No. 898,404. PATENTED SEPT. 8, 1908.

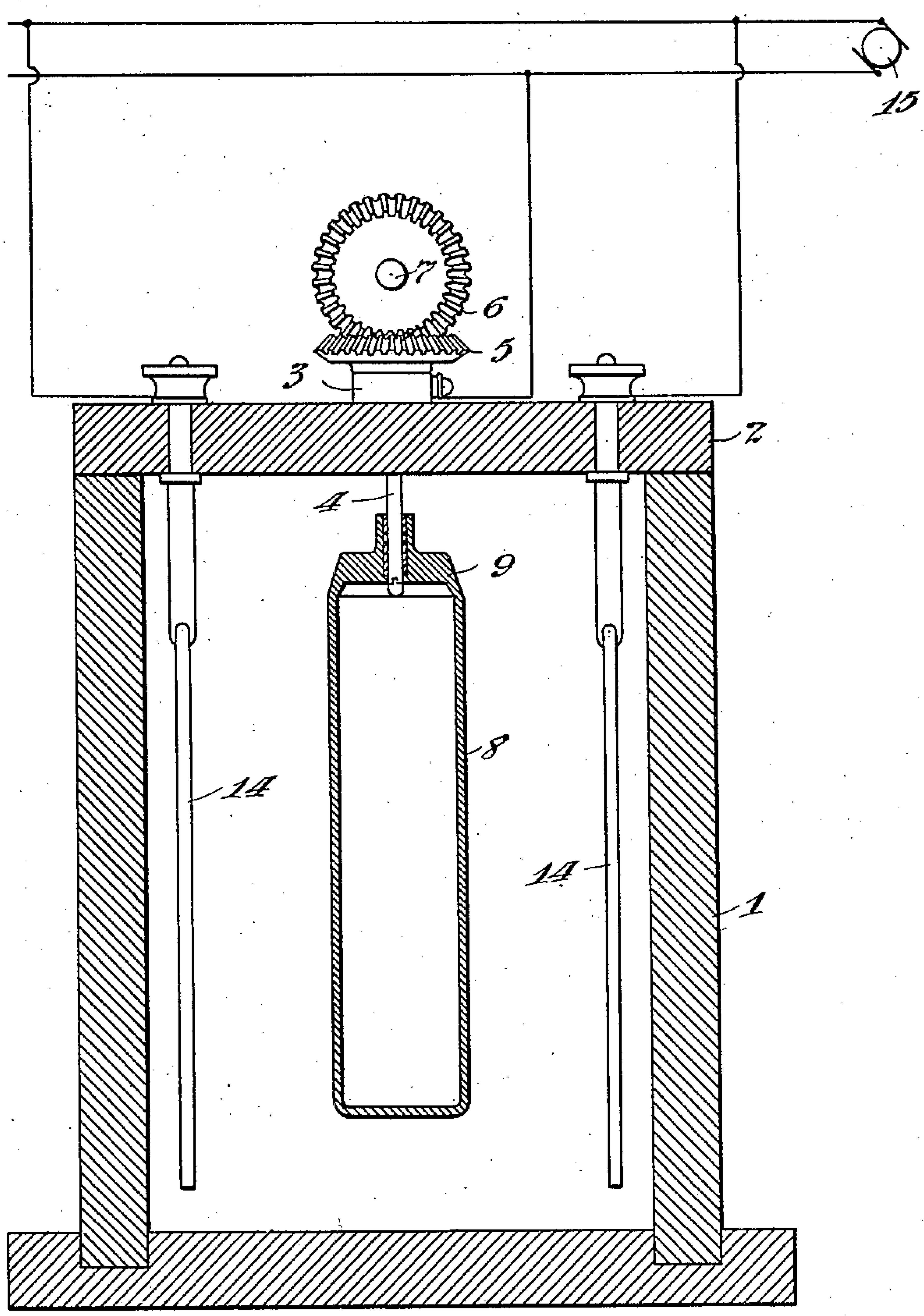
T. A. EDISON.

PROCESS OF MAKING ARTICLES BY ELECTROPLATING.

APPLICATION FILED NOV. 3, 1906.

2 SHEETS—SHEET 1.

Fig. 1



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2 SHEETS—SHEET 2.

Fig. 2

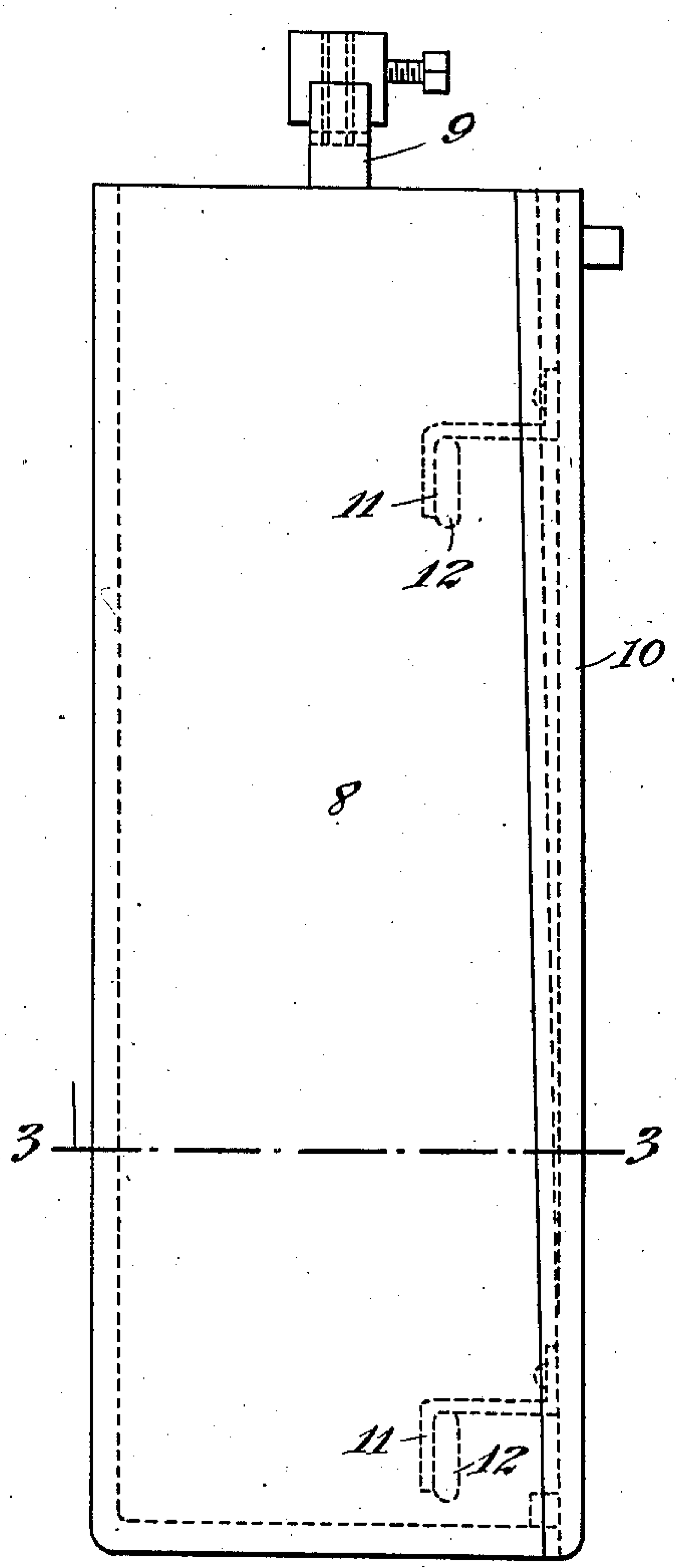


Fig. 3

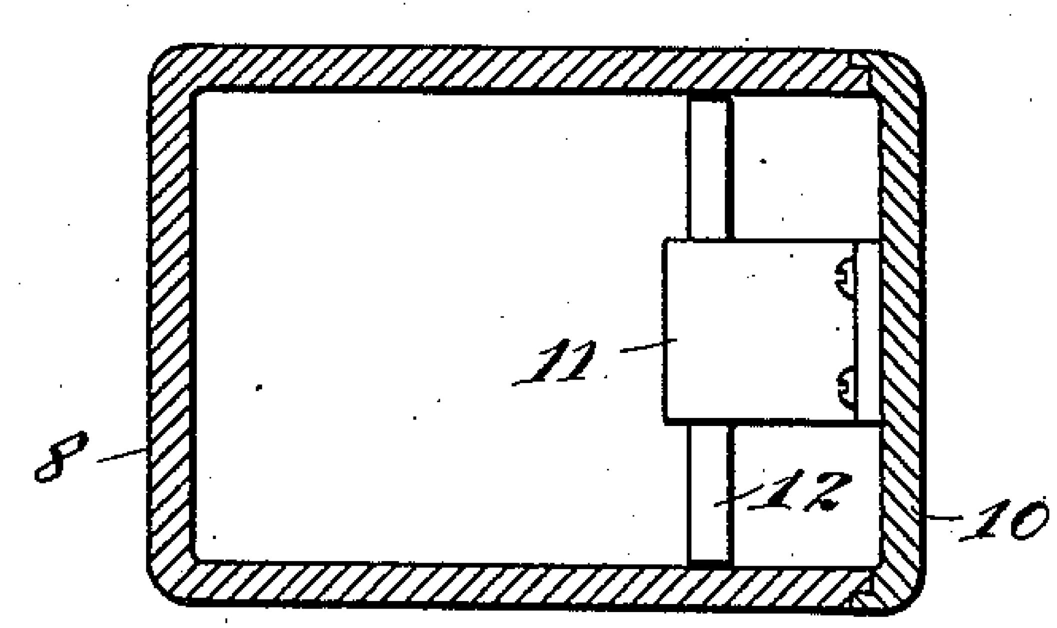
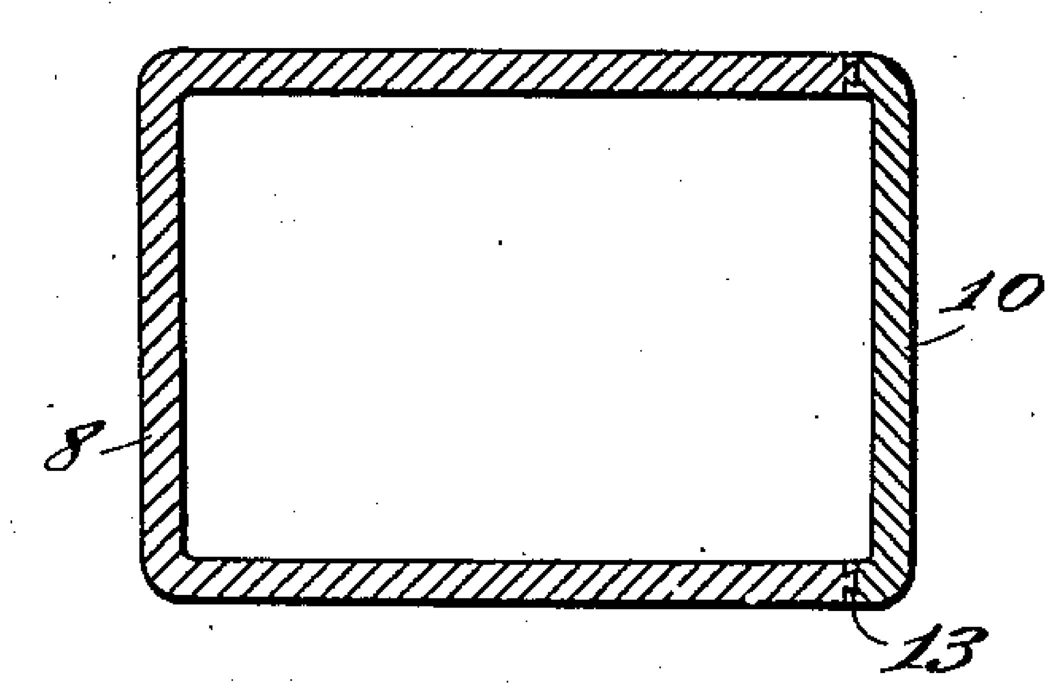


Fig. 4



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UNITED STATES PATENT OFFICE.

THOMAS A. EDISON, OF LLEWELLYN PARK, ORANGE, NEW JERSEY, ASSIGNOR TO EDISON STORAGE BATTERY COMPANY, OF WEST ORANGE, NEW JERSEY, A CORPORATION OF NEW JERSEY.

PROCESS OF MAKING ARTICLES BY ELECTROPLATING.

No. 898,404. Specification of Letters Patent. Patented Sept. 8, 1908.

Original application filed October 5, 1903, Serial No. 175,818. Divided and this application filed November 3, 1906. Serial No. 341,861.

To all whom it may concern:

Be it known that I, THOMAS A. EDISON, of Llewellyn Park, Orange, in the county of Essex and State of New Jersey, have invented certain Improvements in the Process of Making Articles by Electroplating, of which the following is a description.

This application is a division of Patent No. 850,912, granted April 23, 1907.

My invention relates to an improved process for making articles by electro-plating, and, particularly, for making cans or receptacles for use with storage batteries of my improved type, and as I describe in Patent No. 857,041, granted June 18, 1907. The process has been gotten up especially with the object in mind of making such cans or receptacles of iron, but it may be carried out for the manufacture of other articles and from other metals or combinations thereof.

The particular value of a can or receptacle for storage batteries made by a plating process, as I shall describe, resides in the fact that such an article is entirely seamless, so that the necessity is done away with of employing solder, which may be affected by the alkaline electrolyte used with such batteries. The problem of making a storage battery can or receptacle, or other essentially hollow article, by a plating process of iron, presented very great practical difficulties, since such metal during a plating operation tends to contract, and, unless special provision is made to overcome the same, the contraction will result in the metal cracking or scaling from any molds or forms on which it may be plated. Furthermore, in the plating of iron, the formation of gas bubbles would result in the deposited coating being pitted or actually perforated, which would of course, destroy the utility of the completed article. Furthermore, an electro-deposited coating of iron is extremely weak and brittle in nature, and articles made therefrom without subsequent treatment would not be available for commercial use. The process which I have invented and which will be presently described has been evolved after a long series of experiments, and results in the production of a plated article, such as a battery can or receptacle, which may be made of iron, which will be perfectly smooth and coherent throughout, being entirely free of pits or holes, and which, when finished, is very strong and tough.

In order that the invention may be better understood, attention is directed to the accompanying drawings forming a part of this specification, and in which:

Figure 1, is a cross-sectional view, taken through one of the plating tanks which is used in carrying my process into effect, the assumption being made that the articles which are to be produced are one piece battery cans or receptacles; Fig. 2, a separate side elevation of the mold or former used in the manufacture of such cans or receptacles; Fig. 3, a cross-sectional view on the lines 3—3 of Fig. 2, looking downwards; and Fig. 4, a view corresponding to Fig. 3, showing a modification.

In all of the above views corresponding parts are represented by the same numerals of reference.

In the carrying of my process into effect, and in the preferred embodiment thereof, I make use of three plating tanks in which distinct plating operations take place. I prefer to use three separate tanks in order that the operations may be continuous, so that while one plating is going on in one tank a succeeding plating may be taking place in another tank, and so on. It will, however, be understood that the same tank may be used for the several platings, although in that case it will obviously have to be cleaned out and a fresh solution used for the subsequent plating operations. The several tanks used may be all of the same construction, so that a description of one will suffice for all.

The tank 1, is in the form of a long, open trough, having one or more wooden cross-pieces corresponding to the several molds or formers which may be used therein. Each cross-piece 2, is formed with a bearing 3, in which is mounted a vertical shaft 4, having a bevel-gear 5, at its upper end. Meshing with each of the gears 5, is a bevel-gear 6, on a longitudinal shaft 7. In this way it will be obvious that a plurality of the shafts 4, may be driven from the same main shaft. Each of the molds 8, is made of the proper form or shape, being composed preferably of brass or copper, and being hollow so as to be as light as possible. Each mold is provided with a bridge-piece 9, at its upper end, with which the lower threaded end of the shaft 4, engages, so that the mold will be rotated by said shaft. Each of the molds is provided with a removable section 10, which may be separated from the main portion of the mold to facilitate the removal of the completed article, as will be explained. The removable section 10, of each mold may be normally held in position in any suitable way, as, for example, by means of a hook 11, engaging over a bridge-piece 12, (as shown in Figs. 2 and 3), or by a dove-tailed joint 13, between the two sections, (as shown in Fig. 4). The mold 8, constitutes the cathode of the plating bath, suitable anodes 14, being arranged therein, and being connected with a suitable source of supply 15, either a battery or plating dynamo. The mold 8, is preferably slightly tapered towards its lower end to facilitate the removal of the completed article. This taper may be very slight indeed, and need not be more than one-sixteenth of an inch.

Assuming three plating baths to be employed and the preferred process to be carried out in connection with the manufacture of battery cans or receptacles of iron, I proceed substantially as follows: The mold is first dipped in melted paraffin wax maintained at a temperature of about one hundred degrees centigrade, so as to coat the mold with a very thin layer thereof. This layer need not be more than .005 to .025 inch in thickness. After the wax layer has cooled and congealed I apply thereto a conducting material in finely divided form, preferably graphite, so as to entirely coat the mold, the coating of wax being so thin that the graphite apparently makes contact through the same with the mold. I prefer to make use of a preliminary coating of wax, as explained, since this not only facilitates the application of the graphite, but also permits the article, when finished, to be readily removed. The coated mold is now placed in a copper bath with copper anodes, and is copper-plated to a thickness of about .004 inch, more or less. The solution used may be the ordinary copper sulfate ($CuSO_4$) solution.

After the plating of copper has been applied the mold is removed and washed and introduced into a second tank having a nickel plating solution therein. Any suitable solution may be employed, such as a nickel-ammonium sulfate solution. In this bath the mold is plated with an extremely thin coating of nickel, about .001 inch in thickness. The mold is then removed and washed and put into the third tank employing iron electrodes, and having a solution consisting preferably of ferrous-ammonium sulfate $Fe(H_4N)_2(SO_4)_2$. It is important that this iron solution should be absolutely n utral and free from ferric salts, since the presence of any traces of acidity, or of ferric salts, affects the character of the plating, making it very brittle, and causing it to scale or flake off of the mold. It will be understood that a solution of ferrous sulfate may alone be used, but I prefer to use ammonium sulfate therewith, as in this way the conductivity of the bath will be increased while the coherence and smoothness of the resulting coating of iron will be very materially improved. The solution used may be from twelve per cent. to fifteen per cent. of the double salt. In order that the possibility of the bath becoming acid may be prevented, I preferably add small quantities of ammonia or other alkali thereto at suitable intervals. The plating of iron is effected preferably by a current of about 1 to 1.2 amperes per square decimeter of surface. The plating of iron is continued for from thirty to thirty-five hours at a temperature of not below forty degrees centigrade, thereby giving a coating about .020 inch in thickness. If the bath is materially cooler than this, say at the ordinary temperatures, I have found from my experiments that the deposit tends to crack after a few hours. It will, of course, be understood that when heavier or lighter layers of iron require to be deposited, the time during which the coating takes place will be proportionately increased or diminished.

In order to prevent the formation of pits or holes in the deposited iron coating, which would be likely to form by the accumulation of gas bubbles thereon, and to secure a very smooth surface, I introduce a quantity of crushed charcoal into the solution, whereby the added material will rub over and scour the surface of the deposited metal to polish the same and wipe off any gas bubbles which may tend to accumulate thereon. Furthermore, I find that a small percentage of carbon will in this way be incorporated with the deposited iron, which, therefore, in the subsequent annealing, is converted practically into a superior product of soft steel, containing, according to my analysis, almost .4% of carbon. As a result the finished article is considerably tougher and more rigid than when made of pure iron. Such particles of charcoal may vary in dimension between one-sixteenth to one-eighth of an inch in size. Of course, it may be possible that other materials may be used for this purpose, but I have found that charcoal is very desirable for this use. The amount of charcoal which is thus added to the solution may obviously vary within quite wide limits, but good results are secured when the bulk of charcoal introduced is about one-half the bulk of the solution, so that if the charcoal is allowed to float it will form a layer extending about half the thickness of the solution in the tank. During the iron plating the mold is revolved at a speed of about ninety turns per minute, but this speed is also variable and need not be strictly adhered to.

After a plating of iron of the desired thickness has been formed on the mold, the latter is removed from the tank, and washed in water at a temperature of about seventy-five degrees centigrade, thereby melting the wax originally deposited on the mold, after which, by removing the removable section of the mold, the resulting casing or can or other article can be separated therefrom, as will be understood. Iron which has been thus plated on a mold is extremely brittle, and, in order that it may be made tough and strong, I prefer to anneal the same. For this purpose the articles, after plating, are introduced into a closed retort and heated to a red heat, being then allowed to slowly cool. Preferably this heating of the articles is effected in a non-oxidizing atmosphere, such as in an atmosphere of hydrogen gas, so as to remove any possibility of oxidizing, and, after annealing, the articles are allowed to cool in the same atmosphere. In the case of storage battery cans or receptacles, it is necessary that the copper originally deposited on the graphite should be removed, since this metal is slightly soluble in an alkaline electrolyte in the presence of electrolysis. This removal of the original copper coating is preferably effected by filling the can or receptacle with a solution of a mixture of copper nitrate $Cu(NO_3)_2$ and sodium nitrate ($NaNO_3$), or sodium nitrate can alone be used in the solution. The can or receptacle is now used as an anode of a plating bath, a copper cathode being introduced therein and a plating current applied. When the solution contains copper nitrate, as is preferable, the copper will be plated off from the inside of the can or receptacle and be recovered on the cathode; but when sodium nitrate is alone used the copper thus removed forms insoluble copper hydrate, which can be recovered from the solution in any suitable way. I prefer to apply a preliminary coating of copper, since I find that the iron tends to crack after a few hours plating, owing to its tendency to constantly contract, and the copper appears to offer a base or foundation on which the iron is deposited and which resists the tendency to contraction. The deposit of nickel is applied to the copper in order that the final article may be provided with a nickel interior. This is of importance in connection with cans or receptacles for storage batteries, in order that the iron may be protected from the effects of any erratic electrolytic action in the alkaline solution.

After the copper coating has been removed, as explained, the article is trimmed on its upper edge ready to receive the cover or cap, and, if desired, its sides may be provided with horizontal corrugations located within the edges of the can so as to stiffen the same, as I describe in my Patent No. 852,424, granted May 7, 1907. Finally, the can or receptacle is nickel-plated on its outside so as to protect the same from oxidation, and, if desired, an additional coating of nickel may be applied to the inside thereof and welded thereto. The can or receptacle is now finished, and is ready to receive the electrodes, after which the top or cover is soldered in place. Cans made in this way can be manufactured very cheaply, they are of superior appearance, they are very strong and tough, they are free from pits or holes, they do away entirely with the necessity of using solder joints, and they are well suited for the purpose for which they are designed. When articles of other forms or of different materials are made, the process will be modified as will suggest itself to persons skilled in the art.

Having now described my invention, what I claim as new therein and desire to secure by Letters Patent is as follows:

1. The process of making a storage battery can or receptacle, which consists in electro-plating a coating of copper on a former, in electro-plating a film of nickel on the copper coating, and in electro-plating a film of iron on the nickel film, whereby a seamless article will be produced, substantially as set forth.

2. The process of making a storage battery can or receptacle, which consists in electro-plating copper on a former, in electro-plating a film of nickel on the copper coating, in electro-plating a film of iron on the nickel coating, and in finally removing the copper deposit, whereby a seamless can or receptacle having a nickel-plated interior will be formed, substantially as set forth.

This specification signed and witnessed this 2nd day of November, 1906.

THOMAS A. EDISON.

Witnesses:
FRANK L. DYER,
ANNA R. KLEHM.