

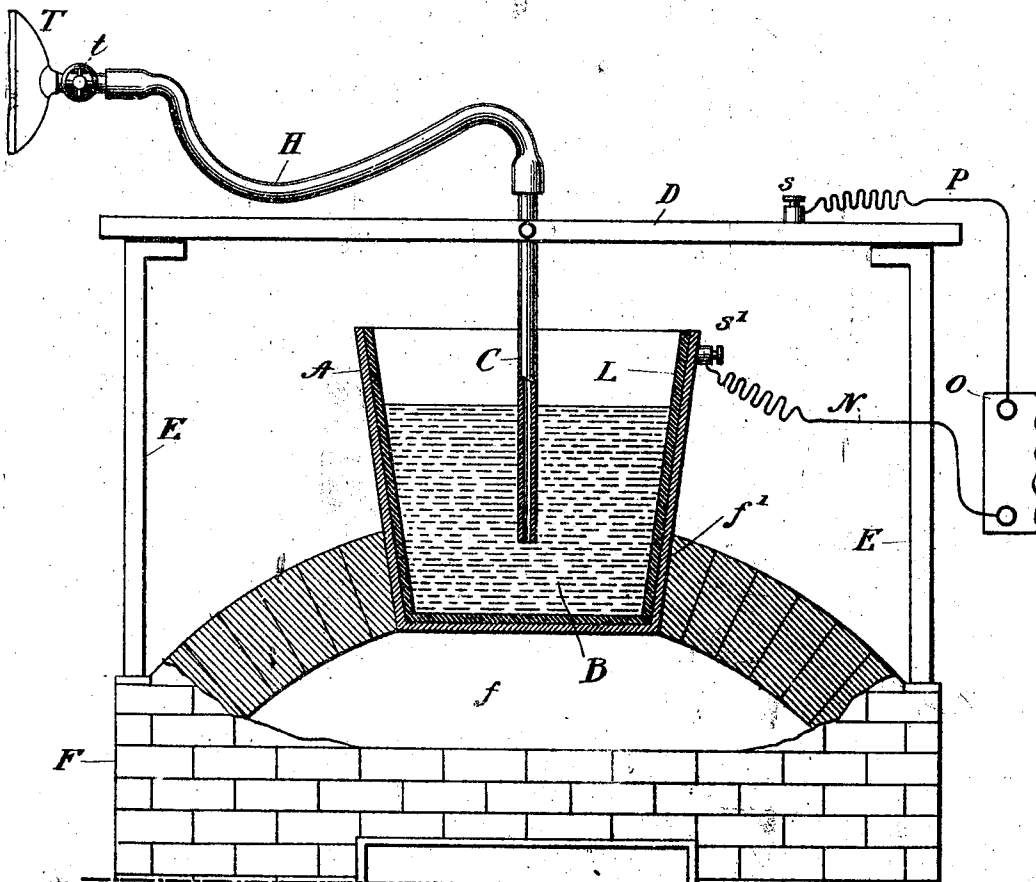
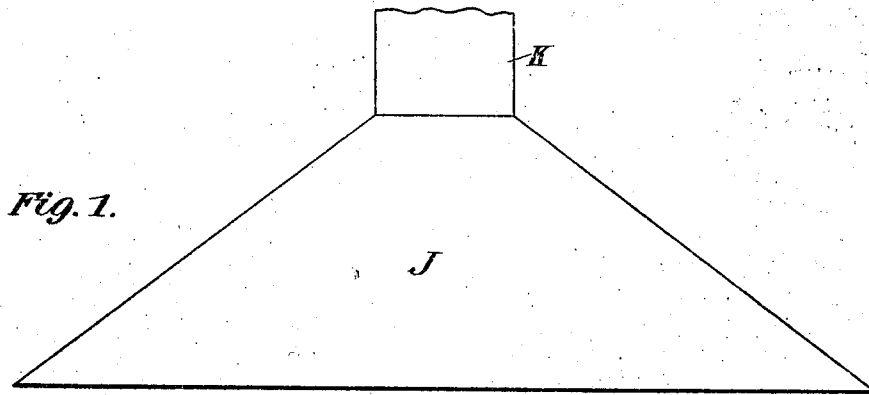
(No Model.)

3 Sheets—Sheet 1.

F. A. GOOCH & L. WALDO.
PROCESS OF REDUCING ALUMINIUM.

No. 528,365.

Patented Oct. 30, 1894.



WITNESSES:

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Herman D. Solomon

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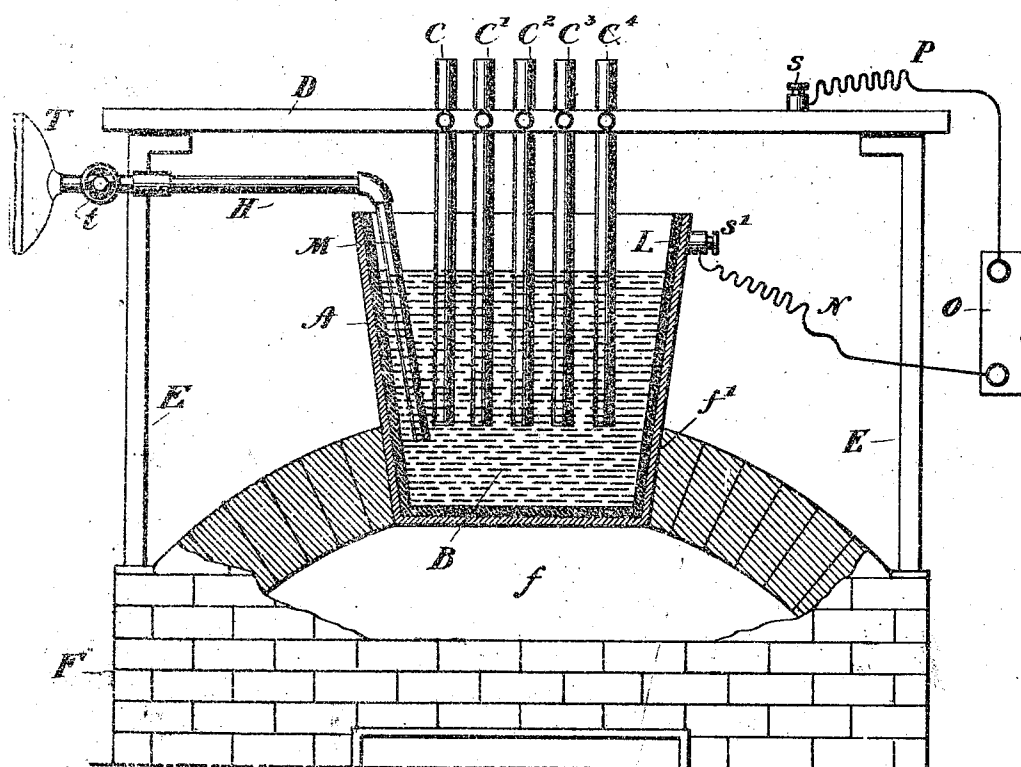
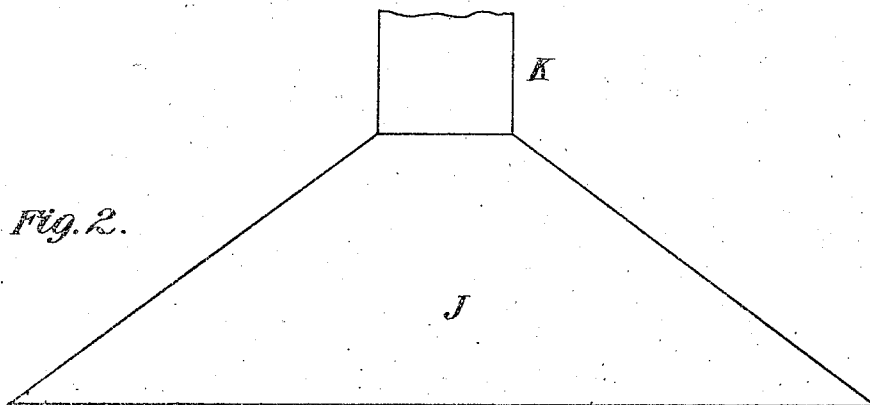
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3 Sheets—Sheet 2.

F. A. GOOCH & L. WALDO.
PROCESS OF REDUCING ALUMINIUM.

No. 528,365.

Patented Oct. 30, 1894.



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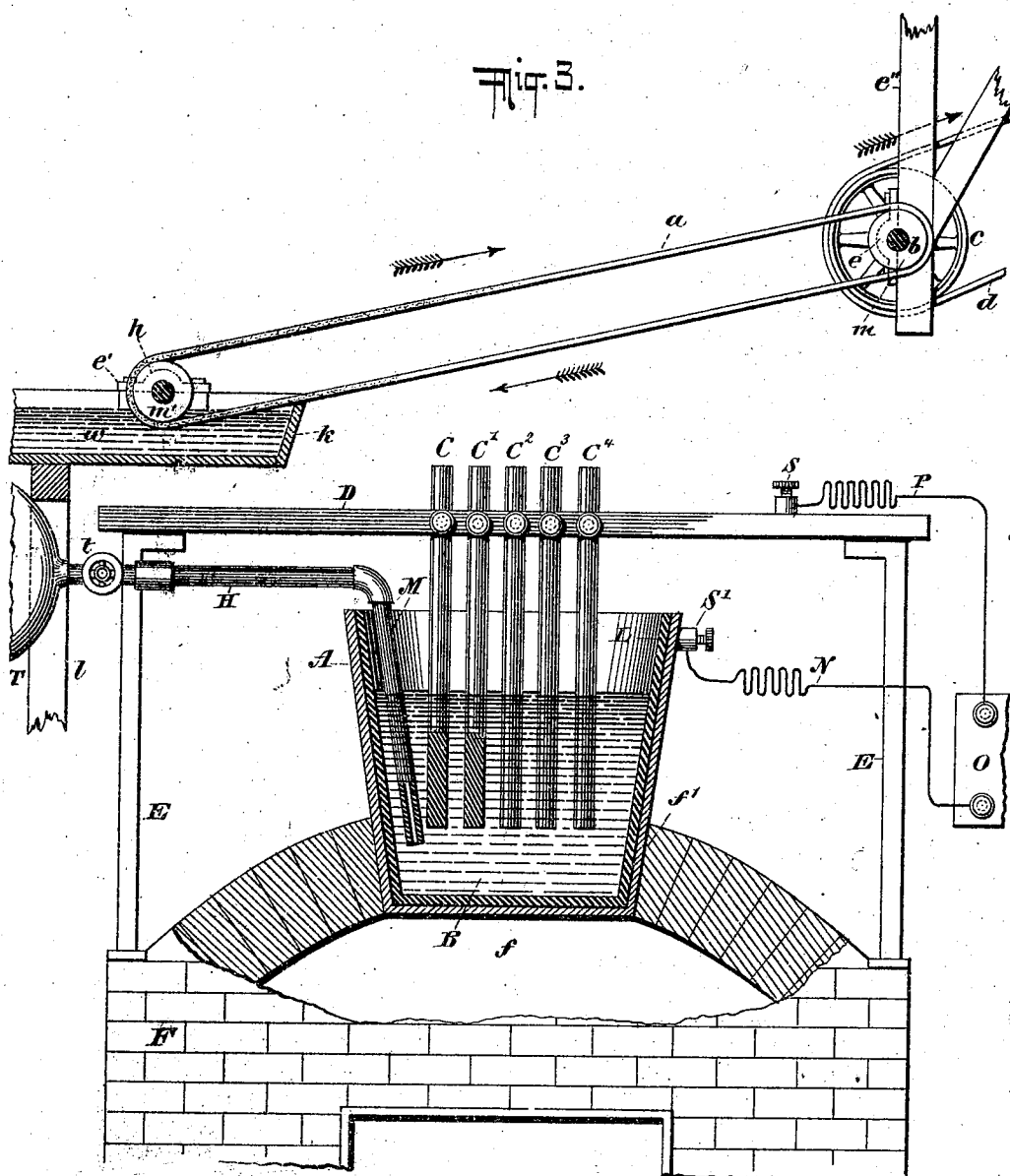
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3 Sheets—Sheet 3.

F. A. GOOCH & L. WALDO.
PROCESS OF REDUCING ALUMINIUM.

No. 528,365.

Patented Oct. 30, 1894.



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UNITED STATES PATENT OFFICE.

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PROCESS OF REDUCING ALUMINIUM.

SPECIFICATION forming part of Letters Patent No. 528,365, dated October 30, 1894.

Application filed September 1, 1893. Serial No. 484,561. (No specimens.)

To all whom it may concern:

Be it known that we, FRANK A. GOOCH, residing at New Haven, in the county of New Haven, and LEONARD WALDO, residing at Bridgeport, in the county of Fairfield, State of Connecticut, have invented certain new and useful Improvements in Processes of Reducing Aluminium; and we 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 invention described herein relates to processes for the reduction of aluminium from its compounds by the electrolysis of a suitable fused mass containing such compounds. The compound of aluminium used should be one which will fuse at a temperature and under conditions which shall be practically attainable.

More especially our invention herein described relates to the reduction of aluminium from its chloride.

In the accompanying drawings, which are hereby made a part of this specification, is shown one form of apparatus suitable to the practice of our invention. We do not, however, limit ourselves to the apparatus shown, since any other suitable apparatus would answer equally well for the practice of our invention.

Figure 1 represents a sectional diagrammatic view of the apparatus employed by us. Fig. 2 represents a sectional view of a modified form of apparatus employed by us. Fig. 3 represents a sectional diagrammatic view of another modified form of apparatus employed by us.

Similar letters refer to similar parts throughout the drawings.

F is a furnace having a fire box *f*, and opening *f'* in the top of the furnace, into which is set a tapering crucible A, the same being supported by the sides of the opening *f'*. The construction of the crucible and the arrangement of the electrodes and conductors are hereinafter fully described.

T is a tank from which the hydrogen is supplied

through the tube II, the supply being regulated by the cock *t*.

ss' are binding posts for the conductors N P.

In the practice of our invention, so far as it relates to the reduction of aluminium from its chloride, we preferably prepare a bath by fusing in a suitable tank or crucible A and in proper proportions, the chloride of aluminium and the chloride of an alkaline metal (preferably sodium) or of an alkaline earth metal, with the fluoride of aluminium and the fluoride of sodium. A convenient way to form a suitable bath is to combine the double chloride of aluminium and sodium (represented by the formula $2\text{NaCl}.\text{Al}_2\text{Cl}_6$) with the mineral cryolite. We find it of advantage to add to the combination just named an additional amount of chloride of sodium in excess of the amount necessary to form the double chloride. These ingredients are preferably mingled together in the following proportions: the double chloride of aluminium and sodium, fifteen parts; cryolite, fifty-five parts; sodium chloride thirty parts; but these proportions are variable serviceably within wide limits, without materially affecting the operation or function of the bath, as, in fact, any proportions which may be found suitable may be employed.

The reason for employing cryolite or the fluorides of aluminium and sodium in the bath is the well known fact that, when they are present and reduction by the action of the electric current takes place, the aluminium melts and flows to globules, while, when the bath contains only the chlorides named, the aluminium is obtained in the form of a powder, which has to be further treated before it can be made commercially available. The object of adding the excess of sodium chloride to the bath is to make the bath more liquid. It is also advantageous in diluting the cryolite. It is not, however, essential to our invention that the excess of sodium chloride should be present; nor that the cryolite, or fluorides of aluminium and sodium should form part of the bath, when the chlorides already mentioned are present.

Instead of forming the double chloride of aluminium and sodium separately and then adding it to the bath, it will be sufficient to place the chloride of aluminium (represented by the formula Al_2Cl_3) in the bath, and then to add the chloride of sodium in such quantity that part of it may unite chemically with the chloride of aluminium to form the double chloride, while the remainder forms the excess of sodium chloride needed for the bath above described; or the order of introduction may be reversed, the former being added first. Usually this order will be found preferable, as the chloride of aluminium is very volatile until brought in contact with the sodium chloride.

In place of the excess of sodium chloride or of a part of such excess, we may employ a certain proportion of chloride of potassium, (which is useful in making the bath more fluid,) or of some other of the alkaline metals. In case of any such substitution in the ingredients of the bath, the proportions of all the ingredients used are suitably readjusted if necessary. For example, if the chloride of potassium be used, in place of a part of the sodium chloride, the ingredients are preferably mingled together in the following proportions: cryolite, fifty-five parts; chloride of aluminium, twelve parts; chloride of sodium, nineteen parts; chloride of potassium, fourteen parts; but with a bath constituted as last above described, the proportions given are variable serviceably within considerable limits without materially affecting the operation or function of the bath, as, in fact, any proportions which may be found suitable may be employed.

The crucible A, preferably employed by us in the operation of our invention, consists of a tank of iron lined with compacted carbon. The carbon lining L of this tank serves as the cathode, the iron of the tank being connected by the conductor N with the negative pole of a dynamo electric machine or other suitable source of electricity, O. The anode C is a detached carbon electrode partially immersed in the bath B; and connected in the following manner with the source of electricity: We preferably suspend the anode from an iron bar D raised above the crucible and resting on wooden supports E E. The bar D is connected by the conductor P to the positive pole of the source of electricity. If desired, the cathode may also be formed of a detached carbon, suspended in a similar way to that just described for the anode, or otherwise supported, and partially immersed in the bath B. If desired, a number of separate carbons may be used to form the electrodes as shown in Fig. 2, where C C' C'' C^3 and C^4 , all suspended from the bar D collectively form the anode. The relative superficial areas of the electrodes in any particular case are adjusted so as to secure the greatest

economy in action. In place of a carbon anode, an anode of any other suitable material, as of platinum may be used. The bath may be fused, and the fusion may be maintained by the application of heat from any suitable source, as from a furnace F. The temperature required to fuse the bath suggested above is that of a dull red heat. We may also fuse the ingredients of the bath in a separate apparatus and introduce the same in a molten condition into the bath at the beginning of the process, the fusion being thereafter maintained in any suitable way. When the electric current is passed through the bath and electrolysis takes place, aluminium is deposited at the cathode and the halogens (chiefly chlorine) are liberated at the anode. It is well known that these gases, in a free state, are highly noxious to health. On this account, and for the further reason that they attack and quickly destroy the positive electrode in the apparatus used in any process similar to the one described, their escape in a free state would render such process commercially useless. To obviate these difficulties, and to accomplish other desirable results, we introduce hydrogen into the bath. The hydrogen is preferably delivered in a substantially continuous supply underneath the surface of the fused mass in near proximity to or through the anode. In the latter case a longitudinally perforated carbon rod C is preferably employed for the anode, and the gas is passed through the same as through a pipe, the gas being supplied through a tube H connecting with the upper end of the anode C, which may project above the bath. The hydrogen may also if preferred be conducted through a separate pipe as the pipe M in Fig. 2. When the halogen elements are liberated by the electrolysis of the bath, they combine instantly with the hydrogen and escape at the anode in the form of hydrochloric acid or hydrofluoric acid, chiefly the former. These gases in the quantities evolved in our process, are easily controlled and disposed of, without injury to apparatus or workmen, by appropriate means external to the bath, as by the use of a flue K, having a strong draft, and provided with a hood J, projecting over the crucible A; or cloths or other absorbent media, saturated with water may be suspended over the crucible, the escaping gases being taken up by the water, whose power of acting as a solvent for hydrochloric acid and hydrofluoric acid is well known. Such an arrangement is shown in Fig. 3, where a represents an endless band or apron of cloth or other suitable fabric, passing over drums m , m' attached to shafts b , h . The shaft b revolves in journal boxes e and is supported in any suitable manner, as by a strip e'' suspended from the ceiling. The shaft h revolves in boxes e' formed on the edges of the trough k . The shafts and band or apron a

are kept in revolution in the direction indicated by the arrows by power from any suitable source transmitted by the belt *d*, passing over the pulley *c*, which is rigidly attached to the shaft *b*. The shaft *b* is hung somewhat higher than the shaft *h*. The drum *m'* on shaft *h* runs close to or under the surface of water *w* contained in a shallow pan or trough *k*, having suitable support *l*. The band or apron *a* being inclined passes through the water *w* at the lower side of the drum *m'* and is thus kept saturated with water. Thus saturated it passes continuously over the crucible.

We do not claim the particular arrangement of devices just described, nor regard it as novel, nor do we confine ourselves to the particular devices shown, since any other suitable means external to the bath might be employed for disposing of the escaping gases.

We preferably supply hydrogen to the bath in excess of the amount required to combine with the halogen elements. The excess of hydrogen substantially permeates the fused mass, thereby securing a more uniform intermixture of the ingredients of the bath and protecting the surface of the molten mass from atmospheric action.

In the practical operation of our invention, where we use the suggested baths composed of the chlorides of aluminium and sodium and the fluorides of aluminium and sodium, with or without an excess of chloride of sodium and with or without the chloride of some other alkaline metal, and with or without the chloride of potassium we have found that we obtain at the anode hydrochloric acid almost exclusively, with very little trace of fluorine. This shows that the aluminium deposited at the cathode is derived chiefly from the chloride of aluminium in the bath; and we have found that, by the occasional addition of chloride of aluminium (Al_2Cl_3) in sufficient quantities, the bath will be replenished and the process will be a substantially continuous one during a considerable period of time. An excess of the chloride of aluminium produces no injurious effect, as it is gradually utilized in the subsequent operation of the process. We have hereinbefore spoken of fluorine being set free, though we are aware that it is considered very difficult to isolate this element. We, however, use the term "fluorine" merely for convenience, meaning thereby to include not only free fluorine, if any be liberated, but also any compound thereof, which might be set free at the anode, if hydrogen were not supplied to the bath. As before stated, the aluminium is deposited at the cathode, where it melts forming globules, which, when either of the suggested baths whose proportions are hereinbefore stated, is employed, gather at the bottom of the bath, the aluminium having a higher specific gravity than the fused bath. The aluminium may then be removed in any suit-

able manner as by means of a ladle lined and covered with carbon, or by drawing it off at the bottom through a suitable opening; or the bath may be poured out, and, after being cooled, the aluminium may be picked out. In case a bath should be used whose specific gravity is higher than that of aluminium, the aluminium would rise to the top, where it could be easily removed.

In the process herein described, we use an electric current of suitably low electro-motive force, usually of from four to ten volts; but the voltage of the current employed will depend on the form and size of the electrodes as well as on the composition of the bath, it being only necessary to have a voltage sufficient to decompose electrolytically the chloride of aluminium in the bath under all the existing conditions of resistance, and of chemical constitution.

The electric current which we employ in our process, and which is herein referred to as being passed through the bath, is employed solely for purposes of electrolysis. The hydrogen may in the first instance be introduced before or after the electric current is passed through the bath or simultaneously therewith, the order of operations being unimportant.

We are aware that hydrogen has been employed heretofore in processes for reducing aluminium, either as the sole agent or as an auxiliary agent in accomplishing the reduction of the metal from the aluminium compounds used. In the process herein described, we do not employ hydrogen as an agent in such reduction, nor do we in this application claim any process in which hydrogen is so employed.

The objects of introducing hydrogen into the bath in our improved process herein described are, to secure a more uniform intermixture of the ingredients of the bath, and to protect the surface of the molten mass from atmospheric action, to protect the anodes from the corrosive action of the halogens set free by the electrolysis of the bath, and to convert such free halogens into a more manageable form.

We do not herein specifically claim those forms of the herein described process which are specifically set forth and claimed in our application, Serial No. 504,763, filed March 23, 1894, the same being a divisional application of this case.

Having described our invention, what we claim, and desire to secure by Letters Patent, is—

1. As an improvement in the art of manufacturing aluminium, the herein described process which consists in forming a bath by fusing together the chlorides of aluminium and sodium and the chloride of another alkaline metal, with the fluorides of aluminium and sodium, passing an electric current

through the fused mass, thereby electrolyzing the same, and supplying hydrogen to the bath, substantially as and for the purposes set forth.

2. As an improvement in the art of manufacturing aluminium, the herein described process, which consists in forming a bath by fusing together the chlorides of aluminium and sodium and potassium, and the fluorides of aluminium and sodium, passing an electric current through the fused mass, thereby electrolyzing the same, and supplying hydrogen

to the bath, substantially as and for the purposes set forth.

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LEONARD WALDO.

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ANNIE G. WYMAN.

Witnesses as to Leonard Waldo:

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GILBERT H. CRAWFORD.