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ELECTROPLATING
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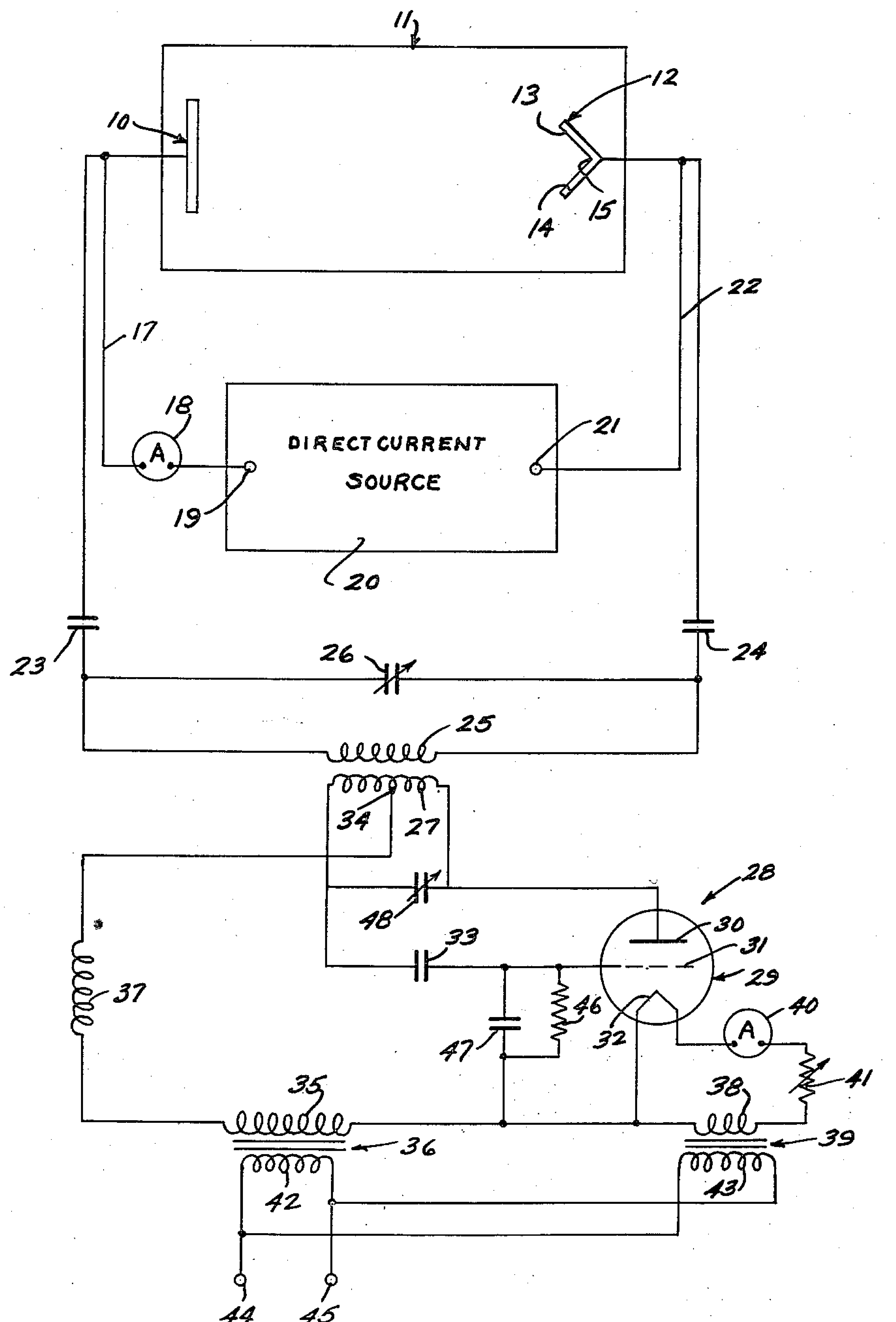

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ELECTROPLATING

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This invention relates to a method for high frequency galvanic separation of metals, and apparatus therefor, and products obtained thereby, and more particularly, to an improved electroplating process and apparatus and the resulting improved electroplated articles.

This application is a continuation in part of my co-pending application, Serial No. 327,402 entitled "Method for High Frequency Galvanic Separation of Metals and Products Obtained thereby," filed December 22, 1952, now abandoned.

In general, the electroplating of a metal onto a given article involves immersing the article to be plated in an electrolyte and passing an electric current through the electrolyte between the article and another electrode also immersed in the electrolyte. The electrolyte contains the metal to be plated and additional plating metal may be added to the electrolyte either by adding additional quantities of a salt of the metal to the electrolyte or, in certain cases, by employing an electrode made of the metal which will supply metal to the electrolyte solution when subjected to the electric D. C. current employed in the plating process.

The instant invention involves the electroplating or electrodeposition of metals under the action of high frequency fields. It has already been proposed, in the electrodeposition of metals, to superimpose alternating currents on the D. C. field in the electrolyte, to reduce passivity of the anodes and to increase the throwing power of the bath or electrolyte. In general, the use of a high frequency field, superimposed on the D. C. field, has not been successful for one reason or another, mainly because this did not favorably influence the deposition process.

The process of the present invention for the electrodeposition of metals, under the action of high frequency fields, is characterized by the fact that at least two high frequency fields, the frequencies of which differ so little that a resultant frequency is of about molecular magnitude, are superimposed on the direct current field as a result of which resonance phenomena occur, which partially cancel or strengthen the characteristic charge of the ions and in this way favor the metal deposition. The electrode arrangement is preferably so tuned with the high frequency oscillator that a "skin effect" is produced on the electrodes, as a result of which, due to the strongly ionizing action of the "skin effect," any overvoltage of the ions to be discharged drops out and thus very high throwing powers and very high electrolytic deficiencies are obtained. It is advisable to tune to intermediate or average frequencies of such magnitude, as, for instance, between 3.50 and 3.56 meters wave length (in air), that the crystal structure of the deposited material is so influenced on the cathode that the deposit can be adapted to the particular purpose of use for which the electroplated material may be intended.

By the application of the process of the present invention, there is obtained a particularly favorable, that is,

extremely dense, finely crystalline metal deposit which is most strongly bonded to its base.

Though all galvanically depositable metals may be used in accordance with the invention, the invention is particularly advantageous for chrome or similar metal plating. The deposits and especially chrome deposits obtained by the invention are characterized by exceptional hardness, resistance to corrosion by acids or moisture, and other unusual properties; and a preferred application of the instant invention is that of hard chroming surfaces, such as of tools, machine elements, bearing surfaces, gun and rifle bores, gramaphone needles, etc.

It is, therefore, an important object of the instant invention to provide an improved electroplating process and apparatus and article produced thereby.

It is a further important object of the instant invention to provide an improved electroplating process which involves superimposing on the D. C. field in the electrolyte at least two high frequency fields whose frequencies differ slightly.

Still another object of the instant invention is to provide an improved process for electroplating metals which comprises imposing a D. C. field on a plating bath and superimposing on the D. C. field at least two high frequency fields whose frequencies, expressed in wave lengths in air, are of a magnitude of 1.8 to 16 meters and which differ from one another by a magnitude of 2 to 40% of their average wave length.

Other and further objects, features and advantages of the present invention will become apparent to those skilled in the art from the following detailed disclosure thereof, and the drawings attached hereto and made a part hereof.

In the drawing, Figure 1 is essentially a diagrammatic view showing a wiring diagram and the plating tank connected thereto, embodying the instant invention.

Although the details of the wiring diagram will be described hereinafter, it will be noted that the high frequency fields employed in the practice of the instant invention, expressed on the basis of wave lengths in air, are of a magnitude within the range of about 1.8 meters to about 16 meters, and preferably about 3.5 meters to about 6.5 meters. The wave lengths of each differ from one another by a magnitude of from about 2 to about 40% of their average wave length (i. e., the average wave length for the two or more high frequencies), and preferably the wave lengths differ from about 5 to about 20% of their average wave length.

Although there are a number of theories which may possibly explain the various advantages obtained in the practice of the instant invention, certain of these advantages may best be described on the basis of operating examples.

For example, plating is carried out in a chrome plating bath (having 266.7 g./l. CrO_3 and 2.8 g./l. HSO_4 content) maintained at 135° F. with a cathode current density of 400 A. S. F. (amperes per square foot) and an anode current density of 200 A. S. F., using a lead anode **10** (Figure 1) at one end of the tank **11** and a V-shaped brass cathode **12** at the opposite end of the tank *t*. The V-shaped cathode **12** is employed facing the anode as shown in the drawing so as to present a number of different surfaces for plating with the chrome. When the D. C. current is turned on (without the application of high frequency fields according to the instant invention) there is a delay of several seconds before bubbling of hydrogen appears at the cathode.

Plating under such conditions for three minutes results in the plating of chrome along the edges **13** and **14** of the front side of the cathode **12**, but a substantial absence of chrome in the central portion **15** of the V-shaped face of the cathode **12**. The absence of chrome on the face of the cathode increases from top to bottom so that there is actually no chrome plated at the top extremity of the cathode even along the edges **13** and **14**. On the back **16** of the cathode **12** chrome is plated along the bottom, but not along the top. After plating for five minutes under these conditions there is very little change in the area on the front or back side of the cathode which is covered by chrome, although a thicker coating of chrome is applied. After plating for ten minutes under these conditions, it will be noted that there is a slight decrease in the uncoated or unplated area on the front side of the cathode along the V-notch at **15**, but there is a definite decrease in the area on the back of the cathode which is coated by chrome. This indicates that a reversible process is apparently involved if the plating is carried out for prolonged periods of time.

If the same coating procedure is now used, except that high frequencies of 5.2 and 6.2 meters wave length magnitude are used, with the average wave length magnitude being about 5.7 meters, a definite difference in the plated cathodes will be noted. For example, as soon as the current is turned on (for the D. C. field and the high frequency fields) it will be noted that hydrogen bubbles appear almost instantly at the cathode, and chrome plating is apparent even after as little as one-half second (whereas it is well known that in the ordinary chrome plating process several seconds are required before plating starts). After three minutes of plating under these conditions, it will be noted that the entire backside **16** of the cathode **12** is chrome plated and the front side of the cathode **12** is chrome plated except for a small portion lying immediately along the bottom of the V-shaped groove at **15**. After plating for five minutes under these conditions the entire cathode on the front and back sides is coated with a thicker layer of chrome, with the exception of a narrower region along the notch **15** than in the case of the cathode plated for only three minutes under these conditions. After ten minutes of plating the uncoated portion along the notch **15** is decreased still more. Depending upon the specific operating conditions, about thirty to forty minutes is ordinarily required to effect complete plating even along the notch **15** under these conditions; but it will be appreciated that complete plating in the absence of the instant high frequency fields cannot be accomplished in any period of time, because of the tendency toward reversal of the action which was noted in the sample plated for ten minutes in the absence of the high frequency fields.

It will also be noted that the cathodes plated in the presence of the high frequency fields just described do not have build up of chrome at sharp edges or at surface irregularities, so that a perfectly smooth or uniform layer of chrome is applied. This feature is of particular advantage in the chrome plating of gun and rifle bores, wherein surface irregularities or alterations of the rifling because of the plating would cause fatal defects. Another unique feature of the invention is that it may be used to plate, for example, a steel file without disturbing the contour of the file surface (and affording a uniform thickness of coating along all points on the filed surface).

As the foregoing example clearly demonstrates, there is a distinct difference between the plating operation involving the use of superimposed high frequency fields as compared to the plating operation not using such superimposed high frequency fields. In addition, a microscopic examination of the chrome layers plated with and without the use of high frequency fields shows clearly that a relatively porous layer of chrome is applied if the high frequency fields are not used. In contrast, if the high frequency fields are used as indicated herein, a dense substantially non-porous chrome coating is obtained with a distinct reduction in pores in the coating lying along the inner face between the chrome layer and the brass cathode. It will also be found that electroplating using only a single A. C. field, even though this field has a frequency within the critical range herein set forth, results in no appreciable improvement over the above described electroplating process using only the D. C. field (and not using the instant plurality of high frequency fields).

As an example of another plating process embodying the instant invention, plating is carried out in an electrolyte containing zinc (content: 4.6 oz. 1 gal. of Zn, 12.5 oz. 1 gal. of NaCN, 10.5 oz. 1 gal. of NaOH) maintained at 95° F. with a cathode current density of 20 A. S. F. and an anode current density of 10 A. S. F., using a zinc anode and a brass cathode **12** in the same type of tank arrangement as that used for the chrome plating. The plating is carried out for three minutes without using a high frequency field, and a comparable run is carried out for three minutes using superimposed high frequencies of 5.2 and 6.2 meters wave length magnitude. Similar runs are carried out for five minutes and for ten minutes; and it is found that in each case, the zinc coating applied is much more dense and more uniformly applied when the high frequency fields are superimposed than when the high frequency fields are not used. Even at the end of three minutes using the high frequency fields, it will be noted that the zinc coating covers the entire electrode (cathode) even in the V-shaped groove, whereas the cathode plated for three minutes without the use of the high frequency fields shows only a very light coating in the V-shaped groove and a number of surface irregularities on the back of the cathode. After five minutes coating without the use of the high frequency fields some of the surface irregularities on the back are cleared up, but the coating is nowhere near as uniformly applied as that applied for five minutes using the high frequency fields. After ten minutes, it is possible to observe a distinct difference in the acutal thickness of the coating applied, with the coating applied using the high frequency fields being thicker and more uniform. Microscopic examination of the coatings also reveals a much more dense non-porous coating layer applied using the high frequency fields.

As another example, plating is carried out in an electrolyte containing copper (content: 3 oz. 1 gal. of Cu, 4.5 oz. 1 gal. of $Cu(CN)_2$, 6 oz. 1 gal. of NaCN) maintained at 120° F. with a cathode current density of 40 A. S. F. and an anode current density of 20 A. S. F., using a copper anode and a brass cathode **12** in the same type of tank arrangement as that used for the chrome and the zinc plating. Plating is again carried out for periods of three, five and ten minutes, with and without the use of superimposed high frequencies of 5.2 and 6.2 meters wave length magnitude. At the end of three minutes plating without the use of the high frequency fields, the backside of the cathode contains some copper plating, with no plating along the extreme rear edge, and only very irregular plating on both of the backsides, particularly along the bottom. The front side of the cathode has no copper plating in the bottom of the V-shaped groove. In contrast, plating for three minutes using the instant superimposed high frequencies results in complete copper plating of the cathode on both the front and back sides, including the very bottom of the V-shaped groove on the front face. Plating for five and ten minutes using the superimposed high frequencies results in a continued complete coverage of the cathode with an increasingly thick layer of copper plating. Plating for five minutes without the use of the high frequency fields results in a somewhat more complete copper plating of the back of the cathode, but an absence of copper plating in the bottom of the V-shaped groove in the front face of the cathode is still very noticeable. Plating for ten minutes without the use of high frequency fields results in what appears to be a substantially complete copper plating coverage of the entire cathode, but it will be appreciated that the plating in the bottom of the V-shaped groove is only a very thin coating. Again, a microscopic comparison of the coatings shows that the copper coating applied using the high frequency fields is much more dense and non-porous and is in contact with the brass cathode surface over a much greater area.

Comparable results may be obtained using other electrolytes and/or electrolytes containing other galvanically depositable metals or mixtures of such metals. Another electrolyte which may be used to obtain substantially the same results as those described in connection with the copper plating is an electrolyte containing cadmium (content: 3.3 oz. 1 gal. of Cd, 12 oz. 1 gal. of MaCn, 2.6 oz. 1 gal. of NaOH) maintained at 90° F. using a cathode current density of 20 A. S. F. and an anode (Cd) current density of 10 A. S. F.

Although there are certain practical considerations which will be discussed hereinafter concerning the generation of the high frequency fields, it is preferable to employ high frequency fields of a magnitude of about 3.5–6.5 meters wave length. In this range, the best plating results are ordinarily obtained using an average wave length in the lower end of this range of, for example, 3.50–3.56 meters, but the generation and control of high frequencies in this region is somewhat more difficult and for practical purposes it may be advantageous to use wave lengths within the range of 4.5–6.5 meters. For example, using high frequencies having wave lengths of 4.4 and 4.8, it will be found that the differences described hereinbefore in connection with the pair of wave lengths 5.2 and 6.2 will be even more noticeable and the advantages obtained thereby in more uniform coating, more complete coating and more dense coating will be obtained much more quickly and much more noticeably. Again, using wave lengths of, for example, 3.4 and 3.6, still a more noticeable improvement is obtained, or the improvement is obtained more quickly. Practical problems in the generation of these frequencies, such as the tendency to cause breakdowns in elements such as the oscillator, may make it more desirable to use frequencies in the higher wave lengths at perhaps a slight sacrifice in plating time and/or quality. Actually, the benefits of the instant invention can be obtained using wave lengths as high as about 16 meters, although no appreciable improvement appears to be obtained using greater wave lengths. In general, it is desirable to use wave lengths that are as close to one another as is practical. Also, wave lengths as low as about 1.8 meters may be employed to advantage in the practice of the instant invention, but below this wave length the problems of generation and control become unnecessarily difficult.

To apply the D. C. field to the plating path, the anode 10 is connected through a conductor 17 and an ammeter 18 to one terminal 19 of a direct current source 20 having a second terminal 21 connected through a conductor 22 to the cathode 12. The source 20 may be any source of steady or pulsating current. Batteries may be used or where standard 25, 50 or 60 cycle alternating current is available, it will ordinarily be preferable to provide rectifiers to convert the alternating current to direct current.

To apply a high frequency field to the plating bath, certain points of the conductors 17 and 22 are respectively connected through coupling capacitors 23 and 24 to the terminals of a coil 25 which may have a variable tuning capacitor 26 connected in parallel therewith. The coil 25 is inductively coupled to a tank coil 27 of an oscillator generally designated by reference numeral 28, which comprises a triode vacuum tube 29 having a plate or anode 30, a control grid 31 and a directly heated cathode or filament 32. The oscillator may be a series-fed "Hartley" type with the plate 30 being connected to one end of the tank coil 27, with the grid 31 being connected to the other end of the tank coil 27 through a D. C. blocking capacitor 33 and with a plate supply voltage being connected between a tap 34 on the coil 27 and the filament 32.

A source of direct current may be used for the plate supply but preferably, to eliminate the need for rectifiers, an alternating current supply is used. In particular, the filament 32 is connected to one terminal of a high voltage secondary winding 35 of a transformer 36 and the tap 34 is connected through a choke coil 37 to the other terminal of the winding 35.

To heat the filament 32, one side thereof is connected to one side of a secondary winding 38 of a transformer 39, the other side of the filament being connected through an ammeter 40 and a rheostat 41 to the other side of the winding 38. The transformers 36 and 39 have primaries 42 and 43 connected in parallel to terminals 44 and 45 which may be connected to a suitable A. C. source, such as a source of 60 cycle, 220 volt current.

Grid-leak bias is preferably used for the oscillator 28 to insure self-starting, the grid 31 being connected through the parallel combination of a resistor 46 and a capacitor 47 to the filament 32.

With the coil 25 being tuned by the capacitor 26, it is not necessary to tune the coil 27. However, it may in some circumstances be desirable to connect a variable capacitor 48 across the coil 27.

It will be appreciated that with the oscillator circuit as thus far described, a high frequency field of one frequency may be readily applied to the plating bath. To apply a high frequency field of a different frequency, a separate oscillator may be used. According to an important feature of this invention, however, the oscillator 28 is used to simultaneously apply two different frequencies to the plating bath, to thus eliminate the need for two separate oscillators.

It has been found that this highly advantageous result is achieved by using a relatively high degree of coupling between the coils 25 and 27. It is believed that a high degree of coupling results in the generation of two frequencies because of the fact that when two resonant circuits are coupled together with a coefficient of coupling greater than a certain amount, two resonant peaks will exist at frequencies respectively above and below the frequency to which the circuits are tuned (which hereinbefore is referred to as the "average" frequency). The oscillator circuit may thus have the greatest degree of application at two different frequencies and can operate simultaneously at both frequencies.

If the oscillator output is viewed on an oscilloscope, for example, the wave will have the same general form as is produced by the addition of two sine waves. As is well known, "beat" frequencies may be produced from waves of two different frequencies and such beat frequencies are produced by the oscillator of the system of this invention.

It should be noted that the greater the degree of coupling, the more prominent are the pair of resonant peaks and the greater is the spacing or frequency difference therebetween. Thus, the relation of the two frequencies can be adjusted by adjusting the coupling between the coils 25 and 27.

In practice, the coupling is generally adjusted until optimum performance is achieved. In any case, the coupling should be such that the mutual inductance in henrys is substantially greater than

$$\sqrt{\frac{R_1 R_2}{w}}$$

where R_1 is the resistance of one coil in ohms, R_2 is the resistance of the other coil in ohms and $w=2\pi f$, f being the frequency to which tuned, in cycles per second. A coupling such that

$$M=\sqrt{\frac{R_1 R_2}{w}}$$

is generally termed "critical coupling" and hence the coupling should be substantially greater than critical coupling.

By way of illustrative example and not by way of limitation, the capacitors 23 and 24 may each have a capacitance of 2000 micro-microfarads; the capacitor **26** may have a maximum capacitance of 125 micro-microfarads; the capacitor **33** may be constituted by two vacuum capacitors each having a capacitance of 250 micro-microfarads; the capacitance **47** may have a capacitance of 100 micro-microfarads; the resistor **46** may have a value of 10,000 ohms; the voltage developed across the secondary **35** may be 5000 volts R. M. S.; and the tube **29** may be an air-cooled high vacuum type with 2000 watts maximum power output. As above indicated, the capacitor **48** is not necessary.

It is a specific feature of the invention that the high frequency source is connected in parallel relation to the direct current source. A series coupling could be used but such would necessitate that the D. C. source have a very low internal impedance to the high frequency currents to obtain efficient operation. This is difficult to achieve, particularly with the relatively long conductors usually used to connect the D. C. source to the electrodes.

With a parallel coupling such as shown, the impedance of the high frequency current path through the plating bath should be much less than the impedance of the path through the D. C. source. With conductors of substantial length as are usually used to connect the D. C. source to the plating bath, this is achieved to a certain extent by merely connecting the high frequency source to points on the conductors **17**, **22** close to the anode **10** and cathode **12**. If desired, in addition, choke coils may be provided between the terminals of the D. C. source and the points to which the high frequency source is connected.

A further specific feature is in the adjustment of a position of connection of the high frequency source to the conductors **17**—**22** to obtain optimum coupling to the bath. With frequencies in the ranges previously specified, the conductors **17**, **22** can form a transmission line of substantial length as compared to one wave length, and by moving the points of connections to the conductors **17**, **22**, resonant and anti-resonant points (or nodes and antinodes) may be found and by using the resonant points, optimum coupling can be achieved. In many cases, points can be found at which the high frequency current path through the bath is resonant with the high frequency path through the D. C. source being anti-resonant so that the ideal coupling can be obtained.

Accordingly, this invention not only provides an improved electroplating process and apparatus utilizing high frequency fields of two different frequencies to produce improved articles, but this invention also provides a method and apparatus for electroplating by which high frequency currents of one or more frequencies can be efficiently coupled to a plating bath. This invention further provides the arrangement by which a single oscillator is used to produce two high frequency currents of different frequencies. This invention also permits the use of a wide range of D. C. current density of, for example, 5 to 1500 A. S. F. generally, although with chrome plating preferably 200 to 1300 A. S. F.

It will be understood that modifications and variations may be effected without departing from the spirit and scope of the novel concepts of this invention.

I claim as my invention:

1. A process for electroplating with an electrolyte which comprises immersing an electrode and an article to be plated in the electrolyte, connecting the electrode and the article to a direct current source through a pair of conductors, connecting to said conductors an alternating current source having a frequency such that said conductors form a transmission line of substantial electrical length as compared to one wavelength, determining the resonant and anti-resonant positions of said conductors by moving the high frequency connection points along said conductors, and obtaining a maximum high frequency field in the electrolyte by adjusting the high frequency connection points to resonant positions.

2. A process for electroplating with an electrolyte which comprises immersing an electrode and an article to be plated in the electrolyte, connecting the electrode and the article to a direct current source through a pair of conductors, connecting to said conductors an alternating current source having a high frequency such that said conductors form a transmission line of substantial electrical length as compared to one wavelength, determining the resonant and anti-resonant positions of said conductors by moving the high frequency connection points along said conductors, and obtaining a maximum high frequency field in the electrolyte by adjusting the high frequency connection points to resonant positions, said high frequency being approximately 3.5 meters as expressed in wavelengths in air.

3. A process for electroplating with an electrolyte which comprises immersing an electrode and an article to be plated in the electrolyte, connecting the electrode and the article to a direct current source through a pair of conductors, connecting to said conductors an alternating current source having a high frequency such that said conductors form a transmission line of substantial electrical length as compared to one wavelength, determining the resonant and anti-resonant positions of said conductors by moving the high frequency connection points along said conductors, obtaining maximum high frequency fields in the electrolyte by adjusting the position of the interconnections of the high frequency source and the conductors to resonant points, said alternating current source supplying at least two alternating currents whose frequencies, expressed in wavelengths in air, are approximately 1.8 to 16 meters and which differ from one another by approximately 2 to 40% of their average wavelength.

4. A process as defined in claim 3 in which the electrolyte contains chromium.

5. A process as defined in claim 3 in which the electrolyte contains copper.

6. A process as defined in claim 3 in which the electrolyte contains zinc.

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