Patented Aug. 15, 1939

2,169,540

UNITED STATES PATENT OFFICE

2,169,540

PURIFICATION OF MANGANESE SULPHATE SOLUTIONS

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No Drawing. Application November 19, 1937, Serial No. 175,538

12 Claims. (Cl. 204—1)

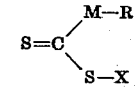
This invention relates broadly to electrolytic processes for the extraction of metallic manganese from aqueous solutions and, more particularly, relates to the purification of manganese solutions.

While the invention to be described and claimed may be employed for the purification of manganese solutions in general, it is particularly adapted and intended for the purification of manganese sulphate solutions from which metallic manganese is to be extracted by processes such as that described and claimed in my co-pending application Serial No. 100,131, filed September 10, 1936, now Patent 2,119,560, issued June 7, 1938.

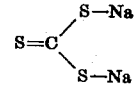
In working with managenese sulphate electrolytes, I have found that even the most minute quantities of nickel and cobalt in the electrolyte are harmful, having the effect of retarding the electrolytic deposition and causing the deposition of impure manganese on the cathodes. I have found that the removal of these metals from the electrolyte must be complete in order to avoid their deleterious effects, the last one or two milligrams per liter of these impurities being as harmful to proper deposition and the securing of a pure deposit as larger amounts. Laboratory processes for the removal of these impurities have been found to be entirely unsatisfactory in commercial operations, not only from the standpoint of proper electrolytic operation and the securing of pure deposits but also by reason of the high cost of the necessary reagents. For example, in laboratory work, dimethyl glyoxime is regarded as an ideal and accurate precipitant for nickel, but this reagent is entirely unsatisfactory for the removal of nickel from manganese electrolytes. This is due not only to the high cost of this reagent but also, and principally, to the fact that it fails to precipitate the last two milligrams per liter of nickel. Alpha furil dioxime is stated by the literature on the subject to be sensitive to one part of nickel in six million but even this reagent fails to precipitate nickel satisfactorily for producing suitable manganese electrolytes. In addition, it is far too expensive to be of value in commercial electrolytic deposition operations. Other means and reagents suggested by the literature for removing nickel and cobalt from manganese solutions have proved to be of equal lack of efficacy in purifying electrolytes of the type under consideration.

This invention provides a method for effecting the purification of manganese solutions, particularly those of manganese sulphate, prior to electrolysis thereof, by precipitating from the solution impurities of the group including nickel and cobalt. The process according to the invention is operable to cause the removal of the last traces of these impurities from the manganese solution and to cause their precipitation as a compound which will not redissolve in the solution. Further, the process employs reagents which will not adversely affect the electrolysis of the solution, either by retarding deposition or by contaminating the deposit.

In the process according to this invention the impurities nickel and cobalt are precipitated from a manganese solution, and particularly from a manganese sulphate solution, by treating the solution with compounds of the so-called xanthate type. These compounds, as is known, are the di-salts of thiocarbonic acid and I have found that while it is probable that all of the xanthate-type compounds are effective to a certain degree in causing the desired removal of nickel and cobalt, certain of these compounds are much more effective than others. In general, the process may be effectively carried out by treating the manganese solution with a compound of a derivative of thiocarbonic acid which is soluble in the manganese solution being treated. Such compounds have the general formula



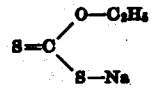
in which M is either a sulphur or an oxygen atom, depending upon whether the compound is a tri-thiocarbonate or a di-thiocarbonate, R is either an alkali metal atom or an alkyl radicle, and X is an alkali metal atom. The tri-thiocarbonates of the type



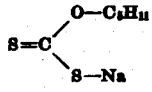
are not satisfactory precipitants of nickel, cobalt, copper, etc., from manganese sulphate solutions. However, I have found that compounds of the di-thiocarbonate class are accurate and complete precipitants of these impurities from maganese sulphate solutions and are effective in removing the last one or two milligrams per liter of nickel, cobalt, and copper from such electrolytes.

The di-thiocarbonates, or xanthates, are formed by simultaneously mixing carbon disulphide with an alkali and an alcohol, in the proper stoichometric proportions. For example, if carbon disulphide, sodium hydroxide and ethyl alcohol are mixed in the proper proportions, sodium ethyl

di-thiocarbonate is formed, having the following molecular structure:



If an amyl alcohol is used in place of the ethyl alcohol in the described reaction, an amyl di-thiocarbonate is formed which may have the following molecular structure:



The amyl radical may exist as pentasol, di-ethyl carbinol or other isomer but retains the formula C_5H_{11} for empirical formula purposes. Any of the alcohols whatsoever may be used in the preparation of the xanthate compound, the choice depending largely upon the required properties of the resulting xanthate compound with respect to the solution to be treated, and it is to be understood that my invention is not limited in any way to any particular alkyl di-thiocarbonate or xanthate compound, but is inclusive of all compounds of this class.

Irrespective of the particular alcohol employed, the alkyl thiocarbonates, or xanthates, are effective precipitants of nickel, cobalt and copper from manganese sulphate solutions. I have found, however, that xanthates of the heavier alcohols are most efficient in effecting this precipitation. For example, less amyl xanthate than ethyl xanthate is required to precipitate the final milligram of nickel or cobalt from a liter of manganese sulphate. The amyl xanthate is more expensive than the ethyl xanthate, however, and I have found that satisfactory results may be obtained by employing a mixture of the two.

In carrying out my process I prefer to use the alkali xanthates, such as sodium ethyl di-thiocarbonate, sodium amyl di-thiocarbonate, potassium ethyl di-thiocarbonate and potassium amyl di-thiocarbonate. The accumulation of alkali in the electrolyte has not been found to have deleterious effects on the deposition of metal from the solution, and the use of the alkali xanthates has the additional advantage of aiding in reducing the acidity of the solution. While any other compound of the xanthate type might be employed, it would be necessary of course to use only those which are sufficiently soluble in the manganese solution being treated.

It is preferable to employ, in actual commercial operation, more precipitating reagent than is required by theoretical considerations. The exact amount of excess required appears to be of no importance in effecting the precipitation, but the purification is facilitated by the use of the excess. A relatively small excess of xanthate in the electrolyte has no deleterious effect on the electrolysis of the solution.

The following procedure constitutes an example of how the process according to this invention may be actually carried out. The solution which is to be purified may constitute a neutral solution of manganese and ammonium sulphates containing five milligrams per liter of nickel and five milligrams per liter of cobalt at room temperature. This solution may be prepared by leaching ores, roasted concentrates or other manganese bearing materials with sulphuric acid or ammonium sulphate solution. To this solution is added 0.2 gram per liter of potassium pentasol xanthate and 0.3 gram per liter of sodium ethyl xanthate. The solution is then stirred slowly or intermittently for about three hours and then filtered. No heating is required and the precipitation may be carried out at room temperature. The filtered solution will contain no measureable quantities of nickel or cobalt and the electrolyte, formerly unsatisfactory for manganese deposition, will now deposit pure metallic manganese at reasonably high current efficiency. The impurities nickel and cobalt will be precipitated as nickel and cobalt xanthates which are insoluble in manganese sulphate solution or in a solution of manganese and ammonium sulphates. If desired, proper amounts of an ethyl xanthate or an amyl xanthate may be employed as the precipitating reagent instead of the mixture of these two as in the procedure outlined. The use of one only of these reagents will be effective in removing nickel and cobalt impurities within the limitations set forth hereinbefore.

If desired, nickel and cobalt values may be recovered from the impurity precipitate by suitable means.

I have found that copper, bismuth, lead, antimony, arsenic, iron and silver may be precipitated with nickel and cobalt by the method and means disclosed in this application. These impurities may be removed by less expensive means, however, and it will usually be found that removal of these impurities by such other suitable means and prior to the precipitation of nickel and cobalt will be more economical practise.

While I have described the process according to my invention specifically and in detail, it is to be understood that the invention is limited only by the scope of the appended claims.

What I claim is:

1. In a process for the electrodeposition of metallic manganese from an aqueous manganese sulphate solution, the step of purifying the solution prior to electrolysis by removing nickel and cobalt therefrom, which comprises adding to the solution a xanthate.

2. In a process for the electrodeposition of metallic manganese from an aqueous manganese sulphate solution, the step of purifying the solution prior to electrolysis by removing nickel and cobalt therefrom, which comprises adding to the solution an alkali metal xanthate.

3. In a process for the electrodeposition of metallic manganese from an aqueous manganese sulphate solution, the step of purifying the solution prior to electrolysis by removing nickel and cobalt therefrom, which comprises adding to the solution an ethyl xanthate.

4. In a process for the electrodeposition of metallic manganese from an aqueous manganese sulphate solution, the step of purifying the solution prior to electrolysis by removing nickel and cobalt therefrom, which comprises adding to the solution an amyl xanthate.

5. In a process for the electrodeposition of metallic manganese from an aqueous manganese sulphate solution, the step of purifying the solution prior to electrolysis by removing nickel and cobalt therefrom, which comprises adding to the solution an alkyl thiocarbonate compound at room temperature.

6. In a process for the electrodeposition of metallic manganese from an aqueous manganese sulphate solution, the step of purifying the solution prior to electrolysis by removing nickel and cobalt therefrom, which comprises adding to the solution an amount of an alkyl thiocarbonate compound which is in excess of the amount

theoretically required to form di-thiocarbonate compounds with the nickel and cobalt in the solution.

7. In a process for the electrodeposition of metallic manganese from an aqueous manganese sulphate solution, the step of purifying the solution prior to electrolysis by removing nickel and cobalt therefrom, which comprises adding to the solution a mixture of alkyl thiocarbonates.

8. In a process for the electrodeposition of metallic manganese from an aqueous manganese sulphate solution, the step of purifying the solution prior to electrolysis by removing nickel and cobalt therefrom, which comprises adding to the solution a mixture of amyl thiocarbonate and ethyl thiocarbonate.

9. In a process for the electrodeposition of metallic manganese from an aqueous manganese sulphate solution, the step of purifying the solution prior to electrolysis by removing nickel and cobalt therefrom, which comprises adding to the solution a mixture of an amyl xanthate and ethyl xanthate.

10. In a process for the electrodeposition of metallic manganese from an aqueous manganese sulphate solution, the step of purifying the solution prior to electrolysis by removing nickel and cobalt therefrom, which comprises adding to the solution a mixture of an amyl xanthate and an ethyl xanthate both of which are appreciably soluble in the solution.

11. In a process for the electrodeposition of metallic manganese from an aqueous manganese sulphate solution, the step of purifying the solution prior to electrolysis by removing nickel and cobalt therefrom, which comprises adding to the solution a mixture of an alkali metal amyl xanthate and an alkali metal ethyl xanthate.

12. In a process for the electrodeposition of metallic manganese from an aqueous manganese sulphate solution, the step of purifying the solution prior to electrolysis by removing nickel and cobalt therefrom, which comprises adding to the solution a mixture of an alkali metal amyl xanthate and an alkali metal ethyl xanthate both of which are appreciably soluble in the solution.

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