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TREATMENT OF ELECTROLYTES FOR THE DEPOSITION OF MANGANESE

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My invention relates in general to the electrodeposition of substantially pure manganese metal from solutions of its salts and more particularly to methods for inhibiting the oxidation of neutral or slightly alkaline solutions of manganous salts, particularly when employed in an electroplating circuit.

In the known art, manganese has been plated from solutions of its salts containing ammonium salts at a pH in the range of 6.5 to 8.0. Within this pH range manganous salts are subject to oxidation by air to produce manganic compounds which are objectionable both through the loss of manganese by the deposition of insoluble hydrated oxides and through the loss of current efficiency by the alternate formation and reduction of these compounds in the electrolytic cell. While this tendency to oxidation of manganous salts is to some extent overcome by the addition of certain ammonium salts, it is found to be advantageous to add an agent to the solution which inhibits still further this oxidation. Such agents are those which will be oxidized in preference to the oxidation of the manganous salts and thereby preserve the latter from oxidation. The usual agent for this purpose is sulphur dioxide. There are, however, several important objections and inconveniences in connection with the use of this reagent. The sulphite of manganese which is formed by its addition to manganous salt solutions is a relatively insoluble compound. Consequently, the effective concentrations of sulphur dioxide which may be used are very low, being of the order of 0.1 gram per liter. As a result of this limited solubility of manganese sulphite continual small additions of sulphur dioxide must be made to the solution in order to maintain a sufficient concentration to effectually prevent oxidation of the manganous salts. Even under these conditions, some oxidation usually takes place. The use of a gaseous addition agent also presents certain inconveniences and there is, further, an accumulation of sulphuric acid in the electrolyte due to this addition which tends to gradually increase the manganese content of a circulating electrolyte, eventually reaching a point where some method of compensation must be employed to remedy the condition.

I have outlined some problems in connection with the use of sulphur dioxide and similar agents to illustrate the features of my invention and those skilled in the art are familiar with other problems, such as the formation of thionates and related sulphur compounds which accumulate in the circuit.

Other agents to stabilize manganous salt solutions and promote improved deposition of manganese have been used, such as acetaldehyde, but they have the objection of causing the accumulation in the re-circulated electrolyte of their undesirable oxidation products.

The principal object of my invention is to so handle solutions of salts of manganese, particularly in re-circulating electrolytic processes, so as to overcome the types of problems discussed hereinabove.

Other objects and features of the invention will be clear to those skilled in the art from the consideration of the following description:

I have discovered that a certain class of compounds is very effective in stabilizing manganous salt solutions and in improving their performance in manganese plating circuits operated in accordance with the known art in such plating operations. This class of compounds is characterized by having as their oxidation products only one or more of the substances water, carbondioxide and nitrogen. It will be obvious that compounds of this class cannot cause the accumulation of objectionable substances in the plating solution. Other characteristics of these compounds are their solubility in the water to a high degree and their compatibility with the other constituents of the solution, consequently permitting their use in any desired concentration.

Among this class of compounds which I have found highly efficacious not only in inhibiting oxidation of the manganous salts but in increasing the brightness and coherence of the manganese metal plate and in increasing the current efficiency of the plating operation are hydroxylamine, formaldehyde, urea, guanidine and derivatives of these substances in which the structural arrangement is such that oxidation to only one or more of the substances carbon dioxide, water, and nitrogen may take place in the solution. Such derivatives, for example, are hydroxylamine sulphate, oximes of aldehydes in which every carbon atom except the final one has attached to it at least one hydroxyl group, such as lactic oxime or glyoxime and compounds of formaldehyde such as hexa-methylene-tetra-amine which in alkaline solutions decomposes to form formaldehyde and ammonia; and amines and amidines which contain only one carbon atom or in which all except the final carbon atom have attached to them at least one hydroxyl group. Since the plating solution frequently contains ammonia, some of which is lost by vaporization, the addition of a small amount of ammonia in

this way is not objectionable. It will be clear that acid derivatives of these compounds may be used providing that the acid radical is the one that is normally contained in the circuit. For example, in the customary plating from a sulphate circuit, hydroxylamine sulphate would be used whereas in plating from a chloride bath hydroxylamine hydrochloride would be employed. While the acid derivatives of substances of the type disclosed may be used, for the reasons indicated hereinabove, I prefer to employ only those substances which oxidize to one or more of the substances nitrogen, water or carbon dioxide. Hydroxylamine is unusually satisfactory and is preferably employed as a salt such as hydroxylamine sulphate.

As an example of the use of my invention, I have used a plating solution containing approximately 25 grams per liter of manganese as manganese sulphate and 200 grams per liter of ammonium sulphate. This solution, after being formed from the leaching of manganous oxide with spent electrolyte from a previous plating operation, has a pH of approximately 7 to 8. After being purified to remove iron, arsenic, nickel, cobalt and copper and other materials which were found in excess in the particular ore under treatment, this solution is relatively unstable, forming a brown precipitate of hydrated manganic oxide within 30 minutes when exposed to the air. The manganese which was plated from such a solution using a diaphragm cell with a current density of 20 amperes per square foot was dense and coherent but of a dark color and the current efficiency was approximately 40%. When the same solution was treated with 0.1 gram per liter of hydroxylamine it was found to remain completely colorless and unchanged over a period of several days. The manganese deposited from this solution was bright, smooth and of excellent quality and the current efficiency was more than 70%. As indicated hereinabove, hydroxylamine may be conveniently added to the circuit in the form of hydroxylamine sulphate using about 0.5 of a gram per liter. Since one addition of hydroxylamine sulphate suffices to stabilize the solution for a relatively long period, the amount of sulphuric acid which is added to the circuit in this way is much less than that introduced by sulphur dioxide to accomplish the same stabilization and, furthermore, the sulphur added in this way is and remains entirely in the form of sulphate ions whereas the oxidation of sulphur dioxide produces not only sulphuric acid but an indeterminate quantity of several thionates whose accumulation in the circuit is objectionable. If even this addition of sulphate ion should prove objectionable, the hydroxylamine can be made immediately before use by the addition of a stoichiometric equivalent of barium hydroxide to hydroxylamine sulphate, for example, and introduced immediately into the circuit.

Another example of my invention is the use of formaldehyde. This may be introduced most conveniently in the form of the commercial formalin solution containing 37% of formaldehyde. I have found that formaldehyde is approximately as effective in a given concentration as sulphur dioxide but not so effective as hydroxylamine. I prefer to use 0.5 gram per liter of formaldehyde since this amount gives increased desirable effects over those obtained, for example, with a saturated solution of the sulphite ion.

Those skilled in the art will understand that the proportion of addition agent which may be employed in accordance with my invention in the electrolyte will vary to a considerable extent with the particular addition agent used, the concentration of manganese salts in a solution and the stabilizing effect desired. For example, in the case of hydroxylamine very much smaller proportions may be employed than given in the illustrative example. So effective is hydroxylamine that an amount of 0.1 gram per liter is at least as effective as a saturated solution of sulphite ions formed by the introduction of sulphur dioxide.

While I have described my invention in considerable detail in order that those skilled in the art may understand how to practice it, the invention is limited only by the scope of the appended claims.

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

1. The method of electrodeposition of manganese from solutions of salts thereof which comprises providing an aqueous solution containing manganous sulphate, ammonium sulphate substantially in excess of the manganous sulphate and a small proportion of hydroxylamine sulphate, introducing said solution into the catholyte compartment of a diaphragm cell, said cell being provided with cathodes and anodes, and passing a current between said anodes and cathodes to electrolytically deposit manganese in the form of a metal onto the cathodes.

2. In the process of producing electrolytic manganese from aqueous electrolyte solutions containing a member selected from the group consisting of manganous sulphate and manganous chloride and, respectively, a member selected from the group consisting of ammonium sulphate and ammonium chloride, said solutions being substantially neutral or slightly alkaline, the steps of introducing into such solution a relatively small proportion of hydroxylamine, and electrolyzing said solution in the catholyte compartment of a diaphragm cell, said cell containing cathodes and anodes, to electrolytically deposit manganese in the form of a metal onto the cathodes.

3. The method of electrodeposition of manganese from solutions of salts thereof which comprises providing an aqueous solution containing manganous sulphate, ammonium sulphate substantially in excess of the manganous sulphate, and a small proportion of hydroxylamine sulphate, said solution having a pH between approximately 6.5 and 8, introducing said solution into the catholyte compartment of a diaphragm cell, said cell being provided with anodes and cathodes, and passing a current between said anodes and cathodes to electrolytically deposit manganese in the form of a metal onto the cathodes.

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