UNITED STATES PATENT OFFICE.

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PROCESS OF REDUCING METAL AND MAKING METALLIC HYDROXIDS.

SPECIFICATION forming part of Letters Patent No. 717,328, dated December 30, 1902.

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To all whom it may concern:

Be it known that I, HENRY SPENCER BLACKMORE, a citizen of the United States, residing at Mount Vernon, in the county of Westchester and State of New York, have invented certain new and useful Improvements in Processes of Reducing Metal and Making Metallic Hydroxids; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

The object of my invention is to reduce metals and make metallic hydroxids from their double oxids or combinations of metallic oxids with metal more electropositive—such as plumbates, chromates, manganates, aluminates, ferrites, &c., of more electropositive metals—in a rapid, efficient, and economical manner; and it consists, essentially, in exposing compound oxids of the character aforementioned to the action of a gaseous substitution or displacing agent, such as hydrogen, and heat.

My invention relates particularly to the reduction of lead from alkali-metal plumbates and production of alkali-metal hydroxids by the action of hydrogen, but is not confined to the reduction of lead, as it may be applied to the reduction of many other metals—such as chromium, aluminium, iron, &c.—or alloys of such metals when deoxidized simultaneously.

It is well known that metallic oxids *per se* may be deoxidized when heated in the presence of hydrogen, hydrocarbons, or other gaseous deoxidizing agent; but it is found in many cases that the temperature at which the affinity of the oxygen content for the deoxidizing agent varies and, as in many cases, the metallic oxid to be reduced is of refractory character, being infusible below temperatures of that obtained by the use of the electric arc, and the said oxid being a non-conductor of heat is naturally exposed at varying temperatures throughout the body—*i. e.*, the exterior being at higher temperature than the interior. Therefore great difficulty is experienced in maintaining a uniform temperature and performing a complete reduction. I have found, however, that by combining metallic oxid with metal of more electropositive nature—such as alkali-metal plumbates, aluminates, ferrites, &c.—the refractory oxid in combination forms compounds of readily-fusible nature, whereby the refractory-oxid content is brought to a condition at which it may be readily maintained at a uniform temperature and in a molten condition without the employment of extremely-high temperatures and by which means when exposed to the action of a gaseous substitution or displacing agent the more electronegative metal or metals may be readily reduced to a metallic state, thereby obviating the difficulties hitherto met with in employing the refractory oxids *per se*.

The manner in which I prefer to carry out my process for the reduction of lead is to melt sodium hydroxid (NaOH) in a proper receptacle and add thereto lead hydrated peroxid, ($PbO_3—OH_2$,) sometimes called "plumbic acid," whereby a reaction takes place which may be illustrated by the following chemical formula or equation, producing sodium plumbate:

$$2NaOH+PbO_3—OH_2=Na_2PbO_4+2H_2O.$$

When the reduction of metal only is desired, I find it of advantage to convert only a part of the sodium hydroxid into sodium plumbate, as the excess of sodium hydroxid assists in maintaining the sodium plumbate in a molten condition at a lower temperature; but the whole can be converted into sodium plumbate, if desired, without rendering the process inoperative. I can also produce sodium plumbate by heating metallic lead in conjunction with sodium hydroxid or sodium carbonate and pass a current of oxygen or air therethrough. I then pass hydrogen through this molten sodium plumbate or sodium hydroxid containing sodium plumbate, whereby the lead-oxid content of the plumbate becomes transformed, displacing the lead in metallic state, producing sodium hydroxid by substituting hydrogen for the lead and liberating steam, as may be illustrated by the following chemical formula or equation:

$$Na_2PbO_4+6H=Pb+2NaOH+2H_2O.$$

Instead of hydrogen I may employ any other gaseous reducing or displacing agent, such as acetylene, (C_2H_2,) in which case the

reaction may be illustrated by the following chemical formula or equation:

$$Na_2PbO_4+C_2H_2=Pb+Na_2CO_3+CO+H_2.$$

In this case the sodium hydroxid first produced by action of the hydrogen content of the acetylene is transformed by action of the carbonic oxid from the carbon content into sodium formate, which in the excess of hydroxid is finally converted into sodium carbonate, with liberation of free hydrogen after all the lead has been reduced.

The employment of acetylene or similar gaseous endothermic reducing agents is particularly advantageous in the reduction of aluminates, ferrites, and similar compounds where the metallic-oxid content is of greater refractory nature, inasmuch as during reduction the decomposition of the acetylene or similar endothermic compound liberates considerable heat within the mass at the point of reaction and facilitates the reduction of the more refractory oxid at lower applied temperatures. The reaction which takes place in the reduction of sodium aluminate with acetylene under similar conditions may be illustrated by the following chemical formula or equation:

$$Na_2Al_2O_4+C_2H_2=2Al+Na_2CO_3+CO+H_2.$$

The presence of calcium aluminate in this process facilitates the reduction.

When a heated aluminate is reduced by hydrocarbon, such as acetylene, it is evident that the temperature must be maintained above the point at which aluminium reduces oxid of carbon in the presence of accompanying ingredients, and when hydrogen is employed as reducing agent sodium hydroxid is regenerated, the aluminate being reproduced by simply adding aluminium oxid or hydroxid thereto from time to time.

The reduction of metals by this process is also facilitated by exposing the material to be reduced to the action of gaseous reducing agent under superatmospheric pressure.

It is obvious that I may reduce other metals—such as chromium, manganese, iron, &c.—by employing a double oxid of such metals or compounds of said oxid with metal more electropositive, it being noted that the oxid of the heavier metallic base of the compound exists as an acid constituent of the salt employed. I can also employ a compound of metallic oxid with more electropositive metal direct—that is, not produced as a step during the process of reduction—without departing from the spirit of my invention.

The term "gaseous substitution agent" employed in this specification and claims is intended to include any gaseous body capable of displacing from the metallic oxid combined with more electropositive metal the electronegative metal the reduction of which is desired and is also intended to include vaporized bodies, such as heavier hydrocarbons heated to a vaporizing-point, as well as bodies which exist as gases *per se* at ordinary temperature and pressure.

It is obvious that I can perform the reduction of the compound of the metallic oxid with metal more electropositive *per se* in a heated or molten condition by the action of gaseous reducing or substitution agent, it not being necessary in some cases to bring the compounds to a state of fusion before reduction takes place without departing from the spirit of my invention, or I can employ in conjunction therewith other compounds which may facilitate the fusion or reduction by dissolving or suspending the same in a state of fusion, the object being to reduce the compound of metallic oxid with metal more electropositive when heated by the action of gaseous reducing agent. I can expose the compound to be reduced to a heat capable of fusing it and introduce either or both the compound to be reduced or gaseous deoxidizing agent after fusion or during fusion, or I can add to the fused bath more compound to be reduced and gaseous deoxidizing agent from time to time, as desired, making the process continuous and withdrawing the reduced metal at intervals, without departing from the spirit of my invention, which consists in displacing from a compound of a metallic oxid with a metal more electropositive the more electronegative metal or metals while the composition is in a heated condition by the action of a gaseous substitution agent. It is also obvious that I can produce alloys of various metals by exposing to the action of a gaseous reducing agent a heated compound or compounds of metallic oxid or oxids with a metal more electropositive, the said compound or compounds containing the metals an alloy of which is desired being reduced in a heated condition simultaneously.

It may be noted that it is advantageous, although not absolutely necessary, that the compound reduced should be heated to a state of fusion or suspended in or liquefied by the action of other ingredients, whereby the reduction is facilitated.

It is seen that the present process consists in its most simple description in the displacement of the heavier metal from its oxid by hydrogen, liberating the metal, and producing a hydrate or hydroxid of the more electropositive metal of the compound employed, as, per example described, the displacement of lead from sodium plumbate by hydrogen and production of sodium hydrate or hydroxid. In cases where the gaseous reducing agent contains carbon as well as hydrogen, such as acetylene, it is obvious that the resultant hydroxid will be finally converted into carbonate.

By adding sodium carbonate to molten lead and passing a current of oxygen therethrough the lead becomes oxidized and de-

composes the sodium carbonate, producing sodium plumbate, with liberation of carbon dioxid. Then exposing the heated plumbate to the action of hydrogen, it is transformed into sodium hydrate or hydroxid, reducing the lead to its metallic state again. Then withdrawing the sodium hydrate thus produced, adding more sodium carbonate and oxygen, it can be readily seen that the process of producing sodium hydroxid from sodium carbonate may be carried on continuously, with simultaneous oxidation and reduction of lead.

Having now described my invention, what I claim as new, and desire to secure by Letters Patent, is—

1. The process of reducing metals which consists in exposing a compound composed of a metallic oxid with a metal more electropositive than the metal of the oxid, to the action of heat and a gaseous substitution agent capable of displacing the more electronegative metal.

2. The process of reducing metals which consists in exposing a molten body containing a metallic oxid combined with a more electropositive metal than the metal of the oxid, to the action of a gaseous substitution agent capable of displacing the more electronegative metal.

3. The process of reducing metals which consists in displacing from a molten body containing a metallic oxid combined with a more electropositive metal than the metal of the oxid, the more electronegative metal, by subjecting the composition to the action of hydrogen.

4. The process of reducing metals which consists in displacing from a compound composed of a metallic oxid with a metal more electropositive than the metal of the oxid, the more electronegative metal, by subjecting the composition to the action of hydrogen and heat.

5. The process of reducing metal and making alkali hydroxid which consists in exposing a compound composed of an alkali metal with a metallic oxid to the action of hydrogen and heat.

6. The process of reducing metal and making sodium hydroxid which consists in exposing a compound composed of sodium with metallic oxid to the action of hydrogen and heat.

7. The process of reducing lead and making sodium hydroxid which consists in exposing sodium plumbate to the action of hydrogen and heat.

8. The process of making compounds of metallic oxid and more electropositive metal, making hydroxid of the more electropositive metal and reducing the heavier metal, which consists in forming a compound of the heavier-metal oxid with the more electropositive metal, by exposing an oxid of the heavier metal to the action of a compound of the more electropositive metal capable of being decomposed thereby, and exposing the product to the action of hydrogen and heat.

9. The process of making compounds of metallic oxids with alkali metal and transforming it into alkali-metal hydroxid and reduced metal, which consists in oxidizing the heavier metal in conjunction with an alkali salt decomposable by the heated metallic oxid and exposing the resultant product in a heated state to the action of hydrogen.

10. The process of making compounds of sodium with oxids of heavier metals and transforming the compound into sodium hydroxid and metal, which consists in oxidizing the heavier metal in conjunction with a sodium salt decomposable by the metallic oxid and finally reducing the metal and making sodium hydroxid by exposing the heated compound to the action of hydrogen.

11. The process of making sodium plumbate, sodium hydroxid and metallic lead, which consists in decomposing a sodium salt by the action of lead oxid and exposing the heated plumbate to the action of hydrogen and heat.

12. The continuous process of making sodium hydroxid, which consists in passing oxygen through metallic lead in conjunction with sodium carbonate in a heated condition, exposing the heated resultant compound to the action of hydrogen, withdrawing the sodium hydroxid so produced, adding more sodium carbonate and oxygen to the lead simultaneously reduced and continuing the process as before.

13. The process of reducing metals which consists in displacing from a compound composed of metallic oxids with a more electropositive metal than the metal of the oxids, the more electronegative metals, by subjecting the composition to the action of heat and a gaseous substitution agent capable of displacing the more electronegative metals.

14. The process of reducing metals which consists in displacing from a compound composed of metallic oxids with a more electropositive metal than the metals of the oxids, the more electronegative metals, by subjecting the composition to the action of hydrogen and heat.

15. The process of reducing metals which consists in exposing a compound composed of metallic oxid or oxids with a more electropositive metal than the metal of the oxid, to the action of a gaseous endothermic reducing agent at a reacting temperature.

16. The process of reducing metals which consists in displacing from a compound composed of metallic oxid or oxids with a more electropositive metal than the metal of the oxid, the more electronegative metal or metals, by the action of a gaseous endothermic displacing agent at a reacting temperature.

17. The process of reducing metals which consists in exposing a compound composed of a metallic oxid with a metal more electropositive than the metal of the oxid, to the action of a gaseous reducing agent at a reacting temperature while under superatmospheric pressure.

In testimony whereof I affix my signature in presence of two witnesses.

HENRY SPENCER BLACKMORE.

Witnesses:
WARREN C. STONE,
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