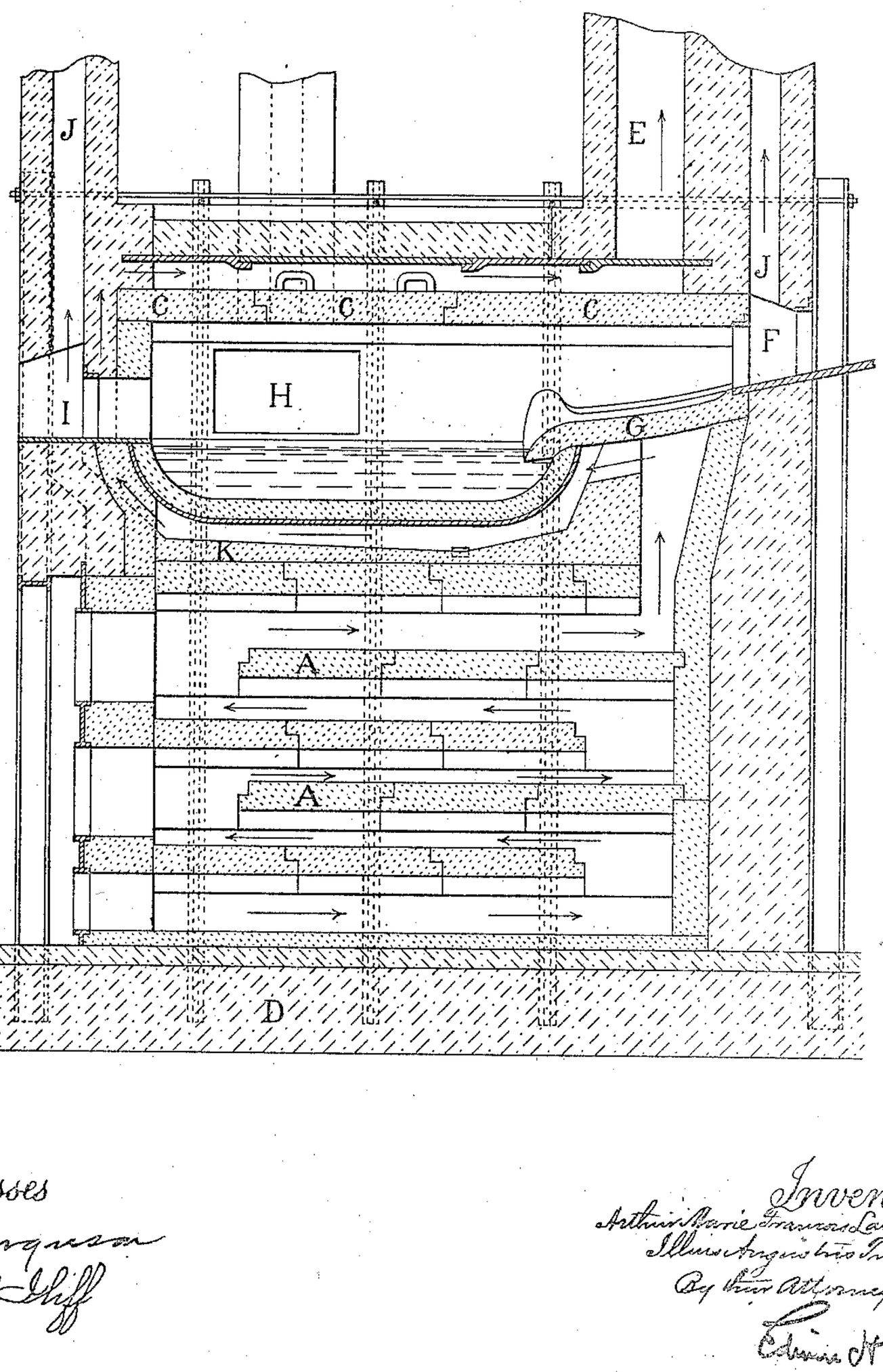
(No Model.) 7 Sheets—Sheet 1.

A. M. F. LAURENT-CÉLY & I. A. TIMMIS.

SECONDARY BATTERY.

No. 446,527. Patented Feb. 17, 1891.

FIG. 1.



Witnesses
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Wm. H. Schiff

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Edwin H. Brown

(No Model.) 7 Sheets—Sheet 2.

A. M. F. LAURENT-CÉLY & I. A. TIMMIS.

SECONDARY BATTERY.

No. 446,527. Patented Feb. 17, 1891.

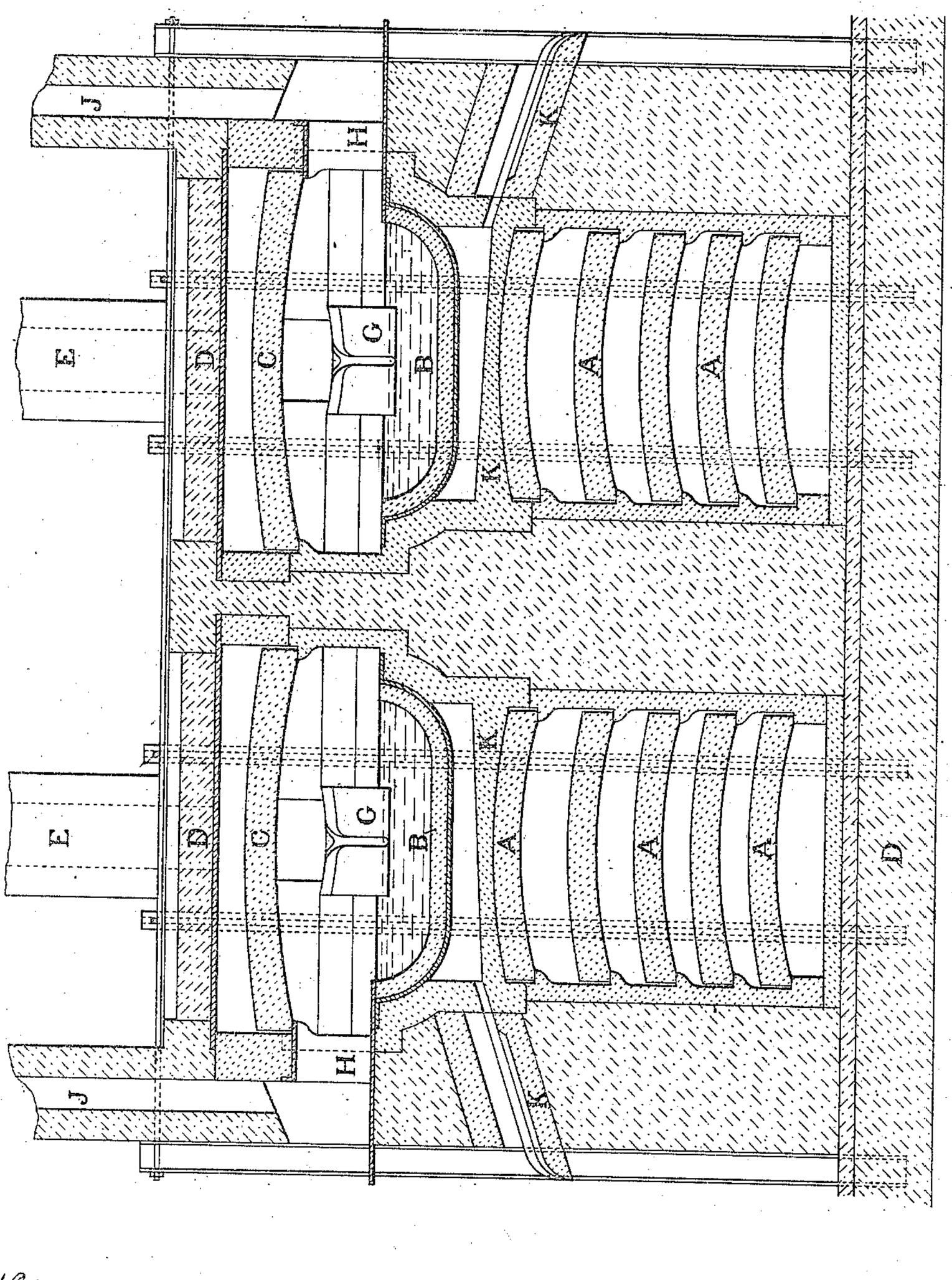

FIG. 2.

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(No Model.) 7 Sheets—Sheet 3.

A. M. F. LAURENT-CÉLY & I. A. TIMMIS.

SECONDARY BATTERY.

No. 446,527. Patented Feb. 17, 1891.

FIG. 4.

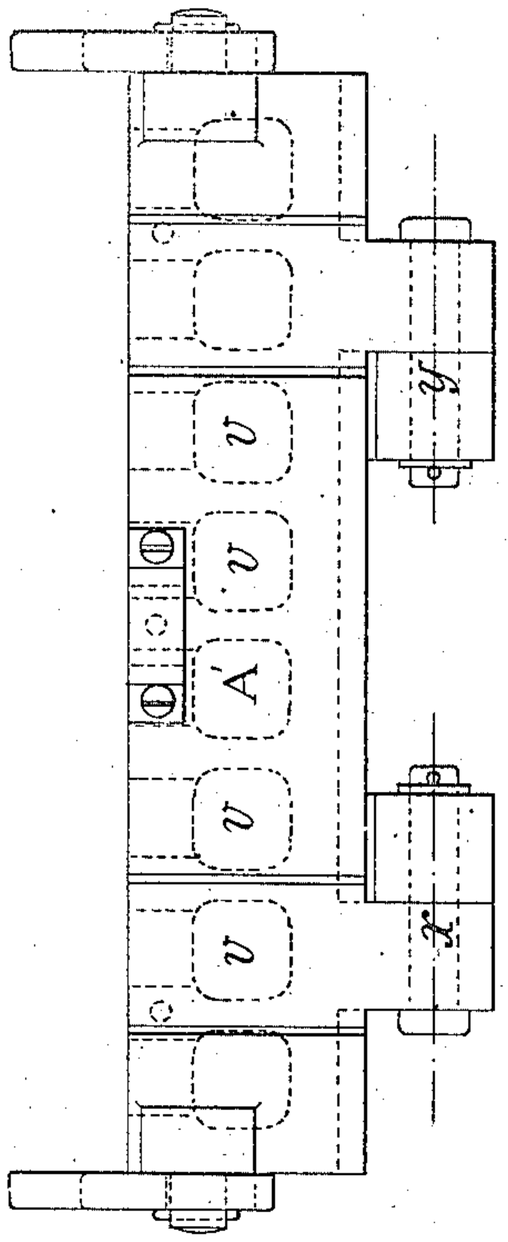


FIG. 5.

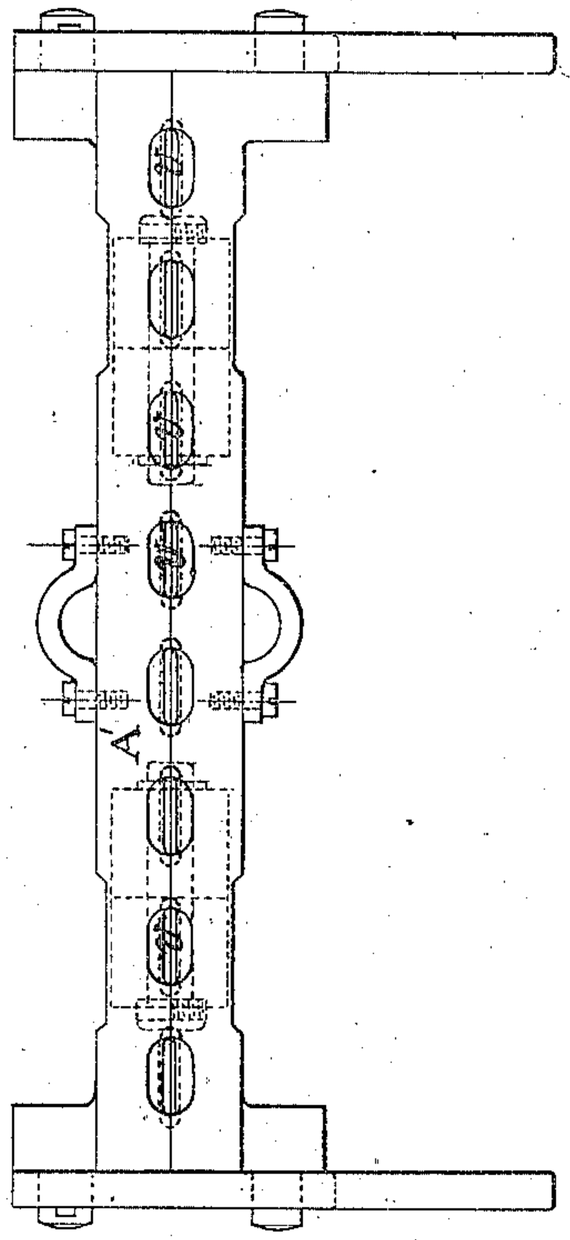
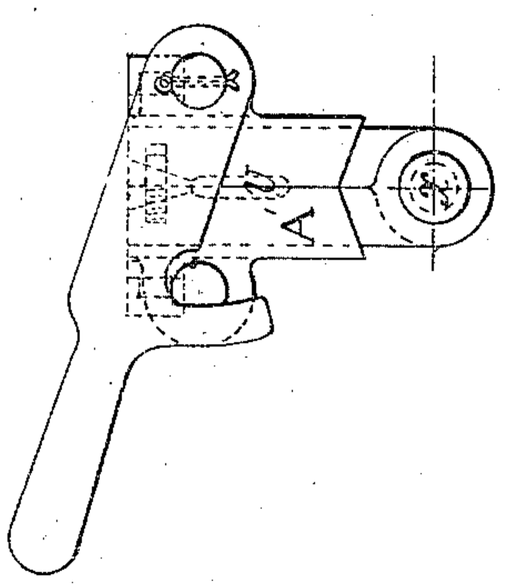


FIG. 3.



a.

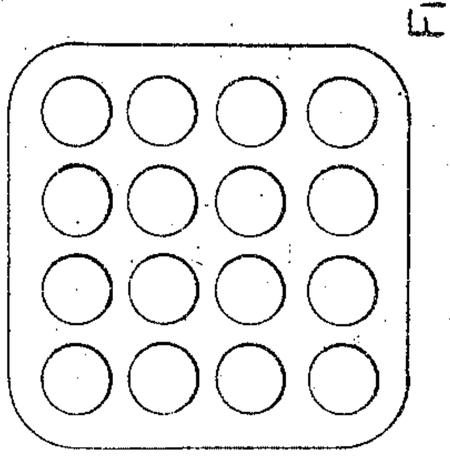
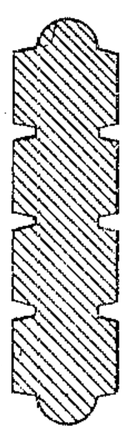


FIG. 18.



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(No Model.) 7 Sheets—Sheet 4.

A. M. F. LAURENT-CÉLY & I. A. TIMMIS.

SECONDARY BATTERY.

No. 446,527. Patented Feb. 17, 1891.

Fig. 8.

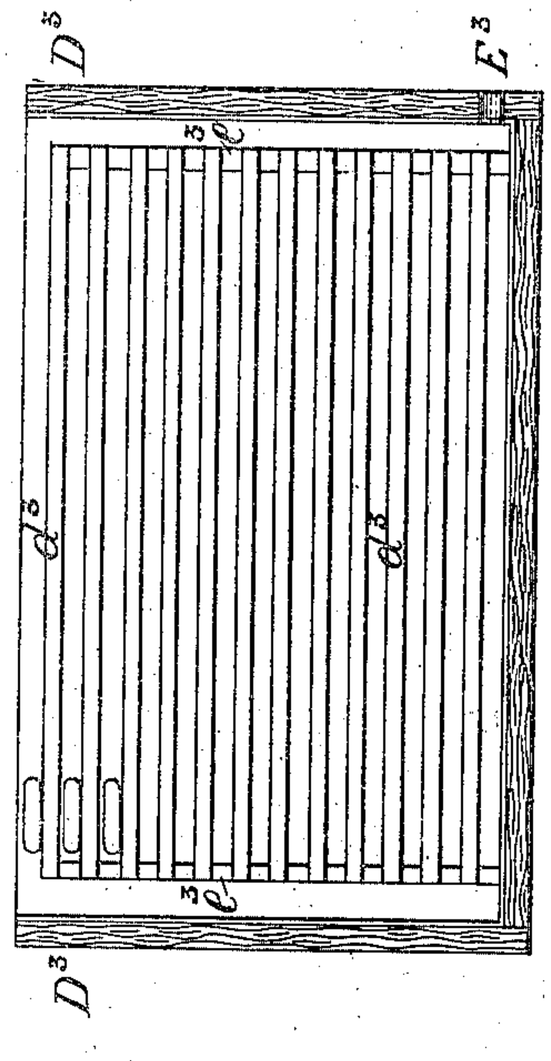


Fig. 9.

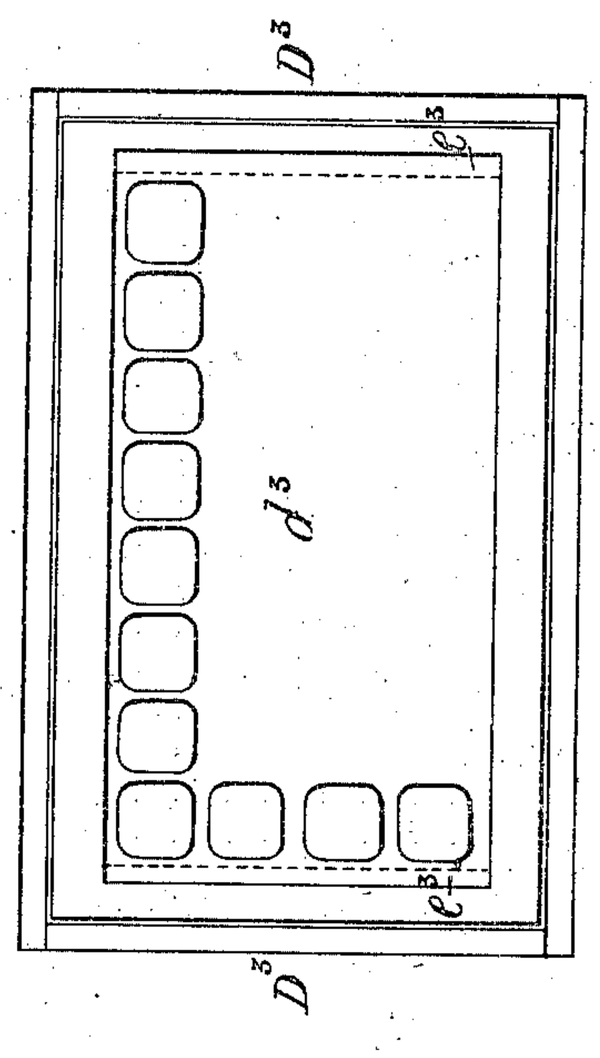


Fig. 6.

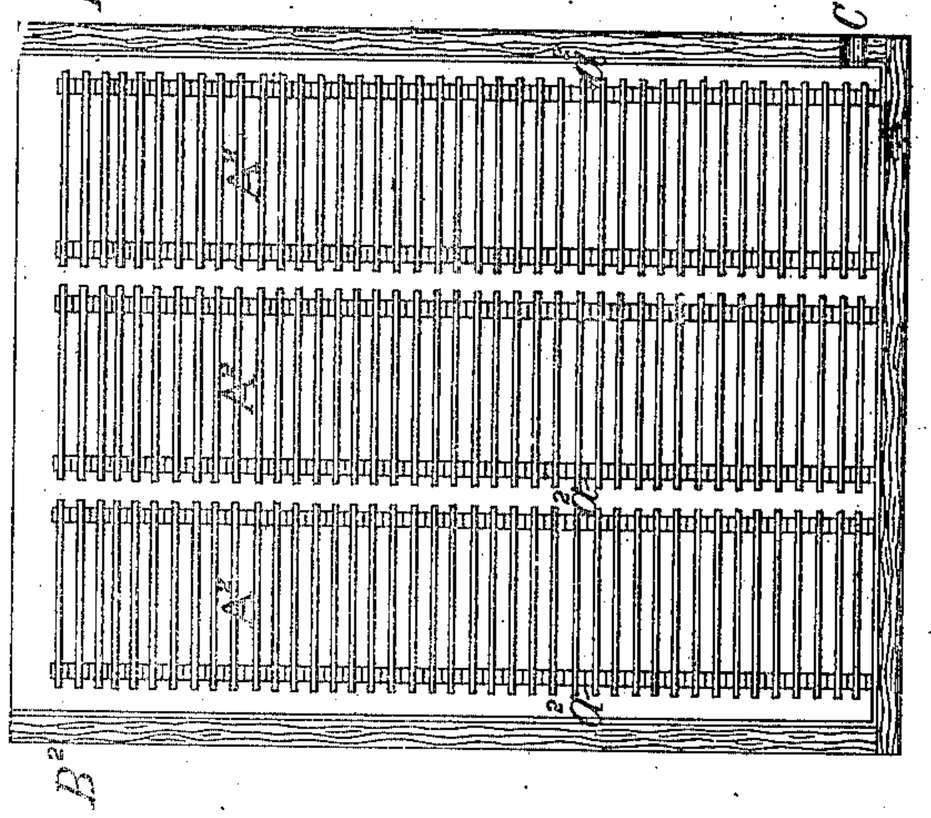
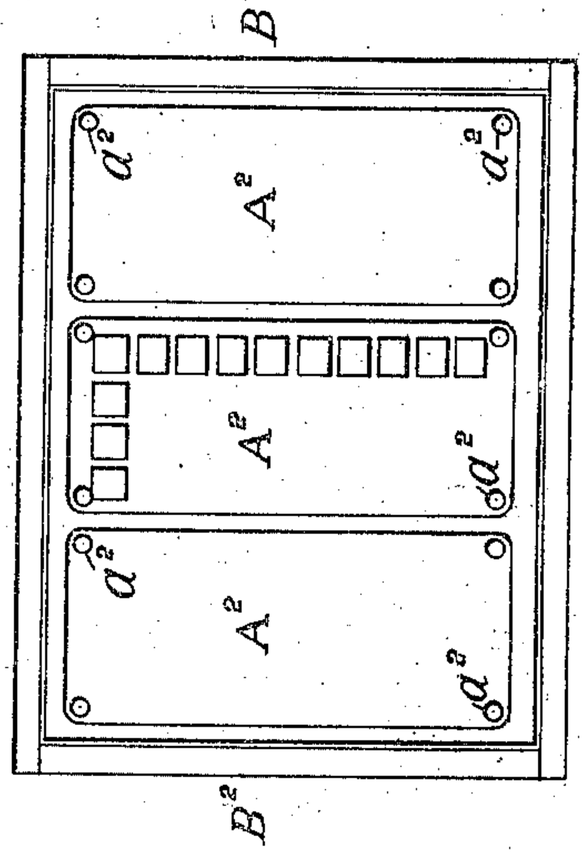


Fig. 7.



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(No Model.) 7 Sheets—Sheet 5.

A. M. F. LAURENT-CÉLY & I. A. TIMMIS.

SECONDARY BATTERY.

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FIG. 12.

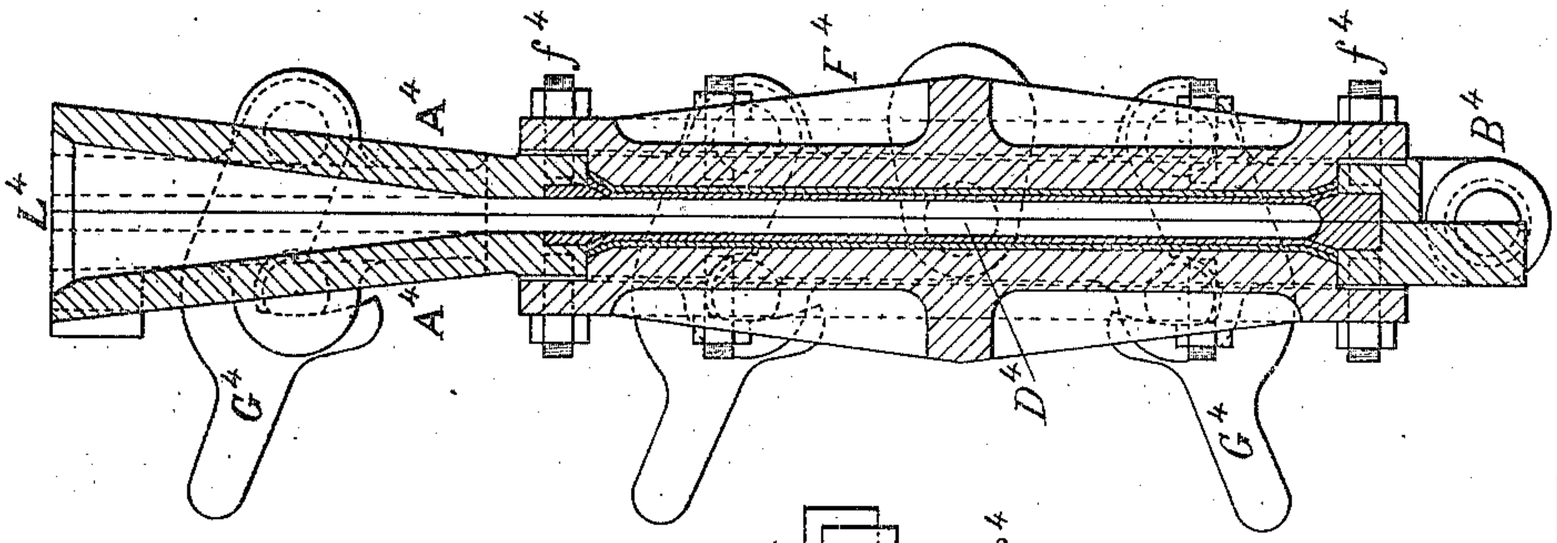


FIG. 11.

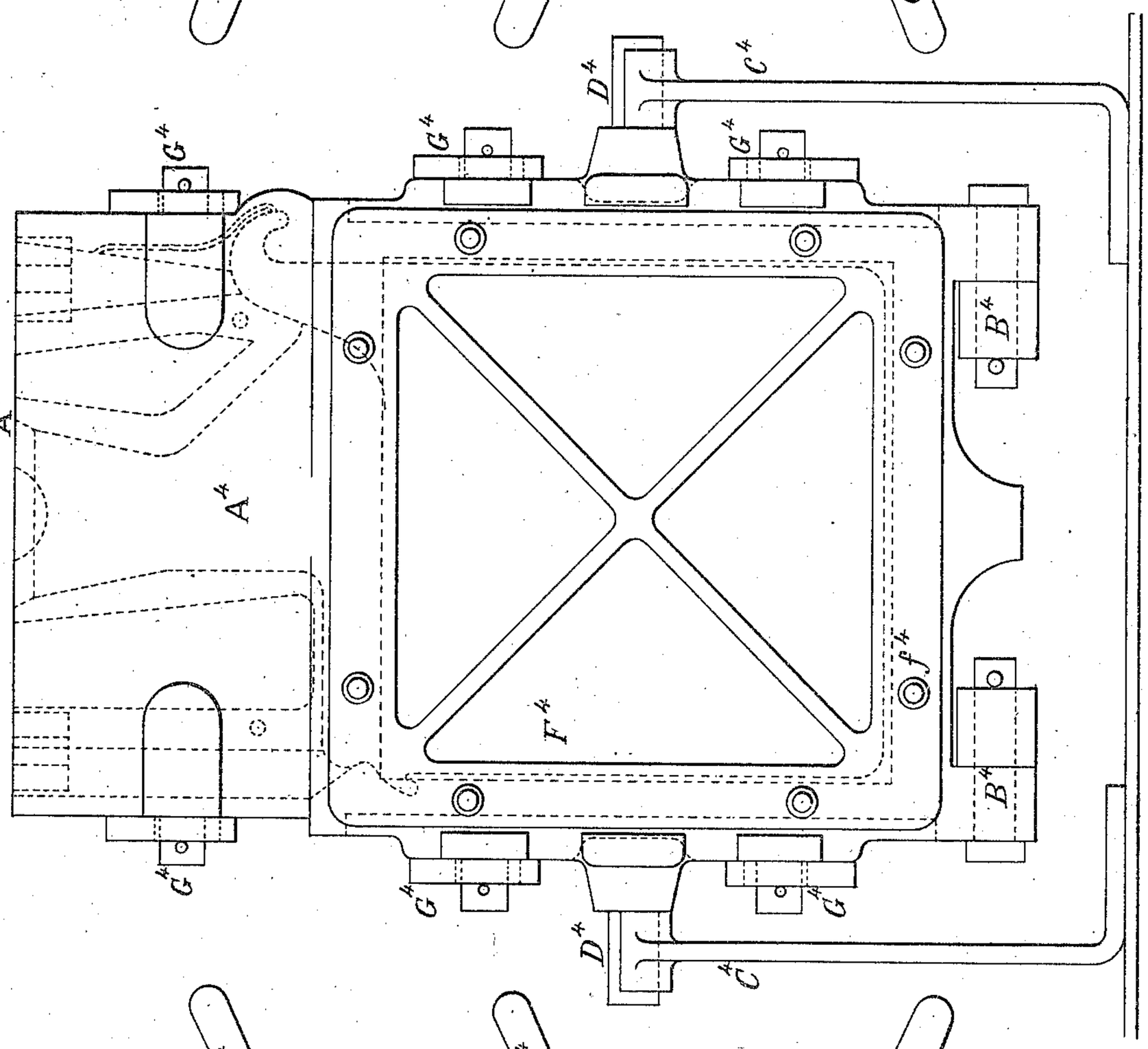
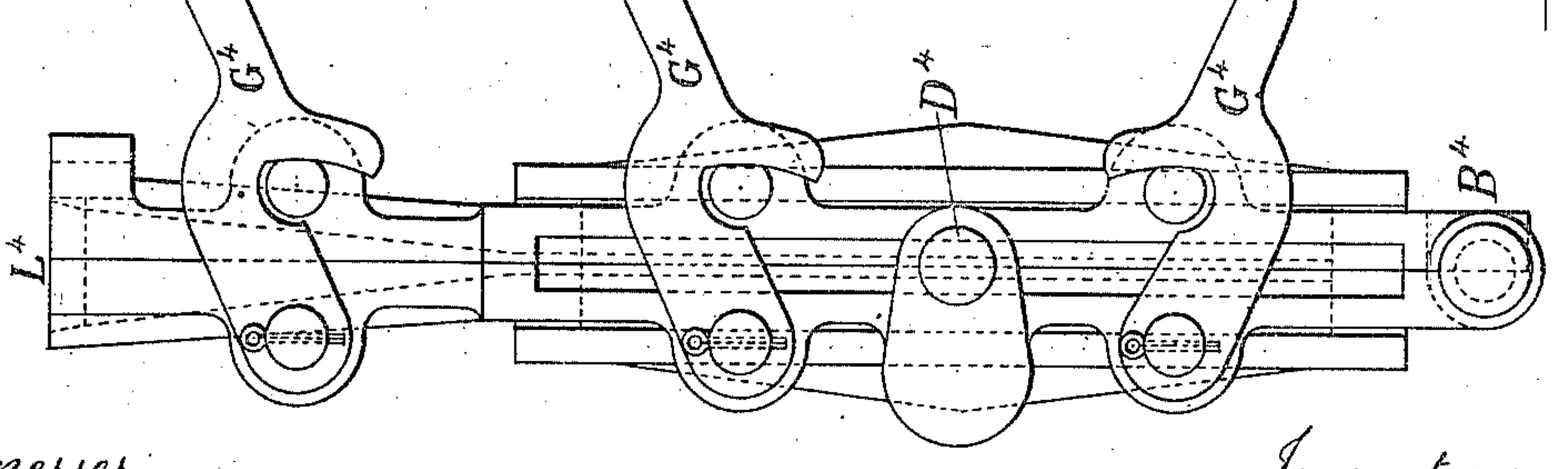


FIG. 10.



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SECONDARY BATTERY.

No. 446,527. Patented Feb. 17, 1891.

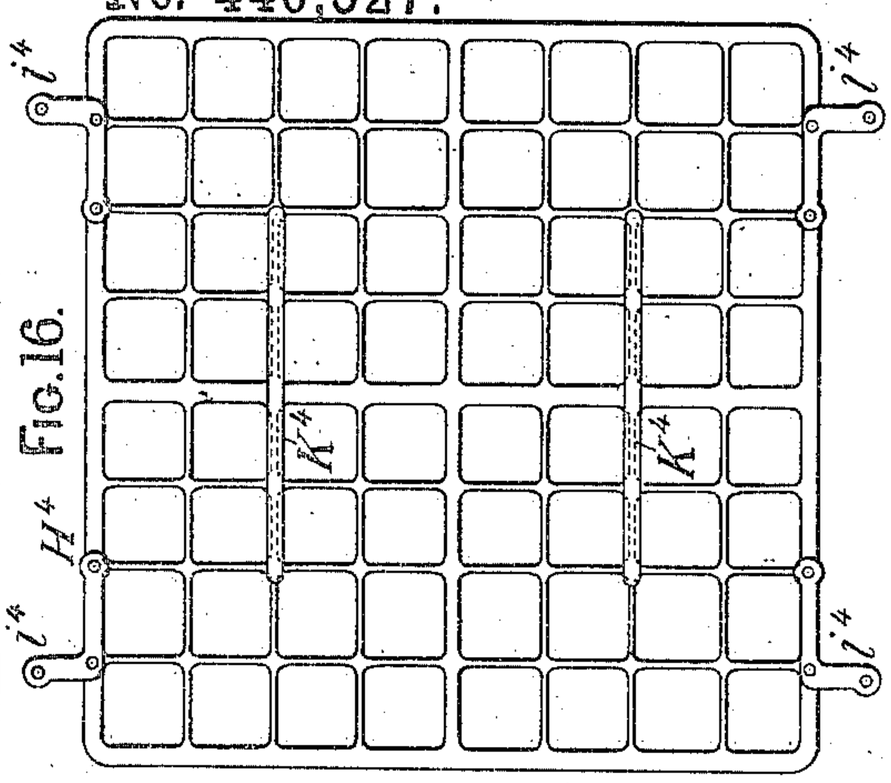

FIG. 16.

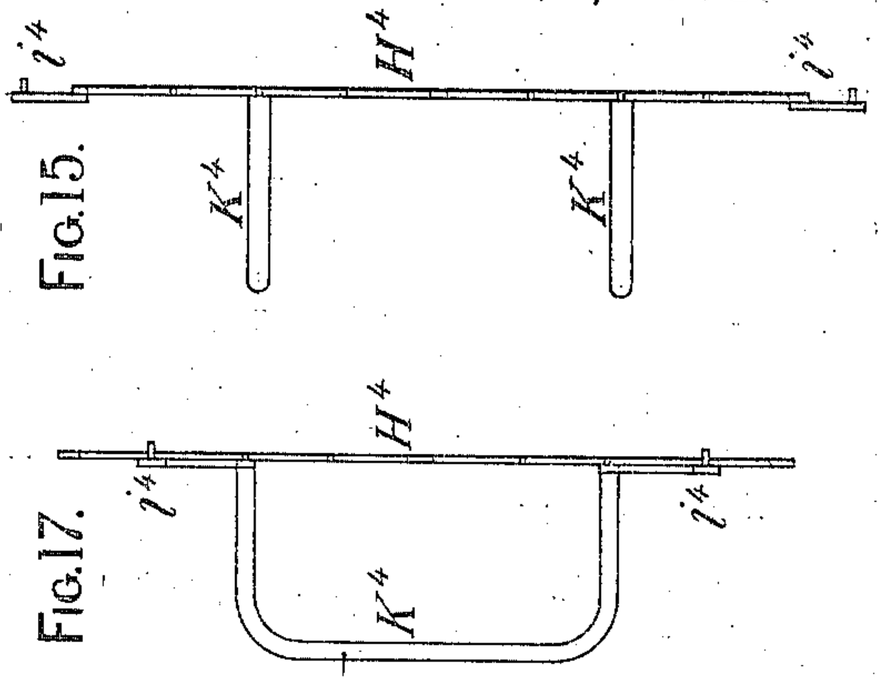

FIG. 15.

FIG. 17.

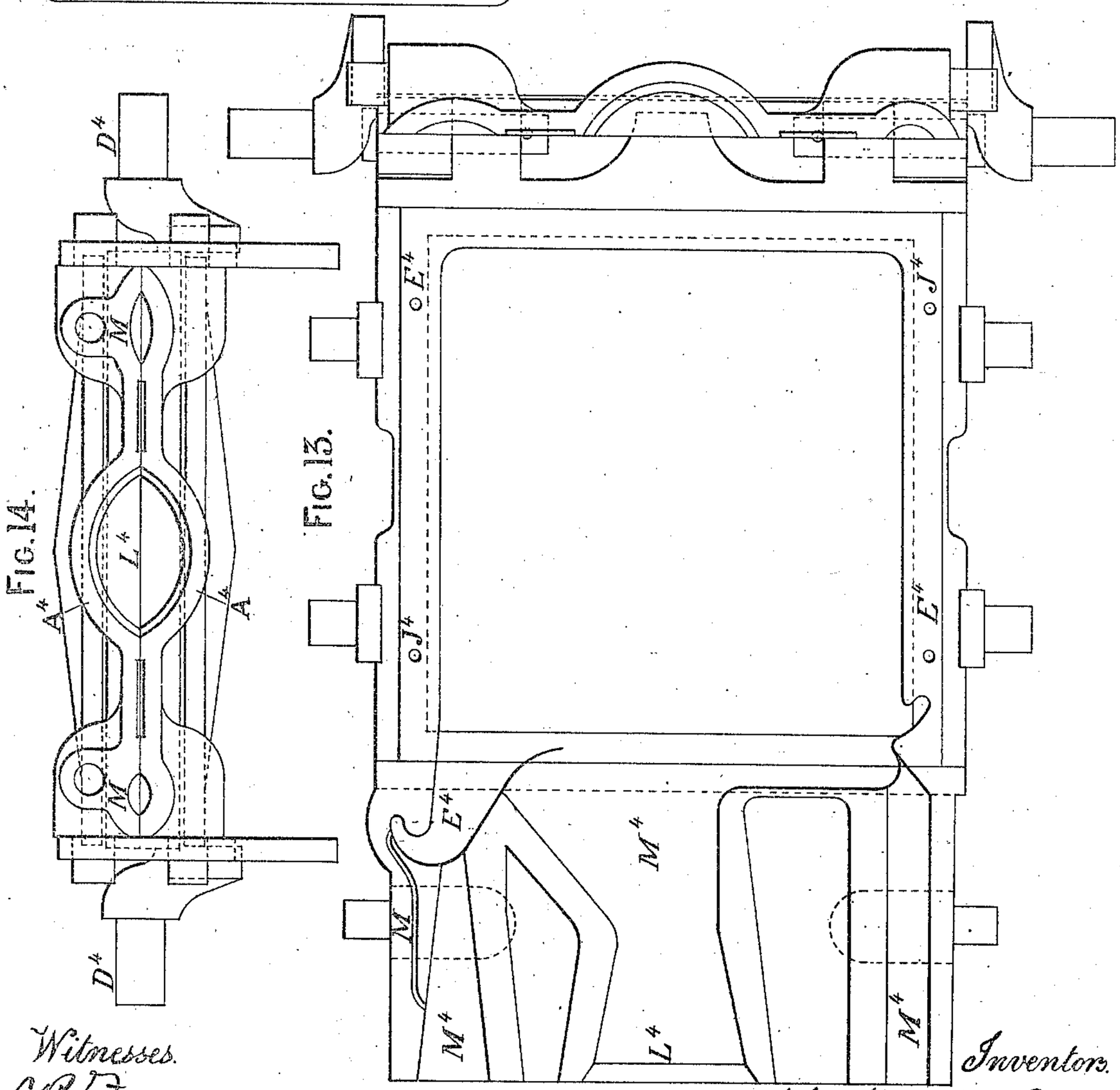

FIG. 14.

FIG. 13.

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(No Model.) 7 Sheets—Sheet 7.

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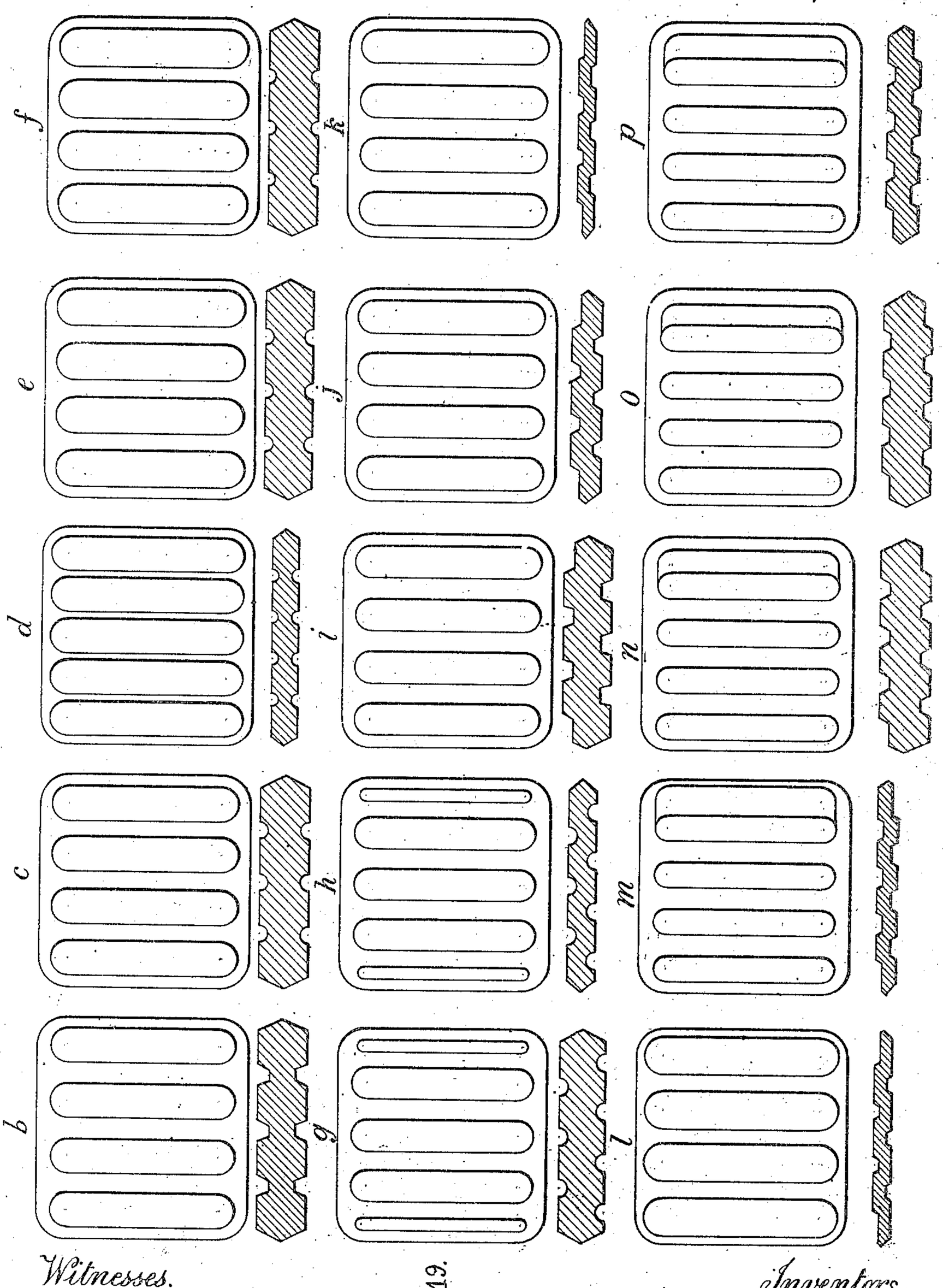

FIG. 19.

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UNITED STATES PATENT OFFICE.

ARTHUR MARIE FRANÇOIS LAURENT-CÉLY, OF PARIS, FRANCE, AND ILLIUS A. TIMMIS, OF LONDON, ENGLAND.

SECONDARY BATTERY.

SPECIFICATION forming part of Letters Patent No. 446,527, dated February 17, 1891.

Application filed April 8, 1890. Serial No. 347,111. (No model.)

To all whom it may concern:

Be it known that we, ARTHUR MARIE FRANÇOIS LAURENT-CÉLY, chemist, a citizen of the Republic of France, residing at 59 Rue de Provence, Paris, France, and ILLIUS AUGUSTUS TIMMIS, civil engineer, a subject of the Queen of Great Britain, residing at 2 Great George Street, Westminster, London, S. W., England, have invented certain new and useful Improvements in and Relating to and in the Manufacture of Electric Secondary Cells; and we do hereby declare the following to be a full, clear, and exact description of the invention, reference being had to the accompanying drawings, which form part of this specification.

The objects of our invention are to produce electrical plates for use in secondary batteries—*i. e.*, positive (or anode) and negative (or cathode) plates—which have much less density and much more storage capacity than any previously made or described.

The density of our anodes (cellular peroxide of lead) is only 4.5 to five as against a density of seven to nine in the best previously-described plates of ordinary peroxide of lead, while the density of our cathodes (cellular lead) is only three to 3.5 as against a density of six to eight in spongy lead. Again, we are able to store thirty-five to forty ampère-hours per kilo of active material in our cells as against twenty-five to twenty-eight ampère-hours in the best previously made or described cells, and the rate of charge and discharge which we employ is nearly double that used heretofore.

In the manufacture of the above plates, anodes, and cathodes we use the following means and processes.

We melt chloride of lead, (which any one can do, as this is common property), and then we add as much as twenty-five per cent. of pure metallic zinc. The heat in the furnace (which is by preference a closed one, so as to exclude the air as much as possible) we prefer to have as high as 550° centigrade. This is a most important feature. The fused mixture is then run into a receiver, and we find it an important feature to make this receiver sufficiently large to enable the impurities to fall to the bottom and so that the fused body forms a store of heat. The vessel which holds the molten mixture is either lined with or made in one piece of refractory material or more than one piece, and we find it convenient to run some ordinary lead, which protects the bottom of the receiver from the attacks of the fused body. Metallic lead is heavier than the mixture. The mixture is then poured into suitable molds, as hereinafter described, and cast into any required forms. The pastiles (or other forms) are then taken from the molds and are treated as follows, after being washed in a cold concentrated solution of hydrochloric acid. The washing of the pastiles in concentrated hydrochloric acid is effected to destroy any metallic oxides which may be in the pastiles, as without this in the course of forming the plates the sulphuric acid used causes soluble sulphates to be formed and the pastiles disintegrate; but we would have it very distinctly understood (as it is one of the main features in our invention) that by our process we do not make and almost entirely prevent the making of metallic oxide, and, further, by way of explanation, chloride of lead contains no hydrate; but chloride of zinc does contain hydrate, and consequently a fused mixture which contains the two chlorides of lead, and zinc contains chloride of lead, chloride of zinc, oxide of lead, and oxide of zinc, and this mixture or combination when treated by sulphuric acid causes the formation of sulphate of lead, and more especially sulphate of zinc, which are most destructible to the plates. On the other hand, if metallic zinc, which contains no hydrate, is mixed with fused or melted chloride of lead a pure compound of chloride of lead and chloride of zinc is obtained which is clear of the oxides of these metals. This is a most important and quite new invention. The negative pastiles are then washed in pure water and afterward dried. (We find 120° centigrade a convenient heat.) They are then placed in molds and spaced, and when the molds are closed, pure lead, with five per cent. to seven per cent. antimony, is run in and forms a frame-work and also a tang, which is used as hereinafter described. The heat requisite to melt the antimonious lead (say about 350° centigrade) is considerably less

than that employed to melt the mixture which forms the pastiles. When the antimonious lead frame-work is cast round the pastiles, the latter have grooves in them very often. In fact we prefer to make them in this way, so that the metallic frame-work in these grooves acts as an additional support and conductor. These molds are lined with asbestus packing, which is a most important feature. These negative plates are now put into suitable boxes with zinc plates, each set coupled, and then the two sets short-circuited, the solution being pure cold water with a few drops of hydrochloric acid. This operation ceases when heat ceases to be given off and when the active material is soft and perfect. It is now cellular lead with a density of three to 3.5. The plates are then washed in pure cold water.

The positive pastiles are placed on zinc plates in pure cold water, with a little hydrochloric acid, till they are thoroughly transformed into metallic cellular lead, and are then washed in cold water. They are then heated at a moderate heat in contact with air, which is increased up to 300° centigrade, when the pastiles become cellular litharge, with a density of five, which is about one-half the density of any other active material.

We do not use any hot water or hot solutions or an electric current to produce the pastiles of cellular lead and cellular litharge.

The fusion and reduction of chloride of lead is not new, but is common property; but the addition of metallic zinc is new, and the consequent formation of a mixture free from hydrate, which enables us to make low-density pastiles which have about double the capacity of any heretofore made.

The heat applied to the positive pastiles is far greater than ever before tried. These pastiles are placed in molds with asbestus packing and a frame-work of antimonious lead cast round them, as above described. The — and + plates are now put in lead-lined or earthenware, glass, or other suitable boxes and coupled up and charged with an electric current of two ampères per kilo of lead plates. This is about double the amount used before this. The arrangement of coupling we believe is quite new. The lead tang allows a rod to be placed in a slot from below and any one or more plates to be removed. A rod is threaded and has nuts on it (and washers, preferably) to make good contacts.

We do not bind ourselves to the exact ingredients named, but to them or their known equivalent.

The drawings herewith, coupled with the following description, will make our invention to be more readily understood.

In the accompanying drawings, Figures 1 and 2 are respectively a cross-section and longitudinal section of the furnace for melting the mixture of chloride of lead and metallic zinc. Figs. 3, 4, and 5 are respectively an end view, a longitudinal elevation, and a plan of a mold for casting the pastiles. Figs. 6 and 7 are respectively a vertical section and a plan of a vat for washing the pastiles in concentrated hydrochloric acid. Figs. 8 and 9 are respectively a vertical section and a plan of a vat for the chemical treatment of the pastiles which are to be turned into cellular lead to form the positive plates. Figs. 10 and 11 are respectively an end view and an external elevation of the frames which we employ to cast a frame-work of antimonious lead around the pastiles. Fig. 12 is a vertical cross-section of Fig. 11. Fig. 13 is an elevation of one-half of this frame and shows the internal face thereof. Fig. 14 is a plan view of the frame. Figs. 15, 16, and 17 are respectively an end view, a plan, and another end view of the templet used for securing in the frame a proper spacing around and between the pastiles which have to be connected together by a frame-work of antimonious lead so as to form an accumulator-plate. Figs. 18 and 19, *a b c d e f g h i j k l m n o p*, show the various forms according to which the pastiles are cast.

The melting-furnace, practically a closed one, (shown in transverse section in Fig. 1 and in longitudinal section in Fig 2,) consists of a furnace having several stories A A of a cast-iron pan B, provided with sole or flag stones of refractory material. This pan is covered with removable flag-stones C, on the top of which we place cast-iron plates D, forming a flue. The hot gases of combustion pass first under the cast-iron pan and then into the flue C D without ever communicating with the inside of the furnace. After leaving flue C D they enter the chimney E.

There are three doors arranged on the outside of the melting-furnace. The first F is for charging in the mixture of chloride of lead and metallic zinc. It has an extension formed by a dead-plate G, under which the hot gases of combustion pass in the beginning of the operation. The chloride of lead fuses on this dead-plate and falls then into the pan. The metallic zinc is then added and the mixture is removed by means of a cast-iron ladle introduced through the second door H, called "casting-door." We may use the equivalent of metallic zinc. A third door I or stirring-up door is used to stir up the mixture while it is in the molten state. At each of these issues there are arranged flues J J, which collect the fumes or vapors. These flues unite into a single one of conical shape opening into a condensation-chamber. Under the pan there is a flagging K of refractory bricks, inclined on both sides, so as to form channels in the middle for the purpose of collecting the molten mixture in case of accident and preventing it falling into the fire. It is very desirable, for the reasons hereinafter appearing, to exclude air as much as possible from the mixture, and the above form of furnace enables this to be done more completely than any other.

After having taken some of the molten

mixture by means of the cast-iron ladle it is run into a hinged cast-iron mold A', Figs. 3, 4, and 5, provided internally with cells V V of any shape. *x y* is the hinge. Cells *v v* permit of any required form being given to the pastiles. We show *a b c d*, &c., a series of pastiles of varied forms. The next stage consists in washing the pastiles in concentrated hydrochloric acid. Although we effect fusion in a closed vessel, it is impossible to entirely avoid the entrance of air through the furnace-door, and consequently to prevent the formation of oxychlorides in a small degree. The zinc and lead oxides which are formed must therefore be eliminated. To effect this we arrange the pastiles, Figs. 6 and 7, on leaden trays A^2 A^2 A^2, provided with holes, permitting easy circulation of the liquid, and with projections a^2 a^2 a^2, so as to leave between them a sufficient space to prevent the crushing of the pastiles. These trays are piled up in any number in wooden vats B^2 B^2, lined with lead. These vats are provided at their lower part with a hole C^2, in which a tap made of stoneware or other material not affected by chemicals is fitted. The vat is filled up with concentrated hydrochloric acid. In this acid any oxides are transformed into chlorides, and the operation is continued until the pastiles contain nothing but pure chloride of lead. The vat is then emptied by means of the stone tap and a circulation of water established for the purpose of removing the excess of hydrochloric acid retained by the plates.

The two aforesaid operations apply equally to the pastiles which are to form the positive plates and to those used in the manufacture of the negative plates.

After the second operation the pastiles are divided into two groups—the positive pastiles and the negative ones. Each group undergoes a different treatment.

First, with respect to the positive pastiles, by means of reduction and transformation into litharge. The positive pastiles, cleaned and washed, as has been explained above, are subjected to a reduction process to be first of all turned into cellular lead. This reduction is effected by an electro-chemical method, Figs. 8 and 9, by means of zinc plates d^3 d^3, separated by lead blocks e^3 e^3 and piled up in a vat D^3, lined with lead. This vat is filled up with water, in which the chloride of zinc resulting from the electro-chemical action is dissolved. It is provided with a stoneware tap, or of any other material not affected by chemicals, for the purpose of emptying the liquid. After the reduction has been effected in these conditions the positive pastiles are deprived of all the chlorine which entered into their previous composition. There remains now nothing but pure cellular lead. The pastiles are then taken into a stove heated to a temperature ranging between 250° and 300° centigrade, (say 480° to 570° Fahrenheit.) Under the oxidizing influence of hot air their transformation into cellular litharge is effected. The next stage consists in casting a frame of antimonious lead round the pastile. The casting of this frame is effected both round the positive pastiles of cellular litharge and round the negative one of chloride of lead not yet reduced by the same means and with the same mold, as we are now going to describe. It consists, essentially, Figs. 10 to 17, of two cast-iron frames A^4 A^4, jointed together by means of a hinge B^4. It can swing round a segment C^4 by means of trunnions D^4. Each hollow frame is all around and internally provided with a hollow E^4 E^4, which correspond to the projection with which the frame of antimonious lead must be provided. It is, besides, lined with asbestus mill-board of a thickness sufficient to form a slightly-elastic surface. A platen F^4 of cast-iron keeps this asbestus mill-board in position and permits of any degree of pressure being imparted by by means of the nuts f^4 f^4. The pressure on the two platens is obtained by means of six cam-levers G^4. To cast a frame the mold is placed horizontally and opened at right angles. A templet H^4, which is an exact counterpart of the spaces left between and all around the pastiles, is laid on the lower platen, Figs. 15, 16, and 17. It is provided with four projections i^4 i^4, which enter holes J^4 J^4 in the platen and serve to insure the exact position of the pastiles. The pastiles are placed in the open parts of the templet, so that spaces of uniform size are therefore left between the pastiles. The templet is removed by means of handles K^4 without disturbing the pastiles. The upper platen is lowered and the tightening cam-levers are operated. The pastiles are thus pressed between the pieces of asbestus mill-board and cannot be shifted. The mold being then brought into a vertical position, antimonious lead is run through the opening L^4. The molten metal fills up the spaces left between the pastiles and around the platens. The pastiles are therefore connected firmly by means of a frame-work of lead. The mold, being brought back into its horizontal position, is opened, the frame-work is withdrawn, and it is sufficient to let the leaders M^4 M^4 drop to obtain the accumulator-plate.

Secondly, with respect to the negative pastiles. These are now provided with a frame-work of antimonious lead, and then it remains only to reduce them into cellular lead. These plates being still in the state of chloride of lead, their reduction is effected in the same manner as in the case of the positive plates—that is, by means of an electrolytic bath in a vat containing the plates to be reduced and zinc plates.

Finally, we have thus obtained positive plates consisting of pastiles of cellular litharge, and on the other hand negative plates of pure cellular lead, the pastiles in either kind of plate being strongly connected with

one another by means of a frame-work of antimonious lead. There remains only to group both kinds of plates, so as to form them electrically by the ordinary means.

Having now particularly described and ascertained the nature of our said invention, we declare that what we claim is—

1. The process of forming material for secondary-battery plates, consisting in fusing or melting chloride of lead, adding metallic zinc thereto, and subsequently running the mass into a large receiver and allowing the impurities of the mixture to fall to the bottom of receiver, substantially as specified.

2. The process of forming positive plates for secondary batteries, consisting in fusing or melting chloride of lead, adding metallic zinc to said chloride of lead, forming the mass in suitable molds, and subsequently washing the formed plates in concentrated hydrochloric acid, substantially as specified.

3. The process of forming positive plates for secondary batteries, consisting in first fusing or melting chloride of lead and metallic zinc, then forming the same in suitable molds, then washing the formed plates in concentrated hydrochloric acid, then reducing the plates to litharge, and then forming a frame-work of antimonious lead around the plates, substantially as specified.

4. The process of forming negative plates for secondary batteries, consisting in first fusing or melting chloride of lead, then adding metallic zinc thereto, then forming the same in suitable molds, then washing the formed plates in concentrated hydrochloric acid, then forming a frame-work of antimonious lead around the plates, and subsequently reducing the plates to cellular lead, substantially as specified.

5. The process of forming plates for secondary batteries, consisting in fusing or melting chloride of lead and metallic zinc, pouring the mass into a receiver lined with or made of a refractory material faced with a protecting stratum of ordinary lead, and subsequently pouring the mixture into a suitable mold and washing the material thus formed in concentrated hydrochloric acid, substantially as specified.

6. The process of forming plates for secondary batteries, consisting in fusing or melting chloride of lead and metallic zinc, then forming said mass into plates, and subsequently coupling the plates in sets and in short-circuit in a vat containing a solution of water and hydrochloric acid, substantially as specified.

In testimony that I, ARTHUR MARIE FRANÇOIS LAURENT CÉLY, claim the foregoing, in conjunction with the said ILLIUS AUGUSTUS TIMMIS, I have hereunto set my hand this 11th day of March, 1890.

ARTHUR MARIE FRANÇOIS LAURENT-CÉLY.

Witnesses to the signature of Laurent-Cély:

FR. LAURENT,
Ingénieur, 77 Rue des Petits Champs, Paris.
E. SEMPTY,
Nég't, 24 Rue Louis le Grand, Paris.

In testimony that I, ILLIUS AUGUSTUS TIMMIS, claim the foregoing, in conjunction with the said ARTHUR MARIE FRANÇOIS LAURENT CÉLY, I have hereunto set my hand this 12th day of March, 1890.

I. A. TIMMIS.

Witnesses to the signature of I. A. Timmis:

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