

GOVERNMENT OF INDIA : THE PATENT OFFICE: 214, ACHARYA JAGADISH BOSE ROAD, CALCUTTA-17.

Complete Specification No.113764. Application and provisional specification filed on 23rd December 1967.

Complete Specification filed on 15th October 1968.

Acceptance advertised on 23rd March 1974.

Index at acceptance—39L[III].

PROVISIONAL SPECIFICATION

IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF PHARMACEUTICAL GRADE MAGNESIUM HYDROXIDE.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH,

RAFI MARG, 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 the invention:

This is an invention by (1) VEERARAGHAVA ARAVAMUTHAN (2) POONAMALLE SRINIVASA DESIKAN and (3) KADATHUR SOMASUNDARA SRINIVASAN, all Scientists and all Indian Nationals and working at the Central Electrochemical Research Institute, Karaikudi.

This invention relates to improvements in or relating to the Production of Pharmaceutical Grade Magnesium Hydroxide starting from magnesium chloride solutions obtained from different source such as from sea bitterns, magnesite, dolomite etc., or mixtures thereof.

Hitherto it has been proposed to obtain very pure magnesium hydroxide from magnesium salt solutions by reacting with caustic alkali under proper conditions or subjecting magnesium salt solutions to aqueous electrolysis.

This is open to the objection in that (1) in chemical precipitation methods the removal of residual salt from the magnesium hydroxide precipitate presents one of the most difficult problems because of the semi-colloidal nature of the precipitate and (2) in the case of electrolysis with metal anodes the contamination by heavy metal impurities particularly lead, copper, silver and so on at some stage or other cannot be entirely eliminated especially to obtain a product satisfying the stringent specification of the National Formulary for magnesium hydroxide for use in pharmaceutical preparations; (3) in cases where the magnesium sulphate or nitrate solutions are used metal anodes have to be necessarily used and the anodes of graphite or carbon will be consumed due to the evolution of oxygen at the anode. If the magnesium chloride electrolyte is contaminated with sulphate and or nitrate, the electrolysis cannot also be successfully conducted with graphite or carbon anodes as the attack of anode is inevitable.

The object of this invention is to obviate these disadvantages by electrolysing magnesium chloride solutions in a diaphragm cell wherein carbon or graphitic carbon functions as an anode producing magnesium hydroxide at the cathode in a very easily filterable form of high purity with simultaneous liberation of chlorine

at the anode compartment wherein a concentrated pure solution of sodium chloride functions as anolyte, the anolyte level being advantageously kept always higher than the catholyte level.

To these ends, the invention broadly consists in electrolysing magnesium chloride solutions free from heavy metal impurities and the like in concentrations from 5-20% containing sodium chloride from 1-7% and employing an anolyte consisting of pure sodium chloride. The cathode is of stainless steel and the anode is graphitic carbon. Synthetic diaphragm materials such as microporous rubber, PVC or porous porcelain and almost any material used as diaphragm in aqueous chloride electrolysis have been tried with success. The experiments were conducted from 30-100°C depending upon the diaphragm material used. The current density is of the order of 6-12 amps/sq. dm., both on the anode and cathode.

The following typical examples are given to illustrate the invention:

Electrolysis of magnesium chloride solution for preparation of magnesium hydroxide was carried out in a diaphragm cell using micro-porous rubber as diaphragm. The chlorine from the anode compartment was continuously removed by partial suction. The various particulars of two typical cell runs are given below. The magnesium hydroxide formed in the cathode chamber was periodically removed from the bottom of the vessel and filtered off the solution, washed free from chloride and dried at about 120°C.

Electrolytic vessel : PVC tank with a tapering bottom for removal of the product.

Cathode : Perforated sheet of stainless steel

Anode : Perforated graphite plate

Price : TWO RUPEES.

TABLE

Particulars	Example 1		Example 2	
1. Catholyte composition	Mag. chloride Sod. chloride]	127 g/l 58 g/l	Mag. chloride Sod. chloride	155 g/l 51 g/l
2. Anolyte composition	Sodium chloride	200 g/l	Sodium chloride	200 g/l
3. Current Passed (total)	80 amperes		82 amperes	
4. Cathodic current density	7.5 amps/sq. dm.		8.5 amps/sq. dm.	
5. Cell voltage	4.5 volts		4.75 volts	
6. Inter electrode distance	1.5-2.0 cms		1.5-2.0 cms.	
7. pH of catholyte	5-5.5		5-5.5	
8. Temperature	45-50°C		45-50°C	
9. Weight of product obtained	65 gms		70 gms	
10. Purity of product	96%		95%	
11. Cathodic current efficiency	72%		75%	
12. Energy consumption kwh/kg	5.77		5.92	

Note: The only variation is change in current density between the two sets of experiments.

ANALYTICAL REPORT OF MAGNESIUM HYDROXIDE

(Analysis done as per N. F. XII Specification, page 224)

Description : Bulky white powder

Solubility : Passes N. F. test

Loss on drying : 0.84% (Max. allowed 2%)

Loss on ignition : 32.32% (Range 30-33%)

Soluble salts : Passes N. F. test

Carbonate : Passes N. F. test

Arsenic : Passes N. F. test (Max. 10 p. p. m.)

Calcium oxide : Passes N. F. test (less than 1%)

Heavy metals : Passes N. F. test (Max 40 p. p. m.)

Assay : 95.35% (Min, 95%)

TABLE B

Effect of sulphate impurity on graphite consumption and cell voltage

Sl. No.	Catholyte	Anolyte	Cell voltage	Graphite consumption gms/kg, of product
1.	MgCl ₂ 150 g/l MgSO ₄ 7.5 g/l NaCl 50 g/l	NaCl soln. 200 g/l	4.25-4.5	Almost negligible
2.	MgCl ₂ 150 g/l MgSO ₄ 15 g/l NaCl 50 g/l	NaCl soln. 200 g/l	5.0	0.231 gm
3.	MgCl ₂ 150 g/l MgSO ₄ 30 g/l NaCl 50 g/l	NaCl soln. 200 g/l	5.0	0.247 gm
4.	MgCl ₂ 150 g/l MgSO ₄ 7.5 g/l NaCl 50 g/l	MgCl ₂ 150 g/l MgSO ₄ 7.5 g/l NaCl 50 g/l	4.25-4.5	0.489 gm

Note: The effect of sulphate was studied with a view to utilise commercially available magnesium chloride contaminated with sulphate.

The effect of sulphate impurity on graphite consumption and voltage is given in foregoing Table.

The following are the main advantages of the invention :

- (1) Very pure magnesium hydroxide acceptable as a pharmaceutical grade preparation has been obtained by the electrolysis of pure magnesium chloride solutions in a simple diaphragm cell.
- (2) The said electrochemical operation utilises carbon and/or graphitic carbon as anode and produces chlorine as a valuable anode-product and magnesium hydroxide as a cathode-product. Stainless steel is employed as a cathode. All diaphragm materials employed in aqueous chloride electrolysis have all been found to be good for the purpose. The electrolysis is simple and conducted at ordinary temperatures. The magnesium hydroxide produced is obtained in an easily filterable form which could be periodically withdrawn from the bottom of the electrolytic cell. Magnesium chloride solution can also be continuously fed.

- (3) This process is applicable also to magnesium chloride solutions contaminated with sulphate, upto a concentration of 20% on the weight of magnesium chloride, without resulting in excessive consumption of graphite anode. Since the process envisages the use of a separate anolyte which is a pure solution of sodium chloride, evolution of oxygen at the anode is effectively prevented thus minimising the graphite consumption, even if the catholyte is contaminated with sulphate. (Ref. foregoing Table B). Thus the invention enables the usage of commercially available magnesium chloride from sea bitterns which is usually contaminated with sulphate, for the production of N. F. grade magnesium hydroxide electrolytically which is not possible by use of metallic anodes.

R. Bhaskar Pai

Patents Officer,

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

Dated this 20th day of December 1967.

Complete Specification No. 113764.

IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF PHARMACEUTICAL GRADE MAGNESIUM HYDROXIDE.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH,

RAFI MARG, 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 (1) VEERARAGHAVA ARAVAMUTHAN (2) POONAMALLE SRINIVASA DESIKAN and (3) KADATHUR SOMASUNDARA SRINIVASAN, all Scientists and all Indian Nationals and working at the Central Electrochemical Research Institute, Karaikudi.

This invention relates to improvements in or relating to the Production of Pharmaceutical Grade Magnesium Hydroxide starting from magnesium chloride solutions obtained from different sources such as from sea bitterns, magnesite, dolomite etc., or mixtures thereof, employing preferably only electrochemical techniques. Pharmaceutical grade magnesium hydroxide is utilised widely in antacid, cutturtic formulations administered orally and therefore cannot tolerate any impurity beyond very low percentage.

Hitherto it has been proposed to obtain magnesium hydroxide from magnesium salt solutions by reacting with caustic alkali, lime etc., under proper conditions or subjecting magnesium salt solutions to aqueous electrolysis.

This is open to the objection in that (1) in chemical precipitation methods the removal of residual inclusions from the magnesium hydroxide precipitate presents one of the most difficult problems because of the semi-colloidal nature of the precipitate and (2) in the case of electrolysis with metal anodes the contamination by heavy metal impurities particularly lead, copper, silver and so on at some stage or other cannot be entirely eliminated especially to obtain a product satisfying the stringent specification of the National Formulary for magnesium hydroxide for use in pharmaceutical preparations; (3) in cases where the magnesium sulphate or nitrate solutions are used metal anodes have to be necessarily used and the anodes of graphite or carbon will be consumed due to the evolution of oxygen at the anode. If the magnesium chloride electrolyte is contaminated with sulphate and or nitrate, the electrolysis cannot also be successfully conducted with graphite or carbon anodes as the attack of anode is inevitable.

The object of this invention is to obviate these disadvantages by electrolysing magnesium chloride solutions in a diaphragm cell wherein carbon or graphitic carbon functions as the anode producing magnesium hydroxide at the cathode in a very easily filtrable form of high purity with simultaneous liberation of chlorine at the anode compartment wherein a concentrated pure solution of sodium chloride functions as anolyte, the anolyte level being advantageously kept always higher than the catholyte level.

The underlying principal of this invention consists in liberating OH ions at the cathode and the *in situ* precipitation of magnesium hydroxide from the catholyte under controlled conditions so as to get an easily filtrable magnesium hydroxide without any excess OH ions and a precipitate of such a character which is easily washable and would not retain any impurities.

To these ends, the invention broadly consists in electrolysing magnesium chloride solutions free from heavy metal impurities and the like in concentrations from 5-20% containing sodium chloride from 1-7% and employing an anolyte consisting of pure sodium chloride. The cathode is of stainless steel and the anode is graphitic carbon. Synthetic diaphragm materials such as microporous rubber, PVC or porous porcelain and almost any material used as diaphragm in aqueous chloride electrolysis have been tried with success. The experiments were conducted from 30-100°C depending upon the diaphragm material used. The current density is of the order of 6-12 amp/sq. dm. both on the anode and cathode.

The typical examples are given in Appendix A to illustrate the invention.

The effect of sulphate impurity on graphite consumption and voltage is given in Appendix B.

According to the present invention, the process for the production of pharmaceutical grade magnesium hydroxide by precipitating magnesium hydroxide is characterised in that a solution of magnesium chloride is electrolysed in a diaphragm cell, using magnesium chloride as catholyte and an anolyte of pure sodium chloride in concentration of 1-7% to precipitate out magnesium hydroxide in the cathode compartment *in situ* in an easily filtrable form, thus eliminating the use of alkali which is employed in the conventional process for the precipitation of magnesium hydroxide from magnesium chloride solutions.

Electrolysis of magnesium chloride solution is conducted at temperatures ranging from 30° to 100°C in a diaphragm cell utilising carbon or graphitic carbon as an anode stainless steel as cathode and porous porcelain, microporous rubber, PVC and the like as diaphragm material producing chlorine as a valuable anode-product, and magnesium hydroxide as a cathode product and periodically withdrawing the magnesium hydroxide produced from the bottom of the electrolytic cell, while at the same time feeding a solution of magnesium chloride into the cell continuously.

Thus, magnesium chloride solutions which are contaminated with sulphate upto a concentration of 20% on the weight of magnesium chloride, similar to the commercially available magnesium chloride obtained from sea bitterns is electrolysed in a diaphragm cell utilising a pure sodium chloride as anolyte and precipitating magnesium hydroxide, effectively preventing the evolution of oxygen at the anode thus minimising consumption of the graphite anodes.

In the present process magnesium hydroxide is precipitated *in situ* in an easily filtrable form without any inclusion, electricity being made use of for the liberation of the necessary OH ions for this purpose, unlike in the conventional process wherein an alkali is employed for the precipitation of magnesium hydroxide from chloride solutions. This invention eliminates the

use of sodium hydroxide which is used in the conventional process of chemical precipitation wherein a soluble magnesium salt like magnesium chloride is reacted with sodium hydroxide. In this procedure about 1.35 kg of sodium hydroxide is consumed per kg of magnesium hydroxide produced. Instead of about 5.8 kwhrs of electric energy are spent per kg magnesium hydroxide produced in the present invention. It is clear therefore, that under Indian conditions it will be economical to adopt the process covered by this invention especially with pharmaceutical grade magnesium hydroxide in preference to the well-established chemical precipitation procedure.

APPENDIX A

Electrolysis of magnesium chloride solution for preparation of magnesium hydroxide was carried out

in a diaphragm cell, using micro-porous rubber as diaphragm. The chlorine from the anode compartment was continuously removed by partial suction. The various particulars of two typical cell runs are given below. The magnesium hydroxide formed in the cathode chamber was periodically removed from the bottom of the vessel and filtered off the solution, washed free from chloride and dried at about 120°C.

Electrolytic vessel : PVC tank with a tapering bottom for removal of the product.

Cathode : Perforated sheet of stainless steel

Anode : Perforated graphite plate.

Particulars	Example 1		Example 2	
1. Catholyte composition	Mag. chloride	127 g/l	Mag. chloride	155 g/l
	Sod. chloride	58 g/l	Sod. chloride	51 g/l
2. Anolyte composition	Sodium chloride	200 g/l	Sod. chloride	200 g/l
3. Current passed (total)	80 amperes		82 amperes	
4. Cathode current density	7.5 amps/sq. dm.		8.5 amps/sq. dm.	
5. Cell voltage	4.5 volts		4.75 volts	
6. Inter electrode distance	1.5-2.0 cms		1.5-2.00 cms	
7. pH of catholyte	5.-5.5		5-5.5	
8. Temperature	45-50°C		45-50°C	
9. Weight of product obtained	65 gms		70 gms	
10. Purity of product	96%		95%	
11. Cathodic current efficiency	72%		75%	
12. Energy consumption kwh/kg	5.77		5.92	

Note : The only variation is change in current density between the two sets of experiments.

ANALYTICAL REPORT OF MAGNESIUM HYDROXIDE

(Analysis done as per N.F. XII Specification, page 224)

Description : Bulky white powder
 Solubility : Passes N.F. test
 Loss on drying : 0.84% (max. allowed 2%)
 Loss on ignition : 32.32% (range 30-33%)
 Soluble salts : Passes N.F. test

Carbonate : Passes N.F. test
 Arsenic : Passes N.F. test (max. 10 p.p.m.)
 Calcium oxide : Passes N.F. test (lets than 1%)
 Heavy metals : Passes N.F. test (max. 40 p.p.m.)
 Assay : 95.35% (min. 95%)

APPENDIX B

Effect of sulphate impurity on graphite consumption and cell voltage

S. No.	Catholyte	Anolyte	Cell voltage	Graphite consumption gms/kg of product
1.	MgCl ₂ 150 g/l MgSO ₄ 7.5 g/l NaCl 50 g/l	NaCl soln. 200 g/l	4.25-4.5	Almost negligible.
2.	MgCl ₂ 150 g/l MgSO ₄ 15 g/l NaCl 50 g/l	NaCl soln. 200 g/l	5.0	0.231 gm
3.	MgCl ₂ 150 g/l MgSO ₄ 30 g/l NaCl 50 g/l	NaCl soln. 200 g/l	5.0	0.247 gm
4.	MgCl ₂ 150 g/l MgSO ₄ 7.5 g/l NaCl 50 g/l	MgCl ₂ 150 g/l MgSO ₄ 7.5 g/l NaCl 50 g/l	4.25-4.5	0.489 gm

Note: The effect of sulphate was studied with a view to utilise commercially available magnesium chloride contaminated with sulphate.

WE CLAIM :

1. A process for the production of pharmaceutical grade magnesium hydroxide by precipitating magnesium hydroxide characterised in that a solution of magnesium chloride is electrolysed in a diaphragm cell, using magnesium chloride as catholyte and an anolyte of pure sodium chloride in concentration of 1-7% to precipitate out magnesium hydroxide in the cathode compartment *in situ* in an easily filtrable form, thus eliminating the use of alkali which is employed in the conventional process for the precipitation of magnesium hydroxide from magnesium chloride solutions.

2. A process as claimed in Claim 1 wherein electrolysis of magnesium chloride solution is conducted at temperatures ranging from 30° to 100°C in a diaphragm cell utilising carbon or graphitic carbon as an anode, stainless steel as cathode and porous porcelain, microporous rubber, PVC and the like as diaphragm material producing chlorine as a valuable anode-product and magnesium hydroxide as a cathode product and periodically withdrawing the magnesium hydroxide produced from the bottom of the electrolytic cell, while at the same time feeding a solution of magnesium-chloride into the cell continuously.

3. A process as claimed in Claim 1 and 2 wherein magnesium chloride solutions which are contaminated with sulphate upto a concentration of 20% on the weight of magnesium chloride, similar to the commercially available magnesium chloride obtained from sea biterms is electrolysed in a diaphragm cell utilising a pure sodium chloride as anolyte and precipitating magnesium hydroxide, effectively preventing the evolution of oxygen at the anode thus minimising consumption of the graphite anodes.

4. A process for the preparation of pharmaceutical grade magnesium hydroxide substantially as herein before described.

R. Bhaskar Pai

Patents Officer,

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

Dated this 9th day of October 1968.