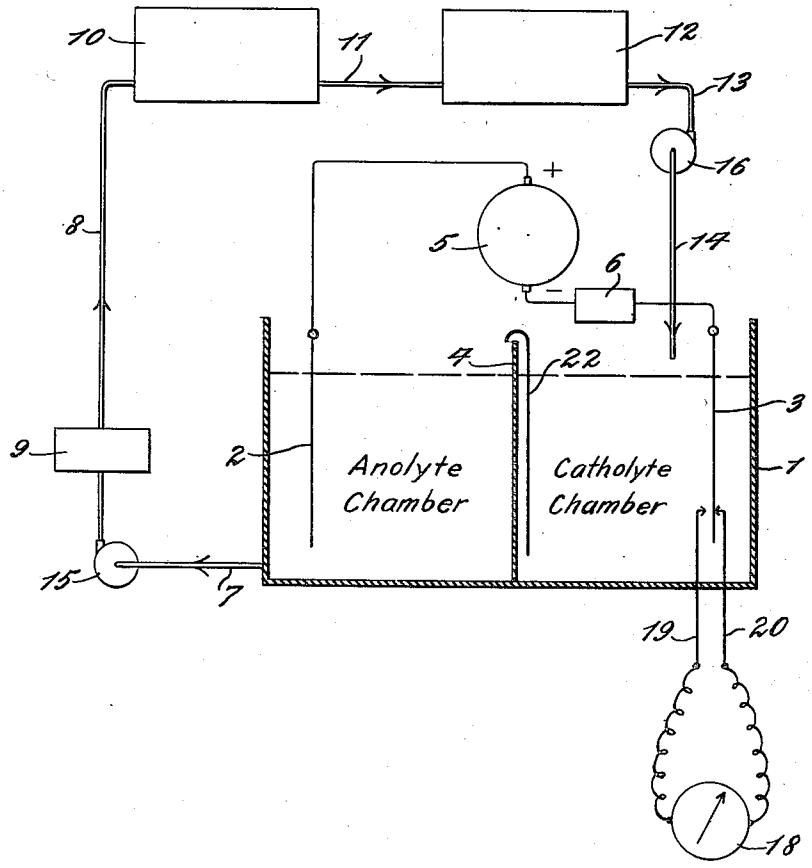
June 9, 1942. C. L. MANTELL 2,286,148

MANGANESE CATHODE VOLTAGE CONTROL

Filed July 11, 1941 3 Sheets-Sheet 1

Fig. 1.



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Filed July 11, 1941 3 Sheets-Sheet 2

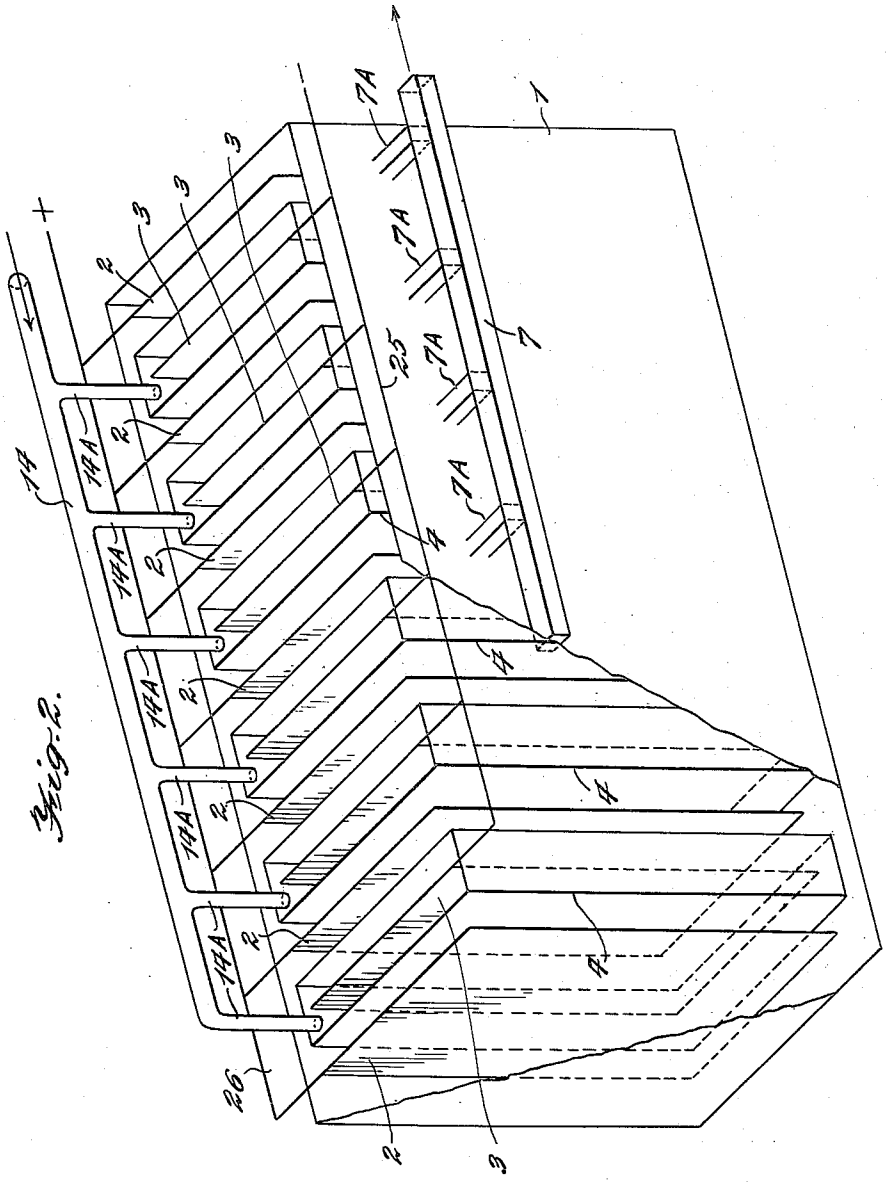


Fig. 2.

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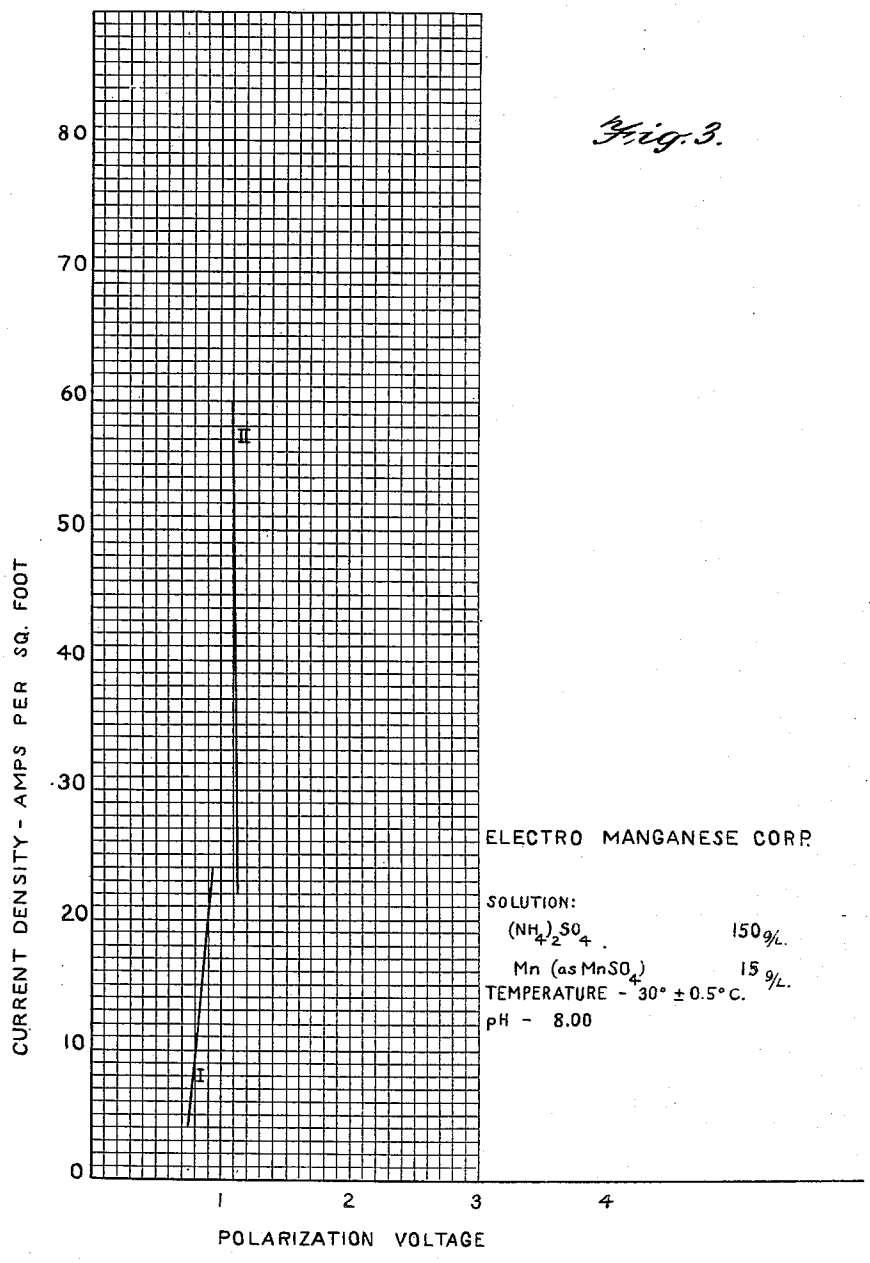


Fig. 3.

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Patented June 9, 1942

2,286,148

UNITED STATES PATENT OFFICE

2,286,148

MANGANESE CATHODE VOLTAGE CONTROL

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Application July 11, 1941, Serial No. 401,893

2 Claims. (Cl. 204—105)

This invention relates to the commercial electro-deposition of manganese from solutions of its salts and is a continuation-in-part of my application Serial No. 343,180, filed June 29, 1940.

It is a principal object of the invention to solve the problem of controlling the deposition of manganese on a cathode so as to obtain uniform and dependable results especially in continuous day-to-day commercial operation and especially in the electrowinning of manganese from its ores.

The principles of the invention will be defined in the claims appended hereto and will be illustrated by the description herein and the accompanying drawings, in which:

Fig. 1 is a diagrammatic flow sheet of apparatus, including an electrolytic cell, for the electrowinning of manganese;

Fig. 2 is a diagrammatic enlarged view of a form of electrolytic cell for use in commercial operations, showing the anodes and cathodes connected, respectively, in parallel with the group of anodes collectively connected in series with the group of cathodes, each cathode being separated from adjacent anodes by a diaphragm; and

Fig. 3 is a curve or graph showing the relation between polarization voltage and current density.

Notwithstanding the large quantity and high quality of the labor and studies devoted to the subject, successful control has not heretofore been achieved.

Among the variables to which much study has been devoted in an attempt to devise a suitable control are the following:

Cathode current density
Anode current density
Composition of electrolytes, i. e., anolyte and catholyte
Temperature
pH
Composition of cathode
Composition of anode

Insofar as any single criterion has been arrived at, the practical skilled workers in the art have proceeded in the belief that control is to be sought by controlling cathodic current density. The application of this criterion, especially to large scale commercial continuous operations, has proved to be unsound. Sometimes the deposits have been good, sometimes bad. One of the phenomena observed is the gradual disappearance of the deposit characterized as "receding." This means that a good deposit is temporarily maintained only to gradually recede or disappear.

This invention is based on the discovery that among the numerous variables, there is one the control of which permits adequate control of manganese deposition and that is the potential drop at the cathode.

In the electrodeposition of manganese it is necessary to segregate the electrolyte into two parts or chambers known as the anolyte chamber and catholyte chamber, respectively. The acid concentrations in both of these chambers are different and change continuously during the course of electrolysis. The catholyte chamber continuously increases in alkalinity and the anolyte chamber continuously increases in acidity.

Changes in current density produce changes in the resistances of the anolyte and catholyte due to changes in the heating effects thus produced. These heating effects in turn cause changes in acid concentration measured by pH, which in turn cause further resistance changes in the anolyte and catholyte. The changes in acid concentration also affect the potential drop between the anode and cathode, respectively, and the electrolyte surounding them. The electrowinning of manganese therefore involves a continual change in the composition and electrical properties at the various points and parts of the system, including changes in the component potential drops and corresponding resistances which in the aggregate make up the over-all cell or tank voltage and over-all resistance, respectively.

The more important voltage drops and resistances are at the following locations:

(*a*) At the anode.
(*b*) In the anolyte.
(*c*) At the diaphragm.
(*d*) In the catholyte.
(*e*) At the cathode.

Changes in current density may produce indeterminate changes in the potential drops and resistances at the locations (*a*) to (*d*) and therefore if current density is used as a criterion of control, cathode voltage drop (*e*) is then determined solely by the difference between over-all cell voltage and the sum of the indeterminate voltage drops at the locations (*a*) to (*d*) inclusive and the voltage drop at location (*e*) is therefore uncontrollable. However, by fixing (*e*), the other variables can be varied over a considerable range without interfering with the satisfactory deposit of manganese.

In other words, changes in current density produce in the system so many changes other than cathode drop that there is either no controllable response or insufficient controllable response in the cathode drop due to changes in current density, to permit the latter to be used as a means of control.

Increase in current density is, of course, obtained by increase in the over-all cell voltage but in manganese electrowinning an increase in cell voltage does not necessarily produce an increase in current density and may, on the contrary, produce a decrease due to changes in the electrical properties of the various component parts of the system.

Current density may be varied over a wide range in the electrowinning of manganese without ever attaining the critical voltage drop at the cathode necessary for successful depositions. On the other hand, if the critical cathode drop is maintained at the correct minimum point or above, it has been discovered that the current density can be varied over a wide range while maintaining this critical minimum drop. Furthermore, if the critical cathode voltage drop is maintained not only can the current density be varied over a wide range, but also the cell voltage can be varied over a substantial range without adversely affecting the manganese deposition.

Thus it is possible to have variation in all of the components of the system except at the cathode without encountering any destructive effect of these variations in relation to the continuance of manganese deposition, by fixing the minimum cathode potential as the mechanism of control.

This is graphically shown by reference to Fig. 3 in which polarization values at the cathode are plotted against current density. These values were obtained in a cell specially devised to obtain polarization values under conditions having practical significance. The cathode had a composition as follows:

Cr	19
Ni	7
Mo	2

Balance, iron.

A saturated calomel half cell was used. No effort was made to exclude air since air is of course present under practical working conditions. The electrolyte had a composition as follows:

	Grams per liter
$(NH_4)_2SO_4$	150
Mn (as $MnSO_4$)	15

The temperature was 30° C.±0.5° C. and the pH was 8.00.

Referring to the curve marked I, as the voltage increases from about 0.75 to about 0.92 the current density increases from 4 to 22 amperes per square foot and no manganese is deposited. Increase in voltage in the range between about 0.92 and 1.13 occurs without an increase in current density. This range represents the beginning of the transformation of manganese from the basic to the metallic form and when the voltage reaches about 1.13 metallic manganese begins to deposit. Increases in cell voltage then produce, under the conditions of the test illustrated in Fig. 3, an increase in current density which may vary from about 22 to 60 amperes per square foot without substantially affecting the polarization voltage.

Referring to Fig. 1, the cell 1 contains an anode 2 and a cathode 3. The cell is divided into anolyte and catholyte compartments by a diaphragm 4 which may be made of canvas or other suitable permeable material. Direct current from the generator 5 is supplied to the anode and cathode as shown.

The generator 5 is equipped with voltage control mechanism 6. Lines 7 and 8 and pump 15 are provided to deliver anolyte liquid from the anolyte chamber through the filter 9 to ore leaching tank 10. Line 11 delivers leach solution from the leach tank 10 to the purification tank 12. Lines 13 and 14 and pump 16 are provided to deliver purified catholyte from purification tank 12 to the catholyte chamber. A potentiometer 18 or other suitable potential measuring device and leads 19 and 20 are provided to measure the potential drop between the cathode 3 and the catholyte liquid. An overflow pipe 22 is provided to permit catholyte liquid to overflow from the catholyte chamber to the anolyte chamber.

Referring to Fig. 2, the cathodes 3 are connected in parallel by the bus bar 25 and the anodes 2 are connected in parallel by the bus bar 26. The cathodes and anodes are then collectively connected in series to the generator as shown in Fig. 1. Each cathode is placed in a compartment or chamber formed by stretching canvas over a wooden frame, the compartment constituting the catholyte chamber or diaphragm chamber and the canvas constituting the diaphragm 4. The spaces between the anodes 2 and diaphragms 4 constitute the anolyte chambers. Catholyte is supplied from the header 14 to each catholyte chamber by downcomers 14A. Anolyte is withdrawn from the anolyte chambers through the laterals 7A which empty into a header 7. In a typical case the total submerged area of each of the two sides of the cathode may be 18 x 30 inches. There may be 27 cathodes and 28 anodes (instead of the number shown in Fig. 2) in a single cell in a typical commercial installation, and in such case the total submerged area of cathode surface is about 203 square feet for each cell. There may be 24 cells connected in series with a single generator, in a typical case. Therefore the total cathode area served by a single generator may be about 4872 square feet. The total area may be greater or less than this value depending on the number of cathodes in each cell, the area of each cathode and the total number of cells. It will be seen therefore that the submerged area of each cathode and the aggregate submerged area of all the cathodes is extensive. As to the composition and properties of the cathode, this need not be described in detail since the invention does not reside in the nature of the cathode material. Advantageously the cathode is a sheet of resilient corrosion-resistant steel having a polished plane surface. The resiliency is desired in order that the deposit of manganese may be removed therefrom by flexing or bending. The anodes may be lead.

In the operation of the apparatus a suitable quantity of conditioned ore, depending upon the capacity of the equipment, is charged into the ore treatment tank 10 and treated with a leach solution having, for example, a concentration of 150 grams per liter of ammonium sulphate and 44 grams per liter of sulphuric acid. The ore prior to the leaching treatment may be a pyrolusite ore suitably conditioned by reduction with reducing gases. Leach liquor from the tank 10 passes through the line 11 to the purification tank 12

where it is suitably purified to remove metallic constituents other than manganese.

At the beginning of operations the anolyte and catholyte chambers may be respectively charged with electrolytes having the following approximate compositions:

Anolyte

	Grams per liter
Manganese as manganese sulphate	15
Sulphuric acid	25 to 30
Ammonium sulphate	150

Catholyte

	Grams per liter
Manganese as manganese sulphate	24 to 26
Ammonium sulphate	150

pH=7.2 to 7.5.

Current is supplied to the anode and cathode at a controllable cell voltage depending upon the size and construction of the cell and in a typical case may be 4.5 to 6 volts. A series of cells may conveniently be connected in series to a standard voltage generator so that the total fall across the series of cells may be equal to the generator voltage. As hereinafter more fully set forth, the cell voltage of each individual cell is controlled by means of the voltage regulator **6** so that the fall in potential between the cathode **3** and its adjacent liquid is maintained at a minimum of about 1.13 volts as measured by the meter **18**. Having fixed the cathode voltage at not below this critical voltage, which determines whether manganese will or will not be deposited, the rate of deposition depends upon the current density and this may be varied over a wide range substantially independently of this critical cathode voltage drop. This range may be, for example, 25 to 60 amperes per square foot of cathode surface. See Fig. 3.

During operation catholyte is fed from tank **12** through lines **13** and **14** to the catholyte chamber and the composition of said feed is preferably maintained to correspond with the catholyte composition above set forth. The catholyte loses manganese and hydrogen and passes through the overflow pipe **22** and through the diaphragm **4** (by diffusion) into the anolyte chamber. Anolyte liquid is continuously withdrawn through line **7** by pump **15**, filtered in the filter **9** to remove any manganese dioxide which may form in the anolyte chamber and delivered to the leach tank **10**. Catholyte may be fed to the catholyte chamber and anolyte withdrawn from the anolyte chamber at rates which maintain a substantially constant level of liquid in the cell. Due to removal of manganese and increase in alkalinity at the cathode, and increase in acidity at the anode, the composition of the anolyte withdrawn from the anolyte chamber is substantially lower in manganese and higher in acidity than the catholyte feed and may be maintained at a composition corresponding to that of the anolyte liquid above set forth. The corresponding power consumption may be about 3.6 kilowatt hours per pound of manganese metal deposited on the cathode and the current efficiency may be about 50–60 per cent of the theoretical. Owing to the composition of the anolyte withdrawn from the anolyte chamber it is preferably, as shown, employed as leach liquor in the tank **10**. The pH of the said anolyte used for leaching is preferably maintained at about 1.3 to 1.6 and that of the catholyte feed at about 7.2 to 7.5.

By continuously regenerating spent anolyte with manganese salt as, for example, by employing it to leach conditioned manganese ore, and suitably purifying the regenerated anolyte particularly by removal of iron, cobalt and nickel, fresh catholyte liquor may be continuously produced and continuously fed to the catholyte chamber and the process of deposition continued until a suitable deposit of manganese is built up on the cathode to the desired and predetermined depth which may be of the order or magnitude of $\frac{1}{8}$ of an inch. When the desired depth has been obtained the cathode is removed and the manganese separated from the cathode plate by suitable manipulation. The removal of the plate from the cell constitutes the end of the plating cycle.

The plating cycle is a function of numerous variables among which are current density, temperature, efficiency of deposition at various plating thicknesses, the mechanical means provided for removal of the cathode with its attached weight of manganese from the cell, the thickness of plate desired and the character of the plate, and in typical cases may vary from thirty-six to over several hundred hours. During the entire plating cycle it is necessary at all times to continuously maintain the voltage drop at the cathode and over the entire submerged area of each cathode and all cathodes at a value not less than the polarization value of manganese and preferably somewhat above it. The importance of this factor may be appreciated when it is realized that in the commercial deposition of manganese a fifteen second power failure may be a sufficient time to cause the manganese deposit to redissolve to the extent that all cathode deposits will be so affected that it is necessary to remove them from the cells, strip the deposits and recondition the cathodes.

The value of the polarization voltage varies to some extent with variations in the concentration and nature of the electrolyte, temperature, pH and current density as illustrated by the examples shown in the following table:

Examples	$(NH_4)_2SO_4$, grams/liter	Mn (as $MnSO_4$), grams/liter	Temp., ° C.	pH	Current density, amps./sq. ft.	Manganese polarization voltage
1	150	15	20	8	15 to 50	1.12 to 1.06
2	150	15	30	8	25 to 60	1.12 to 1.09
3	150	15	40	8	28 to 70	1.15 to 1.00
4	150	15	30	7	28 to 55	1.08 to 0.99
5	150	10	30	7	32 to 60	1.15 to 1.10
6	100	15	30	8	18 to 50	1.13 to 1.00
7	150	25	30	7	24 to 55	1.08 to 1.04
8	150	15	15	8	14 to 50	1.10 to 0.97
9	170	15	30	8	24 to 65	1.10 to 1.09

Under conditions other than those above described, the polarization voltage may be determined by the technique for determining polarization voltages described by Haring, Trans. Electrochem. Soc. 49, 417 (1926).

Manganese salts in general may be used. The sulphate is preferred because of the cheapness of

sulphuric acid. In addition to the manganese salt, a substance acting as a stabilizer is also desirable and for this purpose ammonium salts in general may be employed.

The invention is not primarily concerned with the composition of the electrolytes or anodes but rather with a process of controlling the deposition of manganese from any electrolyte adapted for the electrolytic deposition of manganese therefrom on any cathode adapted for the electrolytic deposit of manganese thereon in the form of a lamina or sheet having a predetermined area and thickness, by continuously maintaining the potential drop at the cathode at a value not less than the polarization voltage of manganese until said sheet or lamina, having said predetermined area and thickness, has been deposited on the cathode.

I claim:

1. The process of controlling the electrolytic deposition of manganese, in the electrowinning thereof, in an electrolytic cell having an anode in an anolyte and a cathode in a catholyte said anolyte and catholyte containing manganese sulfate and ammonium sulfate, said cathode having a surface submerged in the electrolyte, said surface being adapted for the building up thereon of a sheet of manganese having a predetermined area and depth deposited thereon from the electrolyte during electrolysis, which comprises passing a direct current from the anode to the cathode through the electrolyte and maintaining the efficiency of manganese deposition by continuously maintaining the potential drop on the submerged portion of the cathode at a value not less than the polarization voltage of manganese until manganese has been deposited on said cathode to said predetermined area and depth.

2. The process of controlling the electrolytic deposition of manganese, in the electrowinning thereof, in an electrolytic cell having an anode in an anolyte and a cathode in a catholyte said anolyte and catholyte containing manganese sulfate and ammonium sulfate, said cathode having a surface submerged in the electrolyte, said surface being adapted for the building up thereon of a sheet of manganese having a predetermined area and depth deposited thereon from the electrolyte during electrolysis, which comprises passing a direct current from the anode to the cathode through the electrolyte and maintaining the efficiency of manganese deposition by continuously maintaining the potential drop at the cathode and over substantially all parts of the submerged area thereof at a value not less than the polarization voltage of manganese until manganese has been deposited substantially on all parts of said submerged area to said predetermined depth.

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