

No. 829,778.

PATENTED AUG. 28, 1906.

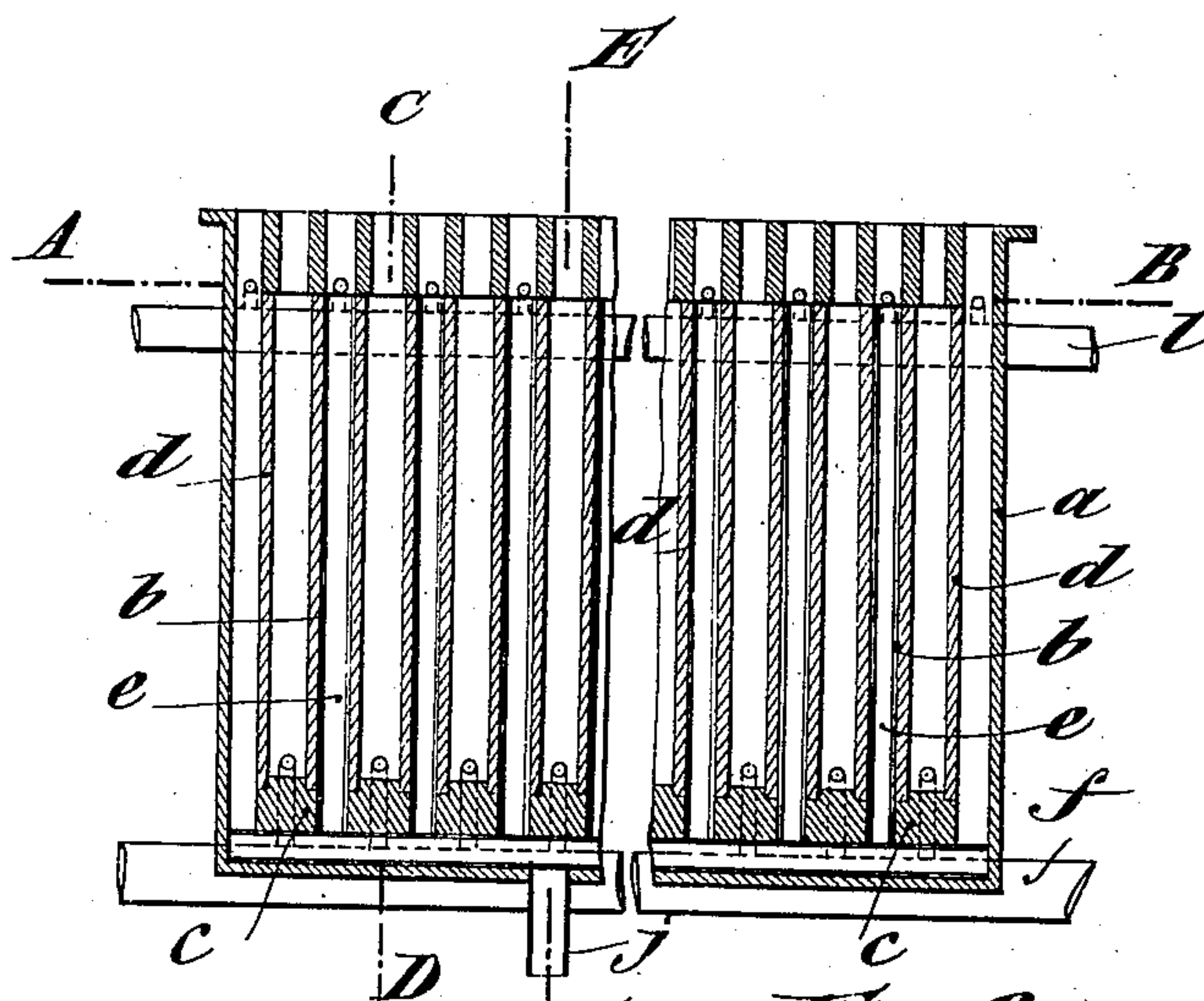
H. M. GRANIER.

MANUFACTURE OF SULFATE OF COPPER AND CAUSTIC ALKALIS.

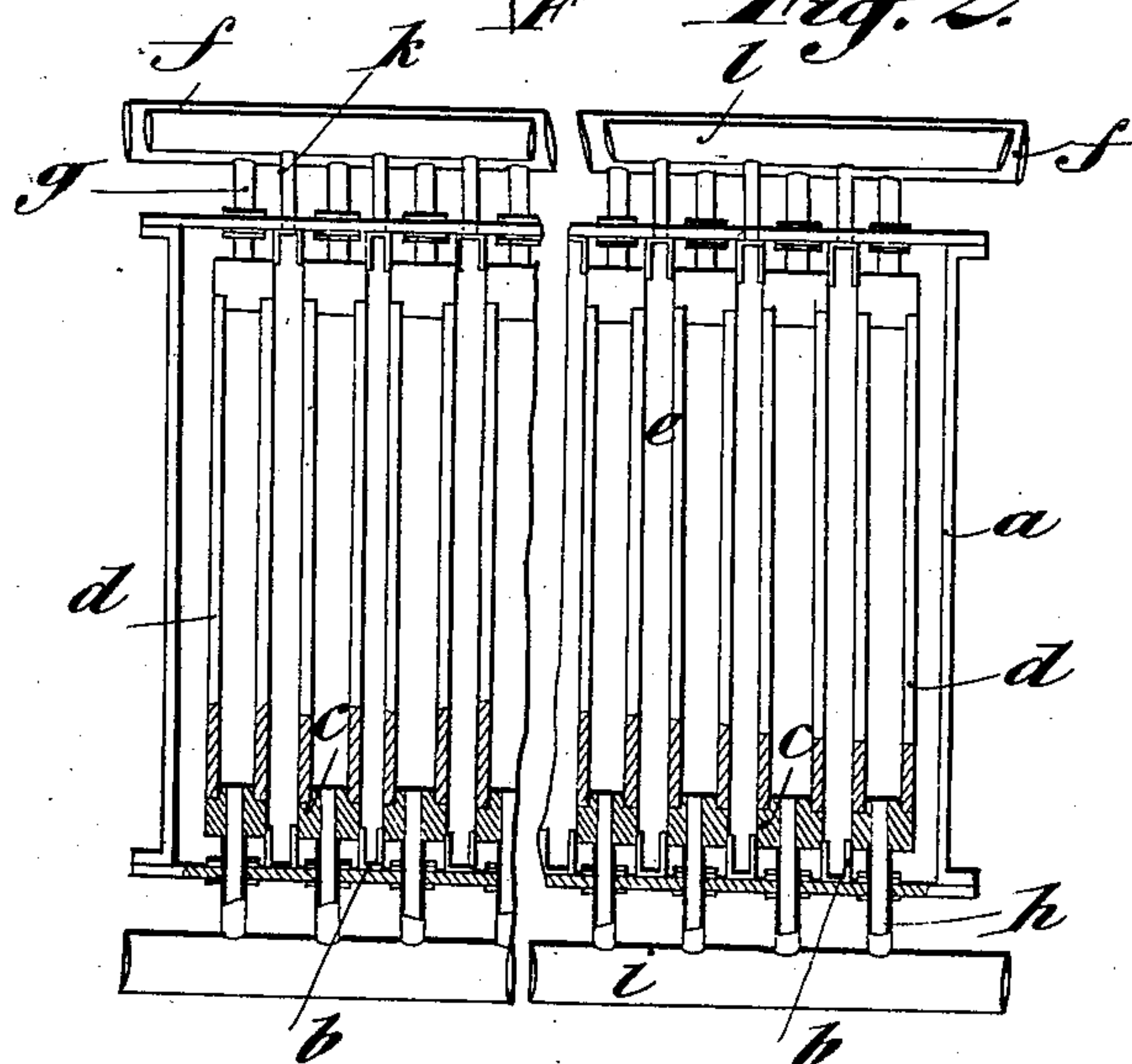
APPLICATION FILED MAR. 12, 1904.

2 SHEETS—SHEET 1.

*Fig. 1.*



*Fig. 2.*



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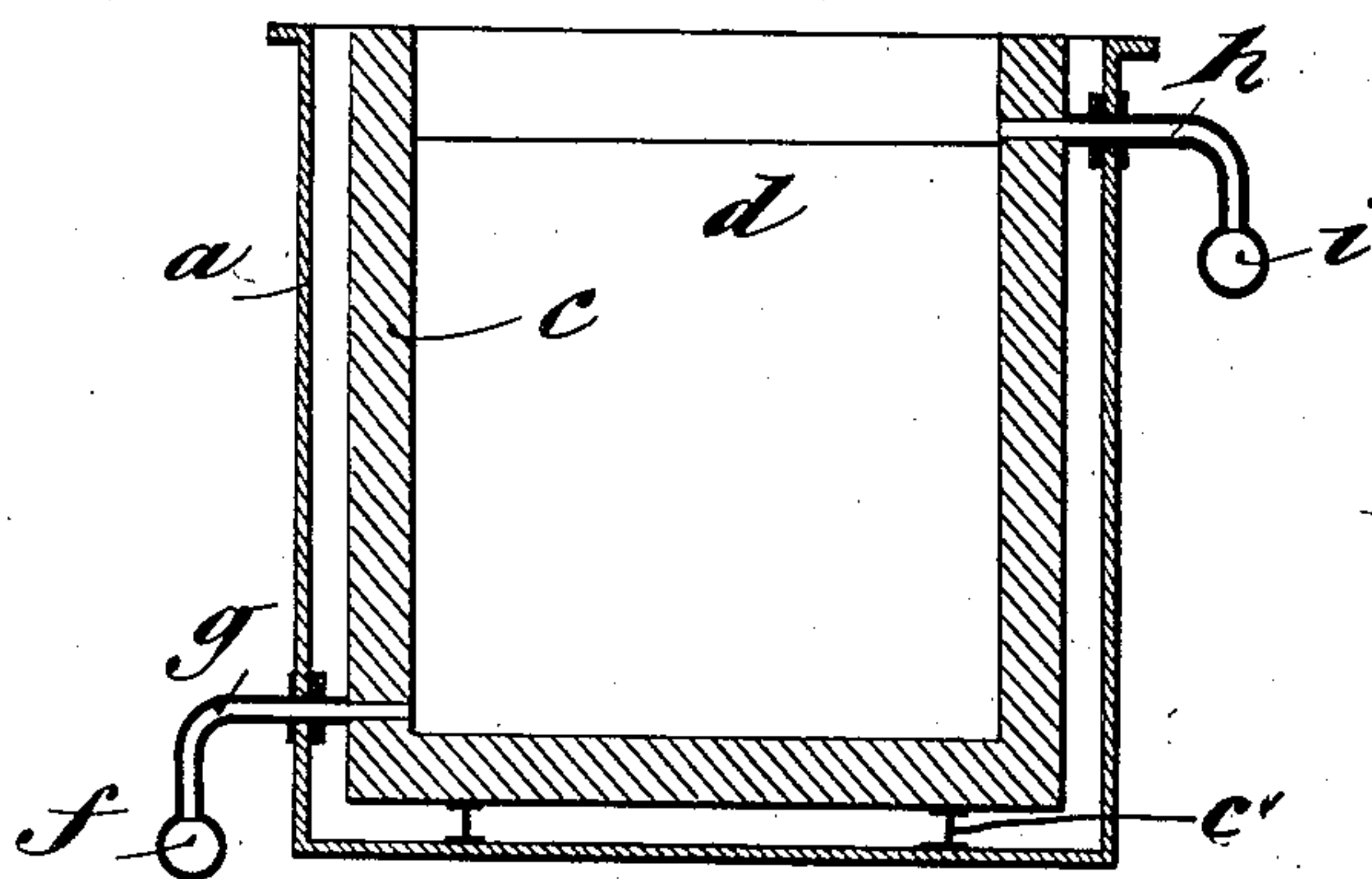
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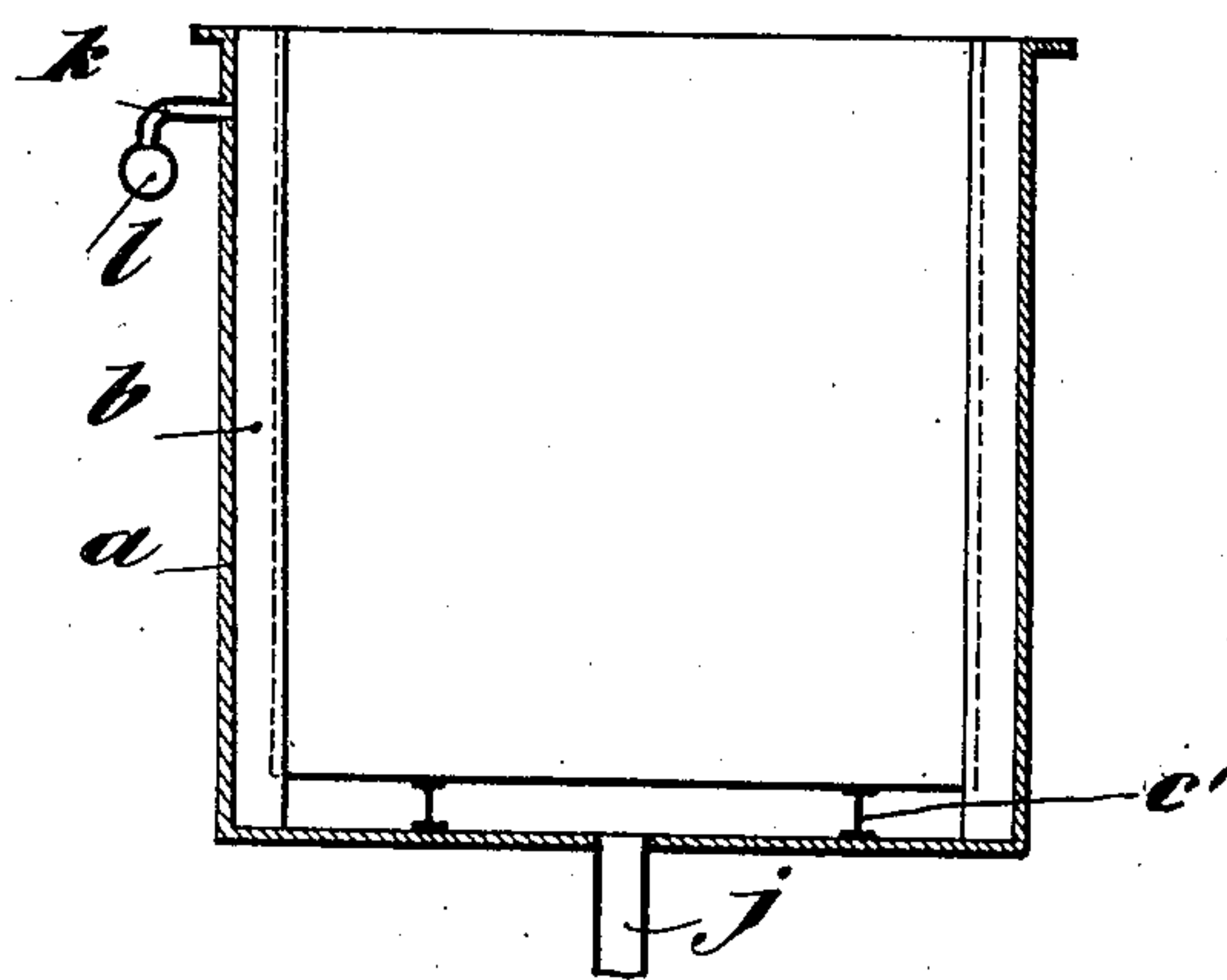
APPLICATION FILED MAR. 12, 1904.

2 SHEETS—SHEET 2.

*Fig. 3.*



*Fig. 4.*



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# UNITED STATES PATENT OFFICE.

HENRI MICHEL GRANIER, OF VILLEMOMBLE, SEINE, FRANCE.

## MANUFACTURE OF SULFATE OF COPPER AND CAUSTIC ALKALIS.

No. 829,778.

Specification of Letters Patent.

Patented Aug. 28, 1906.

Application filed March 12, 1904. Serial No. 197,879.

*To all whom it may concern:*

Be it known that I, HENRI MICHEL GRANIER, a citizen of the French Republic, and a resident of No. 3 Avenue des Ecoles, Villemomble, Seine, France, have invented a certain new and useful Process for the Manufacture of Sulfate of Copper and Caustic Alkalis by the Electrolysis of Alkaline Chlorids, of which the following is a specification.

It is well known that if an aqueous solution of an alkaline chlorid—for instance, chlorid of sodium—be electrolyzed by means of electrodes which are unaffected by the electrolyte soda is produced at the negative pole and chlorin is evolved at the positive pole; but the presence of chlorin and soda, notwithstanding the best diaphragms, give rise to the formation of hypochlorites and chlorates, and in consequence of secondary electrolytic reactions oxygen is evolved at the positive pole and combines with the chlorin to form oxygen compounds of chlorin, which destroy very quickly the anodes and the diaphragms.

Now this invention has for its object to provide an improved process which remedies completely those two drawbacks.

The improved process allows of producing sulfate of copper as well as caustic alkalis.

It consists, substantially, in employing anodes of copper or copper alloys and in employing as the electrolytes an alkaline chlorid at the negative pole and a mixture of alkaline chlorid saturated with cuprous chlorid at the positive pole.

The cathodes may be composed of any material which is not affected by the alkali that is formed—such as, for instance, iron. Under these conditions the chlorin which is evolved at the positive pole forms cuprous chlorid, ( $\text{Cu}_2\text{Cl}_2$ ), which is precipitated in the form of a white powder that is deposited in the path of the positive liquid during the circulation of the latter. The caustic alkali is deposited at the negative electrode, as in the other processes; but in the present process the chlorin is eliminated as soon as it is produced, thereby obviating the formation of oxygen compounds of chlorin. The anodes and the diaphragms are thus no longer destroyed. On the contrary, the consumption of the anodes enters as profit into the manufacture, because it gives rise to an industrial product. In fact, the copper of the anodes combining to form cuprous chlorid ( $\text{Cu}_2\text{Cl}_2$ ) can be converted very easily into sulfate of

copper. The chlorid-of-copper powder is collected and washed in water. In order to obtain sulfate of copper therefrom, it is merely necessary to treat this dry powder with concentrated sulfuric acid up to calcination-point. Hydrochloric acid is evolved and is collected by the ordinary means of condensation, and a white powder of anhydrous sulfate of copper is produced which only requires to be dissolved in water and recovered by crystallization.

In cases where the anodes are composed of alloys (such as copper and zinc) and used with a saturated aqueous solution of cupric chlorid and sodium chlorid the cuprous chlorid will be precipitated and the zinc will remain in solution.

The process may conveniently be carried into effect by means of the improved electrolyzing apparatus illustrated in the accompanying drawings, in which—

Figure 1 is a vertical section thereof. Fig. 2 is a plan, partly in section, on the line A B of Fig. 1. Figs. 3 and 4 are two vertical cross-sections taken, respectively, on the line C D and E F of Fig. 1.

In the figures the same letters of reference indicate the same parts.

As shown in the drawings, the improved electrolyzing apparatus comprises a vessel *a*, composed of cast-iron coated with ebonite or of any other insulating substance, whose longitudinal walls are formed internally with guides *b*, designed to keep the frames *c* in place. Each of these latter is provided on each of its two faces with a diaphragm *d*, so that each frame, with its two diaphragms, forms a compartment for the reception of an anode. The frames *c* are mounted upon any suitable support. By way of example, the I-beams *c'* are shown for such purpose.

The cathodes are arranged in the spaces *e*, comprised between the anode or positive compartments. By this arrangement the anodes are operative on both faces.

The anodes and the cathodes are not shown in the drawings in order to avoid complicating the latter. The positive liquid is supplied in a clear state to the electrolyzer through a supply-pipe *f*, from which are branched small pipes *g*, discharging, respectively, into the lower parts of the several positive compartments, Fig. 3, from which the liquid issues charged with cuprous-chlorid powder through small pipes *h*, that branch off an exit-pipe *i*. The latter con-



veys the liquid into any suitable decanting apparatus, in which the chlorid of copper is deposited in the form of powder and the clear liquid is returned into the electrolyzer.

5 The clear liquid enters through a pipe *j* at the bottom of the vessel *a*, Fig. 4, wherein after circulating freely between the frames *c* it passes out through orifices *k* and is discharged through an exit-pipe *l*. This construction of apparatus is given here merely  
10 by way of example, and it is to be understood that the improved process may be carried into effect by means of any other apparatus.

Having now described my invention, what  
15 I claim as new, and desire to secure by Letters Patent, is—

1. A process for the manufacture of sulfate of copper and caustic alkali, consisting in submitting anodes of copper and cathodes  
20 composed of material that is unaffected by the alkali formed to an electrolyte composed of a solution of alkaline chlorid at the negative pole and of a solution of an alkaline chlorid with cupric chlorid at the positive  
25 pole and in collecting the pulverulent cuprous chlorid formed by the action of the chlorin evolved at the positive pole on the copper of the anodes and converting it into sulfate of copper.

30 2. A process for the manufacture of sulfate of copper and caustic alkali with the production of hydrochloric acid which consists in submitting anodes of copper and cathodes composed of material that is unaffected by  
35 the alkali formed to an electrolyte composed of a solution of an alkaline chlorid at the negative pole and of a solution of an alkaline chlorid with cupric chlorid at the positive

pole, for obtaining caustic alkali at the negative pole and pulverulent cuprous chlorid at the positive pole collecting said cuprous chlorid, washing it in water and treating it with concentrated sulfuric acid and collecting the hydrochloric acid evolved.

3. A process for the manufacture of sulfate  
45 of copper and caustic alkali, consisting in submitting anodes of copper and cathodes composed of material that is unaffected by soda to an electrolyte composed of a solution of chlorid of sodium at the negative pole and  
50 of a saturated solution of chlorid of sodium with cupric chlorid at the positive pole and in collecting the pulverulent cuprous chlorid formed at the positive pole and converting it  
55 into sulfate of copper.

4. A process for the manufacture of sulfate  
of copper and caustic alkali, consisting in submitting anodes composed of a copper alloy and cathodes of a material that is unaffected by the alkali formed to an electrolyte  
60 composed of a solution of an alkaline chlorid at the negative pole and of a saturated solution of an alkaline chlorid with cupric chlorid at the positive pole and in collecting the pulverulent cuprous chlorid precipitated at the  
65 positive pole by the action of the chlorin evolved on the copper of the anodes and converting it into sulfate of copper.

In witness whereof I have hereunto set my hand in presence of witnesses.

HENRI MICHEL GRANIER.

Witnesses:

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ALEXANDE LAMBERT,  
HANSON C. COXE.