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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 66109, Application No. 66109, dated 11th December 1958. Complete Specification left on 10th September 1959. (Application Accepted 20th January 1960.)

**PROVISIONAL SPECIFICATION.**

**IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF MAGNESIUM METAL.**

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 1960).

*The following specification describes the nature of this invention.*

THIS IS AN INVENTION BY VEERARAGAVA ARAVAMUTHAN AND KUPPUSWAMY VENUGOPALAN, BOTH OF THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, BOTH INDIAN CITIZENS.

The electrolysis of fused magnesium chloride in admixture with alkali metal chlorides accounts for the major world production of magnesium metal. In a widely used cyclic process, the anodic chlorine from magnesium chloride electrolysis is first converted into hydrochloric acid and reacted with (a) pure Magnesite or (b) pure basic magnesium carbonate obtained from Dolomite or (c) pure magnesium hydroxide obtained from sea (by reacting with calcium hydroxide or by reacting with calcined dolomite). Large scale possibilities also exist to get pure basic and normal magnesium carbonates from bitterns with the simultaneous production of potash-nitrogen fertilisers. Such basic and normal carbonates of magnesium can also be treated with hydrochloric acid to get magnesium chloride.

In the second step, the magnesium chloride solution is evaporated to get the hydrated salt and in the final stage magnesium chloride suitable for use as a cell feed is obtained from the hydrated salt. All these steps are time consuming, require a number of equipment and also very careful control of operations.

**NOVELTY IN THE INVENTION.**

In the present invention anhydrous magnesium chloride in admixture with alkali metal chlorides for use directly in electrolysis is obtained in one stage by heating mixtures of suitable proportions of sodium chloride, potassium chloride, ammonium chloride and pure magnesium carbonate or oxide of magnesium or mixture of carbonate and oxide. Ammonia or a mixture of ammonia and carbon dioxide is expelled.

Although magnesium oxide or carbonate can be reacted with ammonium chloride in the solid phase at temperatures above 300° C. with expulsion of ammonia and formation of magnesium chloride, yet the reaction slows down after some time possibly owing to the formation of magnesium oxy chloride. Magnesium chloride that is formed as the first product of the reaction may envelope the magnesium carbonate and thus slows down the rate of reaction. However, if the magnesium chloride formed is continuously removed from the sphere of action with the formation of double salt of magnesium chloride with alkali metal chlorides, fresh surfaces of magnesium carbonate can be continuously exposed, to the action of ammonium chloride and the rate of reaction can be maintained practically constant throughout. This has been fully borne out by experiments in which magnesium carbonate alone was reacted with ammonium chloride (time taken 6 1/2 hours) and (2) mixtures of the same weight of the magnesium carbonate with sodium, potassium and or calcium chlorides with ammonium chloride were heated from the beginning (time taken 3 hours).

By adopting the above procedure, for e.g., a double salt having sodium chloride, potassium chloride and magnesium chloride in the ratio of 26:33:41 respectively was obtained and subsequently electrolysed to get magnesium metal under the same conditions of voltage, current density and temperature used in industrial practice viz., a cathodic current density of 3-4 amps. per sq. in a temperature of 700-750° C. and cell voltage of 7 to 7.5.

**ADVANTAGES OF THE PROCESS.**

In comparison with the existing practice this method of obtaining anhydrous chloride consumes less time and eliminates the use of a number of equipment. Less technical skill is needed for the present process. By a suitable arrangement the preparation of anhydrous magnesium chloride in admixture with sodium and potassium chlorides can be done in the same vessel in which electrolysis can also be conducted. The most important advantage of this process is the production of chlorine economically as by-product in the manufacture of sodium carbonate by the ammonia soda process. The ammonia or mixtures of ammonia and carbon dioxide expelled in the production of anhydrous mixed chloride is employed for obtaining sodium carbonate from sodium chloride and the by-product ammonium chloride in the solid state is employed for producing anhydrous chloride. Thus in the cyclic process, the chlorine of the sodium chloride is first fixed as ammonium chloride, then as magnesium chloride and finally liberated as free chlorine by electrolysis.

This process is of special interest whenever ammonia is to be recovered from ammonium chloride for re-use in the process. For, this can be combined with the production of anhydrous magnesium chloride provided raw materials and power are cheap. Thus, e.g., a mixture of ammonia and sulphur dioxide can be employed to produce sodium sulphite from sodium chloride and the ammonium chloride is employed to produce anhydrous magnesium chloride and finally magnesium and chlorine.

The following are among the noteworthy features of the invention :

1. A process for the production of anhydrous magnesium chloride in admixture with alkali metal chlorides from magnesium carbonate or oxide obtained from different sources such as Magnesite, Dolomite, Sea, bitterns etc., in one stage by heating suitable mixtures of alkali metal chlorides, magnesium oxide or carbonate and ammonium chloride.
2. By following the procedure mentioned in (1) the production of magnesium metal can be economically combined with the production of sodium carbonate, sodium sulphite etc., and chlorine of the sodium chloride can be ultimately recovered as free chlorine.

R BHASKAR PAI,

*Patents Officer,*

*Council of Scientific & Industrial Research.*

Dated this 8th day of December, 1958.

Price : TWO RUPEES.

## COMPLETE SPECIFICATION.

### IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF MAGNESIUM METAL BY THE ELECTROLYSIS OF ANHYDROUS MAGNESIUM CHLORIDE.

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 ARAVAMUTHAN AND KUPPUSWAMY VENUGOPALAN, BOTH OF THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, BOTH INDIAN CITIZENS.

The electrolysis of anhydrous magnesium chloride in admixture with alkali metal chlorides accounts for the major world production of magnesium metal. In a widely used cyclic process, the anodic chlorine from magnesium chloride electrolysis is first converted into hydrochloric acid and reacted with (a) pure magnesite or (b) pure basic magnesium carbonate obtained from dolomite or (c) pure magnesium hydroxide obtained from sea (by reacting with calcium hydroxide or by reacting with calcined dolomite). Large scale possibilities also exist to get pure basic and normal magnesium carbonates from bitterns with the simultaneous production of potash-nitrogen fertilisers. Such basic and normal carbonates of magnesium can also be treated with hydrochloric acid to get magnesium chloride.

In the second step, the magnesium chloride solution is evaporated to get the hydrated salt and in the final stage magnesium chloride suitable for use as a cell feed is obtained from the hydrated salt. All these steps are time consuming, require a number of equipments and also very careful control of operations.

In the production of magnesium metal according to the present invention, the step of preparing anhydrous magnesium chloride as such or in combination with alkali metal chlorides consists in reacting magnesite, dolomite, magnesium carbonate (or hydroxide or oxide) obtained from sea or bitterns with ammonium chloride at 300° C. to 750° C.

Thus, in the invented process, there is only one step involved in the production of anhydrous magnesium chloride. Alkali metal chlorides could be incorporated in this one step process. The reaction can be conducted at temperatures starting from 300° C. upto 750° C. to get anhydrous magnesium chloride in one step, either as solid or as liquid, together with sodium chloride, potassium chloride, and calcium chloride. The physical state of the anhydrous chloride depends only upon the temperature under which it is prepared. The anhydrous magnesium chloride thus prepared and containing over 90 per cent. of anhydrous magnesium chloride could be used as the cell feed either in the solid anhydrous state or in the fused or in the molten state, while electrolysis is taking place in the production of magnesium metal.

All the three steps involved in the conventional process have been avoided in the direct reaction practised by us which simply consists in heating magnesium carbonate or oxide with solid ammonium chloride, with the recovery of excess ammonium chloride, if any, and also the by-product a mixture of ammonia and carbon dioxide. The equipment is very simple in construction. It has only a device for heating the materials out of contact with air with condensation systems for the recovery of ammonium salts.

Several compositions of double salts ranging from 0 per cent. of alkali metal chlorides upto 40 per cent. of alkali and alkaline earth chloride mixtures namely sodium, potassium and calcium chlorides—rest being magnesium chloride—have been prepared by this procedure and used as cell-feed for the successful production of magnesium metal.

In partial modification of the process, for treatment of magnesium ores containing a high percentage of silica, the initial dissolution of magnesium from the ore in hydrochloric acid is done. It is followed by the precipitation of magnesium carbonate by reacting this magnesium chloride solution with the ammonium carbonate by-product formed in the later stage of the process as will be clearly seen from the flow sheet at Figure 4 of the accompanying drawings.

Ammonium chloride by-product from processes such as the manufacture of sodium carbonate, sodium sulphite, sodium sulphate or the like can be used.

The mixtures of magnesium carbonate and ammonium chloride are practically in theoretical proportions to get anhydrous magnesium chloride. Sodium chloride and potassium chloride are added to the magnesium carbonate, ammonium chloride mixtures in amounts depending upon the amount alkali metal chloride content needed in the cell feed. To give a typical example, magnesite of about 98 per cent. purity (24 lbs.), ammonium chloride (26 lbs.) Sodium chloride (3 lbs.), Potassium chloride (3 lbs.) are heated to get 30 lbs. of anhydrous salt.

The time required is 5 hours for the production of 30 lbs. of the cell-feed by this one step process. The conventional procedure will take thrice this time to produce anhydrous magnesium chloride starting from the same source. Such conventional steps involve (1) dissolution of the ore in hydrochloric acid, (2) filtration, (3) evaporation of the solution and (4) partial or full dehydration of the salt.

It will be seen that in the invented process the chlorine of the sodium chloride is first fixed as ammonium chloride in the production of sodium carbonate or sodium sulphite by reacting sodium chloride solutions with ammonia and carbon dioxide or sulphur dioxide. The chlorine of the ammonium chloride is then fixed as anhydrous magnesium chloride and finally the chlorine is liberated as free chlorine in the production of magnesium metal. The ammonia evolved in the production of anhydrous magnesium chloride is used again in the process to produce more sodium carbonate or sulphite from sodium chloride.

Thus in the present process, anhydrous magnesium chloride in admixture with alkali metal chlorides for use directly in electrolysis is obtained in one stage by heating mixtures of sodium chloride, potassium chloride, ammonium chloride and pure magnesium carbonate or oxide of magnesium or mixtures of carbonate and oxide. Ammonia or a mixture of ammonia and carbon dioxide is expelled.

By adopting this procedure, for e.g., a double salt having sodium chloride, potassium chloride and magnesium chloride in the ratio of 26:33:41 respectively is obtained and subsequently electrolysed in a non diaphragm 500 (five hundred) ampere cell. Magnesium metal is obtained under the same conditions of voltage, current density and temperature used in industrial practice viz., a cathodic current density of 3-4 amps. per sq. in a temperature of 700-750° C. and cell voltage of 7 to 7.5.

By the same procedure, a cell-feed containing 80-90 per cent. anhydrous magnesium chloride—rest being sodium and potassium chlorides—have also been obtained and utilized.

#### ADVANTAGES OF THE PROCESS.

In comparison with the existing practice this method of obtaining anhydrous chloride consumes less time (5 hours for obtaining 30 lbs. of cell feed, as compared with about 15 hours by the conventional process) and eliminates the use of a number of equipment. Less technical skill is needed for the present process. The most important advantage of this process is the production of chlorine economically as by-product in the manufacture of sodium carbonate by the ammonia soda process. The ammonia or mixtures of ammonia and carbon dioxide expelled in the production of anhydrous mixed chloride is employed for obtaining sodium carbonate from sodium chloride and the by-product

ammonium chloride in the solid state is employed for producing anhydrous magnesium chloride. Thus in the cyclic process, the chlorine of the sodium chloride is first fixed as ammonia chloride, then as magnesium chloride and finally liberated as free chlorine by electrolysis.

This process is of special interest whenever ammonia is to be recovered from ammonia chloride for re-use in the process. Thus for e.g., a mixture of ammonia and sulphur dioxide can be employed to produce sodium sulphite from sodium chloride and the ammonium chloride is employed to produce anhydrous magnesium chloride and finally magnesium and chlorine.

We claim:

1. In the production of magnesium metal the step of preparing anhydrous magnesium chloride as such or in combination with alkali metal chlorides which consists in reacting magnesite, dolomite, magnesium carbonate (or hydroxide or oxide) obtained from sea or bitterns with ammonium chloride at 300° C. to 750° C.

2. A process as claimed in Claim 1 wherein alkali metal chlorides are also incorporated.

3. A process as claimed in Claim 1 or 2 wherein anhydrous magnesium chloride thus prepared is used as a cell feed for electrolysis in mixed alkali-alkaline earth chloride bath for the production of magnesium metal.

4. A process as claimed in any of the preceding claims wherein anhydrous magnesium chloride thus prepared is used as cell feed in the solid anhydrous state, in the fused state or in the molten state, during electrolysis.

5. A process as claimed in any of the preceding claims wherein after heating magnesium carbonate or oxide with solid ammonium chloride excess of ammonium chloride is recovered, and also the by-products, consisting of a mixture of ammonia and carbon dioxide.

6. A process as claimed in any of the preceding claims wherein the materials are heated out of contact with air, and ammonium salts are recovered by condensation.

7. A process as claimed in any one of the preceding claims wherein double salts ranging from 0 per cent. alkali chloride up to 40 per cent. of alkali and alkaline earth chloride mixtures, namely, sodium, potassium and calcium chloride—rest being magnesium chloride—are prepared for use as cell feed.

8. A process as claimed in any one of the preceding claims wherein for the treatment of magnesium ores

containing a high percentage of silica, the initial dissolution of magnesium from the ore is done by hydrochloric acid, and magnesium carbonate is precipitated by reacting the magnesium chloride solution with ammonium carbonate.

9. A process as claimed in any of the preceding claims wherein ammonium chloride by-product from processes such as the manufacture of sodium carbonate, sodium sulphite, sodium sulphate or the like, can be used.

10. A process as claimed in any one of the preceding claims wherein for example magnesite of 98 per cent. purity (24 lbs.), ammonium chloride (26 lbs.), sodium chloride (3 lbs.), potassium chloride (3 lbs.) are heated to get 30 lbs. of anhydrous salt.

11. A process as claimed in Claim 10 wherein the time required is 5 hours for the production of 30 lbs. of cell used.

12. A process as claimed in any of the preceding claims wherein the chlorine of the sodium chloride is first fixed as ammonium chloride in the production of sodium carbonate or sodium sulphite by reacting sodium chloride solution with ammonium and carbon dioxide or sulphur dioxide, the chlorine of the ammonium chloride is then fixed as anhydrous magnesium chloride and finally the chlorine is liberated as fresh chlorine.

13. A process as claimed in any of the preceding claims wherein the ammonia involved in the production of anhydrous magnesium chloride is used again in the process to produce sodium carbonate or sulphite from sodium chloride.

14. In the production of magnesium metal the step for production of anhydrous magnesium chloride substantially as hereinbefore described.

15. A process for the production of magnesium metal substantially as hereinbefore described.

16. Magnesium metal whenever prepared according to a process substantially as hereinbefore described.

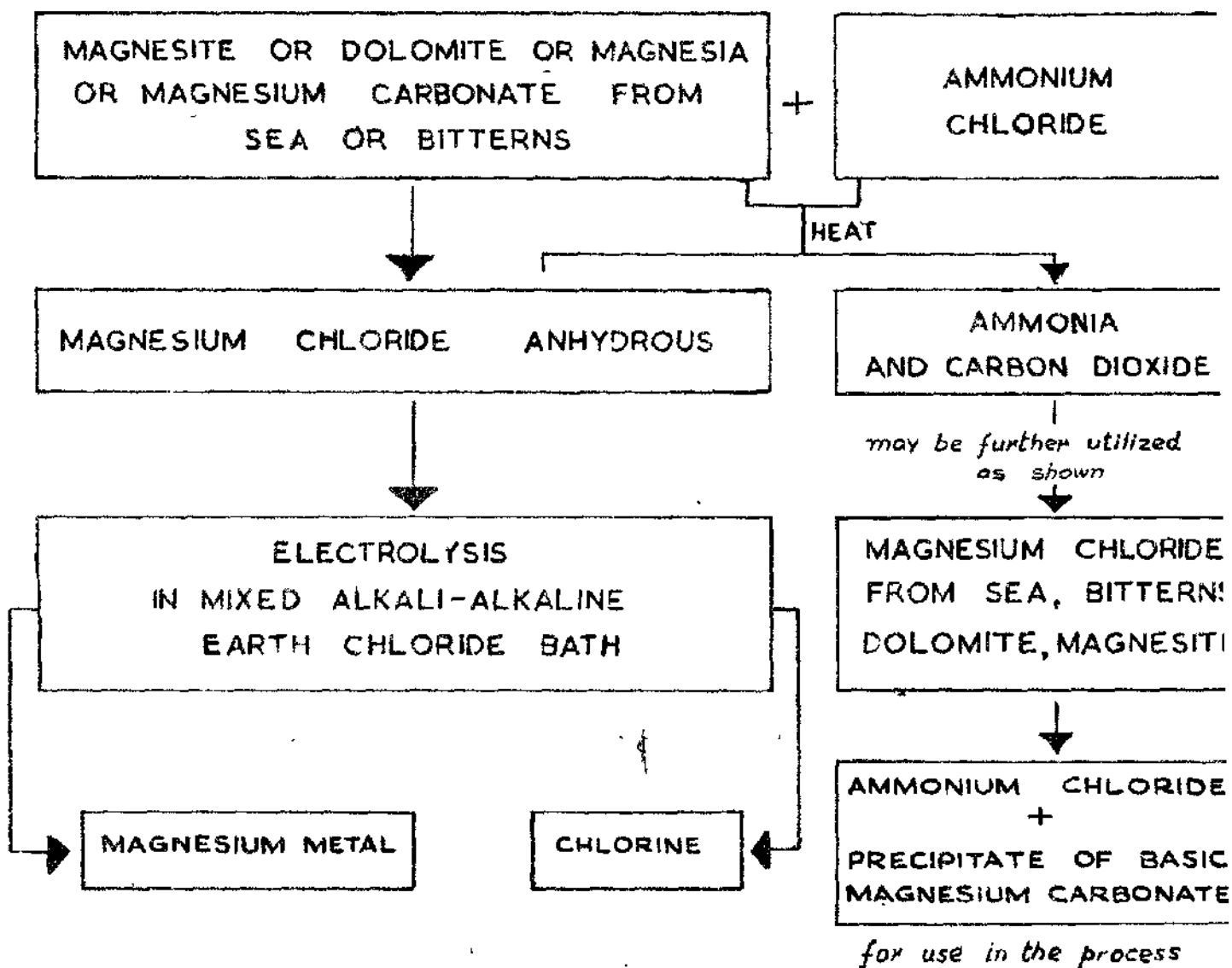
R. BHASKAR PAI,

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Dated this 7th day of September, 1959.

NO. 66109.



FLOW SHEET FOR THE PRODUCTION  
OF  
MAGNESIUM METAL

Fig

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