Patented Feb. 9, 1954

2,668,750

UNITED STATES PATENT OFFICE

2,668,750

PURIFICATION OF BY-PRODUCT HALIDE SALTS

Ignace Joseph Krchma, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application February 7, 1952, Serial No. 270,500

5 Claims. (Cl. 23—91)

1

This invention relates to the purification of by-product halide salts obtained from metal halide reduction processes, especially those resulting from titanium metal manufacture through $TiCl_4$ reduction. More particularly, it relates to the removal of impurities from such by-product salts in order to obtain a product suitable for use in and recycling to an electrolytic cell employed for the production of the active reducing metal utilized in the reduction operation.

Useful methods for producing many of the refractory metals, in which reduction is effected of a halide salt of the metal by means of an active reducing metal, also yield a considerable quantity of by-product salt. The active reducing metals employed in such reduction process comprise in most cases those obtained from the electrolysis of molten halides. Methods for the preparation of reducing metal halide salts have been developed for certain raw material sources. Among examples of such processes are those involving the preparation and purification of magnesium chloride from sea water, brine, and dolomite.

In a completely integrated system for economically producing a refractory metal such as, for example, titanium and zirconium, provision must be made for recycling for reuse the reducing metal and halogen values present in the residual by-product salt. Thus, in reducing titanium tetrachloride with magnesium at temperatures ranging from 750–1000° C. to produce titanium metal, the magnesium used usually comprises that produced electrolytically. The electrolyte present in the electrolytic cells usually consists of magnesium chloride plus other metal halide salts added thereto to obtain desirable electrolytic and physical salt bath properties. Impurities in the cell electrolyte usually act in two ways. The magnesium metal produced by the electrical current in the cell will remove those impurities which alloy with it. Other impurities which do not alloy with magnesium may be liberated at the cathode, be reduced by the metal floating in the bath, or remain unreactive in the bath. The reduced impurities which do not alloy with the magnesium metal tend to collect as a sludge on the bottom of the cell. If the cell operating conditions are not correct, some of these latter impurities may form heavy shells around small particles of magnesium and settle into the sludge at the bottom of the cell, thereby causing undesired loss of product metal. Titanium does not appreciably alloy with magnesium and therefore tends to act like these latter materials. An urgent need

2

exists therefore for a useful method, economical and relatively simple, for removing these impurities because of their extremely harmful effect on the electrolytic process.

The magnesium chloride produced in titanium metal-producing processes in which magnesium and titanium tetrachloride are employed as reactants is contaminated with various impurities which, if present when the magnesium chloride is recycled back into the magnesium electrolytic cells, will be found to prove very harmful and deleterious. Of these impurities, titanium metal, present in the form of fine particles, and various subhalides of that metal, such as the lower chlorides (the dichloride or trichloride) are particulary harmful.

It is among the objects of this invention to eliminate these and other undesirable impurities from by-product halide salts obtained from a metal reduction process and to provide novel methods and means for attaining such objects. A further object is to effectively purify and particularly eliminate titanium and its subchlorides from such by-product salt and by means of relative inexpensive, simple and novel techniques. A specific object is to provide a highly useful method for purifying by-product magnesium chloride from a $TiCl_4$ reduction in which magnesium is utilized as the reducing metal, whereby the purified anhydrous by-product recovered can be effectively used in the electrolytic recovery of the magnesium metal. Other objects and advantages will be apparent from the following description of the invention:

These and other objects are attainable in this invention which broadly comprises reacting a halogen gas selected from the group consisting of chloride, bromine, and iodine, at an elevated temperature with a molten by-product halide from the reduction of a metal halide with a reducing metal.

In a more specific and preferred embodiment, the invention comprises reacting with gaseous chlorine, and at temperatures ranging from 750–1050° C., residual by-product magnesium chloride in which titanium and its subchlorides are present as impurities, to obtain volatile, vaporized chlorides adapted to be separately recovered from the purified by-product, and continuing said reaction until said by-product is freed of said impurities.

In practically adapting the invention, an impure or residual form of metal halide, particularly the by-product obtained from a metal halide reduction process, such as the methods dis-

closed in U. S. Patents 2,205,854, 2,171,439, 2,214,211, 2,148,345, or 2,556,763, etc., can be suitably halogenated to produce a relatively pure, anhydrous material useful for treatment in an electrolytic cell system to effect recovery of its reducing metal and halogen values. Thus, for example, the magnesium chloride salt recovered in molten state by draining from the reduction reactor, or in the form of a liquid or solid condensate from a distillation recovery step, or as a solid mechanically removed from the reactor at the conclusion of the reduction operation, can be charged into a conventional type corrosion-resistant chlorination vessel suitably associated with said reactor and while in molten or fused state therein can be brought in direct contact for reaction at temperatures ranging from about 750–1050° C. with gaseous chlorine, such contact and reaction being continued until the salt is freed of undesirable soluble and insoluble titanium. The anhydrous magnesium chloride product thus freed of undesired contaminants can then be introduced into a conventional magnesium and chlorine recovery system such as an electrolytic cell, wherein the chloride, in fused state, is subjected to electrolysis and separation of its magnesium and chlorine values effected. Droplets of pure electrolyzed magnesium metal collect at the cathode in such system to coalesce and float to the top of the fused mass and can be withdrawn to storage or recycled for reuse to the metal halide reduction stage of the metal producing operation. Chlorine freed and evolved at the anode can likewise be withdrawn to storage or recycled for reuse in the halogenation or metal halide production stages of the system.

To a clearer understanding of the invention, the following specific examples are given. These are merely illustrative and not in limitation of the invention.

Example I

100 parts by weight of impure magnesium chloride comprising the by-product salt from a titanium reduction process of the type disclosed in U. S. Patent 2,205,854, and containing 4 parts by weight of insoluble titanium in the form of dispersed fine titanium metal particles and 7 parts by weight of soluble titanium in the form of lower chlorides, was melted in a silica brick-lined molten-salt type reactor furnace using electrical conductance of the molten salt as the heating means. The heating was done by A. C. current through two graphite electrodes. The solid magnesium chloride added to the furnace was melted initially by using a small shorting bar of graphite between the two graphite electrodes. This shorting bar became highly heated due to the conduction of electrical current and subsequently melted the surrounding solid magnesium chloride to provide a molten charge. After about ¼ of the charge had been added and melted, the shorting bar was knocked loose and removed with the subsequent heating achieved by conduction through the molten bath. The remaining portion of the charge was then added and melted.

The molten charge was heated to about 800° C. and halogenation of the charge effected by feeding gaseous chlorine through a graphite tube under the surface of the molten magnesium chloride. The volatile titanium tetrachloride and excess chlorine resulting from the chlorination were led from the reactor through a ceramic duct to an associated, water-cooled, nickel-constructed condenser wherein the titanium tetrachloride was condensed and collected. The chlorine gas was collected, compressed and recycled for reuse in the system. The flow of chlorine gas to the molten charge was continued until the gas discharging from the chlorination reactor was substantially pure chlorine. Thereupon, the molten, purified magnesium chloride was removed from the reactor, a small amount of molten salt being left therein for use in starting the heating for the next batch of impure salt to be treated.

The purified magnesium chloride product was substantially free of soluble and insoluble titanium upon being tested by the peroxide method which is quite sensitive to titanium content.

Example II

4230 parts by weight of the saline residue separated from the zirconium metal product produced in accordance with the precedures of U. S. Patent 2,214,211 and containing 1.3% fine Zr metal and 1.42% Zr in the form of chlorides associated with the magnesium chloride and potassium chloride present was melted in a chlorination reactor of the type utilized in Example I and the molten mass was heated to 800° C. Chlorine gas was then bubbled through the mass at a rate of 200 parts by weight per hour for 1.25 hours. The zirconium tetrachloride issuing from the reactor was collected on associated water-cooled metal coils with the excess Cl_2 being collected for reuse. From this operation approximately 290 parts by weight of zirconium tetrachloride and 70 parts of chlorine were collected. The purified magnesium chloride-potassium chloride, essentially free of Zr contamination, was then removed from the chlorination reactor and employed in an electrolytic cell to produce magnesium metal therefrom.

Example III

A molten impure salt mixture from the reduction of titanium tetrachloride in accordance with the procedures of U. S. Patent 2,148,345, employing sodium metal as the reductant, was drained from the titanium metal product. About 250 parts by weight of this molten salt, containing approximately 5% Ti as metal, 3% Ti as chlorides, 17.3% KCl and 69.2% NaCl was introduced into a chlorination cell maintained at about 750° C. The molten salt was then contacted with 46 parts by weight of chlorine gas, the gases and vapors from the cell being tested occasionally by allowing small amounts to escape into the air. When these gases no longer fumed violently on such escape, production of titanium tetrachloride from the reaction had ceased. Products collected in water and ice-cooled condensers and a gas collector showed recovery of 60 parts of titanium tetrachloride and 3.5 parts of chlorine.

The purified molten salt substantially free of titanium was then transferred to a sodium cell for electrolytic recovery of sodium.

While described as applied to certain specific embodiments, the invention, as already noted, is not to be construed as restricted thereto. Thus, while temperatures ranging from 750–1050° C. are preferred for use in the halogenation of the metal halide by-product, such halogenation can be effected within a relatively broad temperature range bounded generally by the following limits: The lower temperature range to be above the melting point of the by-product salt and also high enough to insure sufficient vapor pressure of the volatile halide which is produced, the upper

limit to be below the temperature at which attack on the halogenation reactor materials of construction and loss of by-product salt undergoing purification by vaporization occurs. The halogenation reaction is more rapid at higher temperatures and therefore, if an increased rate is desired, resort to a temperature increase can be had.

Similarly, while a magnesium chloride by-product from a titanium tetrachloride reduction process is especially useful for treatment in accordance with the invention, other by-product salts and mixtures thereof are contemplated for treatment hereunder. The halides, particularly chlorides, of the alkali metals (sodium, potassium, lithium), alkaline earth metals (calcium, barium, strontium), and magnesium, are also effectively useful for treatment. Single or multiple component salt mixtures are equally advantageous for use and treatment herein. Multiple components systems are often more useful as electrolytes for the electrolytic recovery of the reducing metal. These by-product salts are recovered from reduction systems of the type set forth in the patents mentioned above. In general, in such systems a metal halide, particularly a chloride, bromide, or iodide, of a metal such as titanium, zirconium, columbium, molybdenum, tantalum, tungsten, etc., is subjected to reduction within a closed reactor, under an inert atmosphere, and at temperatures ranging from 750–1100° C. with a reducing metal such as magnesium, calcium, barium, sodium, potassium, lithium, etc. In some of these reaction systems the by-product salt is drained from the metal reduction reactor in the molten state and therefore can be transferred directly to the halogenation reactor. In other processes the by-product salt is obtained in the solid state and the remelting step prior to introduction of the material into the halogenation reactor can be resorted to, if desired. Alternatively, the solid may be melted within the reactor by means of a conventional reactor heating system. If desired, the solid by-product can be added to a molten starting mass in the reactor. Preliminary separation steps can also be resorted to between the discharge of the by-product salt from the metal reduction reactor and its addition in molten state to the halogenation reactor, especially if large lumps of metal product are inadvertently discharged from the metal reduction reactor. Simple separation methods may be used to separate out these large lumps as, for instance, by recourse to sedimentation, screening, or other suitable means.

Halogenation reactors useful in the invention preferably comprise those constructed of a suitable corrosion-resistant metal or alloy, lined with molten salt-resistant refractories, as for example high silica acid-proof brick, graphite, or ceramic materials, etc. Construction materials and methods of the type employed in active metal electrolytic cells can also be used in assembling the halogenation reactor, as can cooled-wall types of metal reactors wherein a protective liner of frozen salt material is employed. Melting and heating of the salt mass within the reactor can be effected by using electrical conduction or other desired heating means adapted to reduce the salt mass to the desired molten or fluid condition prior to subjecting it to contact with the halogenating gas. In the instance of electrical heating, an alternating current is preferably resorted to which current can be introduced into the salt mass by immersed graphite electrodes. The

halogenation inlet to the chlorination reactor can be constructed of molten salt-resistant materials of which silica, graphite, and some ceramics, such as sintered aluminum oxide, are useful examples. The halogenating agent used comprises the same element as that present in the metal halide and is introduced into the reactor in gaseous state. Vaporization and/or preheating of the halogenating agent can be accomplished by passing it through a hot halogen inlet tube leading to the reactor or can be effected by any other desired method.

A number of modifications are possible in the simple type of liquid-gas contactor employed in the above examples in the halogenation reactor. Such modifications include flowing film contactors, spray contactors, packed towers, etc. Obviously, the invention can be adapted as a batch or a continuous process with the consideration that the molten salt and halogen are retained in contact a sufficient length of time at the temperature of operation used to insure the degree of purification desired.

From the foregoing, it will be readily apparent that the invention provides a novel method for purifying by-product halide salts and improves upon prior methods which have proved technically and economically unsuccessful. In addition, it affords an integrated process for the production of the refractory metals and insures satisfactory recovery of both the halogen and the metal values present in the by-product salt. The purity of the reducing metal is insured because of this purification step. The pure magnesium chloride obtained by the method of this invention comprises a superlative electrolytic cell feed material due to its high purity and freedom from oxides and water contents.

I claim as my invention:

1. A method for purifying an impure by-product metal halide salt recovered from the reduction of a metal halide with a reducing metal which comprises reacting said salt while in molten state with a halogen gas selected from the group consisting of chlorine, bromine and iodine, and continuing said reaction until soluble and insoluble metal product impurities from the reduction present in said salt become removed therefrom in the form of a volatile halide of the halogen employed in the reaction.

2. A method for purifying a by-product metal chloride salt recovered from the reduction of a metal halide with an active reducing metal, comprising subjecting said by-product while in molten condition to chlorination with gaseous chlorine, and continuing the chlorination until soluble and insoluble metal product impurities from the reduction are removed from said by-product in the form of volatile chlorides.

3. A method for purifying a by-product metal chloride salt recovered from the reduction of a metal chloride with an active reducing metal, comprising subjecting said by-product salt while in molten state to intimate contact at temperatures ranging from 750–1050° C. With gaseous chlorine within a reaction vessel, and continuing said contact until the soluble and insoluble metal product impurities from the reduction present in said by-product are removed therefrom in the form of volatile chlorides.

4. A method for purifying a by-product metal chloride salt obtained from the reduction of a metal chloride with an active reducing metal, comprising subjecting said salt while in molten state to chlorination by direct contact with

gaseous chlorine at temperatures ranging from 750–1050° C. within a closed reaction vessel, continuing said chlorination until soluble and insoluble metal product impurities from the reduction are removed from said salt in the form of volatile chlorides, removing said volatile chlorides from the reaction vessel, and separately recovering the purified by-product chloride and condensed volatile metal chlorides.

5. A method for removing titanium impurities present in by-product magnesium chloride obtained in the reduction of titanium tetrachloride with magnesium which comprises subjecting said chloride while in the molten state and at temperatures ranging from 750–1050° C. to direct contact with sufficient gaseous chlorine to convert its titanium values to titanium tetrachloride, removing the titanium tetrachloride formed from the molten bath by vaporization, and separately recovering the purified magnesium chloride and titanium tetrachloride products.

IGNACE JOSEPH KRCHMA.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,730,548	Welch	Oct. 8, 1929
1,878,013	Staib	Sept. 20, 1932
1,923,594	Suchy et al.	Aug. 22, 1933
2,205,854	Kroll	June 25, 1940
2,214,211	von Zeppelin	Sept. 10, 1940
2,253,470	Muskat et al.	Aug. 19, 1941
2,384,479	Lepsoe et al.	Sept. 11, 1945
2,463,396	Krchma	Mar. 1, 1949
2,522,679	Kroll	Sept. 19, 1950
2,556,763	Maddex	June 12, 1951
2,589,466	Wilcox	Mar. 18, 1952

OTHER REFERENCES

Journal of Metals, April 1950, pp. 634–640.

Report of Ductile Titanium at Boulder City, Nev. U. S. Dept. of the Interior; R. I. 4519; Aug. 1949.

Titanium; Barksdale; pp. 316–317; Ronald Press Co., New York; copyright 1949.