

UNITED STATES PATENT OFFICE.

LUDWIG HÖPFNER, OF BERLIN, GERMANY.

PROCESS OF OBTAINING POROUS METALS BY ELECTROLYSIS.

SPECIFICATION forming part of Letters Patent No. 585,359, dated June 29, 1897.

Application filed October 5, 1896. Serial No. 607,882. (No specimens.)

To all whom it may concern:

Be it known that I, LUDWIG HÖPFNER, a subject of the German Emperor, residing at 6 Anhaltstrasse, Berlin, Germany, have invented certain new and useful Improvements in Processes of Obtaining Porous Metals by Electrolysis; and I 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.

Many metals, such as lead and copper, when used for certain special purposes, particularly in electrical storage batteries, prove more valuable if they can be employed in a porous state without sacrificing their strength or cohesion.

The object of the method herein described is to precipitate metals by electrolysis, either in the same electrolytic process by which they are obtained or refined or, if preferred, in a bath specially prepared for the purpose, in such a manner that they combine the property of cohesiveness with great porosity.

The daily practice of electroplating has shown that the structure of metals separated by electrolysis depends upon many conditions—viz., the qualitative composition of the bath, the concentration, temperature, and motion of the electrolyte, and particularly the density of the current. By a proper adjustment of these conditions it is always possible, for instance, to obtain a porous precipitate of the metal, while in the case of non-compliance with these necessary conditions the metal must be precipitated in a compact form. By the term "porous state" I mean a state in which the several metallic particles adhere to each other at one or more points in such a manner that between the particles in contact there remain hollow spaces or interstices. This term, therefore, covers, besides precipitates in the form of powder, matter precipitating in the form of threads, leaves, or moss, such as is obtained in dealing with lead. The main feature of this method for obtaining sufficiently cohesive porous metals by electrolysis is that the metal is precipitated alternatively in a porous form and in a compact state in regular rotation. In the stage of precipitation of porous metal thin-walled pores are produced, while in the compact pre-

cipitates the walls of the pores become more solidified.

The means for securing such alternate precipitation consists in changing (in the proper order of succession) one or the other of the conditions above named, as will be fully explained farther on. As there are several such conditions it might be supposed that there are also several different methods derivable therefrom necessitating a different treatment in each case; but inasmuch as the conditions referred to are inseparable from each other, since in determining the density of the current, for example, the qualitative composition of the bath and the concentration and temperature of the electrolyte must always be taken into account, this method, although the form in which it is carried out may vary in its general bearings, presents one complete and connected whole.

A few specific examples may serve to illustrate the process.

To obtain porous copper, the ordinary solution of sulfate of copper used in electroplating may be employed. By starting with a dense current (exceeding four hundred amperes per square meter at the ordinary temperature) copper in the form of powder is first obtained, and a current of less density is then allowed to follow until the dark color of the precipitate changes into the well-known light-red hue of copper obtained by electrolysis. The current is then again increased to obtain copper in powder, which upon the current being once more reduced becomes a porous mass, and this regular alternation is continued. If it be desired to work with a smaller current, generally a less concentrated solution is used. In the case of lead the method is similar. However, it is preferable to precipitate lead in leaf or moss-like crystals instead of in powder. The suitable current in this case is an intermediate one between the current required to obtain spongy (powdered) lead and that which should be used to produce compact metal. Such current is allowed to act for some time. Then its density is reduced in order that the leaves, which at first are very soft, may become more firm.

An application of the process with a view to obtaining porous metal by a regular alterna-

tion of porous and compact metallic precipitates consists in a regular alternation of two equally different and distinct densities of current, one yielding porous and the other compact or solid metal. The absolute density of the currents to be applied from time to time is best determined for each bath of a certain composition, concentration, and temperature by experiment. It may be stated that a single alternation of the current is sufficient to obtain a stratum of porous metal, and the number of alternations is determined by the thickness of the porous metal which may be required in each particular case.

It has been stated that if it be desired, for example, to work porous copper with currents of great density the ordinary bath of a solution of sulfate of copper is suitable, but that a less concentrated bath should generally be employed in the case of currents of less density. Now this, for one thing, involves the following alteration in the process: Instead of changing the density of the current for a solution of the same degree of concentration the density of current may be left unaltered and the change be effected in the concentration of the solution, as it has been ascertained by special tests that the structure of the metal precipitate is determined by the ratio of the density of the current to the density of the electrolyte, the metal precipitated being the more porous or spongy the greater the ratio and the more cohesive or dense (or the more nearly approaching the solid state) the smaller the ratio in question. A change in the structure or texture of the metal obtained may therefore be effected by correspondingly changing either the densities of current only or the degree of concentration of the solution, or both the density of current and degree of concentration at the same time, and the last-mentioned alternative has proved to be the most advantageous in actual practice. In other words, the best course in obtaining porous or spongy metal deposits is to employ an increased density of current and a solution of a less degree of concentration, and the best course in obtaining solid metal to employ a more highly concentrated solution and a current of less density.

As has already been stated above temperature also affects the question of determining the proper densities of current. Experiments made to ascertain this have, as a result, established the fact that the texture of the metal precipitate is dependent upon the ratio of the density of current to the temperature, and that generally the greater this ratio the more spongy is the metal obtained and the smaller the said ratio the more dense will be the metal precipitated. A high temperature therefore exercises a concentrating action upon the electrolyte. In point of fact when the temperature is high a greater number of the molecules of the electrolyte are found to approach the cathode in the same time than when the temperature is low. Ap-

parently this is the main cause of the influence which temperature exerts. Intensified dissociation, owing to an increase of temperature, will also, however, bring about a greater concentration of the metal ions. Given, therefore, equal densities of current and equal concentration, the required alternation of the metal precipitates may also be obtained by a change of temperature. In most cases, however, the operation will be conducted under the most favorable circumstances, when for spongy metal a higher density of current is combined with a lower temperature and a reduced concentration of the fluid of the bath, and for compact metal a suitably-reduced density of current in conjunction with the higher temperature and greater concentration are employed.

In the same way that concentration and temperature influence the course of the operation so does the manner in which the cathodes move or in which the fluid near the cathodes flows affect the issue of the process. When the quiescence of the electrolyte at the cathode is disturbed, it promotes the separation of metal in a more solid form. Motion therefore also has a concentrating action, more especially because it compensates for or equalizes the rarefaction which is caused at the cathode by the various movements of the ions. The electrolyte can be disturbed sufficiently at the cathodes for the production of the denser metal by any desirable means—as, for instance, the attendant may from time to time stir the electrolyte with a stick or move the cathodes themselves so as to agitate the liquid, or a mechanically periodically-operating agitator may be used, and as I do not claim the particular device used to agitate or disturb the quiescence of the electrolyte at the cathode any other well-known means for producing motion in the electrolyte may be employed. This effect of motion should be taken into account, particularly in those cases where, for the purpose of depolarizing the anodes, moving electrodes are used. Again, all other conditions being equal, a change in the form of the metal precipitate may be obtained by suspending the cathodes alternately in baths varying in qualitative composition, or by combining this change in the qualitative composition (in order still further to enhance the effect) with a corresponding modification of the density of current, temperature, or conditions of motion in such a manner as to obtain spongy metal at one stage and dense or solid metal at the next alternately.

The proper density of current, concentration, temperature, or motion in the case of each individual bath of a given qualitative composition may be best determined by experiment, the appearance of the metal precipitate being the criterion.

The regular alternation of the conditions named may, generally speaking, be secured by two different methods—viz., either by the

employment of two separate cells and separate fluids used in the baths in which the cathodes are suspended alternately, or by always working in the same cell, in which case the values of, say, the density of current, temperature, and motion will have to change, in addition to which it may be expedient to cause liquids varying in composition and concentration to circulate at predetermined periods of time. It is suggested that the two systems should be combined, the spongy precipitate being allowed to partly solidify in its cell, the density of current being somewhat reduced and the temperature correspondingly raised for the purpose. Then it is transferred to another cell, wherein it may be further solidified.

Owing to the fact that the surface of the cathode is constantly increased or extended during the electrolytical process, the ratio of the density of current to the cathode-surface and also consequently—all other conditions remaining equal—the ratio of the density of current to the density of the electrolyte must become gradually smaller—that is to say, the spongy metal separated becomes itself gradually converted into more solid metal, provided the initial density of current has been so determined as but slightly to exceed the limit of current density required for producing solid metal. Accordingly, the passage of the metal from the spongy to the solid state may be allowed to take place automatically by causing the combination of conditions necessary for producing spongy metal to approach as nearly as possible from the beginning the set of conditions required for the formation of solid metal.

A particularly advantageous method for the automatic regulation of the alternate changes in the structure of the metal precipitate, in addition to the changing of the density of current, has been found to be the alternation of temperatures, the temperature being capable of being readily and automatically controlled, so as to uniformly rise or fall, as may be required.

In obtaining porous lead by electrolysis all solutions are not equally well suited. Where a nitric-acid solution is used, for example, rigid plates or scales or needles are obtained which will break under pressure, whereas in experimenting for the present invention it has been found that the small sheets, plates, or scales obtained from a solution of oxid of lead in caustic alkalies are very resistant to fracture. Now where plates obtained in this manner are to be used in storage batteries this is a most important feature, as the oxidation of the lead occurring in this connection is attended with considerable changes in the volume of the oxidized particles, so that it is preferable that the several little leaves of which the whole consists should be capable of performing lateral movements without becoming disconnected from each other. Thus by changing or altering the electrical,

chemical, and physical characteristics or conditions independently or simultaneously we can deposit alternately spongy metal and then a dense metal. For instance, the electrical conditions can be changed by alternately diminishing and increasing the density of current, as by putting in and cutting out a suitable resistance or by shifting from a strong to a weak current alternately.

The chemical constituents of the bath may be changed from alkaline to acid alternately, or from the solution of one salt to that of another by causing one electrolyte to flow into the forming-cell and then another, alternately, or the plates may be lifted from a bath of one salt to that of another.

The physical conditions are, quiescence of the electrolyte, as above described, and the density, by varying the degree of saturation or the temperature, by alternate cooling and heating, both of which can also be accomplished by first using one solution and then another, or lifting the plates from one bath to another.

To form a uniform surface on the spongy metal before causing the denser metal to be deposited, the plates may be pressed by any well-known means, as a platen, or rolled, or otherwise. This will give an even surface over which the denser metal may be deposited, but this may be dispensed with and the spongy metal will then have deposited within its pores or holes a dense deposit that stiffens and hardens them, and the size of the pores or holes in the sponge can be regulated by varying the chemical, physical, and electrical conditions above described, likewise within certain limits the character of the dense deposits.

In view of the fact that the formation at the cathode of a metal is simultaneous with the solution of the anode in the bath this solution or decomposition is taken advantage of in my process by using an impure lead anode, from which the lead is dissolved and deposited at the cathode as a pure metal, and the other metals contained in the anode form the anode slimes, from which they can be recovered by any of the known processes and form valuable by-products. These slimes are more readily deposited or formed when the density of the current is high and the temperature of the electrolyte is low, and this is confirmed by experiments made at temperatures between 100° and 90°, which showed that the anodes became more rapidly covered with insoluble slimes or undissolved oxids as the temperature approached the lower limit. A raised temperature and a reduced density of current will give a purer product and cause an increase in the formation of slimes and a denser metal, while a high current density and a low temperature will tend to lessen the formation of the slimes and cause the formation of an impure cathode. The process would, however, remain the same if the phenomena at the anode—the main features of

the electrolytic process being identical—be on the contrary dealt with as the main object of the operation and if the porous metal obtained at the cathode be regarded as a by-product.

Any well-known apparatus now used for the formation of storage-battery or galvanoplastic plates can be used in connection with my process and I have deemed it unnecessary to illustrate the same.

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

1. An electrolytic process of obtaining a composite metal plate, which consists in electrically precipitating a porous or spongy metal, and stiffening the same by precipitating thereupon a denser metal, for the purpose set forth.

2. An electrolytic process of obtaining a composite metal plate, which consists in alternately electrically precipitating a porous or spongy metal and thereupon a dense metal by changing the density of the current, for the purpose set forth.

3. An electrolytic process of obtaining a composite metal plate, which consists in electrically precipitating a porous or spongy metal, changing the density of the current and electrolyte, and precipitating thereupon a dense metal, substantially as set forth.

4. An electrolytic process of obtaining a composite metal plate, which consists in electrically precipitating a porous or spongy metal, changing the density of the current and electrolyte and the temperature of the electrolyte and thereby precipitating a dense metal upon the porous metal, substantially as set forth.

5. An electrolytic process of obtaining a

composite metal plate, which consists in electrically precipitating a porous or spongy metal, changing the density of the current and the temperature and chemical nature of the electrolyte and thereby precipitating a dense metal upon the porous precipitate, substantially as set forth.

6. An electrolytic process of obtaining composite metal plates, which consists in electrically precipitating a porous or spongy metal, changing the density of current and electrolyte and the temperature, and moving the electrolyte at the cathode thereby precipitating a dense metal upon the porous precipitate, and so on, alternately, as set forth.

7. An electrolytic process of obtaining a composite metal plate, which consists in electrically precipitating a porous or spongy metal at the cathode, producing a uniform surface by pressure thereon, and then causing a dense metal to be precipitated upon the porous metal, for the purpose set forth.

8. An electrolytic process of obtaining a composite metal plate, which consists in electrically precipitating a porous metal and at intervals changing the chemical and physical conditions of the electrolyte, thereby precipitating a dense metal upon the porous layer, substantially as described.

9. A plate for storage batteries which consists of alternate electrodeposits of dense metal and spongy metal, substantially as described.

In testimony that I claim the foregoing as my invention I have signed my name in presence of two subscribing witnesses.

LUDWIG HÖPFNER.

Witnesses:

W. HAUPT,
CHARLES H. DAY.