

Specification No. 60333, Application No. 60333 dated 27th April 1957. Complete specification left on 27th February 1958. (Application accepted 24th October 1958.)

PROVISIONAL SPECIFICATION

IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF BATTERY GRADE MANGANESE DIOXIDE FROM LOW GRADE MANGANESE ORES.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification describes the nature of this invention.

THIS IS AN INVENTION BY VEERARAGAVA ARAVAMITH AN AND THIRUMANGALAM RENGASWAMI VENKATASUBRAMANIAN, BOTH OF THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, BOTH INDIAN CITIZENS.

The invented process for the electrodeposition of manganese dioxide consists in the addition of 7-12 cc. of nitric acid of 1.42 specific gravity per litre of manganese sulphate solution in water. The advantages of addition of proper amounts of nitric acid as stated above and conducting electrolysis under conditions herein after claimed in this patent have not so far been reported in literature. The beneficial effects of addition of nitric acid in general and more so in quantities stated above to produce battery grade manganese dioxide by electrolysis of manganese sulphate solution in water have not so far been reported in literature. By such an addition it is possible.

- (i) to work with high current densities which are of the order of 3 times the anode current densities employed (30 amps per sq. ft. instead of 9 amps per sq. ft.) When pure manganese sulphate solutions are electrolysed commercially to get the desired quality of manganese dioxide (gamma form of manganese dioxide containing not less than 68 per cent. manganese dioxide and not more than 2.5 per cent. iron, 0.5 per cent. lead, 0.03 per cent. copper, 0.1 per cent. arsenic, etc.) as in WECCO process described in Chemical Engineering, January 1954 issue;
- (ii) to keep the cell voltage between 1.8 to 2.2 volts, although in the latest commercial practice (WECCO process) the cell voltage ranges from 2.2 to 2.6;
- (iii) to get an easily stripable deposit with uniform characteristics; and
- (iv) to conduct the electrolysis at about 90°C., i.e., at the same temperature conditions employed in WECCO process.

Forty pounds of manganese dioxide of uniformly acceptable grade have been prepared by electrolysing manganese sulphate solution (obtained from low-grade manganese ores by reaction with pickle liquor as covered in the Indian Patent 59713 by the same authors) after adding nitric acid under the following conditions:

- Concentration of manganese sulphate: 250 grams of manganese sulphate per litre of the solution.
- 4 C.c. of sulphuric acid of 1.84 specific gravity per litre.

10 C.c. of nitric acid of 1.42 specific gravity per litre.
Volume of liquid electrolysed: 8 litres.
Size of the vessel (inner dimension) 12" x 6" x 10".

Material of construction	Glass, hard rubber, chemical stoneware, lead lined, rubber lined etc., vessels.
Size of graphite anodes and cathodes	Graphite plates of about 1/4" thick, 4 inches broad and 12" high and about 10" of the total height dipping in solution (3 anodes and 4 cathodes) or rods of 5/8" to 1" inner diameter, 12" height and about 10" of the total height dipping in solution (3 rods arranged in a row forming one anode or cathode unit—3 such anodes and four such cathodes are employed).
Spacing of the electrodes	1 inch.
Anode current density	30 amps. per sq. ft.
Voltage across the cell	1.8 to 2.2 volts.
Time of electrolysis	8 hours continuous (minimum period 65% (minimum)
Current efficiency	period 65% (minimum)

CHARACTERISTICS OF THE PRODUCT.

Manganese dioxide	82.04%
Total manganese	56.15%
Iron	0.1405%
Carbon	4.82%
Gangue and acid insoluble	4.848% (4.82% is carbon which is not considered as impurity but has beneficial effects).
Moisture	3.83%
Real Density	3.914 gms/cc
pH-EMF Relationship	
F _{H2}	0
O	1.11-.069 pH
Average energy consumed	0.975 kwh per pound of manganese dioxide produced, whereas in WECCO process 1 kwh is needed to produce 1 lb. of manganese dioxide.

R. BHASKAR PAI,

Patents Officer,

Council of Scientific & Industrial Research.

Dated this 23rd day of April 1957.

COMPLETE SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF BATTERY GRADE MANGANESE DIOXIDE FROM MANGANESE ORES.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

THIS IS AN INVENTION BY VEERARAGAVA ARAVAMITH AN AND THIRUMANGALAM RENGASWAMI VENKATASUBRAMANIAN, BOTH OF THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, BOTH INDIAN CITIZENS.

The invented process for the electrodeposition of manganese dioxide particularly for the production of battery grade manganese dioxide from manganese ores consists in

added per every litre of manganese sulphate solutions containing 150-250 grams of manganese sulphate per litre and 4 to 8 ccs. of sulphuric acid of 1.84 specific gravity. The

manganese sulphate solution in water have not so far been reported in literature. By such an addition, it is possible.

- (i) to work with high current densities which are of the order of 3 times the anode current densities employed (30 amps. per sq. ft. instead of 9 amps per sq. ft.) when pure manganese sulphate solutions are electrolysed commercially to get the desired quality of manganese dioxide (gamma form of manganese dioxide containing not less than 68 per cent. manganese dioxide and not more than 2.5 per cent. iron, 0.5 per cent. lead, 0.03 per cent. copper, 0.1 per cent. arsenic, etc.), as in WECCO process described in Chemical Engineering, January 1954 issue;
- (ii) to keep the cell voltage between 1.8 to 2.2 volts, although in the latest commercial practice (WECCO process) the cell voltage ranges from 2.2 to 2.6;
- (iii) to get an easily strippable deposit with uniform characteristics; and
- (iv) to conduct the electrolysis at about 90°C., i.e., at the same temperature conditions employed in WECCO process.

Forty pounds of manganese dioxide of uniformly acceptable grade have been prepared by electrolysing manganese sulphate solutions (obtained from manganese ores by reaction with pickle liquor as described in our prior Indian Patent No. 59713) after adding nitric acid under the following conditions:

Concentration of manganese sulphate 250 grams of manganese sulphate per litre of the solution.

4 Cc. of sulphuric acid of 1.84 sp. gr. per litre.

10 Cc. of nitric acid of 1.42 sp. gr. per litre.

Volume of liquid electrolysed: 8 litres.

Size of the vessel (inner dimensions): 12" x 6" x 10".

Material of construction : Glass, hard rubber, chemical stoneware, lead lined, rubber lined etc., vessels.

Size of graphite anodes and cathodes : Graphite plates of about $\frac{1}{4}$ " thick, 4 inches broad and 12" high and about 10" of the total height dipping in solution (3 anodes and 4 cathodes) or rods of $\frac{5}{8}$ " to 1" inner diameter, 12" height and about 10" of the total height dipping in solution (3 rods arranged in a row forming one anode or cathode unit—3 such cathodes and four such cathodes are employed).

Spacing of the electrodes : 1 inch.

Anode current density : 30 amps per sq. ft.

Voltage across the cell : 1.8 to 2.2 volts.

Time of electrolysis : 8 hours continuous (minimum period.)

Current efficiency : 65% (minimum)

PREPARATION OF MANGANESE SULPHATE SOLUTIONS.

The starting material for the production of manganese sulphate shall be of any type of manganese ore. Even low grade manganese ore containing high iron, silica and alumina contents and in which the percentage of manganese varies from 5 to 30 can be used as a starting material.

Manganese sulphate suited for electrolysis is obtained from the manganese ores by any standard procedure such as by roast-reduction followed by leaching with cell effluent containing dilute acid and small amounts of manganese sulphate, etc., and purification OR by treatment with waste pickle liquor of the Iron and Steel industries such as the mixture of ferrous sulphate and dilute sulphuric acid OR by employing other reducing agents such as carbon, saw dust, sulphur dioxide, iron or the like, in sulphuric acid medium, etc.

ANALYSIS AND PHYSICO-CHEMICAL PROPERTIES.

Manganese dioxide . . .	82.04%
Total manganese . . .	56.15%
Iron	0.1405%
Carbon	4.82%
Gangue and acid insoluble	4.848% (4.82% is carbon which is not considered as impurity but has beneficial effects).
Moisture	3.83%
Real density	3.914 gms/cc.
pH-EMF Relationship	
$E_{H_2=O}$	1.11-0.069 pH.

AVERAGE ENERGY CONSUMED.

0.975 Kwh per pound of manganese dioxide produced.

We claim:

1. A process for the electrodeposition of manganese dioxide particularly for the production of battery grade manganese dioxide from manganese ores which consists in electrolysing manganese sulphate solution (obtained from manganese ore) in water and wherein not less than 5 cc. of nitric acid of 1.42 sp. gr. or its equivalent in any other concentration of nitric acid is added per litre of manganese sulphate solution in water.

2. A process as claimed in Claim 1 wherein 7 to 12 cc. of nitric acid of 1.42 specific gravity are added per litre of manganese sulphate solution containing 150-250 grams of manganese sulphate per litre and 4 to 8 cc. of sulphuric acid of 1.84 specific gravity.

3. A process as claimed in Claim 1 or 2 wherein the starting material for the production of manganese sulphate consists of low grade manganese ore containing high iron, silica and alumina contents and in which the percentage of manganese varies from 5 to 30.

4. A process as claimed in any of the preceding claims wherein manganese sulphate suited for electrolysis is obtained from the manganese ores by any standard procedure such as by roast-reduction followed by leaching with cell effluent containing dilute acid and manganese sulphate, and purification OR by treatment with waste pickle liquor of the iron and steel industries such as the mixture of ferrous sulphate and dilute sulphuric acid OR by employing reducing agents such as carbon, saw dust, sulphur dioxide, iron or the like in sulphuric acid medium.

5. A process as claimed in any of the preceding claims wherein electrolysis is carried out in an electrolytic cell of which both anode and cathode are of graphite.

6. A process as claimed in any of the preceding claims wherein the voltage across the electrodes in close circuit is 1.8 to 2.2 volts.

7. A process as claimed in any of the preceding claims wherein the electrolysis is carried out in electrolytic cell which has no diaphragm.

8. A process for the electrodeposition of manganese dioxide substantially as hereinbefore described.

9. Battery grade manganese dioxide from any grade manganese ore whenever obtained according to a process substantially as hereinbefore described.

R. BHASKAR PAI,

Patents Officer,

Council of Scientific & Industrial Research

Dated this 13th day of February 1958.