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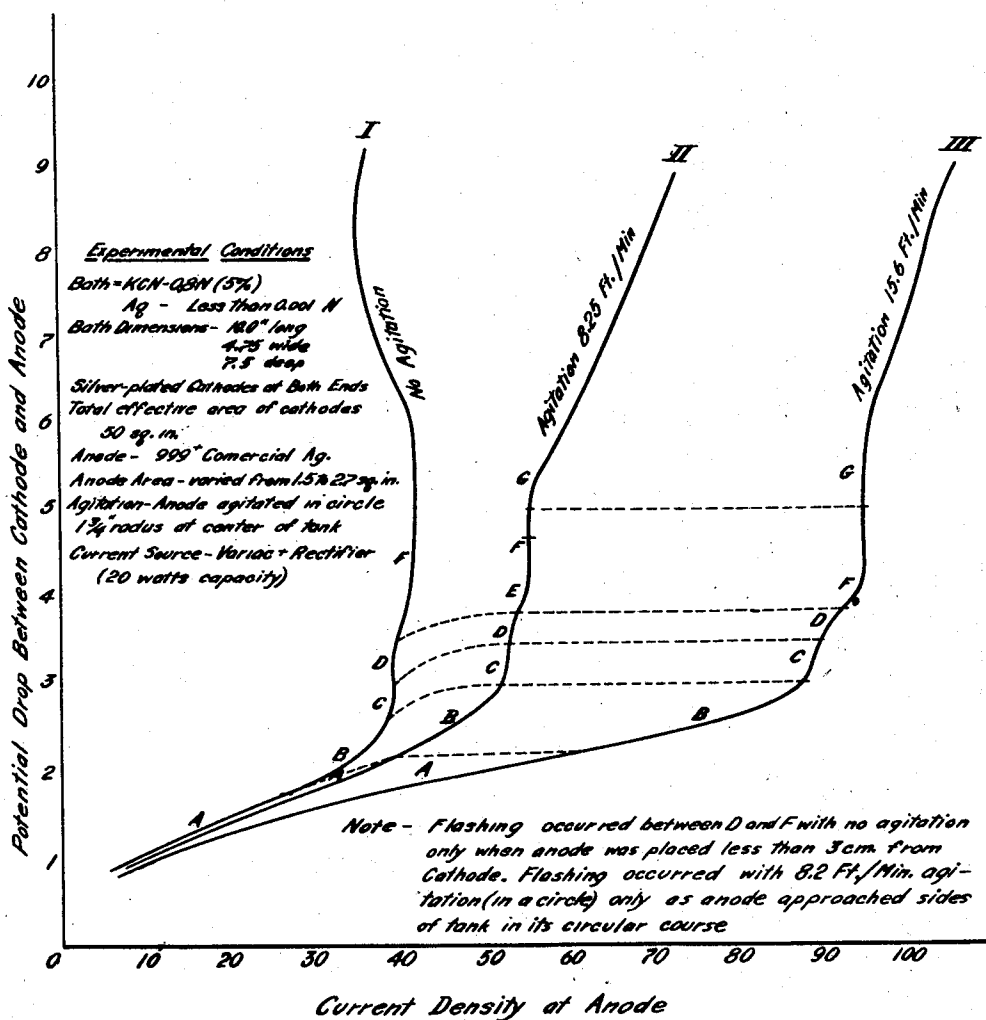
2,416,294

METHOD OF POLISHING METAL SURFACES

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Chart

Showing Typical Potential Drop vs Current Density Relationships
At Various Agitation Rates



Legend

- A-Dulling (low current density)
- B-Edges bright center dull
- C-Practically all bright
- D-Continuous Discoloration (golden to brown)
- E-Flashing
- F-Light gray film (dulling)
- G-Dark gray film (dulling)

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METHOD OF POLISHING METAL SURFACES

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7 Claims. (Cl. 204—141)

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This invention relates to the discovery of an improved method of polishing certain metals by the action of electrolysis.

It has been observed by E. S. Hedges (Chemical Society Journal, (London), 1926, pages 1533-46 and 2580-2595) that copper and silver, for example, as anodes in an electrolytic cell, upon being subjected to the action of low current densities (of the order of 60 to 145 milliamperes per square centimeter with respect to copper), present the phenomenon of forming surface coatings which rapidly alternate, which are, respectively, light and dark, and which accordingly produce a visible flashing effect. These film formations are accompanied by corresponding fluctuations in potential and conversely in the current density of the cell, and the range of such fluctuations increases with increased potential. But, with a current density of the order of 145 milliamperes per square centimeter under consideration therein and a potential difference of 12 volts, such film formations and flashings cease and after passing through this cycle the potential of the cell rises continuously while the current density falls continuously and the film remains permanently upon the metal. This alternating film formation is attributed to the formation and separation of relatively insoluble salts of the metal such as cuprous chloride and silver cyanide, which are white, followed by the dark films which are attributed to the formation of the corresponding metallic oxides.

It is now discovered that if an object (presenting certain metallic surfaces, namely of silver, copper, or cadmium or of alloys consisting of two or more of these metals or of alloys consisting primarily of one or more of these metals, though with some zinc or nickel present therein in their composition) is subjected, in an electrolytic cell containing a soluble simple cyanide and in which such surface constitutes the anode (which is at a free space from the cathode and from other solid surfaces sufficiently to prevent the effects thereof which are found to promote periodicity or flashing) to a voltage above the polarization potential but below that at which the relatively water insoluble films would tend to form and re-form periodically as above described, or permanently accumulate, and diffusion is, per se, sufficient or further promoted by agitation of the electrolyte, and such conditions are maintained for some time, that is, until an appreciable amount or proportion of the metal is removed and dissolved in the electrolyte, the metal surface thus treated will be prevented from undergoing

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the formation of insoluble films and be caused to acquire a high lustrous polish.

The conditions under which such electropolishing may be effected are determined by immersing the surface to be polished, as the anode, in an electrolytic bath containing essentially a soluble simple cyanide (such as an alkali metal cyanide) and, with or without agitation, subjecting to an increasing potential (and current density) to a value greater than that at which polarization occurs, and below that at which the relatively water insoluble films would tend to form and re-form periodically or permanently accumulate.

In developing these conditions, increase of the current density will accompany an increase of the potential difference between the poles of the cell, up to the polarization point. Above this point the potential difference may be increased continuously but will be without appreciable corresponding increase in current density. This point of sharp potential rise without further increase in current density may be regarded as the critical point for electropolishing with respect to potential and current density for the metal surface in question, the electrolyte, and other prevailing conditions of temperature, composition of the electrolyte, type of electric current and potential employed, and the like, under which the determination is made. Above a certain point, further increase in the potential difference between the poles of the cell without corresponding increase in current density also leads to permanent film formation, as indicated by discoloration of the anode.

Below the critical point of potential difference and current density, the metal surface will tend slowly to dissolve and diffuse in the electrolyte. But it will do so uniformly throughout the surface and hence preserve those irregularities which prevent it from presenting or acquiring a mirror-like or specular surface, which is the principal object of the present invention. On the other hand, excessive potential or current density may cause gassing at the anode or formation of the insoluble film.

On the other hand, agitation of the electrolyte promotes diffusion of the dissolved metal from the anode, raises the current densities to be employed at a given potential, for best results, and assures more reproducible results in effecting polishing of the metal surface.

Moreover, it is now found that whereas turning the current on and off, or repeatedly altering it, close proximity or approach of the anode to

the cathode or to the side walls of the retaining vessel or like solid surfaces, or variations in the kind or degree of agitation of the electrolyte promote the flashing effects above noted, the gradual change or continuous control of the current and of the agitation of the electrolyte and provision of sufficient free space in the electrolyte about the anode will effect or promote an electropolishing action upon the surface of the anode, instead of the formation of such resistant dull films, either temporary or permanent.

While the presence of a soluble cyanide is necessary to the procedure of electropolishing in accordance with this invention, some of it at least must be present in the form of a "free," soluble simple cyanide, with or without complex ions of the metal or metals to be polished. Accordingly, both free cyanide ions and complex ions are present in the electrolyte. The "free" alkali cyanide is the soluble cyanide which is present in excess of that required to form and maintain the complex cyanide ion of the metal which dissolves.

The free cyanide promotes the conductivity of the electrolyte and hence increases and maintains the current density of the cell at a higher value at any given potential than would be produced if it were omitted. Further, increased conductivity may also be accomplished by the addition of an inert electrolyte such as potassium carbonate or sodium sulphate. But of these sodium sulphate is to be preferred since it is more inert than the carbonate and is more economical.

The soluble cyanide also performs the specific and important novel function, in the practical application of the invention for electropolishing, of forming both soluble and insoluble compounds with the metal of the anode surface. This is utilized to advantage when the potential and current density are set to maintain a balance between the metal-dissolution rate and the rate of diffusion of the metal complex ions adjacent to the anion into the body of the electrolyte, leading, it is believed, to the formation in the low "valleys" of the metal surface of the insoluble salt and/or oxide, and to the formation of soluble salts on the high "mountains" of the metal surface, where an excess of free cyanide is more apt to be present because of diffusion or agitation.

It is a matter of actual observation that the film or thin layer of electrolyte solution adjacent to the metal surface of the anode, under such conditions, presents a markedly different index of light refraction from the rest of the electrolyte solution. The presence of such a liquid film is a prerequisite for the polishing action to be induced and maintained so as to be carried to completion. The phenomenon of polishing is accompanied by a loss of metal to the electrolyte, and such polishing is in fact actually measured in part in its completeness and brilliancy by the time of operation and amount of such dissolution of metal from the surface being polished.

With cyanides, therefore, although they may be capable of forming insoluble salts with the metal of the anode, it is now found that they are also capable of forming soluble complex anions with the metal and going into solution under appropriate conditions of electrolysis. Hence, if diffusion of the metal cyanides into the electrolyte and of "free" cyanide ions into the fluid film of electrolyte adjacent to and contacting the anode is effected, at sufficient rate and concentration, soluble ions of the metal will be formed in this film instead of or more rapidly than the

insoluble cyanides. Consequently, a complete insoluble film formation will not occur under such circumstances, but, on the contrary, the irregularities or "mountains" will be removed and dissolved until the remaining surface is of uniform, dense and mirror-like or specular with respect to the reflection of light.

The concentration of the anode film of electrolyte, with reference to the ions of the metal of the anode, will be greatest immediately adjacent to the anode surface. It presents a sharply declining gradient of concentration as the distance increases but very slightly therefrom. Accordingly, extremely minute protuberances of metal from the general surface of the anode are sufficient to project through such thin film and be subjected to the action of films of electrolyte which are of less concentration with respect to silver ions, for example, but of much greater concentration with respect to free cyanide ions. Hence, such projections will be subject to the selective dissolving action of the cyanide ions thereon to form soluble complex (e. g., silver) cyanide ions. As a result of such action, the protuberances of metal may be dissolved progressively, in accordance with the present invention, the higher protuberances first, followed by those of less height until finally the entire metal surface is reduced to a continuous surface and reflection of light therefrom is substantially specular and uniform throughout, giving it mirror brilliancy.

As an aid to such electrolysis, dissolution and polishing off of the high points of the anode metal surface and subsequent diffusion of the dissolved metal ions into the body of the electrolyte (as distinguished from complete film formation by precipitation upon the anode) and diffusion of fresh cyanide ions into contact with remaining high points in the metal surface, agitation of the electrolyte is effective. But such agitation should be carefully controlled, so that each portion of the surface will have the same degree of agitation and therefore require and utilize the same current density. It should be disposed in streamline relationship, as nearly as practicable, to the metal surfaces. Typically the agitation is uniformly in one direction rather than back and forth. In this way the liquid film adjacent to the anode surface is not disrupted and yet its effective thickness may be thus reduced and controlled. Its concentration gradient, therefore, is believed to be increased and the metal protuberances of the surface (thus passing through a thinner layer of the protective concentrated metal ion layer of electrolyte) are subjected to greater dissolving action, and such action is effective more closely to the main body surface, that is, to the first continuous surface above which all of the protuberances project. This surface will, therefore, ultimately constitute the finished, polished free surface of the metal when the polishing action has been completed by the reduction and removal of all of the visible or light diffusing or dispersing protuberances which stand above it.

In order that the current density may be thus set up with a relatively low potential across the cell, an amount of "free" soluble simple cyanide, such as one of the alkali-metal cyanides, in solution in excess of the cyanide which will continue with the dissolved metal salt to form a soluble anion therewith, as above stated, will be effective, but an added electrolyte may be employed. In any event, however, the "free" cyanide present must be equivalent to at least .01 mol per liter, us-

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ing potassium cyanide, for example, and may be increased up to saturated solutions.

Since increased temperatures and decreased concentrations of the metal to be polished in the electrolyte tend to increase the current density at which the critical point is reached in any given case, room temperatures or lower and relatively high concentrations of solution are more efficient, preferably a fraction of a mol per liter.

In practicing the invention, the article to be polished is made anodic and provided with sufficient free space about it in a bath containing water soluble simple cyanide radicals and a current is passed through the bath at a voltage which is maintained above that at which anode polarization begins and below that at which permanent discoloration or dulling occurs, as set forth above. Preferably suitable agitation of the electrolyte is set up and provided before the electric current is applied and kept constant.

The following is a typical example of how the proper voltage may be determined, especially with respect to the polishing of silver:

A bath was prepared containing 0.77 mol per liter of potassium cyanide and less than .001 mol per liter of silver. The anode was a plate whose immersed area averaged 2.7 square inches, and which was made from a 999+ commercial silver anode.

The dimensions of the container for the electrolyte were 10.0" long, 4.75" wide and the liquid 7.5" deep. Two cathodes were used, having an aggregate effective area of about 50 square inches, and were equally spaced from the circular path of the anode, at distances of $2\frac{3}{4}$ ", and the anode was rotated in a circle of $1\frac{3}{4}$ " radius approaching to a point approximately .8" from the side walls of the container at a linear rate of 15.6 feet per minute.

The following is a table showing typical voltage-amperage relationship in a 5% KCN bath:

Average voltage	Average amps./sq. ft.	Remarks
0.6	5	Dulling of anode.
1.0	18	
1.4	37	
1.6	43	
1.8	53	
2.0	62	Bright $\frac{1}{8}$ in. at edge only.
2.2	72	
2.3	76	
2.4	79	
2.5	82	
2.6	85	Bright $\frac{1}{4}$ in. at edge only.
2.7	87	
2.8	90	
2.9	90	
3.0	90	
3.2	91	Bright all over optimum voltage.
3.4	92	
3.6	93	
3.8	95	Bright all over and amperage.
4.0	95	
4.2	97	
4.4	95	
4.6	94	
4.8	95	Light gray film $\frac{1}{4}$ in. from edges.
5.0	95	
5.2	95	
5.4	95	
5.6	95	
5.8	97	Light gray film all over.
6.0	96	
6.5	98	
7.0	102	
8.0	102	
8.9	107	Dark gray film all over.
		Do.

It will be seen that in this case the range of optimum average voltage was between about 3.0 to 3.2 volts. It is to be noted that the best range of voltage occurs just after the break in

the volt-ampere curve. Once this voltage is determined for a particular set of conditions, reproducible brightness can be obtained. It is important that the voltage is maintained at the level determined to obtain optimum operating conditions.

The determination and maintenance of the critical voltage is essential to the invention, as is also the presence of cyanide radicals in the bath.

The above example illustrates the fact that electro-polishing may be accomplished by the addition of only cyanide radicals to the aqueous bath.

A graph, showing typical relationships of potential drop, between the anode and cathode, and the corresponding current densities with reference to the polishing of silver in an electrolytic bath, as described on the chart, is given in Fig. 1, in which curves are plotted for conducting the process (I) without agitation of the anode; (II) with agitation of the anode at 8.25 feet per minute; and (III) with agitation of the anode at 15.6 feet per minute, respectively, the conditions for effective results being as indicated in the legend.

Although polishing was satisfactorily accomplished by the foregoing method, better reproducibility was desired. Gas bubbles were evolved at the cathode which reduced cathodic efficiency. This gas also diffused to the anode causing pin points on the surface. It was found that if a soluble salt of the metal to be polished were introduced into the bath, in a quantity equal to less than that required to form the complex with all the cyanide radicals present, improved reproducibility occurred and gassing was eliminated. As an example, a silver salt, $\text{AgK}(\text{CN})_2$, was used in the presence of 0.3 mol per liter of free potassium cyanide, and the quantity of the silver was varied up to 0.5 mol per liter. Results showed polishing in all concentrations, and very satisfactory results when 0.1 mol per liter of silver was used.

The use of the cyanide bath alone requires an optimum voltage which is higher than is economically desirable. A water-soluble electrolyte, such as potassium carbonate, may be used to lower the optimum voltage. The optimum quantity was in the order of 0.3 mol per liter, although any concentration below that at which a black insoluble film is formed on the anode is effective. In certain experiments a silver anode was used together with a bath containing in addition to the carbonate of 0.3 mol per liter of free potassium cyanide and 0.1 mol per liter of silver. Sodium sulfate was substituted for the carbonate and equally favorable results obtained with corresponding concentration.

To increase the reproducibility of results, the anode is preferably agitated in any bath, in accordance with the present invention, so that there is a uniform flow of solution over all parts of the anode. For example, violent motion interferes with the control of voltage, but agitation at a uniform speed of about 20 to 40 inches per minute is satisfactory, using the bath mentioned in the paragraph above. The best voltage was 1.58 volts at 20 inches per minute, and 1.75 volts at 40 inches per minute, thus as the rate of agitation increases, the optimum voltage increases. The materials to be polished should be hung in the most streamlined position possible to avoid turbulence. The following table gives optimum current densities and voltages at different circular agitation rates for teaspoons in the bath mentioned above. The rates are approximate values only.

It is seen that they vary nearly linearly with each other.

Rate, inches per minute	Best voltage	Best current, amps.
0.....	1.25	0.50
10.....	1.50	.50
20.....	1.68	.60
40.....	1.75	.82
85.....	2.25	1.25

It was observed that in the foregoing experiments satisfactory polishing was obtained if the plate to be treated was still wet after plating. In fact it is generally most convenient to carry on the polishing operation in conjunction with and directly after a plating operation. In any case it is highly desirable that the plate be clean.

An example of optimum silver bath is as follows:

	Mol
AgK(CN) ₂ per liter solution.....	0.1
KCN (free) per liter solution.....	0.3
Na ₂ SO ₄ per liter solution.....	0.2

Agitation at the rate of 50 inches per minute and a voltage of 1.8 and current density of about 12 amps. per square foot gives a mirror bright polish to the silver anode, which was of electrolytically deposited silver. The bath measured the same as above described, and the voltage was maintained constant.

Although the examples given were for polishing silver, the following illustrations serve to show the effect of the other metals.

An example of cadmium polishing is as follows:

With a bath containing 1 mol potassium cyanide per liter solution, at 5.0 volts, 300 amps. per square foot, and agitation at 40 feet per minute, a bright polish is obtained. If 0.1 mol of cadmium cyanide Cd(CN)₂ per liter is added to this bath and agitation is uniform at about 8 feet per minute, a bright polish is obtained at 1.5 volts and 80 amperes per square foot.

An example of copper polishing is as follows:

With a bath containing 2 mols potassium cyanide per liter of solution at 3.0 volts and 110 amps. per square foot, and with agitation at 40 feet per minute, a bright polish is obtained.

Brass was polished in a bath containing 1 mol of potassium cyanide per liter at 8 volts and 86 amps. per square foot and with agitation at 20 feet per minute.

It is to be understood that the scope of this invention is not limited to the particular conditions described in the examples but includes the range of variation from such conditions as indicated for silver.

It is also to be noted that alloys which contain a minor proportion of nickel and/or zinc as compared with one or more of the metals falling in the group of silver, copper and cadmium will also polish by the process of this invention. Alloys of 25% nickel and 75% copper and nickel silver were polished by this method. Nickel and zinc themselves do not, however, polish satisfactorily.

If the concentration of the silver or other metal is increased and the concentration of free cyanide kept constant, the optimum current density is lower. As before, where the surface of the silver has high spots, the film is less rich in silver and the low spots most rich in silver. Therefore, the tendency is for the high spots to dissolve faster than the low and a smoothing action results. If the electric potential at the anode surface is maintained at the proper level, the potential

causes silver from the anode to enter into the surface film of electrolyte adjacent to the anode, thus balancing the loss of silver from such film by thermal diffusion or agitation into the solution. If the voltage is too low, the diffusion rate exceeds the rate of formation and the film disintegrates, producing a dull anode. If the voltage rises considerably above the amount necessary to maintain this film, gas which results from decomposition of the solution at the high voltages forms at the anode and breaks the film momentarily. This is visually apparent. The constant removal of silver from high spots in excess of that from the low spots soon erases all surface roughness and the anode takes on a polished appearance.

In the practical application of the invention, it is observed that under the conditions above described a good polishing effect requires sufficient time for the complete removal of the surface protuberances which interfere with the reflection of light so that the whole may be reduced to a geometrically perfect light-reflecting surface which is characteristic of polished surfaces. On the other hand, the time required to produce this polished effect will vary with the irregularity or roughness of the original surface to be polished. If extremely rough, obviously too much metal would require removal for economical employment of the metal. In such cases frostiness may persist in such areas or surfaces, unless the action is sufficiently prolonged.

It is further observed that good polishing may be accomplished even though the original surface be grainy and of poor uniformity. Milkiness also may be present, without preventing a satisfactory polish.

When cyanide is used alone, blisters may occur but are not serious even then.

Low reflectivity or polish may occur if too short a time is allowed for the treatment, but, as already pointed out, this is to be expected and will be overcome by subjecting the surface to be polished to the electrolysis for a longer period of time.

The evolution of gas at the anode may occur when potassium cyanide is used alone or when potassium carbonate is present in the electrolyte with no soluble silver cyanide ions in solution.

I claim:

1. In the anodic polishing of silver, copper, cadmium, alloys consisting of these metals, brass and nickel silver, in cyanide baths, the improvement which comprises employing a substantially constant potential difference between the electrodes which is below the point at which periodic flashing or permanent film formation occurs, and as an aid in establishing and maintaining the constant potential difference, moving the anode with respect to the electrolyte and solid objects in such a manner that turbulence is avoided and the anode does not approach another solid so closely that flashing is produced, and maintaining these conditions for a period of time to effect the dissolution of superficial protuberances from the surface and to leave the surface polished.

2. In the anodic polishing of silver, copper, cadmium, alloys consisting of these metals, brass and nickel silver, in cyanide baths wherein the anode is moved in a continuous unidirectional path with respect to the electrolyte and solid objects, and wherein the potential difference is maintained above the point at which polishing begins to take place and below the point at which periodic flashing or permanent film formation

occurs, the method of inhibiting flashing which comprises maintaining the interelectrode potential difference substantially constant, and maintaining the conditions for a period of time to effect the dissolution of superficial protuberances from the surface and to leave the surface polished.

3. In the anodic polishing of silver, copper, cadmium, alloys consisting of these metals, brass and nickel silver, in cyanide baths wherein the anode is moved in a continuous unidirectional path with respect to the electrolyte and solid objects, and wherein the potential difference is maintained above the point at which polishing begins to take place and below the point at which periodic flashing or permanent film formation occurs, the method of inhibiting flashing which comprises controlling the movement of the anode so as to preclude turbulence, and maintaining the conditions for a period of time to effect the dissolution of superficial protuberances from the surface and to leave the surface polished.

4. In the anodic polishing of silver, copper, cadmium, alloys consisting of these metals, brass and nickel silver, in cyanide baths wherein the anode is moved in a continuous unidirectional path with respect to the electrolyte and solid objects, and wherein the potential difference is maintained above the point at which polishing begins to take place and below the point at which periodic flashing or permanent film formation occurs, the method of inhibiting flashing which comprises controlling the movement of the anode so that the anode does not approach any other solid so closely that flashing is produced, and maintaining the conditions for a period of time to effect the dissolution of superficial protuberances from the surface and to leave the surface polished.

5. In the anodic polishing of silver in cyanide baths wherein the anode is moved in a continuous unidirectional path with respect to the electrolyte and solid objects, and wherein the potential difference is maintained above the point at which polishing begins to take place and below the point at which periodic flashing or permanent film formation occurs, the method of inhibiting flashing which comprises maintaining the interelectrode potential difference substantially constant, and maintaining the conditions for a period of time to effect the dissolution of superficial protuberances from the surface and to leave the surface polished.

6. In the anodic polishing of copper in cyanide baths wherein the anode is moved in a continuous unidirectional path with respect to the electrolyte and solid objects, and wherein the poten-

tial difference is maintained above the point at which polishing begins to take place and below the point at which periodic flashing or permanent film formation occurs, the method of inhibiting flashing which comprises maintaining the interelectrode potential difference substantially constant, and maintaining the conditions for a period of time to effect the dissolution of superficial protuberances from the surface and to leave the surface polished.

7. In the anodic polishing of brass in cyanide baths wherein the anode is moved in a continuous unidirectional path with respect to the electrolyte and solid objects, and wherein the potential difference is maintained above the point at which polishing begins to take place and below the point at which periodic flashing or permanent film formation occurs, the method of inhibiting flashing which comprises maintaining the interelectrode potential difference substantially constant, and maintaining the conditions for a period of time to effect the dissolution of superficial protuberances from the surface and to leave the surface polished.

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