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RECOVERY OF MANGANESE BY ELECTROLYSIS

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This invention relates to the process of recovering metallic manganese by electrodeposition from an electrolyte containing manganese and ammonium sulfates, and has for its object the provision of certain improvements in that process.

In recovering manganese by electrodeposition from an electrolyte containing manganese and ammonium sulfates, a diaphragm cell is used to permit the deposition of metallic manganese from a neutral or alkaline catholyte while sulphuric acid and unavoidably some manganese oxides are produced at the anode. The diaphragm separates anolyte from catholyte and permits maintaining a pH above 6.0 in the catholyte, thereby reducing re-solution of metallic manganese and excessive evolution of hydrogen. The diaphragm also prevents contamination of the catholyte with manganese oxides and lead compounds formed at the lead anode, and further permits the maintenance of a sufficiently high sulfuric acid concentration in the anolyte for recycling to dissolve fresh manganese-bearing material, such as roasted manganese ore, thereby providing manganese sulfate solution for electrolysis.

While the process would theoretically be expected to give satisfactory results, certain difficulties are encountered in practice which greatly impair its usefulness. The principal difficulty is the nature of the deposit of metallic manganese. Using stainless steel cathodes as starting sheets, only a relatively small deposit of smooth and coherent manganese is obtained before the deposit starts to become rough and porous and nodules or "trees" start to form, thereby rapidly impairing the current efficiency until the deposition of manganese ceases entirely. Various additive agents (such as a sulfite ion, alcohol, glycerine, formaldehyde, gum arabic, gelatine, ammonium oxalate, ammonium citrate etc.) have been included in the electrolyte in an attempt to obtain smoother deposits of manganese, but my own investigations indicate that while the use of some of these agents do improve the deposit, no noteworthy improvement in the over-all electrolytic process is obtained.

I have discovered, in the course of an extended investigation of the manganese electrodeposition process, that certain organic acids and certain substitution products thereof, when included in the catholyte in suitable amount, effect a marked improvement in the quality of the manganese deposit without significantly impairing the current efficiency before an economically sufficient amount of manganese has been deposited. The organic acids which I have found suitable for the purpose are dibasic and contain at least three carbon atoms in the molecular formula, and may be either aliphatic (saturated or unsaturated) or aromatic. Based on that discovery, the present

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invention, in its broad aspect, involves the inclusion in the catholyte in the aforementioned manganese electrodeposition process of a small amount of a smoothing agent selected from the group consisting of (1) dibasic organic acids having at least three carbon atoms in the molecular formula and (2) non-hydroxy substitution products of such dibasic acids. More specifically, such dibasic acids and their substitution products may be represented by the formula

$$\begin{matrix} R{=}(COOH)_2 \\ | \\ R_1 \end{matrix}$$

where R is a radical selected from the group consisting of saturated and unsaturated aliphatic radicals and aromatic radicals, and R_1 is a non-hydroxy radical selected from the group consisting of hydrogen, a halogen and an amine. In a more restricted aspect of the invention, the smoothing agent is selected from the group consisting of dibasic aliphatic acids of the general formula $(CH_2)_n(COOH)_2$ where n is one or more and non-hydroxy substitution products thereof. Among the many such dibasic organic acids that I have investigated especially satisfactory results have been obtained with adipic, glutaric, succinic and phthalic acids.

The amount of the organic smoothing agent included in the catholyte may vary generally from about 0.1 to about 1 gram per liter. The optimum concentration of the smoothing agent, for the purposes of the invention, varies somewhat with the concentration of the other constituents in the electrolyte, the type of diaphragm cell employed, the temperature and other operating conditions. Simple tests will usually be found desirable to determine the optimum concentration of any particular smoothing agent under the prevailing operating conditions. A concentration of smoothing agent smaller than the optimum results in decreased effectiveness, while a concentration above the optimum gives smooth but strained deposits, which tend to peel off the starting sheet prematurely. The concentration of smoothing agent for optimum results increases with increase in the temperature of the electrolyte.

The following Table I gives the results obtained in several tests carried out in a laboratory diaphragm cell having a rotating (stainless steel) rod cathode operating at a current density of 80 amperes per square foot. The catholyte contained 180 grams per liter of ammonium sulfate ($(NH_4)_2SO_4$) and 30 to 40 grams per liter of manganese (Mn) as the sulfate, and also contained the indicated smoothing agent in approximately its optimum concentration (grams per liter) for the conditions of the tests. In these tests, the electrolyte temperature was 20° C., and electrolysis was continued until the deposit of manganese

started to become rough. For purposes of comparison, the results of tests are given in which pyruvic, tartaric and citric acids, respectively, were used in lieu of a smoothing agent of the invention. Pyruvic acid is monobasic. While tartaric acid is dibasic, it is a dihydroxy substitution product of succinic acid, and citric acid is a hydroxy substitution product of tricarballylic acid.

Table I

Acid Smoothing Agent	Chemical Formula	Concentration	Weight of Deposit	Current Efficiency
Malonic	$CH_2(COOH)_2$	0.3	2.5	63
Succinic	$(CH_2)_2(COOH)_2$	0.4	2.6	70
Glutaric	$(CH_2)_3(COOH)_2$	0.4	2.5	70
Adipic	$(CH_2)_4(COOH)_2$	0.4	2.3	65
Azelaic	$(CH_2)_7(COOH)_2$	0.15	2.2	63
Maleic	$(CH=CH)(COOH)_2$	0.6	2.3	65
Aspartic	$CH_2CHNH_2(COOH)_2$	0.3	2.6	70
Glutamic	$(CH_2)_2CHNH_2(COOH)_2$	0.5	3.0	64
Pyruvic	$CH_3COCOOH$	0.6	0.7	59
Tartaric	$(CHOH)_2(COOH)_2$	0.15	1.4	61
Citric	$(CH_2)_2COH(COOH)_3$	0.05	1.4	58

The weight of the deposit is reported in pounds per square foot of cathode surface. In judging the results of the tests, the weight of the deposit, its quality and the current efficiency must be considered together. In electrodeposition tests of this type, it is usual to grade the quality of the deposit as "good," "fair" and "poor," the deposit obtained in the absence of any smoothing agent being nodular and "poor." In each of the tests reported in Table I, the quality of the deposit was "good," except in the case of tartaric acid where the deposit was "fair." As the weight of the deposit increases, the roughness and porosity of the deposit increase and the current efficiency decreases. In the tests using a smoothing agent of the invention, an economically sufficient weight of deposit was obtained before manganese began to deposit in a rough and porous state, with consequent lowering of the current efficiency. On the other hand, in the tests using pyruvic acid and citric acid, while the quality of the deposits was good, a much smaller weight of deposit was obtainable before the deposit started to be rough and porous, and the current efficiencies were lower at all times.

In another series of tests carried out under the same general conditions (Table II) electrolysis was continued for 14 hours, the temperature of the electrolyte being 20–25° C.

Table II

Acid Smoothing Agent	Chemical Formula	Concentration	Weight of Deposit	Current Efficiency
Phthalic	$C_6H_5(COOH)_2$	0.35	1.8	70
Adipic	$(CH_2)_4(COOH)_2$	0.45	1.9	74
None			1.4	57

The following Table III records the results of an operation carried out in a commercial size diaphragm cell. The anode was of lead and the cathode was a stainless steel sheet measuring overall 18 inches by 36 inches. The catholyte contained 35–40 grams per liter of manganese as sulfate, and 150–160 grams per liter of ammonium sulfate, and was separated by a 16 ounce cotton diaphragm from an acid anolyte containing less manganese and ammonium sulfate per liter. The current density was 80 amperes per square foot, the temperature of the catholyte was 25° C., the distance between anode and cathode was 2 inches, and the deposition time was 12 hours. The first two deposits were made in the presence of 0.4 gram of adipic acid per liter in the catholyte, and the last two deposits were made in the absence of any soothing agent.

Table III

Deposit	Adipic Acid Concentration	Weight of Deposit	Current Efficiency
1	0.4	1.58	73
2	0.4	1.56	72
3	0	1.41	65
4	0	1.35	62

The first two deposits were homogeneous throughout and their outer surfaces were sufficiently smooth to continue with the electrodeposition for several hours more without serious decrease in the current efficiency. On the contrary, the last two deposits were nodular and porous and their outer surfaces were so nodulized that further electrodeposition would result in a marked decrease in current efficiency. The presence of adipic acid occasions no special starting requirements. However, from 1 to 10 milligrams of zinc per liter of catholyte is a definite help when starting trouble arises. Starting troubles appear to be due to incomplete elimination of impurities, and the zinc seems to promote adhesion of the initial deposit to the starting sheet and minimizes the formation of pin holes in the deposit.

In addition to the dibasic organic acids themselves non-hydroxy substitution products thereof may be used as the smoothing agent. The substitution of a hydroxy radical impairs the current efficiency as well as the quality of the deposit (see tartaric acid in Table I). On the other hand, amino (NH_2) substitution products (aspartic and glutamic acids, Table I) increase the adherence of the deposit. Halide substituted products (such as the chloride, bromide and iodide) act similarly to the unsubstituted acid.

The structure of polybasic organic acids is believed to account, to some extent at least, for their effectiveness as smoothing agent. Of the many theories advanced to explain the effects of additive agents on the character of metallic electrodeposits, those attributing the effect to adsorption appear the most acceptable. According to such theories, the additive agent is adsorbed on the surface of the metal being deposited and its presence so affects the deposition of additional

metal ions that a more uniform growth of the deposit takes place. Since polar compounds are generally concentrated at an interface in an oriented arrangement, it is believed that a dibasic acid may be more strongly adsorbed or may present more active carboxyl groups to the approaching manganese ions than is possible in the case of monobasic acids. Whatever the explanation, the dibasic acids minimize the disordered or localized growth of the deposit which results in excessive nodulizing or "treeing," and their inclusion in the manganese-ammonium sulfate catholyte has a marked beneficial effect on the quality of the deposit, the amount of good quality deposit obtainable, and the current efficiency.

I claim:

1. In the recovery of metallic manganese by electrodeposition in a diaphragm cell from an electrolyte consisting essentially of a solution of manganese and ammonium sulfates, the improvement which comprises including in the catholyte from 0.1 to 1 gram per liter of an organic smoothing agent of the group of organic acids consisting of adipic, aspartic, azelaic, glutamic, glutaric, maleic, malonic, phthalic, and succinic acids.

2. In the recovery of metallic manganese by electrodeposition in a diaphragm cell from an electroylte consisting essentially of a solution of manganese and ammonium sulfates, the improvement which comprises including in the catholyte from 0.1 to 1 gram per liter of adipic acid.

3. In the recovery of metallic manganese by electrodeposition in a diaphragm cell from an electrolyte consisting essentially of a solution of manganese and ammonium sulfates, the improvement which comprises including in the catholyte from 0.1 to 1 gram per liter of succinic acid.

4. In the recovery of metallic manganese by electrodeposition in a diaphragm cell from an electrolyte consisting essentially of a solution of manganese and ammonium sulfates, the improvement which comprises including in the catholyte from 0.1 to 1 gram per liter of phthalic acid.

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