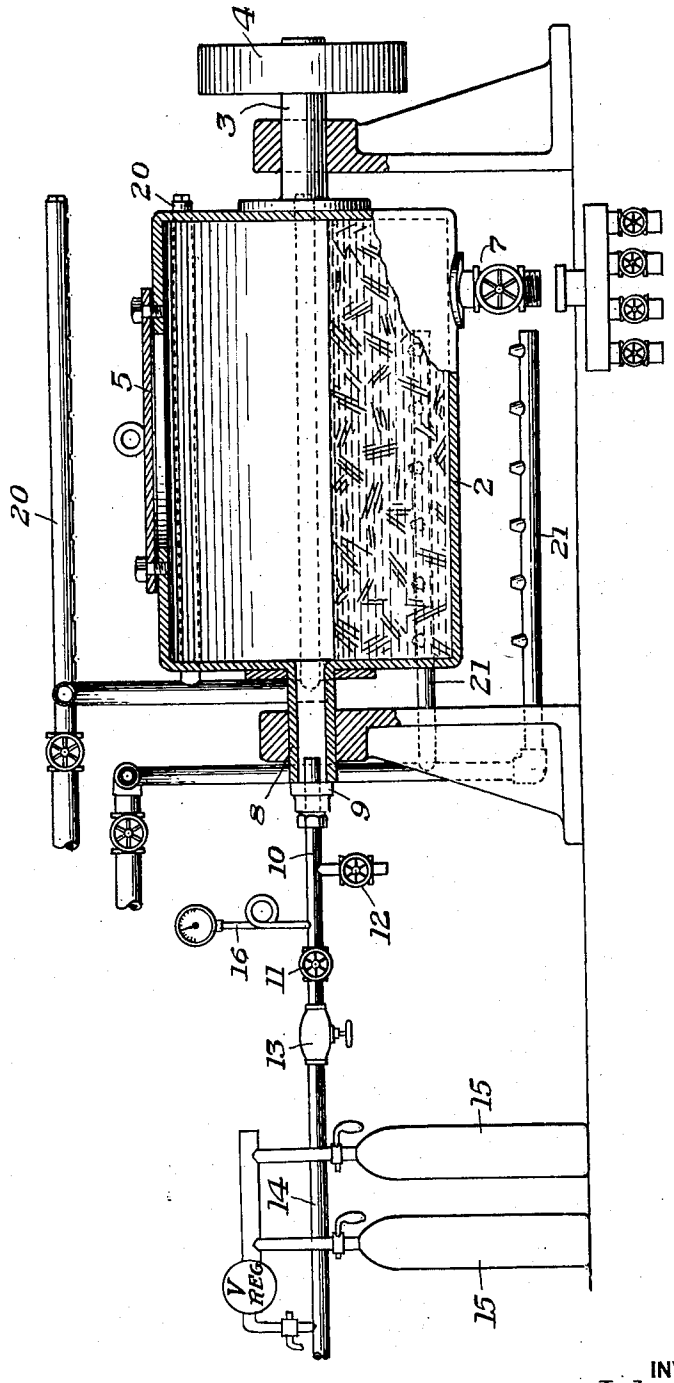
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CONVERSION OF METALS INTO METAL OXIDES AND HYDROXIDES

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## CONVERSION OF METALS INTO METAL OXIDES AND HYDROXIDES

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6 Claims. (Cl. 23—147)

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This invention relates to the conversion of metals into metallic compounds, and constitutes a continuation-in-part of my copending application Serial No. 488,323 filed May 25, 1943, now abandoned.

The conversion of metals into metallic compounds by the present invention finds importance in the preparation of metallic compounds usable as such for industrial purposes, or usable as base substances for conversion into other compounds. It is also useful for the separation and recovery of physically associated metals. By way of illustration, copper may be converted from metallic form into almost colloidal size copper oxide which, of itself, is a desirable commercial material. Alternatively, the copper sheathing or copper-clad steel may be converted into copper oxide while the ferrous base is left untouched, so that the copper oxide may be used as such, or it may be smelted into copper, and the ferrous base can be used as ferrous melting scrap. Thus the invention is applicable either to making metal compounds from a metal, or for separating physically combined metals by converting one of them into a compound.

This invention differs from all known methods of converting metals to metallic compounds by leaching or like reactions, in that metal is continuously reacted in the presence of an electrolyte and continuously precipitated as a compound at the same time from the same body of electrolyte without exhaustion of the electrolyte. This, so far as I can ascertain, is a new phenomenon. In all usual operations of leaching, the metal is reacted with the electrolyte until the electrolyte is spent, or will no longer react with metal. The electrolyte is then processed to recover the metal compound dissolved or contained therein, and the electrolyte so used is exhausted. It must be constantly replenished. With my process, except for certain inevitable handling losses, the electrolyte is usable over and over without processing in any way.

My invention has been successfully employed with several metals and in the making of several compounds, and according to my invention the following conditions are required:

(1) The electrolyte used must be one which is corrosive to the metal to be converted into compounds. That is, it will be capable of attacking the metal from which the compounds are to be made.

(2) The process must be carried out in a closed environment where alternate exposure to the atmosphere and liquid in the environment may be effected.

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(3) There must be present in the closed environment or reactor a gas which enters into combination with the metal.

Essentially my invention contemplates the tumbling of the metal in a corrosive liquid and an atmosphere of a gas which is consumed in the reaction so that the metal is alternately immersed in the liquid and exposed to the gas. Temperature conditions and the concentration of the electrolyte may also in some cases control the character of the product.

My invention may be more fully understood by reference to the accompanying drawings, in which the figure is a view partly in section and partly in elevation and schematic in character of an apparatus embodying and capable of effecting my invention.

In the drawing, 2 designates an enclosed vessel or reactor, preferably rectangular in shape, having a trunnion 3 at one end on which is a pulley 4 by means of which the vessel may be rotated. The vessel has a cover member 5 removably sealed thereto so as to be liquid and gas-tight, but which affords access to the interior of the vessel for charging and discharging the contents of the vessel. The vessel is also shown as having a drain valve 7.

At the other end of the vessel is a hollow trunnion 8 having a gland 9 into which a gas supply pipe 10 is entered. This pipe 10 is provided with a cut-off valve 11, a drain valve 12, a pressure regulating valve 13, and an extension 14. With this arrangement the vessel may be selectively connected through a pressure regulator and manifold to one or another gas storage vessel 15, so that when one vessel is exhausted, another may be used while the first is replaced, or when necessary, two different gases may be supplied simultaneously or successively to the reactor.

In the drawings, spray nozzles 20 are shown for directing jets of cooling fluid against the outside of the drum. The drum may be provided with heat dissipating fins, not shown, to accelerate the rate of heat transfer. Water, or even air currents may be directed through the nozzles. Other nozzles 21 may also be provided for directing a heating fluid such as steam against the reactor. It will be apparent that various other temperature regulating or modifying means may be used.

In the operation of the device, the metal to be processed is charged into the drum. The corrosive liquid or electrolyte is then introduced into the reactor until the reactor is preferably from a half to two-thirds full, after which the

lid 5 is sealed shut. The reactor is then set into rotation, and gas is admitted to build up and maintain a desired pressure therein. After a period of time, depending upon the metal, the amount of metal and the product to be produced, the reactor is stopped and opened. The metallic compound is present in the bottom of the reactor as a sludge of very small particles. Usually the valve 7 is opened and the contents of the reactor are run into a thickener or filter to separate out the metallic compound which is subsequently washed and dried, while the electrolyte from which the compound is separated or filtered is kept for reuse in the reactor. It will be found that during the reaction the metal compound is continuously formed and precipitated without exhaustion of the electrolyte, and that no matter how long the electrolyte is used, it will remain active.

With the reactor about one foot in diameter and about six inches long revolving at 72 R. P. M., the following are typical examples of my method.

*Example 1*

Black copper oxide was prepared by making a solution containing 160 grams of ammonium carbonate-carbamate (ammonium carbonate, commercial grade) and 1000 c. c. of ammonium hydroxide containing 28% $NH_3$ and 2000 c. c. of water. These proportions are not critical, however. It will be noted that the solution is corrosive to copper.

This solution filled the reactor to about one-third of its capacity. Commercial copper scrap was then put into the reactor until it was about two-thirds full. The amount of copper is not critical. The cover was then sealed on and oxygen from one of the tanks 15 was admitted, the regulating valve being set to maintain a pressure of 7 p. s. i. in the reactor. Rotation of the reactor was continued for about an hour, and the sludge and electrolyte were then drawn off. The sludge was separated by filtration, the electrolyte recharged into the reactor with additional copper, and enough fresh solution to offset the amount that remained in the sludge was added and the operation repeated. The electrolyte lost none of its effectiveness.

While the operation could have continued until all of the metallic copper had been converted, it is more efficient to replenish the copper from time to time and so keep a good mass of metal in the reactor.

The sludge was black copper oxide, 99+% of which was 1 micron or under in its greatest dimension. The temperature during reaction reached between 165° F. and 175° F., the oxidation of the metal being an exothermic reaction.

*Example 2*

The same procedure was followed with the metals cobalt, zinc, cadmium, nickel and silver, with the production in each case of the corresponding metal oxide.

*Example 3*

The ammonia concentration of the solution of Example 1 was decreased about 50%, the same amount of copper scrap was charged into the reactor, the oxygen pressure was about the same, small amounts of water were intermittently added, and the reactor was cooled to keep the contents below 165° F. Copper hydroxide was precipitated as a sludge and the electrolyte reused after the hydroxide was separated. Water was added because the formation of the hydroxide tended to remove water and increase the concentration of the ammonia solution. The electrolyte was not depleted by use.

*Example 4*

Using the solution of Example 1 and a like amount of copper, $CO_2$ and oxygen were both introduced in about equal amounts into the reactor. The gas pressure was around 7 p. s. i. and the temperature was of the order of 165° F. Copper carbonate was precipitated.

*Example 5*

A solution was prepared with 300 grams of commercial ammonium chloride and 2700 c. c. of water. This was put into the reactor with enough iron scrap to fill the reactor about two-thirds full. Oxygen was supplied during reaction at about 7 p. s. i. pressure. Very finely divided red iron oxide was produced. The electrolyte was reused for the treatment of other iron. The temperature reached was approximately 165° F., no control being used. Magnetic black iron oxide may be produced with slight variation of this procedure, which consisted in cutting of the oxygen after red oxide had been produced, whereupon $Fe_2O_3$ with additional unreacted iron in the reactor iron formed $Fe_3O_4$. Instead of using a solution of ammonium chloride, a corrosive liquid was prepared using sodium chloride.

*Example 6*

A solution was prepared using 300 grams of commercial ammonium chloride and 2700 c. c. of water. It was put in the reactor with iron scrap. Instead of oxygen, chlorine was introduced into the reactor, and maintained at a pressure about or slightly above 5 p. s. i. Iron chloride in finely divided form was precipitated. The electrolyte was successfully reused.

The same procedure may be followed using sodium chloride as the corrosive agent, or by using HCl or $H_2SO_4$ solution, it being desirable where an acid is used as the corrosive agent, to keep the reactor open during the initial reaction while hydrogen is being generated.

In the above example, fluorine may be used in place of chlorine, to produce fluorides. Other gases are $SO_2$ and $SO_3$. The gas in each case must be an active one, that is, one which may form salt or compounds of the metal to be converted, and the inert gases, such as helium, argon, neon, etc. Gases such as HCl or $H_2S$ are not used, because their reaction with metal will occur directly and hydrogen is liberated. The gas therefore is one which may be combined with metal, but which in entering into the combination does not itself decompose.

*Example 7*

Into a larger reactor, for use in separating copper or gilder's metal from ferrous sheet metal on which it is clad, there was charged 2240 lbs. of scrap containing 80% steel, carrying on its surface 20% (average) gilder's metal. A solution was then introduced, made with:

370 lbs. of ammonium hydroxide 26° Bé.
66 lbs. of ammonium carbonate (commercial)
825 lbs. water

During rotation of the reactor over a period of two hours, 1600 cubic feet of oxygen were consumed, pressure being maintained at about 5 p. s. i. above atmospheric. After two hours, the oxygen was shut off and the reactor rotated for

an additional period of time, about three hours, to remove by attrition copper oxide clinging to the metal scrap. At the end of this time, the ferrous scrap was clean and bright and the coating metal associated with it converted to oxide. The solution, which quickly becomes saturated with copper oxide, was reused each time after the sludge of copper oxide was separated from it, with only sufficient new solution to make up for that which was retained in the solid material.

After separation the precipitate is washed with water, and water used in washing the precipitate may in all cases be used as make-up water for fresh solutions, to thereby conserve electrolyte which otherwise would be lost. The solution used is highly corrosive to copper or gilder's metal, and considerably less corrosive to iron, so that its action is selective, and little, if any iron oxide was found in the precipitate.

Instead of ammonium carbonate or ammonium carbonate-carbamate, I may use ammonia compounds that will give free ammonia ions. Some such materials are ammonium bicarbonate and urea. I may also use carbon dioxide in place of ammonium carbonate, with a compensating increase in the ammonium hydroxide employed.

In all cases, I have found that the electrolyte is one which is corrosive to the metal to be converted into a compound. In all cases the metal compound is constantly precipitated and new compound is constantly formed so that the electrolyte is not exhaused and continues to be usable indefinitely, only the gas in the reactor being consumed. The process is preferably a cyclic one in which the electrolyte is used over and over, and the solution loss during each cycle should not exceed more than 3%.

With my invention a relatively small compact plant can produce metallic compounds of a high quality and very fine particle size more rapidly and with a much less expense for plant outlay and materials than plants using conventional leaching methods.

It is of course well known to use ammonium-hydroxide—ammonium carbonate solutions for preparation of copper oxide by immersing the metal in a tank containing the solution and blowing air through the same. Oxide is formed which is dissolved in the solution until the solution will take up no more oxide, when reaction ceases, and the electrolyte is processed to recover the metallic oxide, but in such case the electrolyte is destroyed. In such procedure much of the ammonia in the solution is carried off with the air constituents not used in the reactor, necessitating expensive ammonia recovery facilities. In distinction to this, with my process the same electrolyte is used indefinitely; reaction does not stop when saturation of the solution is reached; a small body of solution will convert a large amount of metal into metallic compound, the metal compound is directly precipitated, and by using oxygen instead of air and having the reaction proceed in a closed environment, no ammonia or other valuable gas is carried away.

It is also known that ammonia solutions of the kind described may be rubbed upon brass or copper, as in brass polish, and upon drying, leave a deposit that may be brushed or wiped off, but in the evaporation of the solution, the electrolyte is lost, which is contrary to my present invention wherein precipitation occurs concurrently with reaction and the solution remains continuously in the liquid phase—a phenomenon effected through the tumbling or mechanical agitation of the metal and electrolyte in a closed environment to which a consumable gas is supplied.

While I have been unable to exhaust the number of metals and compounds that may be produced, the foregoing is believed to adequately inform those skilled in the art of the procedure to be followed and the practices which are desirable in carrying into effect my invention and discovery, and various modifications in the equipment may be made to facilitate particular operations or plant conditions. Wetting agents such as "Aerosol" may be used, particularly when the metal to be processed is dirty or greasy. In the examples given above I have indicated amounts and pressures which I have found to be satisfactory, but these are not critical and may be varied within wide limits with some resulting change in the speed of reaction or the quality of the oxide in some cases, and while I have indicated that the gas pressure be above atmospheric pressure in the reactor, it is possible to operate with less than atmospheric pressure. Pressures are preferably kept below 60 p. s. i., and pressures of the magnitude indicated as around 5 to 7 p. s. i. are quite satisfactory. For the purpose of efficiency, I have indicated that the reactor be from one-half to two-thirds full, but this again is not critical. There is no advantage in operating it with too small a charge, and if the reactor is too full, the alternate exposure of the metal to the gas and its subsequent immersion is less effective.

I claim:

1. The method of making a metal compound of the group consisting of an oxide and hydroxide from pieces of the raw metal which comprises tumbling the metal pieces in an environment closed against the escape of gas and vapors during the tumbling process containing part liquid and part gas so that in the tumbling process the metal is alternately immersed in the liquid and then exposed to the gas, the gas being commercial oxygen and the liquid being an ammoniacal solution which corrodes the metal, the metal being a metal of the group consisting of copper, nickel, cobalt, zinc, iron, cadmium and silver supplying additional oxygen to the environment as the oxygen is consumed therefrom and continuously during such operation using the same ammoniacal solution and producing during such operation a metallic compound of said group consisting of the oxide and hydroxide from the metal so treated, the ammonia in the ammoniacal solution remaining substantially fixed as such in the solution throughout the process and recovering such metallic compound so formed.

2. The method of making a copper compound of the group consisting of the oxide and hydroxide from pieces of copper which comprises tumbling the copper pieces in an environment closed against the escape of gases and vapors during the tumbling process containing part liquid and part gas so that in the tumbling process the metal pieces are alternately immersed in the liquid and then exposed to the gas, the gas being commercial oxygen and the liquid being a solution of an ammonium compound, and supplying additional oxygen to the environment as the oxygen is consumed therefrom continuously during such operation precipitating the compound of the group consisting of copper oxide and copper hydroxide from the one body of solutin, the ammonia in the solution remaining substantially

fixed in the solution as such during the process, and thereafter recovering precipitate.

3. The method of forming a copper compound of the group consisting of the oxide and hydroxide from ferrous metal having copper physically associated therewith for the separation and recovery of copper and the refinement of the ferrous metal, which comprises tumbling the metal pieces in an environment closed against the escape of gases and vapors during the tumbling process containing part liquid and part gas so that in the tumbling process the metal is alternately immersed in the liquid and then exposed to the gas, the gas being commercial oxygen and the liquid being an aqueous solution of an ammonium compound, and supplying additional oxygen to the environment as the oxygen is consumed continuously forming in said environment during the tumbling operation the cuprous compound of the group consisting of the oxide and hydroxide as a precipitate, the strength of the ammonia solution remaining substantially constant and unaltered throughout the process, and subsequently separating out said precipitate and reusing the said ammonia solution so separated in a succeeding similar operation.

4. The method of converting copper to its respective oxides which comprises introducing pieces of the metal to be converted into an environment closed against the escape of gases, introducing a starting aqueous solution of ammonia and commercial ammonium carbonate into said environment to partially fill it, mechanically tumbling the metal and solution about within the environment, and introducing commercial oxygen into the environment during such tumbling continuously precipitating the metal oxide which is produced, the ammonia in the ammonia solution remaining substantially fixed as such in the solution throughout the process and being retained in the solution without substantial depletion by the reaction.

5. The method of converting metals of the group consisting of copper, nickel, cobalt, zinc, iron, cadmium and silver to their respective compounds of the group consisting of the oxide and hydroxide which comprises introducing a charge of the metal pieces to be processed into an environment closed against the escape of gases and vapors, tumbling it in such environment into and out of an aqueous solution containing metal-ammonia compounds of the metal being treated, simultaneously introducing commercial grade oxygen into the closed environment during such tumbling, continuously forming and precipitating in the environment a compound of the metal, which compound is one of the group consisting of the oxide and hydroxide, regulating the water content of the solution to selectively produce the oxide or hydroxide, the ammonia in the ammonia solution remaining substantially fixed as such in the solution throughout the process and being retained in the solution without substantial depletion by the reaction, separating the precipitate from the solution after substantial depletion of the metal to recover the precipitate and re-using the solution less only the precipitate in processing other like metal to make more of said compound.



6. The method of stripping copper from copper clad steel by oxidation of the copper which comprises introducing pieces of the clad metal into an environment closed against the escape of gas and vapors, said environment containing a body of an aqueous solution of a copper-ammonium compound and containing an atmosphere of commercial grade oxygen, tumbling the charge of metal pieces about in said environment to alternately expose them to the oxygen and immerse them in the solution and effect also mechanical motion of the pieces against one another, whereby the copper on the metal pieces is reacted and stripped, supplying additional commercial grade oxygen to the environment as it is consumed, precipitating in the environment during such tumbling the compound so formed which is a compound of the group consisting of copper oxide and copper hydroxide, the ammonia in the ammonia solution remaining substantially fixed as such in the solution throughout the process and being retained in the solution without substantial depletion by the reaction, terminating the tumbling when the copper has been so stripped and removed therefrom, subsequently separating the compound from the solution to recover such compound and re-using the solution to process more such metal.

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