

No. 679,824.

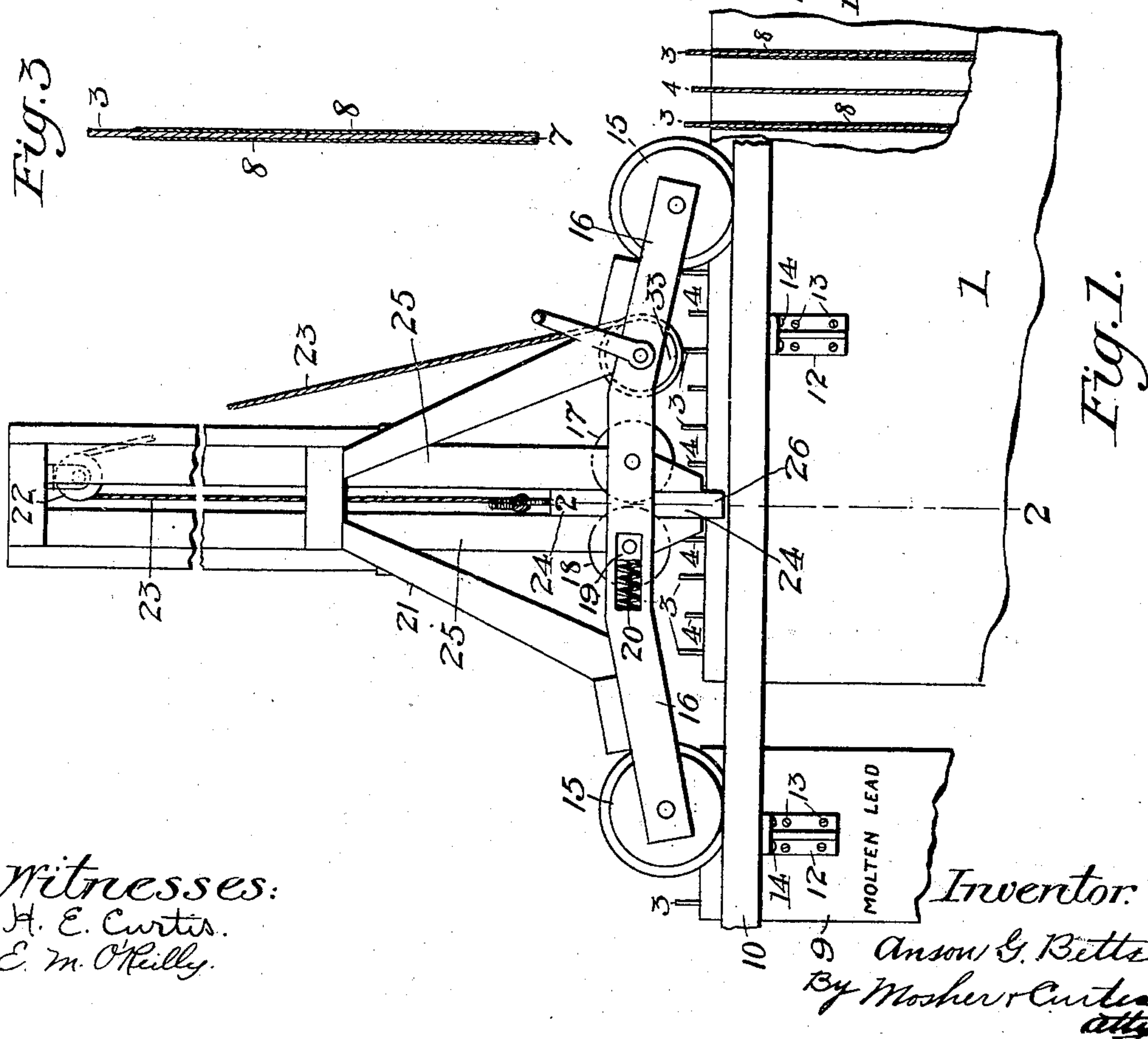
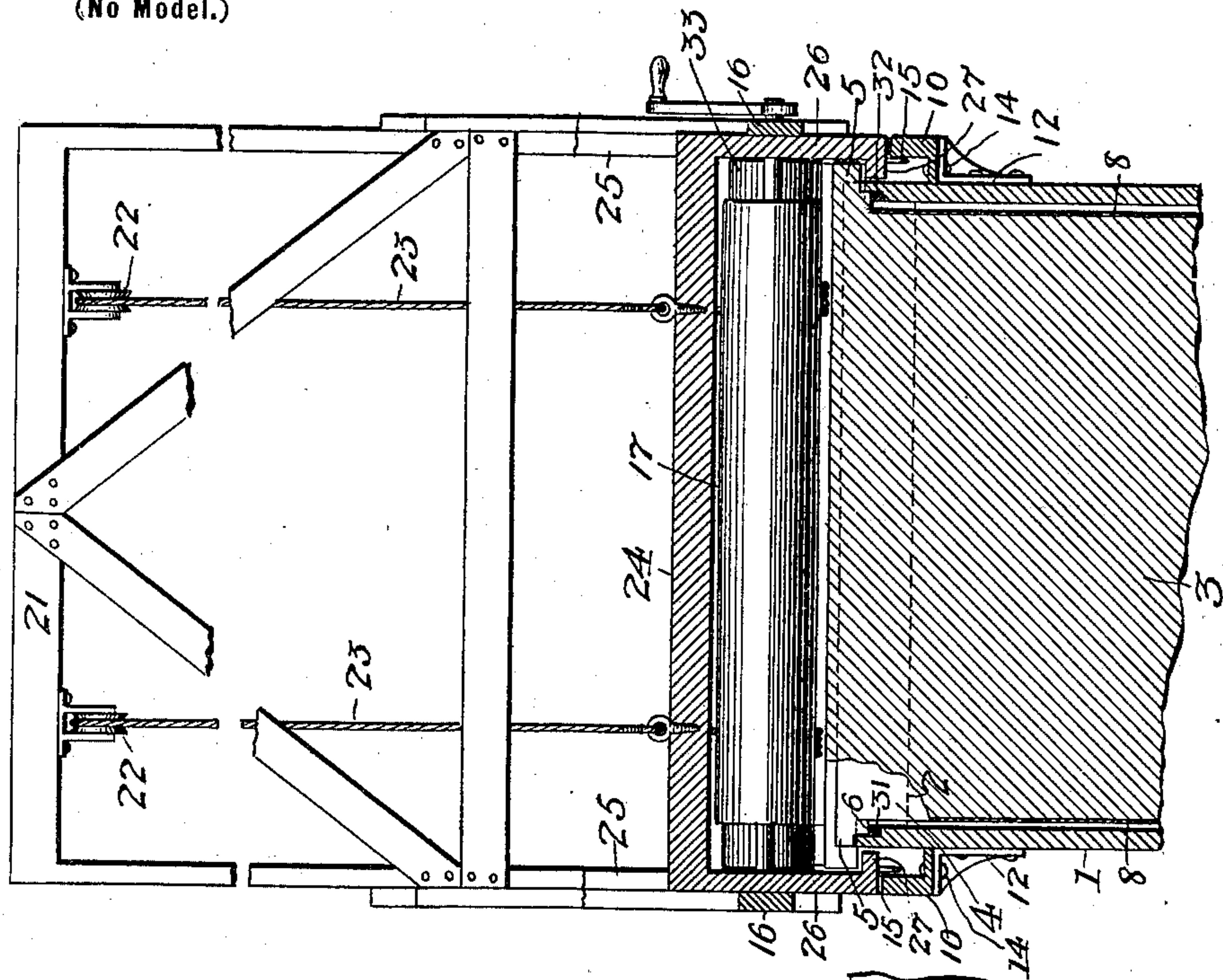
Patented Aug. 6, 1901.

A. G. BETTS.

ART OR PROCESS OF REFINING LEAD BY ELECTROLYSIS.

(Application filed Oct. 12, 1900.)

(No Model.)



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UNITED STATES PATENT OFFICE.

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ART OR PROCESS OF REFINING LEAD BY ELECTROLYSIS.

SPECIFICATION forming part of Letters Patent No. 679,824, dated August 6, 1901.

Application filed October 12, 1900. Serial No. 32,842. (No specimens.)

To all whom it may concern:

Be it known that I, ANSON G. BETTS, a citizen of the United States, residing at Lansingburg, county of Rensselaer, and State of New York, have invented certain new and useful Improvements in Processes of Refining Lead, of which the following is a specification.

Reference may be had to the accompanying drawings, and the reference characters marked thereon, which form a part of this specification.

Similar characters refer to similar parts in the several figures.

This invention relates to improvements in the art or process of refining lead by electrolysis.

The principal objects of my invention are to reduce the amount of electrical energy required for the electrolytic refining of lead and lead alloys and the separation therefrom of pure lead and to carry on such refining without the formation of lead peroxid or other insoluble lead compounds on the anode during electrolysis.

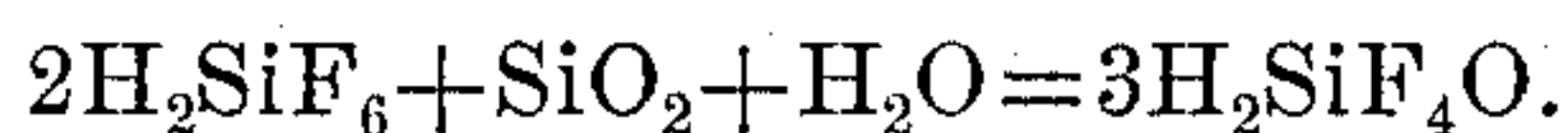
Other objects of my invention are to get the electrodeposited lead into such condition that it may be subsequently fused without loss by mechanically compacting from time to time during the progress of electrodeposition the electrodeposit upon the cathode.

My invention consists of the process of subjecting the lead alloy as anode to an electric current in a solution of a lead salt of a fluorin acid and simultaneously electrodepositing pure lead on the cathode.

The invention further consists in the use of a cathode comprising a metallic core coated with lead and having greater tensile strength and a higher fusing-point than lead; also, in subjecting the electrodeposit on the cathode to a mechanical pressure from time to time during the progress of electrodeposition and after the electrodeposition is concluded in subjecting the electrodeposit to sufficient heat to remove it by fusion from the core, all as hereinafter more fully described, and pointed out in the claims.

By the term "fluorin acid" I mean to include all the acid-fluorin compounds of those acid-forming elements which are less easily separated from their solutions by electrolysis

than lead is. A fluorin acid is defined as an acid which may be derived from an oxygen acid by the simple replacement of the oxygen wholly or in part by fluorin, two atoms of fluorin replacing one of oxygen. The fluorin acid of silicon, for instance, may be derived from silicic acid and water (SiO_2 and H_2O) or H_2SiO_3 by replacing oxygen by fluorin, resulting in fluosilicic acid, (H_2SiF_6 .) I have ascertained by experiment that a solution of a lead salt of such an acid constitutes an electrolyte which can be used for the electrolytic refining of lead with the consumption of a small amount of electrical energy, the electrolysis of which in electrically refining lead will not cause the production of any lead peroxid on the anode and which is itself not subject to decomposition or deterioration by secondary electrolysis. Further, the lead salts of such fluorin acids are very soluble in water and their solutions afford electrolytes of high conducting power. The acid fluorin compound of silicon or fluosilicic acid, (H_2SiF_6 .) often called "hydrofluosilicic acid," which may be made by the simple solution of silica or quartz in hydrofluoric acid, is the fluorin acid which I prefer to use in carrying out my improved process. The hydrofluosilicic acid may contain some silicic acid (SiO_2) without materially affecting the result, such silicic acid probably being in combination with fluosilicic acid in the form of an oxyfluosilicic acid, ($\text{H}_2\text{SiF}_4\text{O}$.) The equation representing its formation would be



I prefer to have the electrolytic solutions strongly acid from the presence of an excess of fluosilicic acid, which prevents the formation of basic insoluble salts and results in a higher electrical conductivity. A solution of lead fluosilicate and fluosilicic acid, in which about half the acid is combined with lead as fluosilicate and in which the acid and lead salt amount together to about twenty-five per cent., offers a resistance to the electric current of about one and two-tenths ohms per column of solution one inch long and one square inch cross-sectional area. This is believed to be much less than that of any electrolyte heretofore used for the purpose of

refining lead and effects great economy in the electrical energy required to carry out the process.

My process of refining is especially applicable to "work-lead," which usually contains such substances alloyed with it as gold, silver, copper, antimony, arsenic, sulfur, bismuth, nickel, iron, zinc, and tin.

In addition to the comparative cheapness of the fluosilicic acid, its stability under the electrolytic influence, and the high conducting power of the solutions made with it there is another advantage in its use not possessed by any acid hitherto used as the basis of an electrolyte, due to the nature of the chemical reactions taking place at the anode.

Lead has a great tendency to form peroxid under oxidizing influences, such as the influence of an electric current on or in the neighborhood of the positive electrode or anode. This tendency manifests itself most strongly in alkaline solutions and to a considerable extent in weakly-acid solutions. Opposed to this tendency is the other one of lead oxid to form salts with acids due to the basicity of this oxid. Considering the lead on the anode by an electrochemical theory, oxygen is there evolved by electrolysis and combines with lead to form lead oxid, and this substance being in an oxidizing zone will either combine with more oxygen to produce the insoluble peroxid or with the acid present to form a salt. Therefore the more acid the character of the electrolyte the greater the tendency of the lead to go into solution properly. With chlorids or solutions containing fluorin acids the action is properly not "oxidizing," but it amounts to the same thing. The use of a strong acid as the basis of an electrolyte is highly desirable in refining lead by electricity, as the production of lead peroxid is very unfavorable to the refining operation. The formation of peroxid requires the consumption of electrical energy and diminishes the supply of lead in the solution, as lead continually deposits on the cathode whether it dissolves at the anode or not, which impoverishment would very soon render the solution useless. Did the common strong acids—sulfuric and hydrochloric—form soluble lead salts, the refining of lead would probably be carried on with solutions of such salts. The other common strong acid—nitric acid—produces a sufficiently soluble salt; but the oxidizing influence of the current with a solution of such a salt is so enhanced by the oxidizing action of the acid itself that lead peroxid is easily separated from such a solution. Solutions containing lead acetate have been used as electrolytes; but the weakness of acetic acid, combined with its susceptibility to continuous oxidation by the peroxid formed and its decomposition by secondary electrolysis, and the low-conducting power of acetate solutions have proven great obstacles in its use. Not only is there loss of acetic acid by electrolytic decomposition and oxidation, but such

decomposition requires the expenditure of extra electrical energy. I have ascertained that the great acidity of the fluorin acids of elements such as silicon, boron, and titanium is sufficient to prevent any formation of lead peroxid at the anode, for in a large number of experiments I have never been able to discover the presence of the peroxid. I have been able to carry on continuous electrolysis with a difference in potential between anode and cathode of from eight to ten hundredths of a volt—about one-fifth of that required to send the same current strength per unit cross-sectional area through the same thickness of a layer of an electrolytic solution of the best acetate compound—double lead potassium acetate—requiring, consequently, about one-fifth the amount of power to do the same work.

After the process of electrodepositing lead upon the cathode has gone on for some time the metallic lead so deposited assumes a loose, rough, and uneven form and crystals of lead may project from the mass sufficiently to reach from the cathode-surface to its neighboring anode-surface, forming "bridges" or "connections" which connect them and make a short circuit. Should the bridging or connections become complete, the process would be interrupted before the cathode received the desired amount of deposit. I overcome this difficulty by subjecting the deposit on the cathode to mechanical pressure, which compacts the deposit without removing any part from the cathode and gives it a smooth and brilliant surface. For the reason that lead deposits more densely on a smooth than on a rough surface this compacting operation serves the double purpose of preventing the surface from becoming rough enough to favor the formation of bridges or projecting crystalline connections and of making the deposit compact enough for subsequent fusion without loss from the formation of dross. Should bridges or connections have been formed, the pressure will reduce the same to approximately the level of the smooth surface. Since the deposited lead is very pure and clean, free from hydrogen and other gases and protected from the air by the solution, the surfaces of the lead crystals are kept perfectly free from dross or other earthy or non-metallic substances by the acidity of the solution, and the crystalline mass of soft lead is changed by moderate pressure into a sound, dense, and homogeneous mass by the inner surfaces of the crystals uniting together and the flowing of the lead to form solid metal. The refining process is continued after the mechanical pressure has been applied with as good results as with a fresh cathode, and the pressing operation may be repeated as frequently as desired until a sufficient load has been deposited upon the cathode, after which the cathode is removed from the solution and denuded of its deposit. Compacting the electrodeposited lead immediately after

removal from the solution is of great importance. If the lead so deposited were removed in its incompact state without quickly pressing, oxidation would soon tarnish the surfaces of the crystals, after which the compacting process would no longer be practicable. Fresh lead surfaces oxidize so rapidly that on drying such a porous mass preparatory to fusion oxidation would occur to a serious and harmful extent. Further, the pores would carry away in them considerable solution, which would not only be lost, but result in the production of more dross.

In carrying out my process I prefer to make use of a cathode consisting of a core of metal which is cheaper and much stronger than lead and which is not fusible except at a much higher temperature than the fusing-point of lead, such as iron or steel coated with lead. The iron or steel having a much greater tensile strength than lead can be made in belt, sheets, or thin plates, which when coated with lead will form as good a cathode for carrying out my improved process as would thicker and heavier pieces of solid lead. By thus providing the cathodes with a core of metal that is infusible as compared with lead the lead which is electrodeposited thereon in carrying out my process can be removed therefrom by fusion—that is, by applying sufficient heat to melt off the electrodeposit—without detriment to the original cathode. As a preferred means for removing from the cathode the lead electrodeposited thereon I pass the cathode into melted lead and support it therein until the electrodeposit fuses, after which the cathode is removed from the melted lead, leaving the electrodeposit therein. When the cathode is removed from the bath of melted lead, a sufficient quantity of the lead will remain adhering to the cathode-piece to make a proper coating on the inner core to protect it from the action of the acid solution and to form a surface suitable to receive the deposition of more lead derived from the anode of lead alloy being treated when the refining process is resumed.

The original cathodes or any which may have had the inner core exposed by removal of the surface coat of lead may be prepared for use by dipping the well-cleaned plates in lead melted at a low temperature, on the surface of which floats a layer of zinc chlorid or other cleansing or fluxing salt, or in any known manner. This layer serves the purpose of effectually cleansing the metallic surface as it passes through into the lead.

The relative amounts of lead fluosilicate and fluosilicic acid in the solution may vary according to the amount of work required to be accomplished by a given expenditure of power. Fifteen per cent. of lead fluosilicate in the solution will be sufficient for all strengths of current up to the practical limit. When for economical reasons it is desirable to have a minimum electrical resistance in

the solution, the proportion of fluosilicic acid only should be increased, as the acid conducts better than the salt.

The porous or slimy residue left at the anode as the lead dissolves away consists mainly of the impurities originally present. It generally becomes gradually detached and falls to the bottom of the electrolyzing vessel or into receptacles placed to receive it, from which it is collected for further treatment.

By the term "lead alloy" I include the lead to be refined, together with all impurities or foreign substances which may be associated with it.

Agitation of the electrolyte is necessary to the successful practice of any electrolytic process for refining metals using solutions as electrolytes. I have not shown any mechanism for securing such agitation, as any of the well-known methods may be employed.

In the accompanying drawings I have shown all the apparatus necessary to enable any one skilled in the art of refining metals by electrolysis to fully understand and practice my improvements in the art of refining lead, in which—

Figure 1 is a side elevation with portions of some members broken away. Fig. 2 is a vertical cross-section of the same, taken on the broken line 2 2 in Fig. 1. Fig. 3 is a cross-sectional view of one of the cathodes detached.

The vat 1 contains the solution forming the electrolyte, which may fill the vat up to the dotted line 2 in Fig. 2. The cathodes 3 and anodes 4 are suspended in the solution by means of the projecting ears 5 and 6, which rest upon the upper edges of the side walls of the vat.

Referring to Fig. 3, 7 is the core of iron and 8 the coating of lead.

The vat 9 is adapted to receive molten lead, which may be poured into the vat or supplied in any known manner. The vat is made of some metal or other material able to resist the heat of the molten lead. Vat 1 is made of wood or other acid-proof material. The opposite sides of the vats are provided with a rail 10, supported by a bracket 12, secured to the side walls of the vats, as by screws 13. The rails are in the form of angle-irons, the horizontal flanges resting upon the brackets and being secured thereto, as by the bolts 14. The vertical flanges of the oppositely-disposed rails form a track adapted to support the wheels 15 of a traveling truck 16. This truck is provided in its main horizontal frame with a pair of parallel horizontal rolls 17 and 18, one of which is journaled in slide-bearings 19, controlled by springs 20, which tend to press such roll toward the other roll. Mounted upon the truck is an upright frame 21, to the upper part of which are secured the pulleys 22, over which pass the ropes or cables 23. One end of each cable is secured to the vertically-movable frame 24 and the other end to the windlass 33, supported by the main frame.

The vertically-movable frame is guided by the uprights 25, which form a slideway for such frame. The vertical end members 26 of the movable frame are each provided at 5 their lower ends with an inwardly-projecting arm 27, adapted to engage the ears of the cathodes, so that the operation of the windlass will lift the cathodes from the solution and up between the rolls 17 and 18, and there- 10 by effect the mechanical pressure, hereinbefore referred to, to give the cathodes a smooth and compact surface. The cathodes will, under the control of the windlass, pass down between the rolls by gravity when returned 15 to the solution. When it is desired to remove the electrodeposit by fusion, as before described, the cathodes are drawn up between the rolls by the windlass and the truck is then moved along its track until the rolls 20 are over the vat containing the molten lead, whereupon the cathode is lowered into the molten lead, where it is allowed to remain until the fusion is complete, after which it is lifted by the windlass from the molten lead 25 and lowered again to its original position in the electrolytic solution when sufficiently cool.

It is obvious that the mechanism may be duplicated so that a plurality of cathodes could be pressed or fused at the same time. 30 I do not desire to be limited to the use of any specific kind of mechanism in practicing my invention.

The anodes are preferably given a form, by casting or otherwise, similar to that of the 35 cathodes.

The electric conductors and means for producing electric currents being old and well-known are not shown, except the conductor 31, which supports the anodes, and the con- 40 ductor 32, which supports the cathodes. These conductors may be copper rods resting on the upper edges of the vats.

The rolls 17 and 18 are preferably made of porcelain or other acid-proof material.

It is obvious that in practicing my inven- 45 tion the form and arrangement of apparatus employed may be varied as desired.

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

1. That improvement in the art of refining 50 lead by electrolysis which consists in subjecting the lead alloy as anode to an electric current in a solution of a lead salt of a fluorin acid, and electrodepositing the lead on the cathode, substantially as described. 55

2. That improvement in the art of refining lead by electrolysis which consists in subject- 60 ing the lead alloy as anode to an electric current in a solution of lead salt of a fluorin acid of silicon and electrodepositing the lead on the cathode, substantially as described. 65

3. That improvement in the art of refining lead by electrolysis which consists in subject- 70 ing the lead alloy as anode to an electric current in an electrolyte containing lead salt, electrodepositing the lead on a cathode consisting of a metallic core comparatively infusible and coated with lead, and removing such electrodeposit from the cathode by fu- 75 sion, substantially as described.

4. That improvement in the art of refining lead, which consists in alternately electro- 80 depositing, and compacting by mechanical pressure, lead upon a cathode consisting of an infusible core of great tensile strength, and removing the compacted electrodeposit 85 from the cathode by fusion.

In testimony whereof I have hereunto set my hand this 6th day of October, 1900.

ANSON G. BETTS.

Witnesses:

GEO. A. MOSHER,
FRANK C. CURTIS.