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


PROVISIONAL SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF MAGNESIUM METAL.

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The following specification describes the nature of this invention.

This is an invention by VIBHA RAGAVA ARABAVU ROTHERAM and KUPPUSWAMY YENUGOPALAN, both of THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARACHI, INDIA, both Indian citizens.

The electrolysis of fused magnesium chloride in a mixture 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 magnesium 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 calcium carbonate from dolomite). Large scale possibilities also exist to get pure basic and normal magnesium carbonates from bitumens with simultaneous production of potash-nitrogen fertiliser. 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 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 solvent 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 ammonium and carbon dioxide is expelled. Although magnesium oxide or carbonate can be reacted with ammonium chloride in the solid phase at temperatures above 500°C with expulsion of ammonium chloride and formation of magnesium chloride, yet the reaction slows down after some time possibly owing to the formation of magnesium oxychloride. Magnesium chloride that is formed as the first product of the reaction may envelop the magnesium carbonate and thus slows down the rate of reaction. However, if the magnesium chloride formed is continuously removed from the sphere of reaction 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 30:33:41 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 4.2 ampere per sq. in. a temperature of 700-700°C and cell voltage of 7 to 7.5.

ADVANTAGES OF THIS PROCEDURE.

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 chloride economically as by-product in the manufacture of sodium carbonate by the ammonia soda process. The anhydrous mixtures of ammonium chloride and carbon dioxide are used 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 if otherwise ammonia is to be recovered from ammonium chloride for reuse in the process. This can be combined with the production of anhydrous magnesium chloride provided raw materials and power are cheap. Thus, e.g. a mixture of ammonium and sulphur dioxide can be employed to produce sodium sulphate from sodium chloride and the anhydrous chloride is employed to produce anhydrous magnesium chloride and finally magnesium chloride.

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, bitumens 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 sulphate etc. and chlorine of the sodium chloride can be ultimately recovered as free chlorine.

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Patents Officer,
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Dated 5th day of December, 1958.

Price: TWO RUPEES.
COMPLETE SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF MAGNESIUM AMMONIUM CHLORIDE OF THE TYPE BOLZAN MAGNESIUM CHLORIDE.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Old Mills Road, New Delhi-1, India, an IANSAK
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 ARAYAMU/HAN AND KUPPUSAMY VENUGOPALAN, BOTH OF THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARAKUNNAM, 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 hydro-chloric acid and reacted with (a) pure magnesite or (b) basic magnesium carbonate obtained from dolomite and sea water or by reacting with calcium hydroxide or by reacting with calciated dolomite. Large scale possibilities also exist to get pure basic and normal magnesia from the anolyte streams with simultaneous production of potash-nitrogen fertilizers. Such basic and normal carbonates of magnesium can also be treated with hydrochloric acid to get magnesium chloride.

In the first 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 and require a number of equipment 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 bitters with ammonium chloride at 150°C.

Thus, in the invention 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 carried out at temperatures ranging from 20°C to 30°C and up to 750°C to get anhydrous magnesium chloride in one step, either as chloride or as an alkali metal salt of magnesium chloride or as a mixture of magnesium chloride and alkali metal chloride.

The physical state of the anhydrous chloride depends on 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.

Thus, in the present invention process, the step of preparing anhydrous magnesium chloride as such or in combination with alkali metal chlorides has been considerably simplified.

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

The mixture 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 58 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 taken 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. On the other hand, the present conventional procedure (1) dissolution of the ore in hydrochloric acid, (2) filtration, (3) evaporation of the solution and (4) partial or full dehydrochlorination of the salt.

It will be seen that in the conventional process the chloride of the sodium chloride is first fixed as ammonium chloride in the production of sodium carbonate or sodium sulphate by reacting sodium chloride solutions with ammonia and carbon dioxide or sulphur dioxide.

The chloride of the ammonium chloride is then fixed as anhydrous magnesium chloride and finally the chloride 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 sulphate 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, 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 38/33/41 respectively is obtained and subsequently used in electrolysis of the obtained solution by anode in carbon brick apparatus. The anode gas evolves 50% of the anode cell. The magnesium metal is obtained under the same conditions of voltage, current density and temperature used in industrial practice with a carbon brick electrode at a 50% current efficiency.

By the same procedure a cell-feed containing 80-50 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 chloride economically as by-product in the manufacture of magnesium carbonate from this process. The ammonia 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 cyclical 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. 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 metals which consists in reacting magnesite, dolomite, magnesium carbonate (or hydroxide or oxide) obtained from sea or bitter ashes with ammonium chloride at 360° C. to 730° 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 ore 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 sulphate, sodium sulphite 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 (28 lbs.), sodium chloride (2 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 anhydrous chloride 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.


Dated this 7th day of September, 1959.

R. BHASKAR PAL,
Patents Officer,
Council of Scientific & Industrial Research.
MAGNESITE OR DOLOMITE OR MAGNESIA OR MAGNESIUM CARBONATE FROM SEA OR BITTERNS

AMMONIUM CHLORIDE

HEAT

MAGNESIUM CHLORIDE ANHYDROUS

AMMONIA AND CARBON DIOXIDE

ELECTROLYSIS IN MIXED ALKALI-ALKALINE EARTH CHLORIDE BATH

MAGNESIUM CHLORIDE FROM SEA, BITTERN

DOLOMITE, MAGNESIUM

AMMONIUM CHLORIDE

PRECIPITATE OF BASIC MAGNESIUM CARBONATE FOR USE IN THE PROCESS

FLOW SHEET FOR THE PRODUCTION OF MAGNESIUM METAL

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