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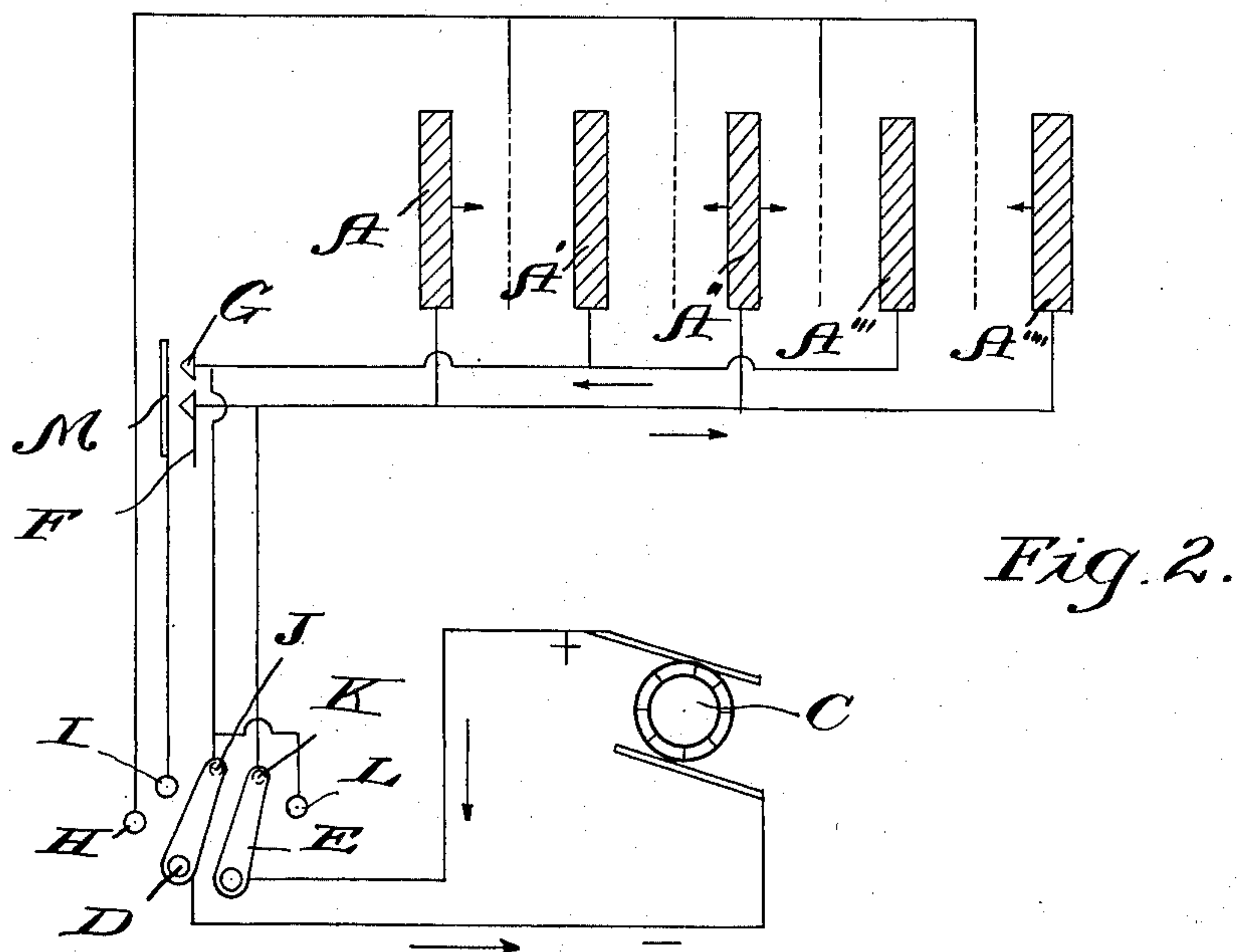
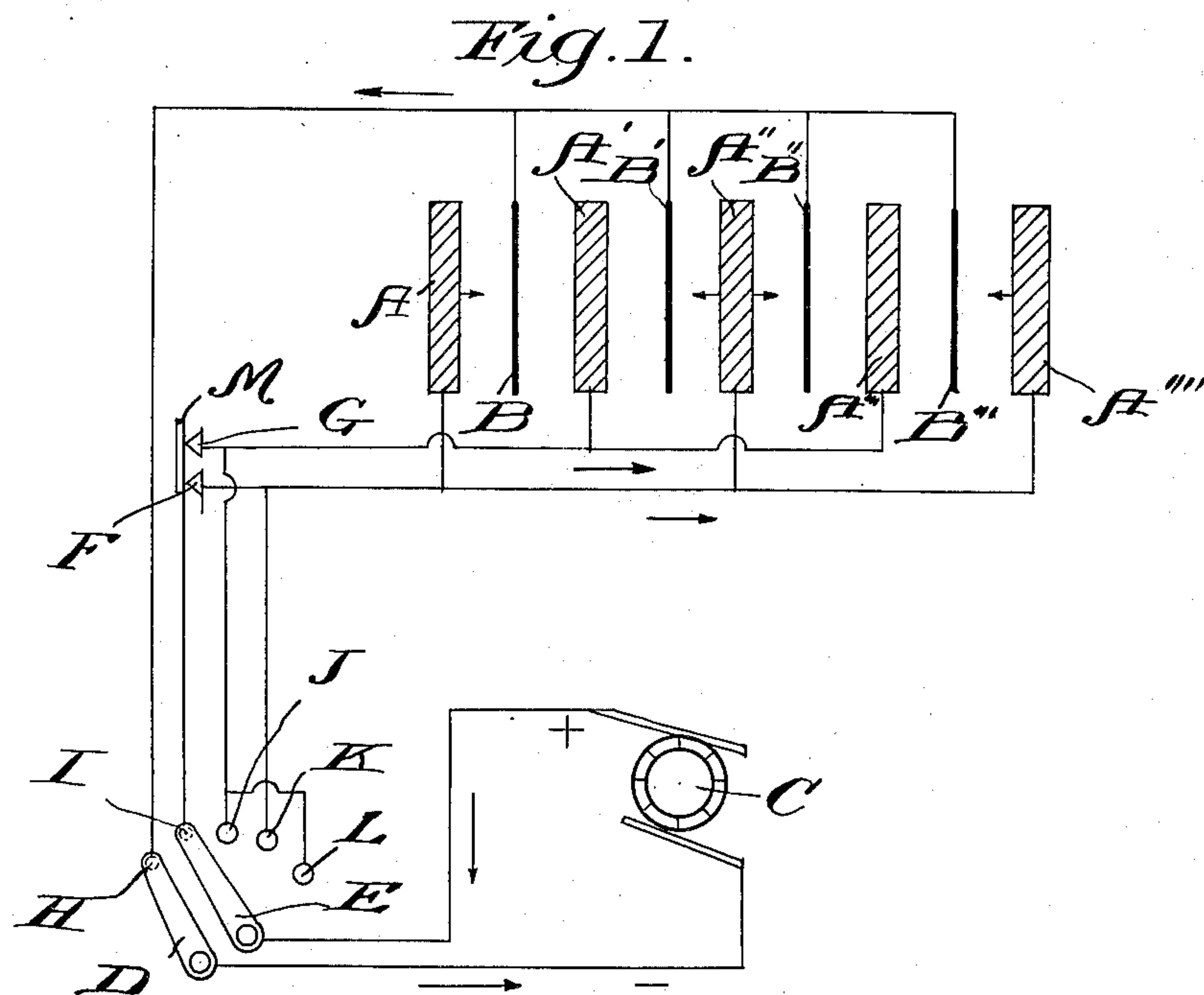
PROCESS OF ELECTROLYTIC REFINING OF ZINC.

APPLICATION FILED MAR. 1, 1911.

998,379.

Patented July 18, 1911.

2 SHEETS-SHEET 1.



Witnesses  
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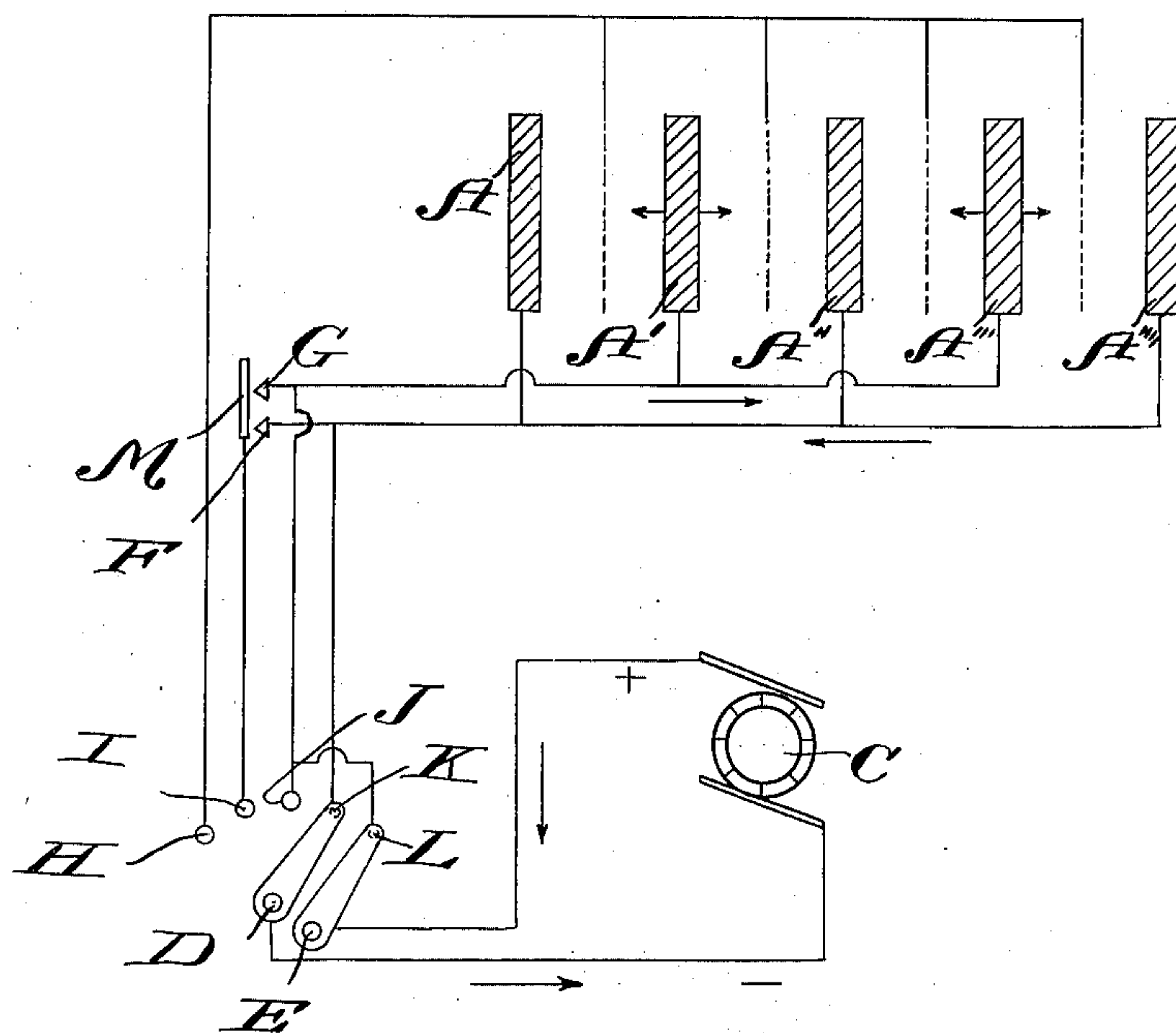
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2 SHEETS—SHEET 2.

*Fig. 3.*



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# UNITED STATES PATENT OFFICE.

KUNIGORO NAMEKAWA AND JISHICHIRO MIYAZAWA, OF SHITAYA, TOKYO, KUMAZO MIYABARA, OF HONGO, TOKYO, AND SHOTARO EMURA, OF SHITAYA, TOKYO, JAPAN.

## PROCESS OF ELECTROLYTIC REFINING OF ZINC.

998,379.

Specification of Letters Patent.

Patented July 18, 1911.

Application filed March 1, 1911. Serial No. 611,581.

*To all whom it may concern:*

Be it known that we, KUNIGORO NAMEKAWA, residing at 88 Minowamachi, Shitaya, Tokyo, Japan, JISHICHIRO MIYAZAWA, residing at 82 Kurumazakamachi, Shitaya, Tokyo, Japan, KUMAZO MIYABARA, residing at 23 Katamachi Nezu, Hongo, Tokyo, Japan, and SHOTARO EMURA, residing at 88 Minowamachi, Shitaya, Tokyo, Japan, all subjects of His Majesty the Emperor of Japan, have invented certain new and useful Improvements in the Process of Electrolytic Refining of Zinc; 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.

Our invention relates to a method of electrolytically separating zinc from a zinc sulfate solution which acts as the electrolyte in the process, and it is characterized by the special arrangement and adjustment of anodes and also by the special preparation of the electrolyte. Its object is to minimize the electric power for the electrolytic process and to produce said metallic zinc of minute crystals and in a thick layer both while refining zinc, or while coating articles with zinc to each of which arts our process is adapted.

The method of electrolyzing zinc from zinc sulfate solutions, which has hitherto been known, has involved the use of insoluble anodes such as lead; and the weak points in this known process are that it requires an increased higher voltage as the electrolytic action commences and the voltage must be proportionately increased as the electrolytic action advances. Further, zinc so deposited soon becomes spongy, and the electrolysis has to be stopped. This is mainly due to the liberation of hydrogen at the cathode and also to a change in the quality of the anode which takes place during the process of electrolysis. One of the advantages of the present invention consists in avoiding these objectionable features.

In our invention, means is devised for changing at will the direction of the electric current flowing from the anode to the cathode, so that the change of quality and conductivity of the anode may be prevented. As electrolysis goes on, lead peroxid or lead persulfate or both are deposited on the anode plate, which gives rise to a polarized

or reverse current; and the novelty of our invention partially consists in changing the polarity of some of the anodes by supplying a negative current thereto, as will be described hereinafter. Consequently, by our process, lead peroxid, lead persulfate, or both, which are deposited on the anodes soon become lead oxid and this falls off from the said anodes by gravity, as these deposits have no affinity with the anode plates. These compounds which it is not necessary to remove from the vats more than twice or thrice a year, can be later reduced to metallic lead by any suitable process. When changing the polarity of the anodes the cathodes or the plates on which zinc is deposited are conveniently removed from the vat or vats and are later replaced after the anodes have become clean. Or if there are inserted anode plates formed of lead or carbon between two consequent polarities, the operation can be continued without removing the zinc cathodes. It should be noted that in case of removing the zinc cathodes into another vat or vats, the change of polarity of the lead anodes should be made so as to let the same polarity occur alternately; or the anodes may be replaced by fresh anodes of the same metal and connected to the negative side of another electric circuit.

Referring to the accompanying drawings forming a part of this specification, in which like characters designate like parts in all the views:—Figure 1 is a diagrammatic view illustrating the depositions of the metal under normal conditions; Fig. 2 is a diagrammatic view showing the apparatus with the zinc cathodes removed and the deposits being stripped from certain of the anodes; and Fig. 3 is a view similar to Fig. 2 showing the deposits being stripped from certain other of the anodes.

A A' A'' A''' A'''' represent anodes, B B' B'' B''' cathodes, C an electric generator, D and E switches acting in unison, G, F and M contacts, and H, I, J, K and L contacts for the switches D and E.

To carry out the invention, we first close the contacts G, F, and M and connect switches D E with contacts H and I, as shown in Fig. 1, when current will flow from anodes A A' A'' A''' A'''' to cathodes B B' B'' B''' and the electrolytic action will take place. As the action proceeds, lead peroxid or lead persulfate, or both, are produced on



the surface of the said lead anodes A A' A'' A''' A''''; and a polarized reverse current will flow between the anodes and cathodes. At this stage, if we remove zinc cathodes or deposited zinc plates B B' B'' B''' as illustrated in Fig. 2 into another vat or vats, break contacts G and F from contact M, and move over switches D E to contacts J and K, current will then flow to anodes A' and A''' from anodes A A'' and A'''' as indicated by the arrows. By this means any lead peroxid or lead persulfate, or both, on the surface of the anodes A' and A''' will be changed into lead oxid, and usually within ten minutes, the time needed depending on the strength of the electric current. These deposits will then fall by gravity to the bottom of the vat. In the next stage as in Fig. 3, if switches D E are moved over to K L, current will flow to anodes A A'' A''' from the anodes A' A''' as indicated in Fig. 3. Lead peroxid or lead persulfate or both on the surface of anodes A A'' and A''' will likewise fall off in the similar manner.

By following the above procedure, polarized reverse currents are not produced and the anodes are restored to a clean condition. It is therefore obvious that the electrolytic action can be continued at a low voltage.

When it is desired to repeat the operation illustrated in Fig. 1 the zinc cathodes are replaced in the solution and the current permitted to flow.

The second part of our invention consists in preventing the formation of spongy zinc plates by use of the following step: namely, sugar, starch or sea-weeds, or all combined, or other similar vegetable substance, each of which has been previously roasted almost to carbonization, is mixed with water, and the liquid squeezed or extracted therefrom of dark brownish color is suitably poured into the electrolyte. By this means, we have observed that the liberated hydrogen does not remain on the surface of cathode plates, but is driven away to the surface of the electrolyte. Consequently the deposited zinc does not assume a spongy form. It follows that the defects inseparable from the hitherto known methods of electrolysis of zinc sulfate solution, are avoided, in our invention and the voltage of electric power may be maintained as low as 3 to 3.5 volts. Moreover, the deposited zinc presents an extremely minute crystalline structure free

from any air-holes. The result is that metallic zinc can be formed in thick layers which was impossible by any process heretofore known to us.

What we claim is:—

1. The process of separating zinc from a zinc sulfate solution by electrolysis, which consists in immersing in said solution a lead anode and a suitable cathode on which the zinc is to be deposited; in passing a current from said anode to said cathode through said solution; and in order to improve the conductivity, passing a current from said solution to said anode at intervals and thereby converting any lead sulfates that may exist on said anode into lead oxid, which may be readily detached from the anode surface, substantially as described.

2. The process of separating zinc in a solid form from a zinc sulfate solution employing a lead anode and a suitable cathode which consists in adding to said solution a compound of vegetable origin which has been heated almost to the point of carbonization; in passing a current from said anode to said cathode; and at intervals passing a current from said solution to said anode to remove any deposit that may have formed thereon, substantially as described.

3. The process of electrolytically forming thick deposits of zinc from a zinc sulfate solution employing a plurality of lead anodes and suitable cathodes, which consist in adding to said solution a compound of vegetable origin which has been heated almost to the point of carbonization; in passing a current through said solution from said anodes to said cathodes; in passing a current at intervals from some of said anodes through the solution to certain other of said anodes to strip the latter of any lead sulfates that may have formed thereon; and in then passing a current from said last mentioned anodes to said first group of anodes to strip any sulfates from said first group of anodes, substantially as described.

In testimony whereof, we affix our signatures, in presence of two witnesses.

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KUMAZO MIYABARA.  
SHOTARO EMURA.

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