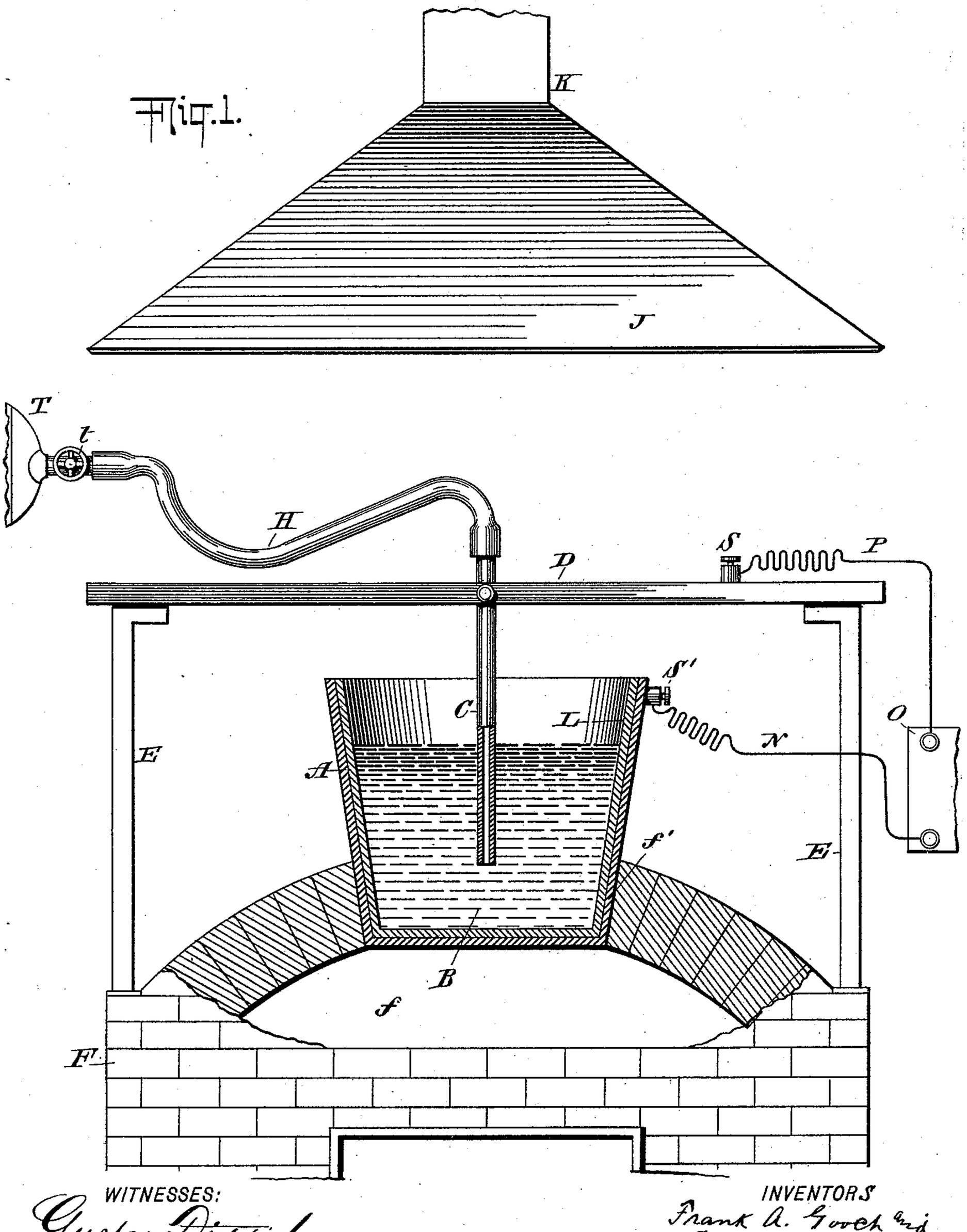
(No Model.) 2 Sheets—Sheet 1.

F. A. GOOCH & L. WALDO.

PROCESS OF REDUCING ALUMINIUM.

No. 527,847. Patented Oct. 23, 1894.

Fig. 1.



WITNESSES:
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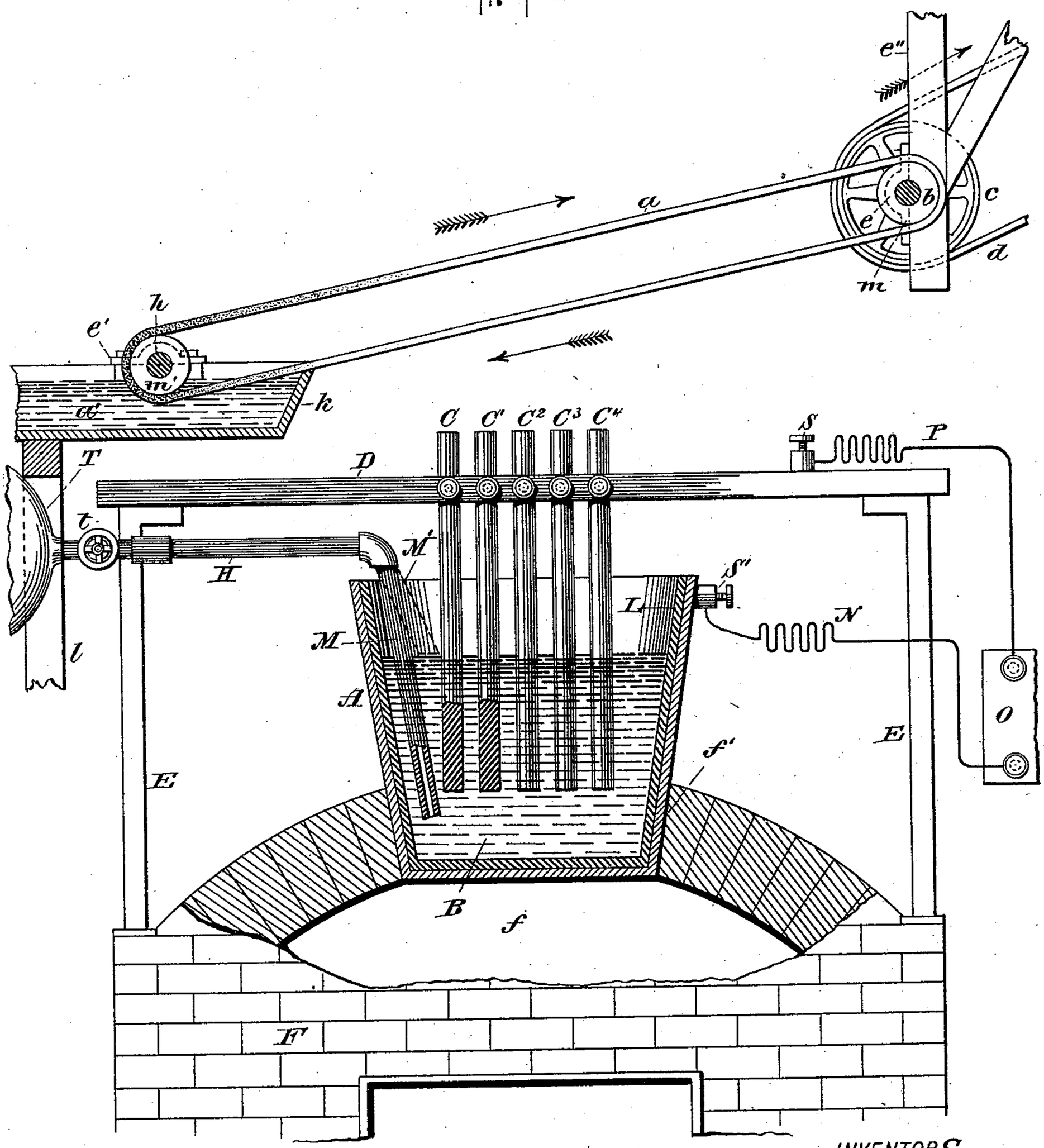
Fig. 2.



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UNITED STATES PATENT OFFICE.

FRANK A. GOOCH, OF NEW HAVEN, AND LEONARD WALDO, OF BRIDGEPORT, CONNECTICUT; SAID WALDO ASSIGNOR TO THE WALDO FOUNDRY, OF NEW JERSEY.

PROCESS OF REDUCING ALUMINIUM.

SPECIFICATION forming part of Letters Patent No. 527,847, dated October 23, 1894.

Application filed April 25, 1894. Serial No. 508,916. (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 herein described relates to processes for the reduction of aluminium from its compounds by the electrolysis of a suitable fused mass containing such compounds.

In an application filed by us September 1, 1893, Serial No. 484,561, we have described and claimed an improved process for reducing aluminium from its compounds, which in general terms consists in passing an electric current through a suitable fused bath containing a suitable compound of aluminium, thereby electrolyzing the bath, and in introducing hydrogen into the bath.

The invention herein described consists, in general terms, in passing an electric current through a suitable fused bath containing a suitable halogen compound of aluminium, thereby electrolyzing the bath, and in supplying to the bath the vapor of water.

In practice, we find that the halogen compounds of aluminium, which are most suitable and best adapted to be used in our process, are the chloride of aluminium and the fluoride of aluminium.

For convenience, we describe our invention with special reference to the reduction of aluminium from its chloride, it being understood, however, that our invention is also applicable to other halogen compounds of aluminium.

Hydrogen in its free state is comparatively expensive to produce. For this reason, we have found it desirable to use some one of the gaseous compounds of hydrogen, many of which are easily and cheaply produced, and answer the purpose to be attained as well as the free hydrogen, as for example the vapor of water.

For simplicity we describe our invention with special reference to the use of steam as the most convenient form of water vapor.

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.

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 boiler, steam-chest or other generator or receiver from which the steam is supplied through the tube H, the supply being regulated by a cock *t*.

s s' are binding posts for the conductors N P.

B is the bath contained in the crucible A through which the electric current is passed.

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 in suitable 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 $2NaCl.Al_2Cl_6$) 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 pro-

portions: 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 electrolysis 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. Our invention, indeed, is applicable to any bath composed of a suitable halogen compound of aluminium, and of any other suitable ingredients which will permit or enable the bath to fuse at a sufficiently low temperature, and which will admit of the halogen compound of aluminium employed being decomposed by electrolysis.

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_6) in the bath, and then to add 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 needed for the bath above described; or the order of introduction of the sodium chloride and the aluminium chloride may be reversed, the former being added first. Usually this 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 are variable serviceably within considerable limits without materially affecting the operation or functions 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 C 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, a number of separate carbons may be used to form the electrodes, as shown in Fig. 2, where C, C′, C^2, 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 being 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 baths 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 tank 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, we supply to the bath the vapor of water, preferably in the form of steam, which we preferably deliver at or beneath the surface of the fused mass in a substantially continuous manner and 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 steam is passed through the same as through a pipe, the steam being supplied through a tube H connected with the upper end of the anode C, which may project above the bar D. The steam may also, if preferred, be conducted through a separate pipe, as the

pipe M in Fig. 2. Where the steam is supplied at the surface of the bath, it may be passed through pipe M′ represented in Fig. 2 by dotted lines, in which case pipe M would be dispensed with. We may dispense with the conduction pipe altogether, and spray water on the surface of the bath. The water will instantly assume the spheroidal condition and quickly vaporize. We may also produce the steam by dropping minute fragments of ice on the surface of the bath.

We do not limit our invention to any particular mode of supplying the steam to the bath, since any suitable mode may be employed without departing from the essential nature of our invention.

The constituents of the steam being dissociated in, or at the surface of, the bath during action, the hydrogen required for our process is supplied in a substantially continuous manner.

When the halogen compounds are liberated by the electrolysis of the bath, they combine instantly with the hydrogen constituent of the steam, and escape at the anode in the form of hydrochloric acid or hydrofluoric acid (chiefly the former). These gases, in the quantities evolved by 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 and hydrofluoric acid is well known. Such an arrangement is shown in Fig. 2, 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 the 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, not regarding it as novel, nor do we confine ourselves to the particular device shown, since any other suitable means external to the bath might be employed for disposing of the escaping gases.

We preferably supply the steam or other form of water vapor to the bath only in an amount sufficient to furnish the hydrogen for the combination with the halogen elements, or slightly in excess of such amount.

In the practical operation of our invention, where we use the suggested bath composed of the double chloride 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, 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 addition to the bath from time to time of chloride of aluminium (Al_2Cl_6) 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 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 either free or in combination were not used in the process.

As before stated, the aluminium is deposited at the cathode, where it melts forming globules, which (when one 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 suitable or convenient manner, as for example by means of a ladle lined and covered with carbon, or by drawing it off through a suitable opening at the bottom. 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 required will depend on the size and form 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 compound 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 steam may in the first instance be supplied to the bath before or after the electric current is passed through the same, or simul-

taneously therewith, the order of the operations being unimportant.

The steam used in our process is likely to cause some oxidation of the anode if the material of the anode is oxidizable; but, unless the material of the anode is very easily oxidizable, the waste of the anode will be usually much less than would be the case if the anode were exposed to the action of free halogens.

As before stated, our invention is applicable to any bath into the composition of which enters a suitable halogen compound of aluminium with other suitable ingredients. It being possible to form a large number of different baths to any of which our invention would be applicable, we do not limit our invention to the use of any particular bath which has been described herein.

In the process herein described, we do not employ the vapor of water as an agent in accomplishing the reduction of the metal from the aluminium compounds used, nor do we here claim any process in which vapor of water is so employed.

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 passing an electric current through a suitable fused bath containing a suitable halogen compound of aluminium, thereby electrolyzing the bath, and in supplying to the bath the vapor of water, 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 passing an electric current through a suitable fused bath containing the chloride of aluminium and in supplying steam to the bath, substantially as and for the purposes set forth.

3. As an improvement in the art of manufacturing aluminium, the herein described process which consists in passing an electric current through a suitable fused bath containing the chloride of aluminium and the chloride of an alkaline metal, and in supplying steam to the bath, substantially as and for the purposes set forth.

4. As an improvement in the art of manufacturing aluminium, the herein described process which consists in passing an electric current through a suitable fused bath containing the chloride of aluminium and the chloride of sodium, and in supplying steam to the bath, substantially as and for the purposes set forth.

5. As an improvement in the art of manufacturing aluminium, the herein described process which consists in forming a bath by fusing the chloride of aluminium and the chloride of an alkaline metal with the fluoride of aluminium and the fluoride of sodium, passing an electric current through the fused mass, thereby electrolyzing the same, and supplying steam to the bath, substantially as and for the purposes set forth.

6. 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 fluorides of aluminium and sodium, passing an electric current through the fused mass, thereby electrolyzing the same, and supplying steam to the bath, substantially as and for the purposes set forth.

7. 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 sodium and potassium, and the fluorides of aluminium and sodium, passing an electric current through the fused mass, thereby electrolyzing the same, and supplying steam to the bath, substantially as and for the purposes set forth.

8. As an improvement in the art of manufacturing aluminium, the herein described continuous process which consists in forming a bath by fusing together the chloride of aluminium and the chloride of an alkaline metal, the fluoride of aluminium and the fluoride of sodium, maintaining an electric current through the fused mass, thereby electrolyzing the same, supplying steam to the bath and replenishing the bath from time to time by adding thereto suitable quantities of the chloride of aluminium, substantially as described.

9. As an improvement in the art of manufacturing aluminium, the herein described continuous process which consists in forming a bath by fusing together the chlorides of aluminium and sodium and the fluorides of aluminium and sodium, maintaining an electric current through the fused mass, thereby electrolyzing the same, supplying steam to the bath and replenishing the bath from time to time by adding thereto suitable quantities of chloride of aluminium, substantially as described.

10. As an improvement in the art of manufacturing aluminium, the herein described continuous process which consists in forming a bath by fusing together the chlorides of aluminium, sodium and potassium, and the fluorides of aluminium and sodium, maintaining an electric current through the fused mass, thereby electrolyzing the same, supplying steam to the bath and replenishing the bath from time to time by adding thereto suitable quantities of chloride of aluminium, substantially as described.

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