

Sept. 9, 1952

S. E. EATON

2,610,144

METHOD OF ELECTROPOLISHING

Filed Feb. 8, 1947

2 SHEETS—SHEET 1

Fig. 1.

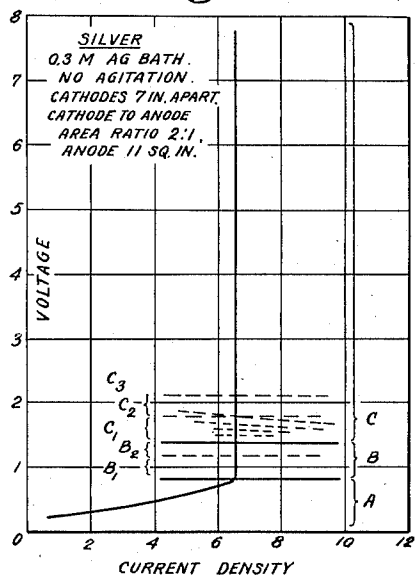


Fig. 2.

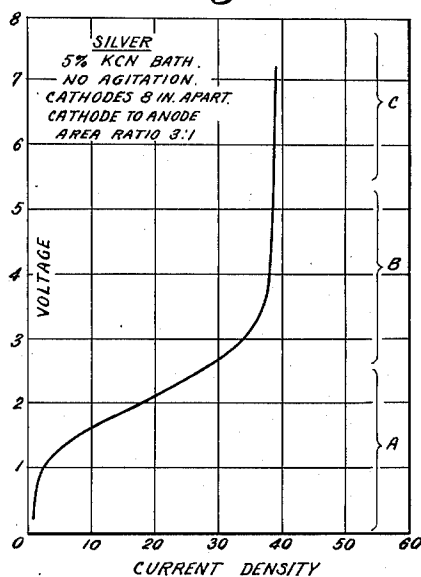


Fig. 3.

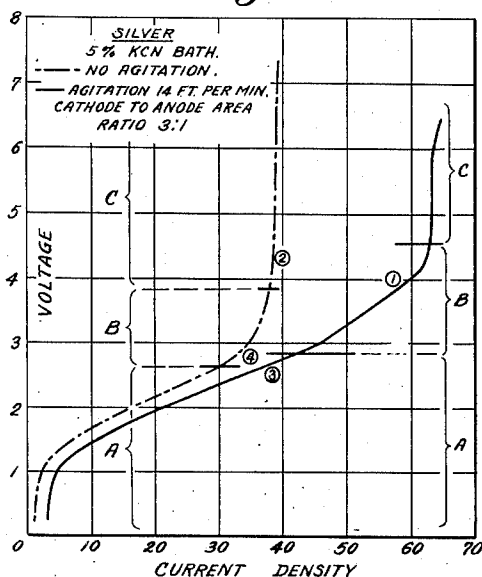
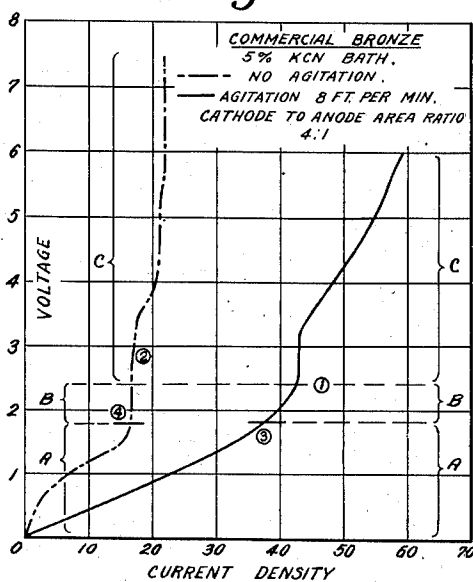


Fig. 4.



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2 SHEETS—SHEET 2

Fig. 5.

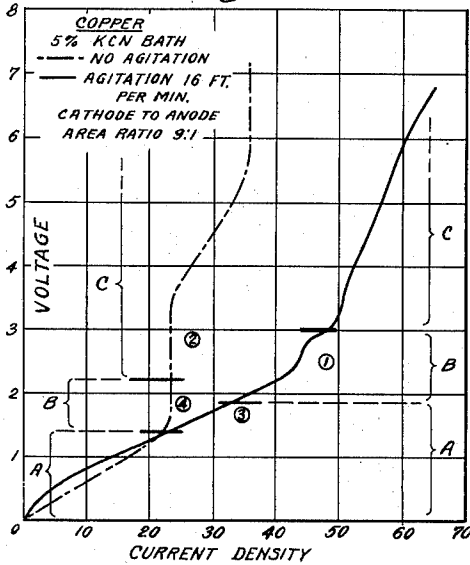


Fig. 6.

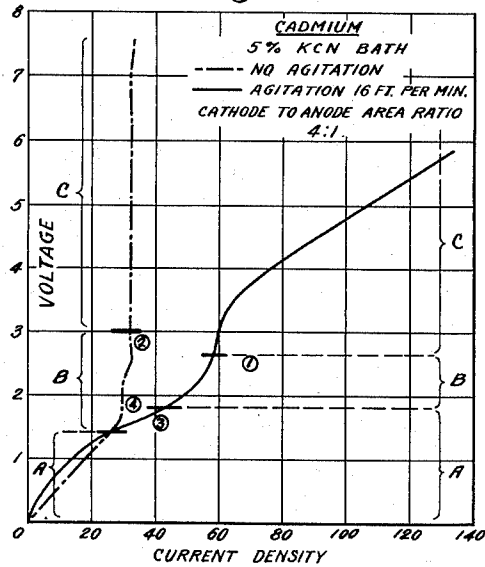


Fig. 7.

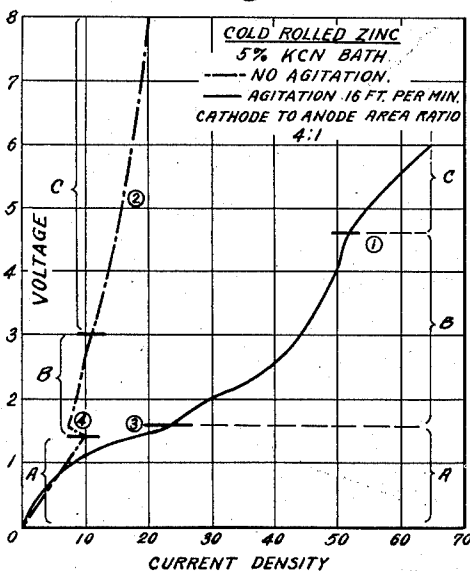
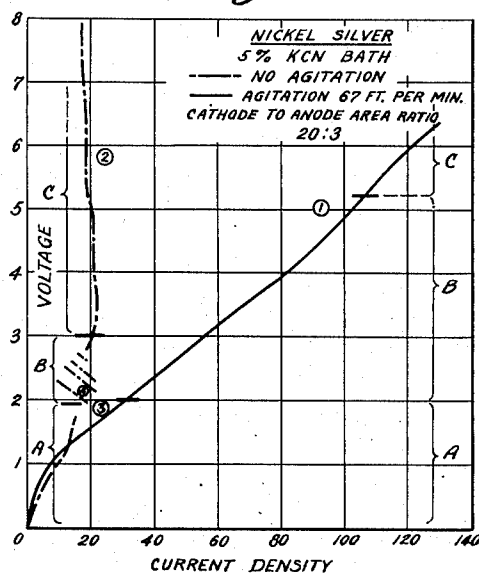


Fig. 8.



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UNITED STATES PATENT OFFICE

2,610,144

METHOD OF ELECTROPOLISHING

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Application February 8, 1947, Serial No. 727,453

12 Claims. (Cl. 204—140.5)

1

This invention relates to a method of electropolishing metal surfaces.

In my copending application Serial No. 474,437, filed February 2, 1943, now U. S. Patent No. 2,416,294 (the disclosure of which is hereby incorporated by reference and of which this application is accordingly a continuation-in-part) a method of polishing metals is described wherein the metal surface to be polished is made the anode in an aqueous electrolyte containing a soluble cyanide and subjected to an electrical potential difference (i. e., the terminal voltage measured between the electrodes of the electrolytic cell) which is between that at which the metal surface manifests a polishing effect and that at which a spontaneous flashing phenomenon takes place or permanent film formation occurs. The potential difference is then maintained substantially constant until the metal surface acquires a polished surface, for example in a quiescent bath. This result may be further promoted by agitation of the anode or of the electrolyte, without turbulence, and by preventing too close an approach of the anode to other solids.

It is now discovered as disclosed in my copending application Serial No. 727,452 that while a controlled and constant potential difference across the electrolytic cell is a useful and desirable method for electropolishing of the metal anode, when commercial application of the method is made the practical problem of accurately maintaining the potential difference at a desired point is sometimes presented.

As disclosed in my said copending application Serial No. 727,452 it is found that a potential difference across the cell, which is positively fluctuated between predetermined limits of voltage and current density and in predetermined periods of fluctuation, results in an improved commercial method yielding reproducible polished surfaces comparable to those obtained by the method of holding the potential difference constant. The factor that is thus left to be closely controlled is that of time which, for commercial practice, is less costly than accurate voltage control.

When a metal surface—which may, for example, be a silver surface which has been formed by electroplating, in which operation it constituted the cathode—is made the anode of an electrolytic cell, containing an alkaline cyanide in an aqueous electrolyte, and the imposed potential difference is varied from zero upward, various changes in the appearance of the surface may be observed.

Considering the surface of only a very small area of the above anode when of silver, for example, the following sequence of changes appears to take place. As the voltage is increased, the current density increases and the surface is etched to a light grey color which remains up

2

to a point called herein the polarization point.

This point marks a change in the relationship between further increase in potential difference with respect to increasing current density in that the current density no longer continues to increase at the same rate. It may increase, but at a slower rate, or it may even not increase at all. If maintained at potential differences slightly above the polarization point the etched appearance of the surface changes to one of specular brightness and covering the surface is a light brown coloration which may be hardly visible. If the potential difference is increased, and the polished area is closely observed, the brown coloration will be seen to become darker, though if the current is cut off or the anode removed from solution such discoloration disappears leaving the surface polished. As the potential difference is raised still further, a peculiarly unstable condition is usually encountered which is termed "spontaneous flashing." In this region the brown discoloration noted above repeatedly and spontaneously fades and returns giving the appearance of flashing. The appearance when faded is one of light brown or grey. Above this potential difference there is a gradual change to a light grey coloration which may be due to an etching effect; and upon increasing the potential difference, it becomes darker. These later colorations which are formed at potential differences above the flashing point, as contrasted with the brown coloration discussed previously, are "permanent"—and especially that coloration which occurs when the anode is maintained at a sufficient potential difference and for a sufficient time tending to produce the dark grey coloration. By "permanent" is meant that the coloration does not readily or completely disappear when the current is cut off or the anode removed from the cell.

The above discussion relates to a given very small area of a silver anode surface. In practice it is observed that corners and sharp edges of the anode become polarized first because of higher current density at these points. Upon gradually increasing the potential difference the brightening and other effects on these parts as described above appear to precede such changes on other parts which are of lower current density. Thus in the case of spoons the edges would exhibit the sequence of change first and the concave center of the bowl would pass through the sequence and hence receive its polish last.

The observed relationships of potential difference to current density with respect to the electrodes and the cell as a whole are therefore averages of the varying effects taking place throughout the entire surface of the anode. This illustrates why if voltage alone is controlled and constant, the potential difference at which all

parts of a spoon, for instance, are brightened at one and the same time, is quite critical. It also illustrates the fact that polishing action begins to take place on at least part of the anode at a voltage below that required to polarize the entire anode.

The exact mechanism of the polishing phenomenon is not understood, in its entirety, but appears to relate to the unequal dissolution of silver from protuberances as compared to depressions in the surface, and to the continual formation of insoluble cyanides of the metal to be polished in the depression and the formation of soluble cyanides on the protuberances.

But by whatever specific mechanism the polishing operates this is the result, that the anode surface progressively develops a dependable and reproducible polish by the imposition of a positively controlled and fluctuated potential difference thereon as above described, as contrasted with an unreproducible surface if uncontrolled voltages or current densities are allowed, as in the spontaneous flashing phenomenon.

Agitation of the electrolyte (preferably without turbulence of the electrolyte) appears to lower the resistance (increase the conductivity) of the system, causing a higher current density at a given potential difference, and effectively promotes the polishing action of the cell.

The process may be carried out by varying the voltage in any of a number of ways. There are, however, certain limitations which should be observed. Excessive time either in the region below the polarization point or in the region of permanent discoloration is to be avoided. While the time period or periods of fluctuation may be varied, no advantage is obtained by too long a period of fluctuation. Short periods of fluctuation are sometimes more effective to develop the polishing action and the polished surface on the anode most satisfactorily.

The principal advantage of the present process is the elimination of the necessity for close control of a constantly maintained voltage. Moreover the positively controlled fluctuation of the voltage into the regions above and/or below the polishing range are not only permissible but found to be advantageous because easier from the standpoint of practical operations. It has been found that best polishing results are obtained if the voltage is not within such regions for a prolonged or dominant proportion of the time of each fluctuation period but is varied substantially all the operating time and predominantly or completely within the polishing range.

Typical examples were carried out in which the potential difference was gradually increased and the values of the voltage and current density were obtained and the characteristic qualities of the anode surface were observed. The results are plotted in the graphs of the accompanying figures showing typical relationships of voltage and amperage for the various metals to which the invention is applicable and successive regions of increasing voltage thereon are labelled A, B and C.

Fig. 1 presents the results obtained with a silver cyanide electrolyte containing 0.3 molal silver and about 0.29 molal free cyanide (above that required to form $KAg(CN)_2$ with the silver present) and 0.1 molal K_2CO_3 , by imposing a gradually increasing potential difference between the anode and cathodes in a quiescent bath;

Fig. 2 shows results obtained with silver in an

electrolyte containing 5% KCN (about 5% molal) with no appreciable silver cyanide or potassium carbonate, in a quiescent bath;

Fig. 3 shows results for the same 5% KCN bath but here the silver anode is agitated in a continuous circular path at a linear speed of 14 feet per minute, with the results shown in the graph to the right, while the results plotted in the graph to the left are quiescent conditions of the electrolyte between the electrodes and of the anolyte and anode specifically;

Figs. 4 to 8 inclusive contain graphs of results obtained similarly to those described in respect of Fig. 3, with bronze, copper, cadmium, zinc and nickel silver respectively.

Referring to Fig. 1, in particular relating to silver, region A represents the low voltage and low current density region in which etching predominates, region B is the polishing region, and region C, the flashing and/or permanent coloration region. As previously explained, though these regions are sharply separated on the graphs—in general, the effects in one may persist into the near parts of the adjacent regions.

Regions B and C of graph 1 have been subdivided typically into subdivisions B_1 , B_2 and into C_1 , C_2 and C_3 , respectively. The upper region of permanent color formation C shows three slightly different effects in the subdivisions labelled C_1 , C_2 and C_3 , respectively. In C_3 , while the current is on, a definitely dark grey coloration gradually forms which is permanent and may become physically separable from the solid metal surface. If voltage is applied suddenly in this region, a period of time, sometimes a few seconds, is required before the coloration becomes permanent. The surface turns a dark grey when first withdrawn from the bath. Part of the dark grey film turns to a light grey and the silver surface appears to be etched under the microscope but part of the dark grey film remains dark and withstands considerable abrasion and withstands at least a few minutes' contact with nitric acid. This dark permanent film can be scratched off of the surface with a probe and under the microscope appears to be a black precipitate—probably of silver oxide.

In C_2 a permanent coloration is formed after a short time, which is grey to dark grey and which does not readily redissolve or disappear upon sharp reduction of the potential difference or cutting off of the current altogether. The lighter grey sometimes appears to be a fine etching of the surface. It also represents the preferred upper limit for the positively imposed fluctuations of potential difference for polishing purposes to avoid the tendencies of permanent film formation.

In C_1 the anode may upon continued maintenance of the potential difference undergo the spontaneous flashing phenomenon over the whole surface or parts of it and with very rapid alternations to very slow alternations, but without accurate prediction, duplication or control. Such flashing may be arrested by, for example, shutting off the current or by increasing the potential difference up into or above the regions C_2 or C_3 or down into region B_2 , B_1 or A.

The electrical power source in the particular instances above plotted had a rated capacity of 25 amperes, 6 volts D. C. The voltage and amperage simultaneously fluctuated with the spontaneous flashing effect. Thus as the brown discoloration fades, the current rises and the voltage falls. Then the coloration reappears, the

5

current falls and the voltage rises. This is what might be expected if the coloration were an insulating film. This cycle of changes is represented in Fig. 1 by the sloping dotted lines of region C₁; each dotted line schematically represents the change in the voltage-amperage relationship during the flashing cycle. Each line corresponds to a different setting of the applied voltage source.

In zone B, two polishing effects are noted and labelled B₁ and B₂. In subdivision B₂ the entire anode develops a uniform polish. A brown coloration covers the surface. This coloration is dark brown at the higher voltages of region B₂ and lighter brown at lower voltages. If the current is lowered or the anode removed from the solution this coloration disappears to leave the surface polished.

The subdivision B₁ is generally that range of potential differences in which the anode surface shows tendencies to acquire polishing preferentially at the margins or corners while the center is usually at lower current density and thus is less polished than the edges.

The other graphs show similar regions A, B and C which have the same general characteristics as those described with reference to Fig. 1. The flashing phenomenon was not observed however and therefore does not appear in the graphs.

The boundaries between different regions are not sharp because the effect in one region graduates somewhat into that of the next, as previously mentioned.

Polishing operations were carried out on silver anodes in electrolytes or compositions, as given in the legends indicated upon the accompanying graphs, with various ranges of imposed fluctuations of potential difference, as indicated below.

Fig. 2 illustrates typical voltage-amperage relationships for a silver anode in a 5% KCN bath with no agitation. A polish was obtained by applying a voltage of 3.5 for 5 seconds, rapidly raising to 3.7 volts and holding there for 5 seconds, then rapidly lowering to 3.5 volts for 5 seconds, etc. The anode showed a brown discoloration when in the solution and this discoloration varied in intensity as the voltage varied. Similar results were obtained in an identical experiment which was like the above except that the time at 3.7 volts was 10 seconds instead of 5; the time at 3.5 volts was 5 seconds.

Fig. 3 illustrates voltage amperage relationship for a silver anode in a 5% KCN bath, the anode being agitated in a continuous circular path at a rate of 14 feet per minute. A voltage of 2.7 was applied for 5 seconds and raised rapidly to 4.6 for 5 seconds, then lowered back to 2.7 for 5 seconds, etc., and this cycle repeated for a total of 2 minutes. The anode appeared grey when at 2.7 volts and brown when at 4.6 volts. The anode developed a polish which was better when withdrawn after the 4.6 volt part of the cycle. When the cycles were lengthened to 15 seconds, the same results were obtained except that the polish was superior.

Results indicate that preferred polishing effect is obtained if a substantial part or all of the cycle of voltage and/or current density includes operation at a voltage above the polarization point and below the point at which permanent discolorations would eventually be formed. As pointed out above a short period of time is required, after applying a voltage sufficient to cause eventual permanent film formation, before a permanent film is actually obtained. It appears that during

6

this short interval, enhanced polishing is obtained because of increased dissolving action on the highest protuberances. In any case, during the remaining part of the cycle, which includes operation at voltages outside this region, the voltage preferably should not be maintained thus for a period of time sufficient for formation of the permanent discoloration, etching, or spontaneous flashing. As in my previous application, Serial No. 474,437, the region of permanent discoloration is that voltage region above (or below) the polishing region which produces a discoloration on the metal surface, which persists when the metal is withdrawn from the bath, as contrasted with the discoloration, either brown or sometimes grey in the case of silver, which disappears almost instantly when the work is withdrawn from the bath or the current is cut off or varied, to leave a polished or slightly milky surface.

Fig. 5 shows relationships for copper in 5% KCN. A voltage of 1.8 was applied for 10 seconds, quickly raised to 2.8 for 10 seconds, lowered to 1.8 for 10 seconds, etc., for a total of 2 minutes, and the polishing effect obtained. These voltages correspond to the upper part of region A and B, respectively. In another run, a voltage of 2.8 volts was applied for 5 seconds and then cut off completely for 5 seconds, reapplied for 5 seconds, etc. for a total of 2 minutes and a polishing effect was obtained.

It may therefore be pointed out from the figures and foregoing description of results that by positively fluctuating the potential difference across an electrolytic cell in which the anode surfaces are of the metal to be polished and the electrolyte contains a soluble cyanide (which is also a solvent of the metal) either continuously or abruptly, and either of equal or of predetermined degrees of variation of the cycle, but including preferably for a substantial part of the cycle a range of values of potential difference above that at which a tendency to polishing is observed and below that at which permanent discoloration occurs, the surface of the anode is developed with a light-reflective quality and mirror characteristics. The period of such fluctuations may also vary.

In addition to the metals specifically referred to above, the present invention is also applicable to alloys consisting of the metals silver, copper and cadmium, and also to surfaces of brass.

Supplemental to the foregoing observations and discoveries, with respect to the anodic polishing of metals by imposing a fluctuating potential difference upon the cell (either with continuous agitation of the electrolyte or in a quiescent bath), which is disclosed and claimed in a co-pending application filed February 8, 1947, Serial No. 727,452, it is now further found that by imposing a fluctuating agitation upon the electrolyte, especially between the electrodes or in the anolyte surrounding the anode surface to be polished, or agitating the anode surface, or both, certain advantages are also obtained.

In this aspect of the invention, voltage-current density relationships were obtained with anodes of different metals in a 5% KCN bath under conditions of no agitation and also with agitation by rotation at a constant circular speed. The results of these experiments are plotted in the accompanying figures showing typical relationship of voltage and current density for the various metals to which the invention is applicable, as above described.

A series of experiments is described below

wherein the polishing effect on the anode caused by changes in rates of agitation of the anode with respect to the electrolyte has been determined.

The general procedure of these experiments was as follows:

The anode was placed in the bath and conditions of voltage, current density, and agitation rate adjusted to one set of conditions, the polishing region for instance. Then the agitation rate was fluctuated (which caused fluctuating changes in anodic conditions accordingly) such that for a substantial part of the time the operation was in the polishing region as above set forth.

It was also noted that a period of time, from a fraction of a second to several minutes, is usually required for conditions to reach equilibrium after each change of agitation. This phenomenon is more marked when agitation rate is decreased than when agitation is increased. During the period of time immediately after agitation rate is decreased and conditions of permanent coloration are approached enhanced polishing action may be observed, thus operation for short periods in this region in which permanent colorations would be formed was found permissible and in some cases was preferred, providing the time was kept short enough to avoid the formation of damaging permanent colorations.

A typical polishing procedure with fluctuating agitation follows.

A pure silver anode was placed in the bath of 5% KCN, and rotated at a surface speed of 14 feet per minute with a potential difference of 4.0 volts resulting in an anodic current density of 58 amps. per sq. ft., corresponding to 1 in the polishing region of the right-hand graph on Fig. 3, for 15 seconds. The agitation was then stopped for 15 seconds and the voltage and current density were observed consequently to approach those values indicated by 2 on the left-hand graph of Figure 3 in the permanent film region. Alternate agitation and no agitation cycles of 15 seconds each were maintained for 2 minutes after which the anode was removed, rinsed and dried. The anode was observed to be polished an estimated one-half perfect mirror.

Another experiment in which the same rate of agitation, voltage and current values obtained, but the timing was different. The silver anode was agitated for 14 seconds, held stationary for 1 second and this cycle continued for 2 minutes. The anode was observed to be polished about one-half mirror.

The same anode was also alternately rotated at 14 ft. per minute for 5 seconds at a voltage of 2.7 volts, current of 39 amps. per sq. ft. corresponding to 3 on the right-hand graph of Fig. 3 in the etching region, then held stationary for 25 seconds during which time the voltage and current approached those indicated by 4 on the left-hand graph of Fig. 3 and repeated for 2 minutes. The anode was then found to be lustrous but not as lustrous as the foregoing runs.

Fig. 4 presents a graph of the conditions and results obtained with an anode surface of commercial bronze. The electrolyte was subjected to fluctuations of agitation of 15 seconds with agitation and 15 seconds without agitation, and 14 seconds with agitation and 1 second without agitation for 2 minutes. Thereupon the potential difference and current density varied between points 1 and 2 and polish of approximately $\frac{1}{2}$ mirror was obtained in each case over

two-thirds to three-quarters of the anode surface.

By subjecting the electrolyte to fluctuations of 5 seconds of agitation and 25 seconds without agitation for 2 minutes, polishing was obtained, which was better on the corners of the anode and the potential difference and current density varied between the points 3 and 4.

Fig. 5 shows typical curves of voltage vs. current density for a copper anode. A polishing effect was observed after 2 minutes of alternate agitation (15 second rotation and 15 second stationary) between points 1 and 2 on the right-hand and left-hand graph 1, respectively of Fig. 5. 14 second rotation alternated with 1 second stationary in the same region for 2 minutes produced a better polish.

A polishing effect was also obtained when the anode was alternately agitated for 5 seconds and held stationary for 25 seconds at points 3 and 4 of Fig. 5 for copper.

Typical curves for a cadmium anode are shown on Fig. 6. Cycles of 15 seconds rotating 15 seconds stationary for 2 minutes total, and also 14 seconds rotation, 1 second stationary for 2 minutes gave potential differences and current densities alternating between points 1 and 2. Periods of 5 seconds rotation and 25 seconds stationary at 3 and 4 produced a third to quarter mirror polish on the cadmium anode.

Fig. 7 shows curves typical of cold rolled zinc. Alternate rotation and then stationary cycles of 15-15 and 14-1 seconds between points 1 and 2 and 5-25 seconds between 3 and 4 produced a luster on the zinc anode.

Fig. 8 shows curves for nickel-silver alloy. The slanting lines on the stationary curves are representative of spontaneous flashing observed. Polishes of $\frac{1}{3}$ to $\frac{1}{2}$ mirror were obtained when a piece of nickel silver alloy was alternately rotated and stopped for 2 minutes in cycles of 15 seconds rotation, 15 seconds stopped, and 14 seconds rotation, 1 second stopped, at points indicated by 1 and 2 on the chart. A polishing effect which was better on the corners of the anode was noted when rotated at a voltage represented by point 3 of Figure 8, 5 seconds and stopped (point 4) for 25 seconds alternately for 2 minutes total time.

The specific cycle is not a critical factor. It is to be understood that other variations in agitation, for example cycling between 28 feet per minute and 14 per minute, agitation would produce variations in voltage in a similar manner and anode polishing would be obtained.

In the adaptation of the invention for various purposes and under specific conditions of equipment and operation, numerous combinations will present themselves from the above disclosure which the invention is especially effective in accommodating.

For example, if it is desired to conduct the process so that it will draw a substantially constant load from the source of electric current, this may be very readily done, and at the same time serve the purposes of the present procedure very advantageously. Thus, the potential difference may be divided or the current may be divided between two or more cells of substantially, equal resistance under analogous conditions of operation by connecting them in series or parallel and interposing an alternating or oscillating switch between them by which the potential difference and/or current through one cell is reduced (and by the same degree) as the

potential difference and/or current through the other cell is increased—and vice versa, substantially complementary to each other at all times.

A similar adjustment of the power requirements may be effected by fluctuating the potential difference and/or current through the cell and the potential difference and/or current through the motor driving the agitating mechanism and thus operating all three in complementary synchronism.

Equilibrium in the etching, polishing or permanent coloration region as discussed above, is that condition which, if it were maintained without change, would develop a gradual permanent etching, polishing or permanent coloration respectively of the metal anode surface.

As indicated above and exemplified in a number of instances described, fluctuations in the agitation of the electrolyte (or of the anode with respect to the electrolyte) include periods of quiescence, as well as variations in the degree of agitation imposed upon the electrolyte or the anode with respect to the electrolyte.

Likewise, it may be emphasized from the foregoing disclosure and data that while changing the rate of agitation, thereby to shift the potential difference-current density values within the polishing region, is effective to promote polishing and enhance the degree of luster obtained on the anode surface, a wider degree of fluctuation in the rate of agitation causing a correspondingly greater shift in the potential difference-current density values and hence carry them outside of the polishing region into the other region designated, will still further enhance the polishing effect and results of the process on the anode surface.

I claim:

1. Method for the anodic polishing of silver, copper, cadmium, alloys consisting of these metals, brass, zinc and nickel silver in an electrolytic cell containing a cyanide bath in which the rate of agitation of the anode with respect to the electrolyte affects the potential difference-current density curve and the location of the equilibrium etching, polishing and permanent coloration regions with respect to said curve, said method comprising the steps of setting up an initial agitation of such metal with respect to the electrolyte, applying a potential difference between the anode and the cathode, said potential difference being in the equilibrium polishing region, cyclically changing said rate of agitation to shift the resulting potential difference-current density values to a point outside said polishing region for a period of time short enough to avoid the formation of a permanent etch or a permanent coloration, and repeating said cycle until at least a portion of the anode acquires a polish.

2. Method for the anodic polishing of silver, copper, cadmium, alloys consisting of these metals, brass, zinc and nickel silver in an electrolytic cell containing a cyanide bath in which the rate of agitation of the anode with respect to the electrolyte affects the potential difference-current density curve and the location of the equilibrium etching, polishing and permanent coloration regions with respect to said curve, said method comprising the steps of setting up an initial agitation of such metal with respect to the electrolyte, applying a potential difference between the anode and the cathode, said potential difference being in one of said regions outside said equilibrium polishing region for a period

of time short enough to avoid the formation of an etch or a permanent coloration, cyclically changing said rate of agitation to shift the resulting potential difference-current density values to a point within said equilibrium polishing region and repeating said cycle until at least a portion of the anode acquires a polish.

3. Method for the anodic polishing of silver in an electrolytic cell containing a cyanide bath in which the rate of agitation of the anode with respect to the electrolyte affects the potential difference-current density curve and the location of the equilibrium etching, polishing and permanent coloration regions with respect to said curve, said method comprising the steps of setting up an initial agitation of such metal with respect to the electrolyte, applying a potential difference between the anode and the cathode, said potential difference being in the equilibrium polishing region, cyclically changing said rate of agitation to shift the resulting potential difference-current density values to a point outside said polishing region for a period of time short enough to avoid the formation of a permanent etch or a permanent coloration, and repeating said cycle until at least a portion of the anode acquires a polish.

4. Method for the anodic polishing of silver in an electrolytic cell containing a cyanide bath in which the rate of agitation of the anode with respect to the electrolyte affects the potential difference-current density curve and the location of the equilibrium etching, polishing and permanent coloration regions with respect to said curve, said method comprising the steps of setting up an initial agitation of such metal with respect to the electrolyte, applying a potential difference between the anode and the cathode, said potential difference being in one of said regions outside said equilibrium polishing region for a period of time short enough to avoid the formation of an etch or a permanent coloration, cyclically changing said rate of agitation to shift the resulting potential difference-current density values to a point within said equilibrium polishing region and repeating said cycle until at least a portion of the anode acquires a polish.

5. Method for the anodic polishing of copper in an electrolytic cell containing a cyanide bath in which the rate of agitation of the anode with respect to the electrolyte affects the potential difference-current density curve and the location of the equilibrium etching, polishing and permanent coloration regions with respect to said curve, said method comprising the steps of setting up an initial agitation of such metal with respect to the electrolyte, applying a potential difference between the anode and the cathode, said potential difference being in the equilibrium polishing region, cyclically changing said rate of agitation to shift the resulting potential difference-current density values to a point outside said polishing region for a period of time short enough to avoid the formation of a permanent etch or a permanent coloration, and repeating said cycle until at least a portion of the anode acquires a polish.

6. Method for the anodic polishing of copper in an electrolytic cell containing a cyanide bath in which the rate of agitation of the anode with respect to the electrolyte affects the potential difference-current density curve and the location of the equilibrium etching, polishing and permanent coloration regions with respect to said curve, said method comprising the steps of set-

ting up an initial agitation of such metal with respect to the electrolyte, applying a potential difference between the anode and the cathode, said potential difference being in one of said regions outside said equilibrium polishing region for a period of time short enough to avoid the formation of an etch or a permanent coloration, cyclically changing said rate of agitation to shift the resulting potential difference-current density values to a point within said equilibrium polishing region and repeating said cycle until at least a portion of the anode acquires a polish.

7. Method for the anodic polishing of an alloy consisting of silver and copper in an electrolytic cell containing a cyanide bath in which the rate of agitation of the anode with respect to the electrolyte affects the potential difference-current density curve and the location of the equilibrium etching, polishing and permanent coloration regions with respect to said curve, said method comprising the steps of setting up an initial agitation of such metal with respect to the electrolyte, applying a potential difference between the anode and the cathode, said potential difference being in the equilibrium polishing region, cyclically changing said rate of agitation to shift the resulting potential difference-current density values to a point outside said polishing region for a period of time short enough to avoid the formation of a permanent etch or a permanent coloration, and repeating said cycle until at least a portion of the anode acquires a polish.

8. Method for the anodic polishing of an alloy consisting of silver and copper in an electrolytic cell containing a cyanide bath in which the rate of agitation of the anode with respect to the electrolyte affects the potential difference-current density curve and the location of the equilibrium etching, polishing and permanent coloration regions with respect to said curve, said method comprising the steps of setting up an initial agitation of such metal with respect to the electrolyte, applying a potential difference between the anode and the cathode, said potential difference being in one of said regions outside said equilibrium polishing region for a period of time short enough to avoid the formation of an etch or a permanent coloration, cyclically changing said rate of agitation to shift the resulting potential difference-current density values to a point within said equilibrium polishing region and repeating said cycle until at least a portion of the anode acquires a polish.

9. Method for the anodic polishing of brass in an electrolytic cell containing a cyanide bath in which the rate of agitation of the anode with respect to the electrolyte affects the potential difference-current density curve and the location of the equilibrium etching, polishing and permanent coloration regions with respect to said curve, said method comprising the steps of setting up an initial agitation of such metal with respect to the electrolyte, applying a potential difference between the anode and the cathode, said potential difference being in the equilibrium polishing region, cyclically changing said rate of agitation to shift the resulting potential difference-current density values to a point outside said polishing region for a period of time short enough to avoid the formation of a permanent etch or a permanent coloration, and repeating said cycle until at least a portion of the anode acquires a polish.

10. Method for the anodic polishing of brass

in an electrolytic cell containing a cyanide bath in which the rate of agitation of the anode with respect to the electrolyte affects the potential difference-current density curve and the location of the equilibrium etching, polishing and permanent coloration regions with respect to said curve, said method comprising the steps of setting up an initial agitation of such metal with respect to the electrolyte, applying a potential difference between the anode and the cathode, said potential difference being in one of said regions outside said equilibrium polishing region for a period of time short enough to avoid the formation of an etch or a permanent coloration, cyclically changing said rate of agitation to shift the resulting potential difference-current density values to a point within said equilibrium polishing region and repeating said cycle until at least a portion of the anode acquires a polish.

11. Method for the anodic polishing of nickel silver in an electrolytic cell containing a cyanide bath in which the rate of agitation of the anode with respect to the electrolyte affects the potential difference-current density curve and the location of the equilibrium etching, polishing and permanent coloration regions with respect to said curve, said method comprising the steps of setting up an initial agitation of such metal with respect to the electrolyte, applying a potential difference between the anode and the cathode, said potential difference being in the equilibrium polishing region, cyclically changing said rate of agitation to shift the resulting potential difference-current density values to a point outside said polishing region for a period of time short enough to avoid the formation of a permanent etch or a permanent coloration, and repeating said cycle until at least a portion of the anode acquires a polish.

12. Method for the anodic polishing of nickel silver in an electrolytic cell containing a cyanide bath in which the rate of agitation of the anode with respect to the electrolyte affects the potential difference-current density curve and the location of the equilibrium etching, polishing and permanent coloration regions with respect to said curve, said method comprising the steps of setting up an initial agitation of such metal with respect to the electrolyte, applying a potential difference between the anode and the cathode, said potential difference being in one of said regions outside said equilibrium polishing region for a period of time short enough to avoid the formation of an etch or a permanent coloration, cyclically changing said rate of agitation to shift the resulting potential difference-current density values to a point within said equilibrium polishing region and repeating said cycle until at least a portion of the anode acquires a polish.

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