(No Model.) 3 Sheets—Sheet 1.

W. SPILKER.

ELECTROLYSIS OF WATERY SALT SOLUTIONS.

No. 583,513. Patented June 1, 1897.

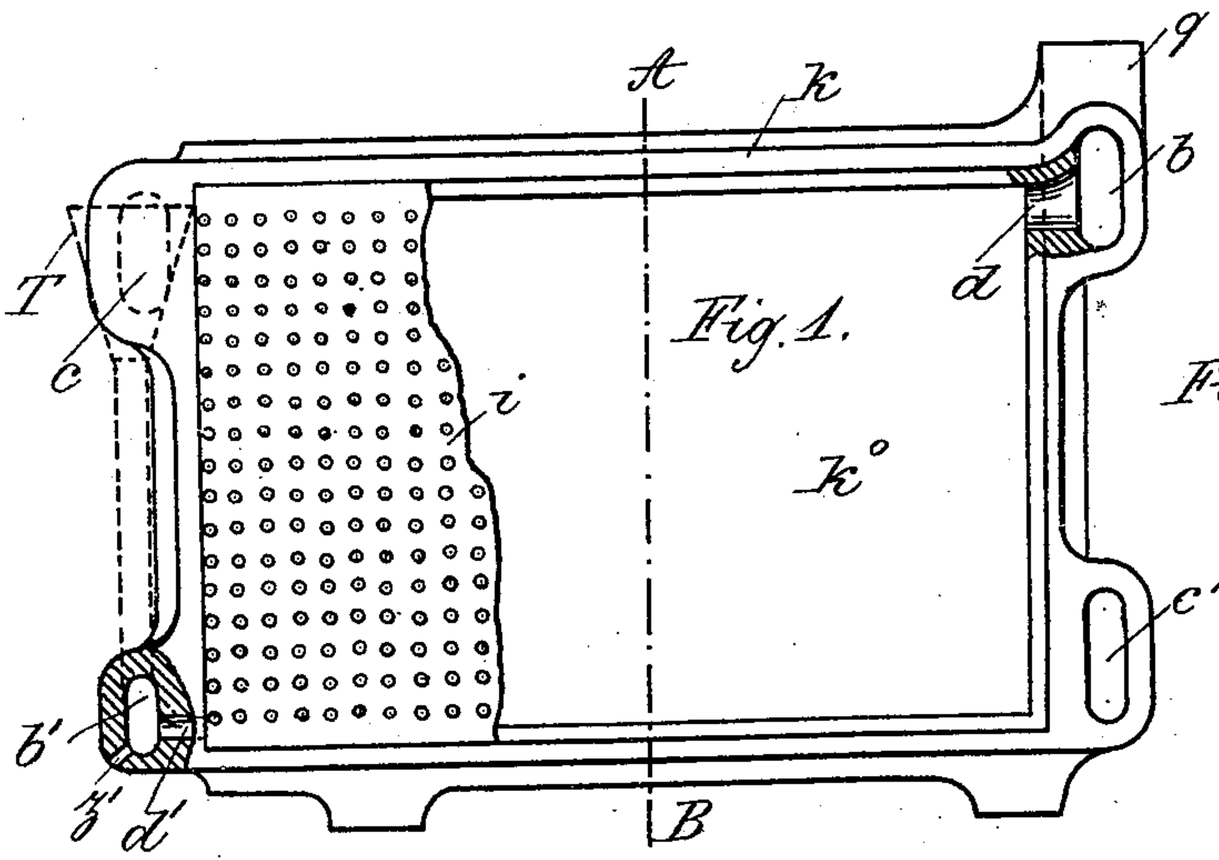

Fig. 1.

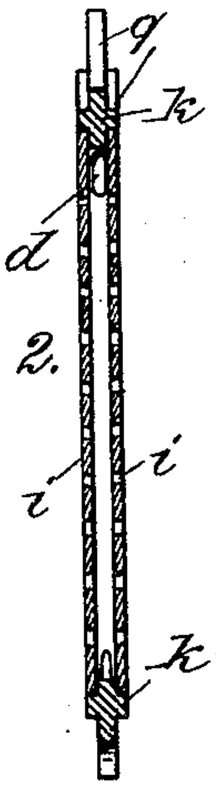

Fig. 2.

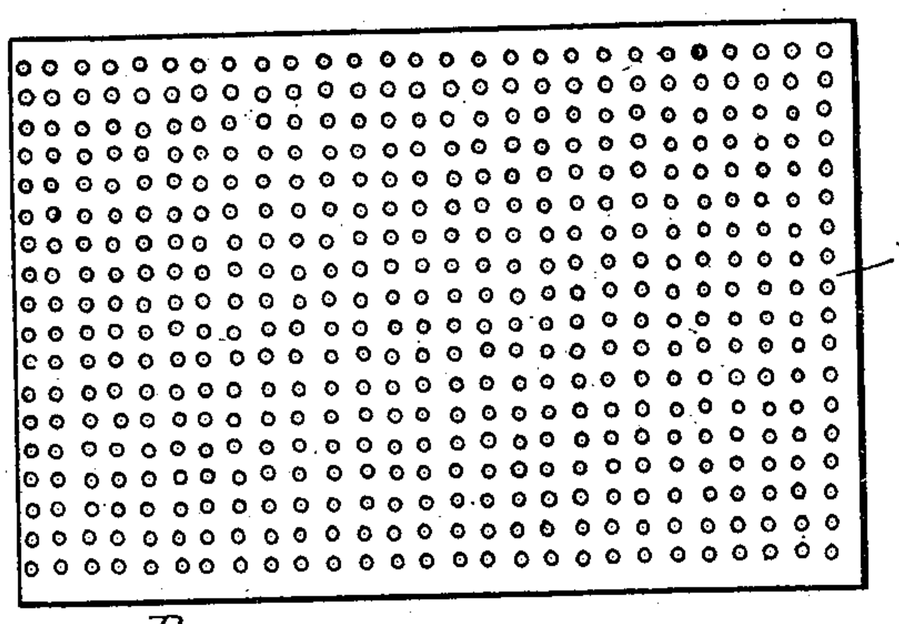

Fig. 1a

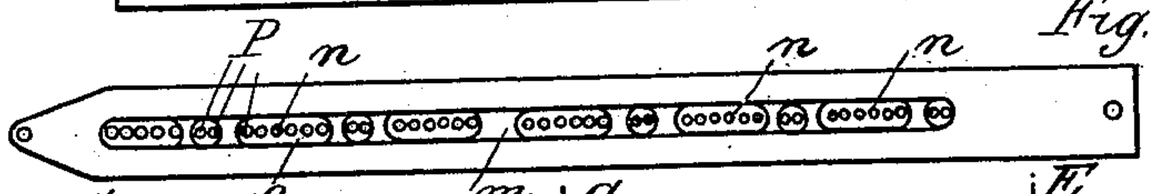

Fig. 3.

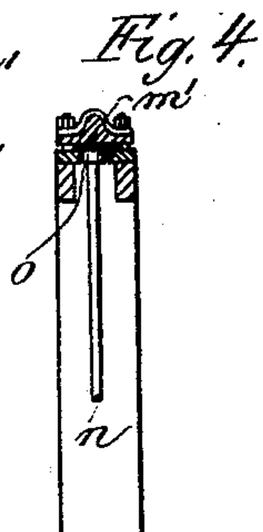

Fig. 4.

Fig. 4a

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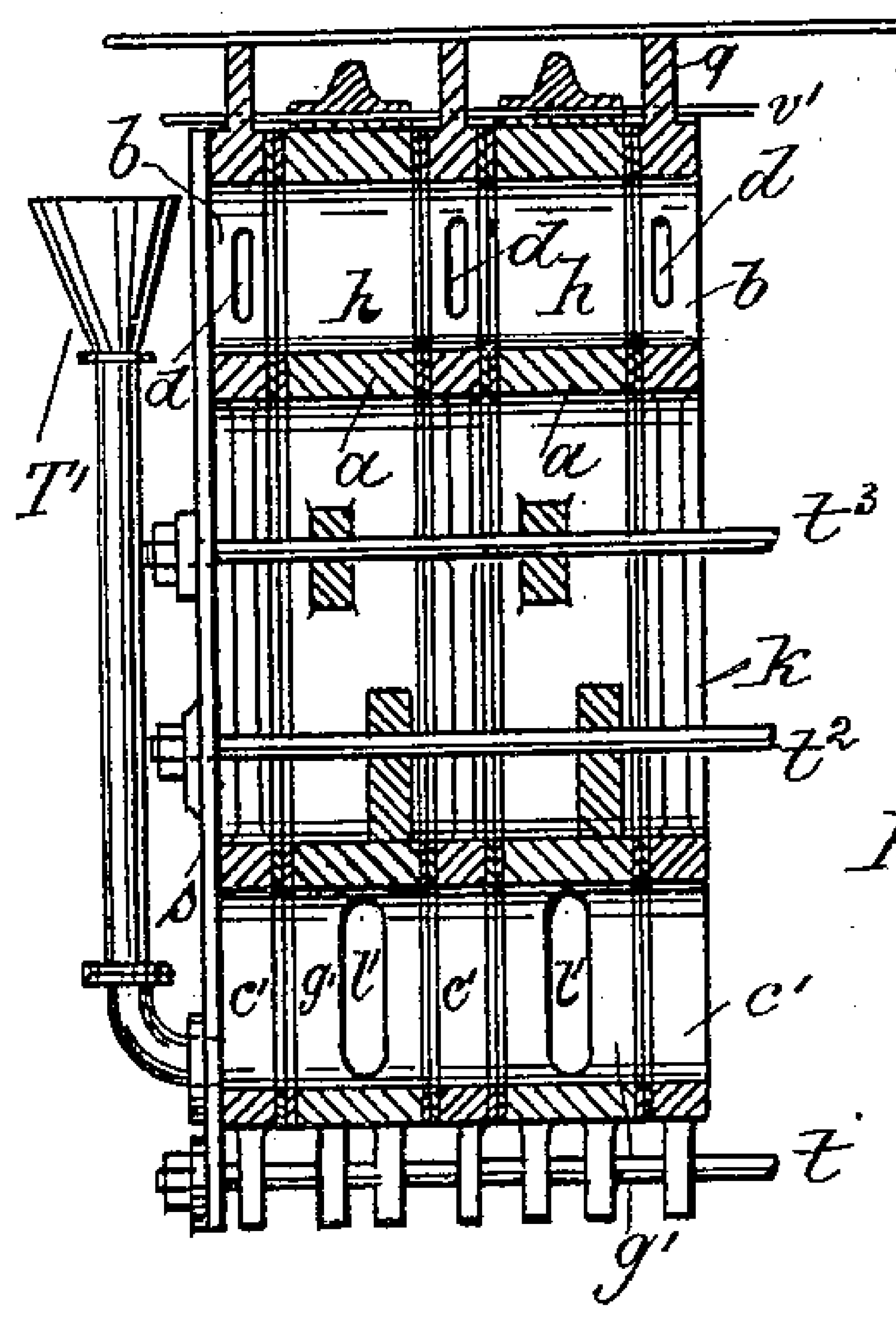


Fig. 5.

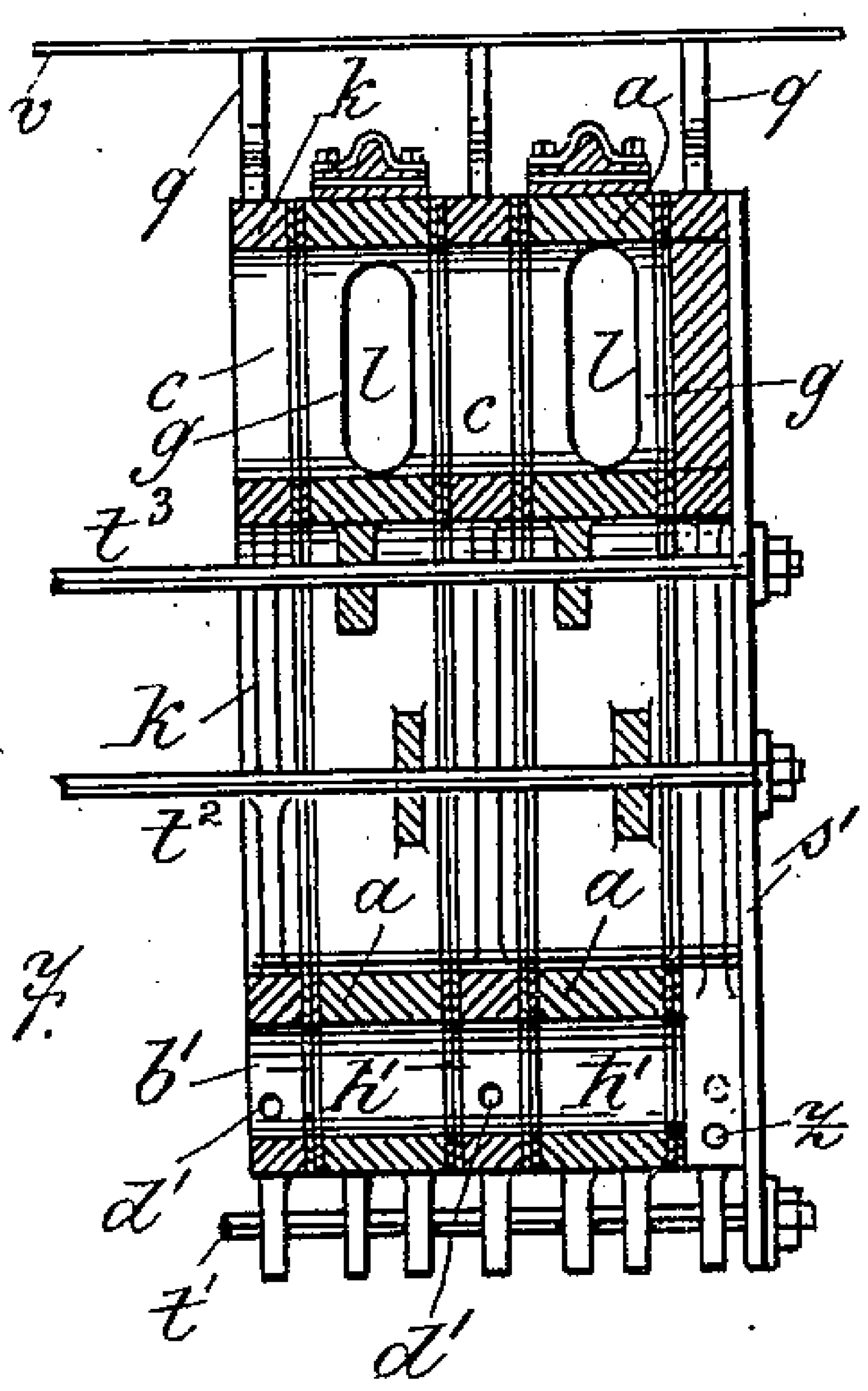


Fig. 7.

Fig. 6.

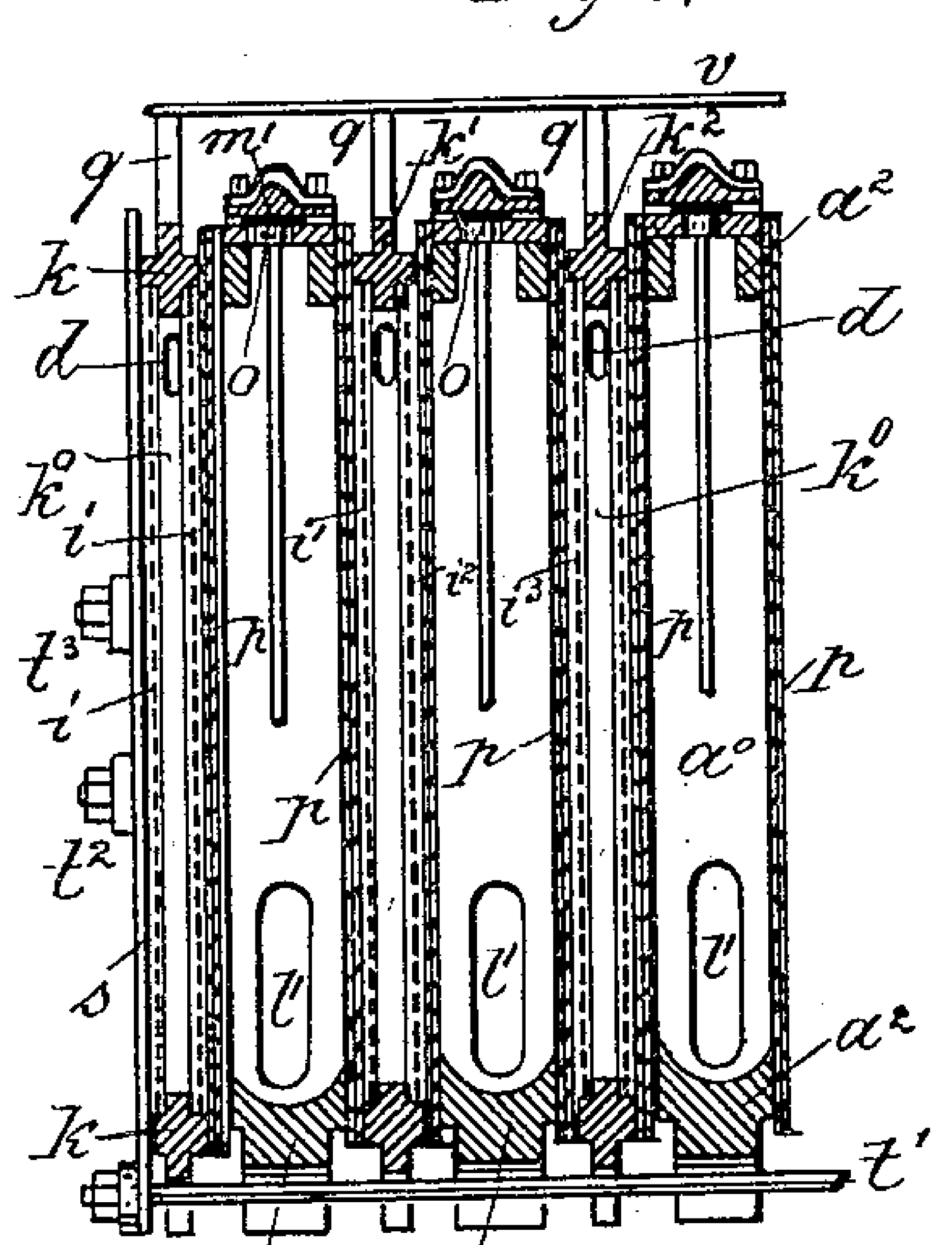


Fig. 8.

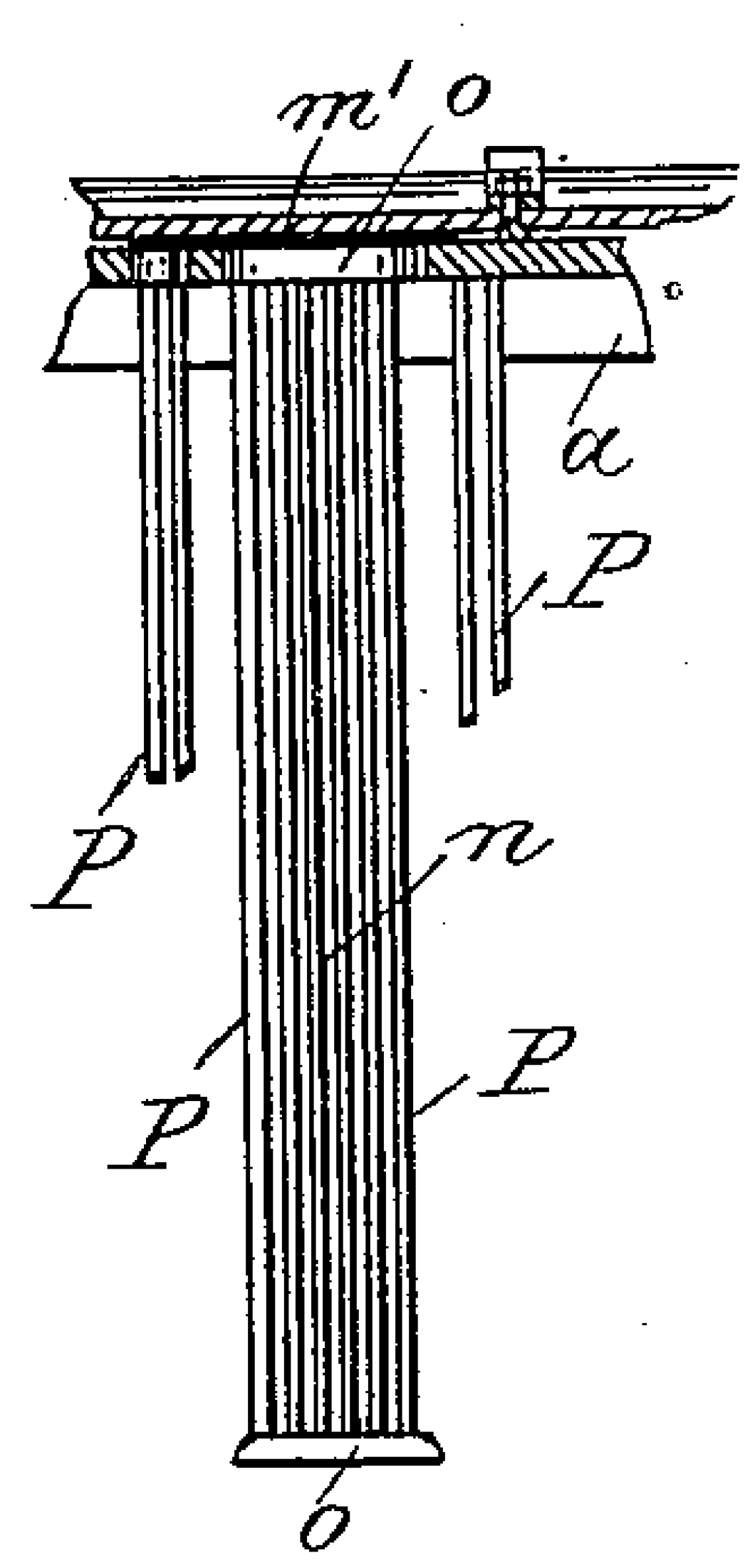
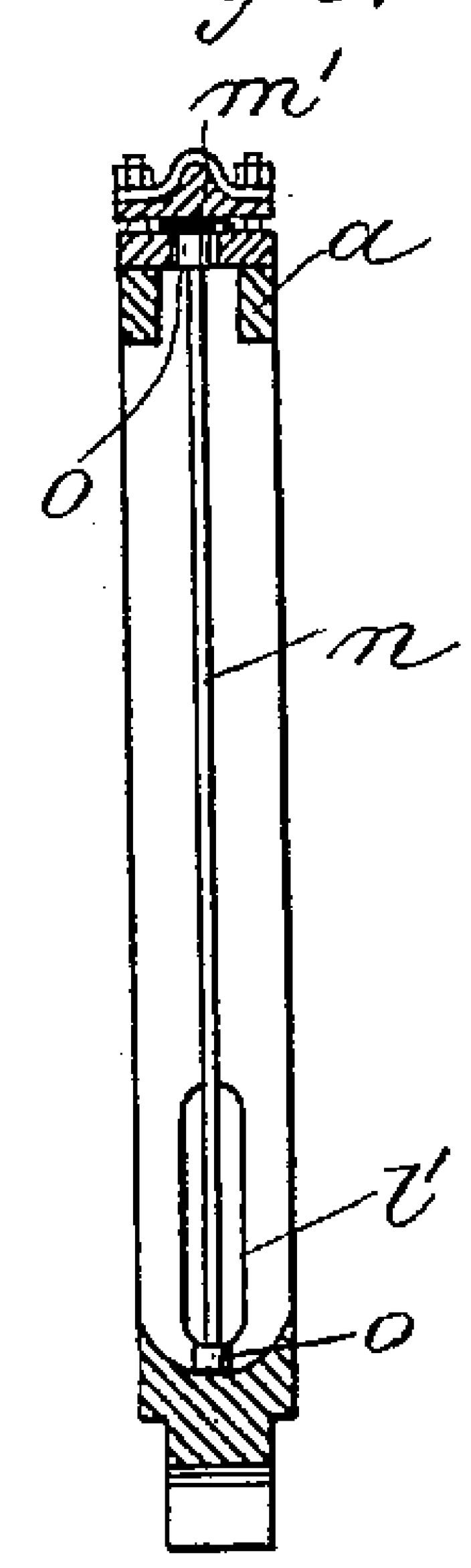


Fig. 9.



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ELECTROLYSIS OF WATERY SALT SOLUTIONS.

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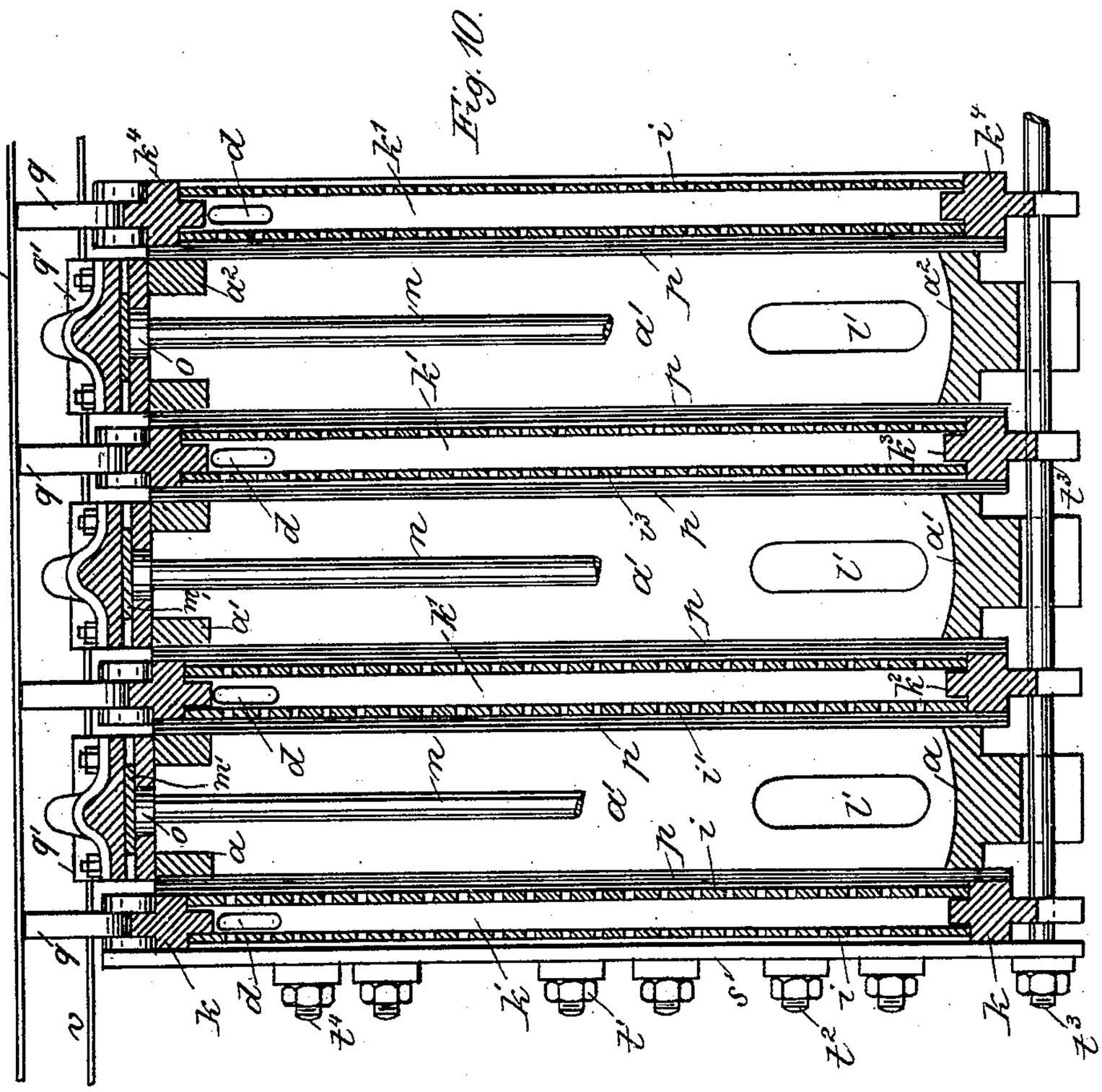
Fig. 10.



Witnesses:

Inventor:

Wilhelm Spilker.

by Heinrich Lade

Attorney.

UNITED STATES PATENT OFFICE.

WILHELM SPILKER, OF BERLIN, GERMANY.

ELECTROLYSIS OF WATERY SALT SOLUTIONS.

SPECIFICATION forming part of Letters Patent No. 583,513, dated June 1, 1897.

Application filed August 15, 1891. Serial No. 402,716. (Specimens.)

To all whom it may concern:

Be it known that I, WILHELM SPILKER, a subject of the King of Prussia, German Emperor, and a resident of the city of Berlin, in the German Empire, have invented certain new and useful Improvements in the Electrolysis of Watery Salt Solutions; and I do hereby declare that the following is a full, clear, and exact description of the invention, which will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to a process for the production of diaphragms for use in electrolytic processes by the electrolytic process itself with the preliminary aid of an endosmotic vegetable, animal, or mineral membrane—such as parchment, asbestos, &c.

In the greater number of electrolytic processes carried out with the use of diaphragms, as in the decomposition of halogen alkali metals, acid solutions or lyes are employed, which rapidly destroy endosmotic membranes—such as parchment, &c.—so that in all these cases it has hitherto been necessary to use expensive fragile clay diaphragms, which is difficult on a large scale; and the object of the invention is to supersede diaphragms of this kind by other and inexpensive membranes suitable for operations on a large scale.

If the membranes of this invention were to be used in the electrolysis of halogen alkali metals by one of the known processes, they would in a short time be destroyed by the chlorin, this being the reason why it has hitherto been necessary to use diaphragms made of clay or other similar mineral substance in electrolytic processes of this kind.

In carrying out the invention a membrane of a substance that is easily destroyed—parchment, for example—is by a particular electrolytic process furnished with a firm, adhesive, and porous coating, forming with the parchment-membrane a firm plate of any suitable dimensions. I employ a bath of any suitable construction, separate the cathode and anode spaces with parchment, charge the anode space with a solution of chlorid of potassium made alkaline by lime, and use caustic-potash lye as the cathode liquid. If now the bath be placed in communication with the source of electricity, hypochlorite will be formed at the anode or positive pole. This would in a very short time destroy the toughest parchment, so that the anode and cathode liquids would mix together and render the apparatus useless. If, however, previous to the passage of the electric current a certain suitable quantity, say about two per cent., of chlorid of calcium be added to the anode liquid, a firm, adhesive, and even coating consisting mainly of lime will, after the electric current has been in operation a short time, be formed on the parchment on the anode side, while the parchment on the cathode side remains free from the coating. If now so much lime be added to the anode solution as to keep the same constantly nearly saturated with lime, the quantity of CaO employed for the purpose being about one per cent., the coating will continue to increase, the process being carried on until it attains a thickness of about ten millimeters. It has the form of a firm even plate fixed to the parchment and gives out a sound similar to that given out by burnt clay or earthenware, which it also resembles in firmness or tenacity. If the electric current did not pass through the bath, the parchment would merely show a pasty lime precipitate which could not protect it from injury.

The diaphragm of this invention is not attacked by hypochlorite, greatly resists the action of chlorin, and may therefore be used in the decomposition of halogen alkali metals and in the electrolysis of watery solutions. The composition consists of lime, respectively, magnesia, and at the same time chlorids. The same process may be performed by employing magnesia, other alkaline earth metals, and similar oxyhydrates instead of lime, also instead of chlorid of potassium, other halogen alkali metals—chlorid of sodium, for example.

The formation of the firm, even, porous diaphragm, of any suitable thickness, inseparable from the parchment, and of only slight resistance, is explained by the fact that in employing such parchment-membranes the potash contents never mount in the same measure as the employed ampere hours generally do, but somewhat less. A portion of the potash formed in the electrolysis, therefore, in consequence of endosmotic action, passes over into the parchment, remaining

therein instead of uniting with the cathode liquid, and at the boundary—that is to say, toward the anode side—is, with the chlorid of calcium there present, transformed into lime and chlorid of potassium or also to fixed basic chlorid of calcium and chlorid of potassium. If now the anode solution contains sufficient lime in solution, this precipitate cannot again dissolve therein, and thus forms the first portion of the coating. This keeps on increasing in thickness and so prevents any attack of the hypochlorite on the parchment. When the coating has become sufficiently thick, the supply of fresh lime to the anode liquid is diminished to a certain extent, say by about twenty per cent., so that said liquid is capable of dissolving further quantities of lime, and from this time the coating remains of the thickness already given to it.

In the performance of the process on a large scale it is desirable to provide the parchment on the cathode side with a firm bearing-surface to prevent the bulging out of the same and the fracture of the unfinished diaphragm, and so that this latter shall be formed in one solid inseparable whole. For this purpose the parchment which is to serve as the substratum for a diaphragm is firmly fixed to the edges of a perforated metal plate serving as a cathode, against the perforated surface of which the parchment bears, and in the course of the building up of the diaphragm becomes firmly attached. Perforated plates are necessary to prevent increase of resistance and to allow of the passage of the potash solution formed at the cathode and also that of the hydrogen, or the cathode-plates may be constructed of several pieces of metal with open spaces between them.

In carrying out the process commercially I employ an apparatus constructed in the manner of a filter-press, as shown in the accompanying drawings, in which—

Figure 1 is a side view, partly in section, of a cathode-frame with a portion broken away to show a perforated sheet-metal plate which, inserted in the cathode-frame, serves as cathode. Fig. 1[a] is a side view of a perforated sheet-metal plate serving as cathode. Fig. 2 is a vertical section taken through line A B of Fig. 1; Fig. 3, a side view, partly in section, of an anode-frame; Fig. 4, a vertical section through line C D of Fig. 3; Fig. 4[a], a plan view of Fig. 3. Fig. 5 is a vertical section, through line E F of Fig. 3, of a portion of the complete apparatus. Figs. 6 and 7 are similar sections, respectively, through line C D and through line G H of Fig. 3. Figs. 8 and 9 are sectional views showing the method of suspending the anodes in the anode-frame. Fig. 10 is a section through line C′ D′ of Fig. 3 on a larger scale.

The apparatus, as shown in Figs. 5, 6, and 7, is constructed of cathode-frames *h* and anode-frames *a* in the following manner: Upon a cathode-frame *k* is laid a perforated sheet-metal plate *i*, then upon the latter a number of parchment-sheets *p*, upon these an anode-frame *a*, then again a number of parchment-sheets *p*, succeeded by a perforated sheet-metal plate *i*′, then a cathode-frame *k*′, a perforated sheet-metal plate i^2, parchment-sheets *p*, anode-frame *a*′, and so on. The cathode and anode frames thus combined are held together by two locking-plates *s s*′, fastened by screw-bolts *t*′ t^2 t^3, &c., in the manner of a filter-press. The iron cathode-frames *k* are provided with apertures *b b*′ and *c c*′, Fig. 1, and serve for the reception of the perforated sheet-metal plates *i*, acting as cathodes. The anode-frames *a* are provided with apertures *g g*′ and *h h*′, corresponding precisely in position and shape to the apertures *b b*′ and *c c*′ of the cathode-frames *k*. The apertures *g g*′ form with the apertures *c c*′, when the apparatus is put together, channels for the passage of the anode liquid, Figs. 5 and 7. The apertures *h h*′ correspond in position and shape to the apertures *b b*′ of the cathode-frames *k*, and with these apertures form, when the apparatus is put together, channels for the passage of the cathode liquid. From the apertures *b* a slot *d* in the frame *k* leads to the inside of the cathode-space k^0, which is shut off on both sides by the perforated sheet-metal plates *i*. From the apertures *b*′ a slot *d*′ in the frame *k* leads to the inside of the cathode-space *k*′. The slots *l l*′ in the anode-frame *a* connect the apertures *g g*′ with the inside of the anode-space *a*′. The apertures *b b*′ *h h*′ and *c c*′ *g g*′ give four channels, which, through slots *d d*′ and *l l*′, permit the supply of the cathode and anode liquids to their compartments k^0 a^0 or the discharge of said liquids therefrom.

When the cathode and anode frames are placed together, as shown in Figs. 5, 6, and 7, the cathode liquid is passed through a funnel T, communicating with the channel formed by the apertures *b*′ of the cathode-frame *k* and the apertures *h* of the anode-frame *a*, into said channel and filling the same and the cathode-spaces k^0 through the slots *d*′, and, further, filling through the slots *d* the channel formed by the apertures *b* of the cathode-frame *k* and the apertures *h*′ of the anode-frame *a*. The anode liquid is passed through a funnel T′, Fig. 5, into the channel formed by the apertures *g*′ of the anode-frame *a* and the apertures *c*′ of the cathode-frame *k*, said anode liquid then passing through the slots *l*′ into the anode-spaces *a*′ and filling the same and through the slots *l* into the channel formed by the apertures *g* of the anode-frame *a* and the apertures *c* of the cathode-frame *k* and filling this channel. *z* is an aperture for the discharge of the cathode liquid and *z*′ an aperture for the discharge of the anode liquid. These apertures are normally closed by plugs or stoppers. In the upper edge of the anode-frames *a* are slots *m*, through which the carbon bodies *n* of the anodes are suspended in the anode-spaces a^0. The carbon bodies—in the form of rods or bars, for in-

stance—are cast in a lead plate *o*, to the top of which is fixed a brass plate *m'*, having an area greater than that of the slot *m*, thereby permitting the carbon bodies to be held suspended from the anode-frame *a*.

P are rods of lead.

All the cathode-frames are connected together by themselves and all the anode-frames by themselves, each set by an electric conductor, the cathode-frames being connected with each other at their projecting part *q* by means of a conducting-rod *v*, placed so as to bear upon all the projecting parts *q*, and the anode-frames being connected with each other at their projecting part *q'* by means of a conducting-rod *v'*. The rod *v* is in connection with one pole and the rod *v'* in connection with the other pole of a source of electricity, so that the current is conducted through the anode and cathode liquid present in the whole of the anode and cathode spaces, which are only separated from one another by the parchment-membranes *p*. The liquids pass through the membranes in contact and the diaphragm now forms on the parchment-membranes *p*.

What I claim as my invention, and desire to secure by Letters Patent, is—

In the electrolysis of watery salt solutions, the process for the production of endosmotic membranes for use in the electrolysis, by the electrolysis itself, which process consists in separating by means of a membrane serving as a foundation-diaphragm, an alkaline-cathode solution from an anode solution consisting of a mixture of the chlorids of the alkali metals and calcium holding the corresponding oxyhydrate, caustic lime, in solution and causing a solid porous coating to be firmly attached to said foundation-membrane on the side of the anode-space by passing an electric current through the bath, substantially as described.

In testimony whereof I have signed this specification in the presence of two subscribing witnesses.

WILHELM SPILKER.

Witnesses:
W. H. EDWARDS,
W. HAUPT.