade manganese ores such as those containing 1% to 7% manganese as well as manganese ores containing 30% to 45% manganese may be treated.

In the improved process for the electrowinning of manganese ores, the ore is crushed and ground to a suitable size. It will be appreciated that the ease of leaching and the nature and texture of each ore affects the degree of fineness to which each ore must be ground. However, since these factors are well understood by those skilled in the art, further elucidation is unnecessary. Since most of the domestic ores, with the exception of the rhodocrosite ores, contain manganese in the quadrivalent state the ground ores are roasted at a temperature of about 650°C. In the presence of reducing gases such as water gas, blue gas, hydrogen etc. The roasted or heat treated or reduced ore is then leached. Preferably spent electrolyte is used for this purpose although a liquor containing about 50 to about 200 grams of ammonium sulfate and about 30 to about 50 grams of sulfuric acid per liter may be used.

The leaching may be carried out by percolation, by solution accompanied by agitation or by any other suitable means until the leach liquor contains about 100 to about 150 grams of manganese sulfate per liter. Iron, arsenic, nickel and cobalt are removed from the solution in any suitable manner. For example, iron may be removed by oxidation and precipitation as the hydroxide whereby the arsenic will also be removed. The nickel and cobalt may be removed by precipitation as xanthates. The precipitates of the above-mentioned impurities are removed in any suitable manner as by means of a pressure filter and the purified leach liquor is fed to the electrolytic cells.

The electrolytic cells may be of any suitable construction and the cathodes may be made of wrought or cast iron, steel, aluminum, aluminum alloy, copper-nickel alloy, etc., depending on the product desired. However, it is important that the anodes be of the type inhibiting the formation of manganese dioxide. In other words, the anodes must contain a catalytic catalyst as described hereinbefore inhibiting the formation of manganese dioxide at the anode. We prefer to use a homogenized lead-tin-cobalt anode made from a 50-50 lead-tin alloy and containing about
0.3% to about 0.4% cobalt, in other words we prefer to employ anodes containing about 50% lead, about 50% tin and about 0.3% to about 0.4% cobalt. However, anodes comprising about 70 parts, i.e., about 65% to about 75% of lead, about 30 parts of tin which is about 25% to about 35% of tin and up to about 4.5% cobalt give satisfactory results. It will be appreciated that it may be said that the cobalt content for practical purposes is only limited by cost and the preparation of an anode which has sufficient strength to have a practical useful life.

Before employing the anodes in the electro-winning of manganese it is preferred to preform them. That is to say, the anodes are made anodes in a dilute ammonium sulfate solution until coated with a film, usually of greenish color, of mixed oxides. Of course, composite anodes having a core, an intermediate layer of lead-tin-cobalt and an outer layer of mixed oxides may be used. The anodes need not be preformed, but may be used directly in the electro-winning process although this is not our preferred procedure.

The purified leach liquor is conveyed to the cell by any suitable means and enters the cell in the region of the cathode. The purified leach liquor contains about 25 grams to about 150 grams of manganese as manganese sulfate per liter and has a pH of about 6.5 to about 7.5. The spent electrolyte coming from the cell has a manganese content of about 3 to about 5 grams of manganese per liter.

The electrolysis of the purified leach liquor is carried out employing our anodes containing a negative catalyst inhibiting the formation of manganese dioxide at the anode. The lead anodes described herein containing tin or cobalt or tin and cobalt or tin, cobalt and antimony are typical of such anodes. The electrolysis is performed at current densities of about 4 to about 12 amperes per square decimeter.

The spent electrolyte may be used for leaching with corresponding economies. When using spent electrolyte or other leaching solutions containing ammonium, it is advantageous to cool the roasting ore below the temperature at which contact with the ammoniacal solution will cause the evolution of ammonia.

At suitable temperature intervals the cathodes are removed from the cell and stored or melted or treated further to obtain the desired end exit ferro-manganese, copper-nickel manganese alloy, metallic manganese, or other manganese-containing products.

From the foregoing description of the improved process, it will be appreciated that the process of electrowinning manganese differs from the prior art including the process of Sheldon and Royer in an important feature. By the use of our novel anodes, the deposition and loss of manganese dioxide at the anode is reduced to insignificant proportions and under optimum conditions practically eliminated. With the reduced formation of manganese dioxide or the practically total elimination of the formation of the dioxide the recycling including reduction and leaching of the dioxide is eliminated. Thus, a tank department of given size will produce more metallic manganese when used in conjunction with our process than when used in conjunction with the prior art process.

Although the present invention has been described in conjunction with certain preferred embodiments thereof, it is to be understood that variations and modifications may be made as those skilled in the art will understand. Such variations and modifications are to be considered within the purview of the specifications and the scope of the appended claims. Thus it is to be understood that in the description of the composition of the anodes of the present invention or of the composition of the cathodes used in conjunction therewith or of the products produced by the process of the present invention the phrase "and balance lead" for example includes other metal or metals not subversive of the characteristics of the anode, cathode or product.

We claim:
1. A process for electrodepositing ornamental or protective platings of manganese which comprises depositing manganese on a cathode from an aqueous solution of manganese sulfate containing glycerine at room temperature and at a current density of about 4 to about 12 amperes per square decimeter in the presence of an anode of which the surface at least contains about 9 to about 50% tin, an effective amount up to about 4% cobalt and the balance lead inhibiting the formation of anodic manganese dioxide at a temperature of about 100 degrees.

2. A process as described in claim 1 wherein the pH of the aqueous solution of manganese sulfate is maintained at about 6.5 to about 7.5 by reacting at least a portion of the electrolyte with an acid neutralizing agent selected from the group consisting of ammonium carbonate and manganese hydroxide.

3. An anode for use in the electrodeposition, including electrowinning, of manganese without substantial formation of anodic manganese dioxide which comprises about 1 to about 15% antimony, about 9% to about 50% tin, a small but effective amount to about 4.4% cobalt and the remainder principally lead.

4. A chill cast anode for use in the electrodeposition, including electrowinning, of manganese without substantial formation of anodic manganese dioxide which comprises about 9% to about 50% tin, a small but effective amount to about 4.4% cobalt and the remainder principally lead.

5. A process for the electrowinning of manganese from its ores including low grade ores containing as little as 1.0% manganese, which comprises leaching comminuted ore of manganese, containing as little as 1.0% manganese, with an aqueous solution containing ammonium sulfate and sulfuric acid, said manganese being in the divalent state, purifying the leaching solution so obtained to obtain a purified leaching solution substantially devoid of iron, arsenic, nickel and cobalt, introducing said purified leach solution into an electrolytic cell having an anode of which the surface at least contains about 10 to about 50% tin, an amount up to about 4% cobalt effective to minimize manganese dioxide formation and the balance lead, and passing a direct current through said cell at a current density sufficient to deposit metallic manganese at the cathode.

6. An anode for use in the electrodeposition, including electrowinning, of manganese without substantial formation of anodic manganese dioxide and having particles of CoSn dispersed throughout the mass thereof which anode comprises an alloy containing about 9% to about 50% tin, a small but effective amount to about 4.4% cobalt and the remainder principally lead.

7. An anode for use in the electrodeposition including electrowinning of manganese at least the
outer layer of which comprises an alloy having particles of CoSn dispersed therein and containing about 9% to about 50% tin, a small amount to about 4.4% cobalt effective to minimize manganese dioxide formation and the balance principally lead and said layer having a surface coating thereon consisting essentially of the oxides of the metals of the alloy.

8. An anode for use in the electrodeposition including the electrowinning of manganese and adapted to minimize the formation of anodic manganese dioxide, at least the outer portion of said anode comprising about 9% to about 50% tin, a small but effective proportion to about 4.4% of cobalt and the balance principally lead.

9. A process for the electrodeposition of manganese including the electrowinning of manganese from its ores which comprises electrolyzing a solution containing manganese sulfate, ammonium sulfate and sulfuric acid in the presence of an anode at least the outer portion of which contains about 9% to about 50% tin, a small proportion to about 4.4% of cobalt effective to minimize manganese dioxide formation and the balance principally lead.

10. A process for the electrodeposition of manganese including the electrowinning of manganese from its ores which comprises electrolyzing a solution containing manganese sulfate, ammonium sulfate and sulfuric acid in the presence of an anode at least the outer surface of which comprises about 30% to about 50% tin and the balance principally lead.

11. An anode for use in the electrodeposition including electrowinning of manganese at least the outer surface of which comprises about 30% to about 50% tin and the balance principally lead.

12. A process for the electrowinning of manganese from its ores including low grade ores containing as little as 1.0% manganese which comprises leaching comminuted ore of manganese, containing as little as 1.0% manganese, with an aqueous solution containing ammonium sulfate and sulfuric acid, said manganese being in the divalent state, purifying the leach solution so obtained to obtain a purified leach solution substantially devoid of iron, arsenic, nickel and cobalt, introducing said purified leach solution into an electrolytic cell having an anode of which the surface at least is constituted of an alloy composition containing about 9% to about 50% tin, a small proportion of cobalt up to about 4.4% effective in inhibiting manganese dioxide and the balance principally lead, and passing a direct current through said cell having the aforesaid purified leach solution as the electrolyte to deposit metallic manganese at the cathode.

13. A composite anode for use in the electrodeposition including the electrowinning of manganese comprising an electrically conducting core and an outer layer containing about 9% to about 50% tin, a small amount to about 4.4% cobalt effective to minimize manganese dioxide formation and the balance principally lead.

14. A process for the electrodeposition of manganese including the electrowinning of manganese, which comprises electrolyzing a solution containing manganese sulfate, ammonium sulfate and sulfuric acid in the presence of an anode comprising an electrically conducting core and an outer layer containing about 9% to about 50% tin, a small amount to about 4.4% cobalt effective to minimize manganese dioxide formation and the balance principally lead.

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