

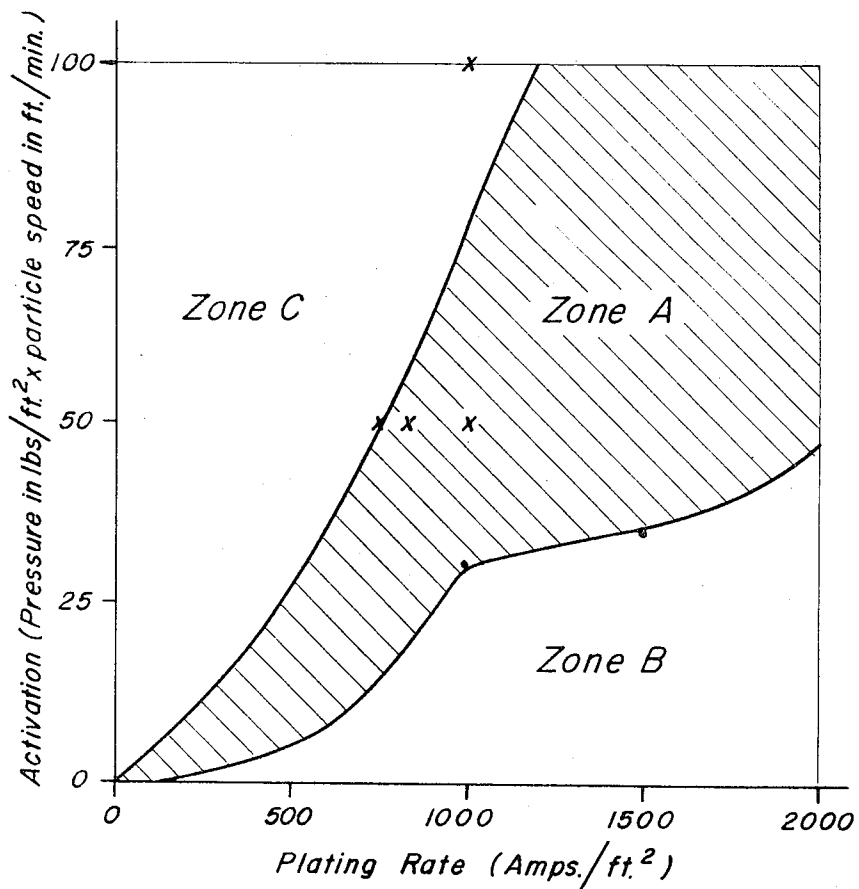
Aug. 21, 1973

S. EISNER

3,753,871

MULTIHARDNESS ELECTRODEPOSITS

Filed Nov. 23, 1971



Inventor :  
Steve Eisner ,  
by *Hugh E. Smith*  
His Attorney.

1

2

3,753,871

**MULTIHARDNESS ELECTRODEPOSITS**

Steve Eisner, Schenectady, N.Y., assignor to

Norton Company, Troy, N.Y.

Filed Nov. 23, 1971, Ser. No. 201,360

Int. Cl. C23b 5/48, 5/20, 5/08

U.S. Cl. 204—35 R

4 Claims

**ABSTRACT OF THE DISCLOSURE**

Electrodeposits having zones of varying hardness are obtained by varying the degree of mechanical activation per unit volume of the electrodeposit during its formation.

**FIELD OF THE INVENTION**

The present invention relates to the field of electrodeposition and, while useful in any electrodeposition process, is of particular utility in the fields of industrial plating and electroforming.

**STATE OF THE ART**

Many methods of producing hardened surfaces on metals have been known in the art. However, in the case of electrodeposited metals such treatments necessitate additional process steps following the electrodeposition reaction. In addition, such prior art methods as case hardening, cold working or the like, will produce only harder outer surfaces and in the event that a softer surface is desired over a hardened inner metal, then such methods fail.

**RELATED APPLICATIONS**

The present invention is directed to a special variation of one or more of the processes disclosed in my earlier copending applications, Ser. No. 34,500, filed May 4, 1970 (now U.S. Pat. No. 3,619,384) and Ser. No. 102,287, filed Dec. 29, 1970 (now U.S. Pat. No. 3,699,014).

**SUMMARY OF THE INVENTION**

By varying the degree of mechanical activation applied in the processes described and claimed in my aforesaid applications during the electrodeposition reaction or by varying the deposition rate while holding the degree of mechanical activation constant or by a combination thereof, the hardness of the electrodeposit can be varied as desired while it is being laid down. The mechanical activation referred to can generally be described as the application to the surface of the electrodeposit during its formation of a plurality of small spaced moving particles which remain in contact with such surface under at least a low degree of pressure throughout the entire electrodeposition reaction. The activation can be carried out by loose particles which are vibrated over the surface of the electrodeposit as described and claimed in U.S. Pat. No. 3,699,014 or by moving an activator belt or disc or the like having the small particles affixed to its surface over the surface of the electrodeposit as described and claimed in U.S. Pat. No. 3,619,384.

**PREFERRED EMBODIMENTS**

Referring now to the drawing, there is illustrated a typical graph showing the plot which results when a large number of specimens of any particular metal are electrodeposited with a given mechanical activation process of either the loose vibratory particle or supported activator particle type referred to above. While the exact configuration of the plot will vary depending upon the particular metal, the specific system and the type of activator, in each instance there will be a zone of conditions where insufficient activation is present for a given

deposition rate so that, as in conventional electrodeposition at such rates, burning of the deposit will occur; a zone of conditions where sound, coherent ductile deposits are obtained; and thirdly, a zone wherein the deposit, while still sound and coherent, becomes hard and brittle. The graph as shown illustrates a plot obtained from a series of samples run of copper electrodeposited from an acid copper sulfate bath using a porous non-woven activator having a plurality of small activating particles secured to its surface. Here the "activation" value is obtained by the product of the speed with which the activator is moved across the electrodeposit and the pressure which is applied in forcing the moving activator against the electrodeposit surface. In the case of the loose vibratory particles, the "activation" value is the function of frequency and amplitude and particle velocity at any given point in the container. This "activation" value, while not an exact correlation of the interaction of speeds and pressures of the particles in these mechanically activated electrodeposition systems, is the best technique known at this time for illustrating in two dimensions the results obtained.

Normally, for most applications of electrodeposition, the desire is for sound, dense, coherent and ductile plate. In such instances, a wide variation of speed and pressure conditions exist, as shown in Zone A of the drawing, for any specific plating rate. The speed or rate of plating is roughly directly proportional to the current density. Rarely would one ever operate of choice at so low an activation value for any given plating rate as to fall within Zone B of the drawing where only burnt, dendritic or powdery deposits are obtained. This is also true for Zone C, the zone of hard, brittle plate, except where one wishes to vary the hardness of the deposit at some portion of its depth. However, if one wishes to provide a hard surface below a softer, more ductile layer of metal, sandwiched between such softer layers or in turn sandwiching such softer layer between harder layers, then such variations can be accomplished by varying the activation value during the deposition or by holding the activation constant and varying the current density used. The most desirable variation in hardness is usually the provision of a harder outer layer, usually quite thin, overlying a softer, more ductile deposit. Such a structure is desirable where an increase in wear resistance of the surface is a benefit as in many electroforms. Provided the outer hard layer produced as described herein is maintained relatively thin, e.g. in the order of 0.0002 inch or less, the more brittle nature of the hard layer does not appear to cause any problem since the layer is cushioned by the underlying ductile and softer deposit. Relative thickness and positioning of the variable hardness zones can be tailored to the end-use specifications desired. The transition from hard to soft metal or vice versa can be either quite sharp and distinct or gradual depending upon the adjustment of current density or activation values. Since the layers of different hardness are produced in a continuous electrodeposition reaction, there is no delamination problem in the resulting structure. Further, with the mechanical activation processes being applicable to essentially all aqueous deposition systems and at extremely wide variations in metal ion concentrations, the present invention is applicable to all metals capable of deposition from conventional systems. The mechanical activation described above, in the instance of either type of activation, results in the imparting of cold work to the electrodeposit while it is forming. As will be seen from the chart illustrated in the drawing, the line marking the demarcation between Zone A and Zone C rises quite steeply as the plating rate increases. The conditions of hard and brittle deposits in Zone C result from an excess of cold work per unit

3

volume of electrodeposit. For an activation value of 50 on the chart, electrodeposition rates below about 750 amps per square foot produce hard brittle plate. Holding the activation value at 50 and stepping the plating rate up to 800 amps per square foot or above produces ductile deposits. The reason for this is that with the activation value held constant, the rate of cold work per unit of time also remains constant, but since the deposition rate has been increased, such cold work is now being distributed throughout a much higher volume of electrodeposited metal. Hence the amount of cold work per unit volume has been lowered and the ductile deposit is the result. Similar results can be obtained by holding the deposition rate constant at a level such as 1,000 amps per square foot and increasing the activation value from 50 where ductile plate was being produced up to 100 which will be seen from the chart to be in Zone C where the harder deposit will result. Variation in the activation value in the case of the supported particle method described and claimed in U.S. Pat. No. 3,619,384, can be obtained by altering either pressures or speeds. Preferably speed is the variable which is altered. Suitable pressures and speeds for the ductile plate in the system illustrated in the drawing are generally in the range of 0.01 to 0.3 p.s.i. and 200 to 400 surface feet per minute. In the case of the loose vibratory particle method described and claimed in U.S. Pat. No. 3,699,014, the variation may be by way of altering amplitude or frequency of vibration, with the frequency being the preferable variable. Suitable amplitudes and frequencies may range quite widely depending upon the particular vibratory unit employed but generally will range from about  $\frac{1}{16}$ " to  $\frac{1}{4}$ " amplitudes and 1,000 to 3,000 cycles per minute.

#### Example 1

Using the type of activation process described and claimed in U.S. Pat. No. 3,619,384, wherein the copper electrodeposit from a copper sulfate-sulfuric acid plating bath having 300 g.p.l. of hydrated copper sulfate and 100 g.p.l. of sulfuric acid, was laid down while the surface of such deposit was constantly activated by contact with a rotating disc, formed from a porous web of Dacron fibers to which was affixed a plurality of 600 mesh aluminum oxide particles bonded thereto by a polyurethane adhesive, moving over such electrodeposit surface at an average surface speed of 1,000 feet per minute and an applied pressure of 3 p.s.i., a thickness of copper of about 3 mils was deposited on a brass disc in approximately 2 minutes at a current density of 2,000 amps per square foot. The final 6 seconds of deposition were carried out at a slower deposition rate by dropping the current density to 500 amps per square foot while maintaining the same degree of activation (surface speed of the activator disc at 1,000 feet per minute and pressure against the deposit of 3 p.s.i.). While the portion of the deposit formed at this slower rate at the end of the deposition cycle was itself too thin to permit a direct hardness measurement, an additional run at 500 a.s.f. under the same degree of activation with the same disc produced a 3 mil deposit which gave a hardness value of 172-175 Knoop. The underlying deposit formed at 2,000 amps per square foot gave a hardness value of 105-109 Knoop. Therefore, it appears that the initial deposit in which the current density was varied as aforesaid had an underlying layer of 105-109 Knoop hardness and a thin skin (estimated at .00005") of 172-175 Knoop hardness.

#### Example 2

Using the type of activation process described and claimed in U.S. Pat. No. 3,699,014, a nickel electrodeposit was laid down using a commercial  $\frac{1}{2}$  cu. ft. vibratory abrasive finishing machine ("Vibratub" Model 33) modified to contain two flat nickel anodes spaced two

4

inches from each side of a flat 2" x 4" steel workpiece cathode; both anodes and the cathode being completely immersed in a mass of irregularly-shaped activating particles consisting of approximately 30-mesh sintered bauxite tumbling abrasives made as described in U.S. Letters Patent No. 3,079,243, and with an electrolyte completely covering the anodes and cathode, said electrolyte consisting of 134 g.p.l.  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , 180 g.p.l.  $\text{NaCl}$  and 32 g.p.l.  $\text{H}_3\text{BO}_3$ . The volume of particles was 8,000 cc. while the volume of electrolyte was 3,000 cc. Plating was carried out for 6 minutes at 2,100 cycles per minute and a  $\frac{1}{8}$ " amplitude of vibration at a current density of 150 amps per square foot. The plating rate was then dropped by reducing the current density to 73 amps per square foot and plating continued for 13 minutes. The resulting plate had an initial layer of nickel on the substrate having a hardness of 198 Knoop and a thickness of 0.5 mil with an outer layer or "skin" of nickel approximately 0.5 mil thick and having a Knoop hardness value of 223.

While the hardness will vary dependent upon metal, degree and type of activation, etc., ordinary acid copper and Watts nickel, as examples, can be made to differ from their usual Knoop hardnesses of 35-190 and 150 respectively as obtained with conventional electrodeposition techniques up to Knoop hardnesses of 105 to 214 for acid copper and as high as 553 for Watts nickel when the deposit is laid down with mechanical activation so as to fall in Zone C as shown in the drawing.

As indicated above, the present invention appears particularly useful in electroforming but is applicable in any electrodeposition process where it may be useful.

I claim:

1. A process for producing a variable hardness, sound and coherent electrodeposit from an aqueous electrodeposition system which comprises mechanically activating the entire surface of the electrodeposit by relative motion between such surface and a plurality of small, hard particles in contact therewith throughout the entire period of electrodeposition so as to introduce cold work into such electrodeposit during its formation and altering the amount of cold work per unit volume of electrodeposit during such electrodeposition so as to vary the hardness of the metal within such electrodeposit.

2. A process as in claim 1 wherein the alteration of the amount of cold work per unit volume of electrodeposit is obtained by varying the rate of mechanical activation.

3. A process as in claim 1 wherein the alteration of the amount of cold work per unit volume of electrodeposit is obtained by varying the rate of electrodeposition.

4. A process as in claim 1 wherein the alteration of the amount of cold work per unit volume of electrodeposit is obtained by varying both the rate of mechanical activation and the rate of electrodeposition.

#### References Cited

##### UNITED STATES PATENTS

3,619,384	11/1971	Eisner	204-35 R
3,619,386	11/1971	Eisner	204-35 R
1,872,709	8/1932	Ernst	204-54 R
3,156,632	11/1964	Chessin et al.	204-DIG. 10

##### FOREIGN PATENTS

231,989	5/1969	Russia	204-DIG. 10
876,484	11/1942	France	204-DIG. 10

FREDERICK C. EDMUNDSON, Primary Examiner

U.S. Cl. X.R.

204-DIG. 10, 49, 52 R