

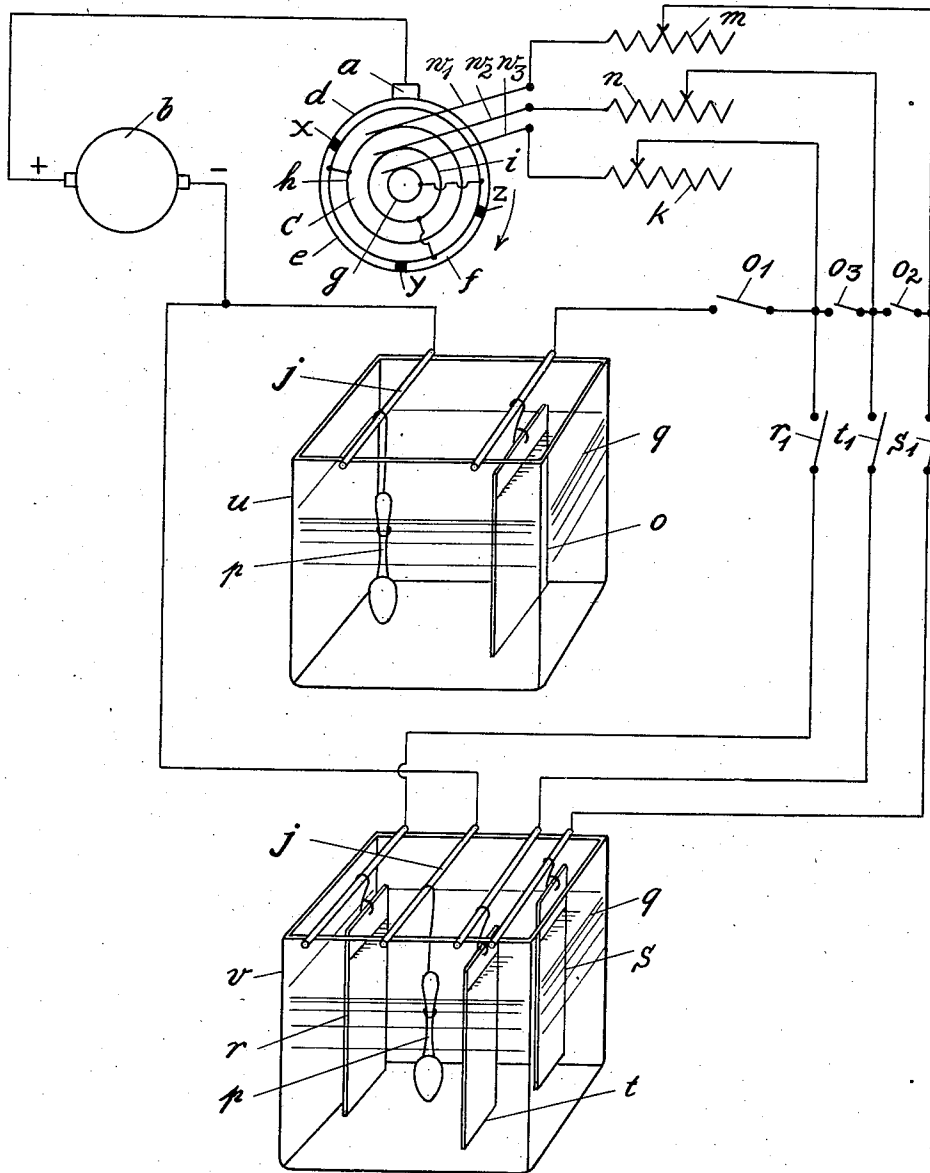
March 20, 1934.

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1,951,893

ELECTRODEPOSITION OF METAL ALLOYS

Filed May 4, 1932



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## UNITED STATES PATENT OFFICE

1,951,893

## ELECTRODEPOSITION OF METAL ALLOYS

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Application May 4, 1932, Serial No. 609,071

In Germany May 13, 1931

12 Claims. (Cl. 204—2)

My invention refers to the art of electroplating and more particularly to the electrolytic deposition of metal alloys on cathodical surfaces.

It is an object of my invention to improve the methods hitherto known for such purpose and to render them more efficient.

It is another object of my invention to provide an improved electroplating method which allows varying the composition of the deposited alloy within particularly wide ranges.

Still another object of my invention is to facilitate the maintaining of an electrolyte for the electrodeposition of metal alloys at a composition suitable for obtaining deposits of the desired composition.

As is well known to those skilled in the art, the deposit obtained in electroplating with a solution of more than one metal does not contain the metals in the same proportion as the solution, since at low cathodical current densities the deposition of the more positive metals such as gold, silver or copper predominates, while at high current densities which cause an increased drop of potential at the surface of the cathode, the deposition of the more electronegative metals such as nickel, iron, zinc and even chromium becomes more and more intense. On the other hand the composition of the electrolytic bath is by no means without influence on the ratio of the metals deposited on the cathode, and the dissolution of alloyed anodes having the average composition of the desired cathodical deposit differs in many cases in accordance with the anodical current density. These phenomena taken together render it rather difficult to produce alloyed electrodeposits, the more so, if the final alloy shall contain both comparatively negative and comparatively positive metals. In many cases the cathodical drop of potential required for the deposition of one metal differs to such an extent from that required for the deposition of another metal, that such alloys cannot be produced at all. Another difficulty encountered in the electrodeposition of alloys is due to the fact that it is extremely difficult to maintain an electrolytic bath at the desired composition by the electrolytic dissolution of metallic anodes irrespective of whether alloyed anodes or a plurality of non-alloyed anodes are used.

According to the present invention I overcome part or all of these difficulties by applying to the electrodes i. e., the cathode on which the alloy is to be deposited, and the anode or anodes, a direct voltage which, however, is not constant

but changes periodically between higher and lower values.

When the voltage is at its higher value, the cathodical current density and the cathodical drop of potential are comparatively high and the deposition of the more negative metals such as for instance nickel is promoted. During the period of lower voltage the deposition of the more electropositive metals such as for instance gold or copper are promoted. Now, if I cause such changes to take place at sufficiently short intervals, the alternating layers of different composition deposited during the alternating periods become so thin, that the deposit ultimately obtained hardly differs, or is altogether identical with an alloy having the average composition. On the other hand I may select the voltage in the period of higher voltage at such values that highly negative metals may be readily deposited, and I may thus incorporate in the alloyed deposit materially greater proportions of electronegative metals than was heretofore possible.

On the other hand my invention enables me to use different anodes in different periods of the voltage applied so as to more precisely control the dissolution of the metals desired in the electrodeposit. In producing for instance an alloyed electrodeposit of copper and nickel I may use for instance a small copper anode inserted during the period of lower voltage, and a bigger gold anode inserted in the period of higher voltage, and I may thus control the dissolution of the two metals at such a rate as is desired for maintaining a constant and satisfactory composition of the bath. In order to facilitate such a control I prefer making the single pulsations substantially constant in voltage at such values as can be readily ascertained by separate tests regarding the rate of dissolution at such voltage.

Instead of a plurality of anodes I may also use alloyed anodes containing the metals to be deposited, in the desired ratio, the even dissolution of such anodes being highly facilitated by the periodically varying voltage. During the period of higher voltage the anodical current density and the anodical drop of potential are also higher, which results in an increased dissolution of the more electronegative constituent of the alloy, the other constituent being more intensely dissolved during the other period.

While the foregoing shows that important advantages are obtained by applying to the electrodes a direct voltage alternating between higher and lower values, it will be understood that my invention is not limited to the use of only two

such alternating periods. If more than two metals shall be deposited in the form of an alloy, and even in other cases, I may advantageously use a voltage which periodically varies between

three or even more values.

In such cases I may adjust the voltage prevailing in the various periods so as to comply with the requirements for a satisfactory cathodical deposition of a corresponding number of metals. Similarly I may use an increased number of anodes consisting of the various metals to obtain a dissolution at the ratio required in the bath.

Going more into the details of my invention I wish it to be understood that my invention, although not limited to a certain duration of the alternating periods, should be carried out with a frequency of pulsations sufficing to obtain a substantially uniform deposit. I have obtained very satisfactory results when altering the voltage applied to the electrolytic cell 150 times per minute, the cycle of for instance three different voltages applied in sequence being completed 50 times per minute. As a rule such a high frequency will not be necessary, while in other cases still higher frequencies may be desirable.

The electrolyte which I use in the practice of my invention does not differ in principle from those commonly in use in the electrodeposition of metal alloys. It contains dissolved compounds of all of the metals to be deposited in a ratio which will depend on various circumstances. It is an advantage of my invention that any desired composition of the bath may be readily maintained throughout very long periods of operation.

In view of the particularly simple way in which I may control the dissolution of the anodes by properly selecting and adjusting the voltage in the different periods or pulsations I may, however, also start from a solution of suitable auxiliary compounds such as alkali salts, alkali cyanides, or the like, and I may introduce the required salts by keeping the bath in operation for a sufficient time, preferably with a comparatively high voltage. During this preparatory stage there occurs the desired anodical dissolution, but no or merely little cathodical deposition. The bath is then ready for regular use.

As regards the number, composition and connection of the anodes many combinations will present themselves without sacrificing the advantages of my invention. I may use a single alloyed anode, or a plurality of such alloyed anodes containing the metals to be electrodeposited, and I may so connect these anodes with the positive pole of the source of electricity that they are permanently inserted in the cycle. In such a case the varying anodical conditions required for the dissolution may be adjusted by controlling the value of the subsequent voltages.

I may, however, also use two or more anodes consisting of the single metals, respectively, or of alloys of part of the metals, and I may so connect them that either all or only part of them is inserted during the period of higher voltage, while the rest is inserted during the period of lower voltage, or vice versa.

I may also combine these two ways of providing and inserting the anodes. In such a case I may provide two or more anodes, each of which contains either one metal only, or an alloy of two or more metals, the only condition being that all the metals to be deposited are present in the anodes. I may connect the anodes in such way that one part is inserted during one period of voltage, and another part during another period of voltage.

In each case the arrangement, the connections, the surfaces and the composition of the various anodes as well as the voltages applied to them should be controlled with respect to each other so that the desired ratio of dissolution is obtained.

In the drawing affixed to this specification and forming part thereof I have shown diagrammatically, by way of example, a device for carrying out my invention.

The positive pole of the source *b* of electric current which may be a galvanic battery or a dynamo, as usual in electroplating, is connected with a brush *a* sliding on a rotary distributor *c*, the surface of which is provided with three segmental metal strips *d*, *e*, *f*. While these strips are insulated from each other by insulating strips *x*, *y*, *z*, they are connected with three slip or collector rings *i*, *h*, *g*, respectively. These rings are connected by sliding contacts *w*<sub>1</sub>, *w*<sub>2</sub>, *w*<sub>3</sub> with three adjustable resistances *m*, *n*, *k*, respectively. The other poles of these resistances may be connected with three separate anodes *s*, *t*, *r*, respectively, of an electrolytic cell *v*, and for such purpose switches *s*<sub>1</sub>, *t*<sub>1</sub>, *r*<sub>1</sub> are provided in the connecting lines. The electrolytic cell *v*, to which these anodes appertain, is further provided with a cathode bar *j*, which carries the cathode *p*—i. e. one or more of the articles to be plated—and is connected to the negative pole of the electrical source.

Another electrolytic cell *u* which may be used instead of the cell *v*, contains a single anode *o* which is connected to the poles of the three resistances *m*, *n*, *k* by switches *o*<sub>2</sub>, *o*<sub>3</sub>, *o*<sub>1</sub>, respectively, all of which should be operated when using this cell. The cathode *p* inserted in this cell is also connected with the negative pole of the electrical source *b*.

When the distributor *c* is rotated the three resistances *m* and the anodes connected therewith will be inserted in the cycle alternately, but as these resistances may be adjusted to different values, the voltage applied to the electrolytic cell *u* or to the electrolytic cell *v* will vary accordingly. In using the cell *u* the three different voltages will be applied to the same anode which is accordingly dissolved at different current densities and drops of potential, i. e. under varying conditions of dissolution. The three anodes *s*, *t*, *r*, provided in the cell *v* are, however, connected each with the poles of one resistance, and it will be understood that during the insertion of one of these anodes the other two will not be inserted.

#### Example

The electrolytic cell *u* shown in the drawing is filled with an electrolyte consisting of a solution of 20 parts by weight sodium pyrophosphate, 20 parts sodium citrate, 8 parts potassium cyanide and 1000 parts water. The anode *o* consists of an alloy of 500 parts gold, 425 parts copper and 75 parts nickel, the distance between the anode and the cathode being about 8 cms, while the ratio of the surfaces of the anode and of the cathode should be about 2:1.

In order to incorporate in the electrolyte the necessary quantity of the dissolved metals, I first apply to the bath a comparatively high voltage, and I continue the electrolysis until the electrolyte contains about 6 grs. dissolved metal per liter. This percentage can be readily ascertained by weighing the anode from time to time. I then replace the cathode by an article or a plurality of articles to be plated and I adjust the three resistances *m*, *n*, *k* in such manner that the pulsa-

tions of the direct voltage applied to the electrodes amounts to 0.5, 2.2, and 10 volts, respectively. The current densities corresponding thereto should be 0.2, 0.8 and 4.8 amperes per dm<sup>2</sup>. The duration of the three alternating pulsations may be equal, and I have obtained highly satisfactory results with 150 single pulsations per minute. The temperature of the bath should be kept at about 20° C.

After one hour the anode is found to be plated with 0.72 grs. of an alloy having a pale red colour and consisting of 695 parts gold, 282 parts copper and 23 parts nickel. It has a particularly fine grain, a considerable hardness and takes a high polish.

By varying the composition of the anodes, or the voltages in each of the three alternating periods or by a combined variation of both I may vary the composition of the alloy deposited on the cathode within particularly wide ranges, and I may impart to it a nickel contents as high as 5 per cent or as low as 0.2 per cent of the whole, and the colour will then vary accordingly between whitish, pale yellowish, yellowish, pale reddish and reddish shades.

Instead of using a single anode, I may also use three separate anodes consisting of gold, copper and nickel, respectively, and in such a case the cell *v* shown in the drawing or a similar arrangement should be used, it being understood that in such case the dissolution of the three anodes occurs alternately during the three alternating pulsations of voltage. While I have given above an example referring to the deposition of a gold, copper and nickel alloy with the aid of an electrolyte containing an alkali cyanide, I wish it to be understood that my invention is not limited to the electrodeposition of alloys of these metals, since all metals can be employed. On the other hand my invention is equally applicable in such cases where the electrolyte does not contain an alkali cyanide, and altogether satisfactory results have been also obtained with alkaline, neutral and even acid electrolytes as are well known to those skilled in the art of electroplating.

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

In the claims affixed to this specification no selection of any particular modification of the invention is intended to the exclusion of other modifications thereof and the right to subsequently make claim to any modification not covered by these claims is expressly reserved.

I claim:—

1. The method of electrolytically depositing a metal alloy on a cathodical surface comprising applying to the electrodes a direct voltage of periodically varying intensity.

2. The method of electrolytically depositing a metal alloy on a cathodical surface comprising applying to the electrodes not less than two alternating pulsations of direct current voltage of different intensity.

3. The method of electrolytically depositing a metal alloy on a cathodical surface comprising applying to the electrodes not less than three alternating pulsations of direct current voltage of different intensity.

4. The method of electrolytically depositing a metal alloy on a cathodical surface comprising applying a direct voltage of periodically varying intensity to a cathode and an anode, the anode containing all the metals to be deposited.

5. The method of electrolytically depositing a gold, copper and nickel alloy on a cathodical surface comprising applying a direct voltage of periodically varying intensity to a cathode and an anode, the anode consisting of an alloy of gold, copper and nickel.

6. The method of electrolytically depositing a metal alloy on a cathodical surface comprising alternately applying a direct voltage of lower intensity to the cathode and one anode, and a direct voltage of higher intensity to the same cathode and to another anode.

7. The method of electrolytically depositing a metal alloy on a cathodical surface comprising alternately applying a direct voltage of lower intensity to the cathode and one anode, and a direct voltage of higher intensity to the same cathode and to another anode, one of these anodes consisting of a single metal.

8. The method of electrolytically depositing a metal alloy on a cathodical surface comprising alternately applying not less than three direct voltages of different intensity to a cathode and to alternately inserted anodes, respectively.

9. The method of electrolytically depositing a metal alloy on a cathodical surface comprising alternately applying not less than three direct voltages of different intensity to a cathode and to alternately inserted anodes, respectively, these anodes consisting of the single metals to be deposited as an alloy.

10. The method of electrolytically depositing a metal alloy on a cathodical surface comprising alternately applying not less than three direct voltages of different intensity to a cathode and to alternately inserted anodes, respectively, these anodes consisting at least partly of alloys of at least part of the metals to be deposited as an alloy.

11. The method of electrolytically depositing a metal alloy on a cathodical surface comprising alternately applying at least two direct voltages of different intensities to a cathode and at least one anode, the frequency of alternation being controlled to obtain a cathodical deposit consisting of a substantially uniform alloy.

12. The method of electrolytically depositing a metal alloy on a cathodical surface comprising alternately applying at least two direct voltages of different intensities to a cathode and at least one anode, the frequency of alternation being about 50 complete cycles per minute.

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