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PROCESS FOR THE ELECTRODEPOSITION OF MANGANESE

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This invention relates to the production of electrolytic manganese. It relates more particularly to improvements in the process for producing electrolytic manganese from its ores by a cyclic process.

In the processes known in the art, manganese is deposited from solutions containing manganese sulphate or chloride and ammonium sulphate or chloride. Other substances such as perchlorates, nitrobenzene, thiocyanate and sulphur dioxide have been suggested as addition agents to the electrolyte to improve the nature of the deposition. Diaphragm cells have been necessary to obtain control of the acidity of the electrolyte surrounding the cathode.

I have discovered that, if the electrolyte contains a substantial proportion of water-soluble hydroxy amines having the property of forming a complexion with manganese as, for example, alcohol amines or alkylolamines or related compounds, manganese may be deposited from sulphate or chloride solutions without the use of a diaphragm cell and without the use of other addition agents such as those heretofore known. A diaphragm cell may be used in the practice of my invention and when it is used addition agents such as sulphur dioxide or other reducing agents may be added to the catholyte with some improvement in the nature of the deposition. When my invention is employed, however, without the use of a diaphragm cell, the addition agents heretofore employed are essentially of no value since they are very quickly oxidized at the anode. I have found, however, that water-soluble alcohols such as ethyl alcohol or amyl alcohol may be used to advantage when depositing manganese from a non-diaphragm cell. It is my conception that these alcohols are slowly oxidized at the anode to form aldehydes which then function as reducing agents to prevent the building up of manganic salts in the solution.

When my invention is used in connection with a cyclic process, the spent electrolyte may be regenerated by treatment with manganous oxide. Manganous carbonate is not entirely satisfactory. In using manganous oxide for the regeneration of the spent electrolyte, my invention has an advantage over the known art in which ammonium salts are used due to the fact that the amine which is regenerated by the action of manganous oxide is not volatile and, therefore, not subject to loss as in the case of ammonia.

As in the known art, the manganese solution which is used for the practice of my invention must be purified from such materials as copper, zinc, iron, arsenic, cobalt and nickel. While the known methods may be used for this purpose, I have found it particularly advantageous to purify the solution containing a salt of a hydroxy amine in addition to the impure manganese salt by agitating with finely divided manganese which may be produced by my process or by known processes. I have found that finely divided manganese used in this way completely removes copper, zinc, iron, arsenic, nickel and cobalt by agitation from five to twenty minutes at a pH of from 7 to 8. While this method of purification may be used on solutions containing ammonium salts as employed in the prior art, its use is not so efficient due to the greater tendency of manganese to dissolve in ammonium sulphate with the evolution of hydrogen. I wish it to be understood, however, that its use with ammonium salts comes within the practice of my invention.

Having described in a general way my invention and its advantages over the known art, I shall now describe in detail and with illustrative examples the method of practicing my invention. I have found that, in the presence particularly of triethanolamine salts, manganese can be maintained in solution up to a pH of about 8 and that an excess of triethanolamine can be added without an increase of the pH above this value. As a result of this behavior, manganese solutions can be purified in the presence of comparatively large amounts of triethanolamine or the like and the electrolysis carried out with much less drop in pH for a given amount of manganese deposition than with ammonium salts. The spent electrolyte can then be regenerated by treatment with MnO to liberate free triethanolamine or the like and restore the pH to its original value. I have found that diethanolamine, hydroxylamine, monoethanolamine, diethylamino-ethanol and other water-soluble hydroxy amines having the property of forming a complex ion with manganese, preferably of relatively low molecular weight, may be substituted for triethanolamine. I have found that triethanolamine is particularly satisfactory and this, as well as the other hydroxy amines, may be employed in pure, impure or commercial form. It will also be understood that any two or more of such hydroxy amines may be employed in admixture with each other.

In order to more completely explain my invention, I give the following technical examples of my process, it being understood that these are given only as illustrative and in no way limitative of the full scope of my invention.

Example I

An electrolyte was made up of 200 grams of diethanolamine, 60 grams of sulphuric acid, 50 grams of manganese sulphate, and 1 liter of water. This solution had a pH of 7.9. Electrolysis was carried out in a non-diaphragm cell through which the electrolyte flowed. The cathode was stainless steel and the anode lead. The rate of flow of the electrolyte was adjusted so that the pH thereof dropped from 7.9 to 3.5 on passing through the cell. The current density was 11.1 amperes per square decimeter. A bright, dense plate of manganese was obtained with a current efficiency of 53%. Regeneration of the electrolyte to the original pH of 7.9 was readily accomplished by shaking with manganous oxide and finely divided manganese.

Example II

An electrolyte was made up containing 200 grams diethylamino-ethanol, 45 grams sulphuric acid and 56 grams of manganese as sulphate per liter. This electrolyte had a pH of 7.12. Electrolysis was carried out in a non-diaphragm cell at a current density of 12 amperes per square decimeter. The line of flow of the electrolyte through the cell was so adjusted that the pH fell to 5.0 in the passage through the cell. The current efficiency was 60% but the manganese obtained, while dense and metallic, was slightly dark.

Example III

The electrolyte contained 200 grams triethanolamine, 50 grams sulphuric acid and 56 grams of manganese as sulphate per liter, electrolysis being carried out in a diaphragm cell. The original pH of the solution was 8.05 which remained practically constant in the cathode compartment. In the anode compartment, the pH was allowed to drop to approximately 1.5. The current density was 10 amperes per square decimeter and the current efficiency was 60%, the plate obtained being bright and dense. Regeneration of the electrolyte was accomplished by shaking with manganous oxide and powdered manganese.

Example IV

In this example, the manganese was plated on an aluminum surface using an insoluble lead anode. The electrolyte contained 250 grams diethanolamine, 68 grams sulphuric acid and 60 grams manganese sulphate per liter. The pH of this solution was 7.58, plating was carried out at a current density of 12 amperes per square decimeter, and the plate was dense, bright and adherent. The pH during electrolysis fell to 6.21.

It will be understood that the above examples are merely illustrative of my invention. Various changes may be made by those skilled in the art in the light of my teachings herein without departing from the spirit of my invention as more particularly pointed out in the appended claims.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. A process for the electro-deposition of high purity manganese comprising introducing an electrolyte into an electrolytic cell containing an insoluble anode, the electrolyte consisting essentially of an aqueous solution of alkylolamine and manganese salts, the salts being selected from the group consisting of sulphates and chlorides, the solution containing at least 5 grams per liter of manganese, the concentration ratio of alkylolamine to manganese being greater than about 3 to 1, and then electrolyzing wtih a minimum cathode current density of about two amperes per square decimeter.

2. A process in accordance with claim 1 wherein the regeneration of the electrolyte is effected by the addition of manganous oxide thereto.

3. A cyclic process for the electro-deposition of high purity manganese comprising introducing an electrolyte into an electrolytic cell containing an insoluble anode, the electrolyte consisting essentially of an aqueous solution of alkylolamine and manganese sulphate, the solution having a minimum concentration of about 5 grams per liter of manganese, the concentration ratio of alkylolamine to manganese in solution being not less than about 3 to 1, and electrolyzing with a minimum cathode current density of about two amperes per square decimeter while causing the electrolyte to circulate through the electrolytic cell at such a rate that the pH is maintained at a desired value.

4. A process of electrolytically depositing manganese to form a bright metallic deposit which consists in introducing an electrolyte consisting essentially of an aqueous solution of manganese sulphate and a salt of an alkylolamine into an electrolytic cell containing an insoluble anode and carrying out the electrolysis at a pH between about 8.0 and about 3.0.

5. A process of electrolytically depositing manganese which comprises conducting the electrolysis in a non-diaphragm cell, having an insoluble anode, the electrolyte consisting essentially of an aqueous solution of an alkylolamine and at least about 5 grams of manganese in the form of manganese sulphate per liter and the current density being at least about 2 amperes per square decimeter.

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