

Dec. 5, 1967

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3,356,597

METHOD AND APPARATUS FOR MEASURING ELECTROFINISHING STRESSES

Original Filed Dec. 24, 1962

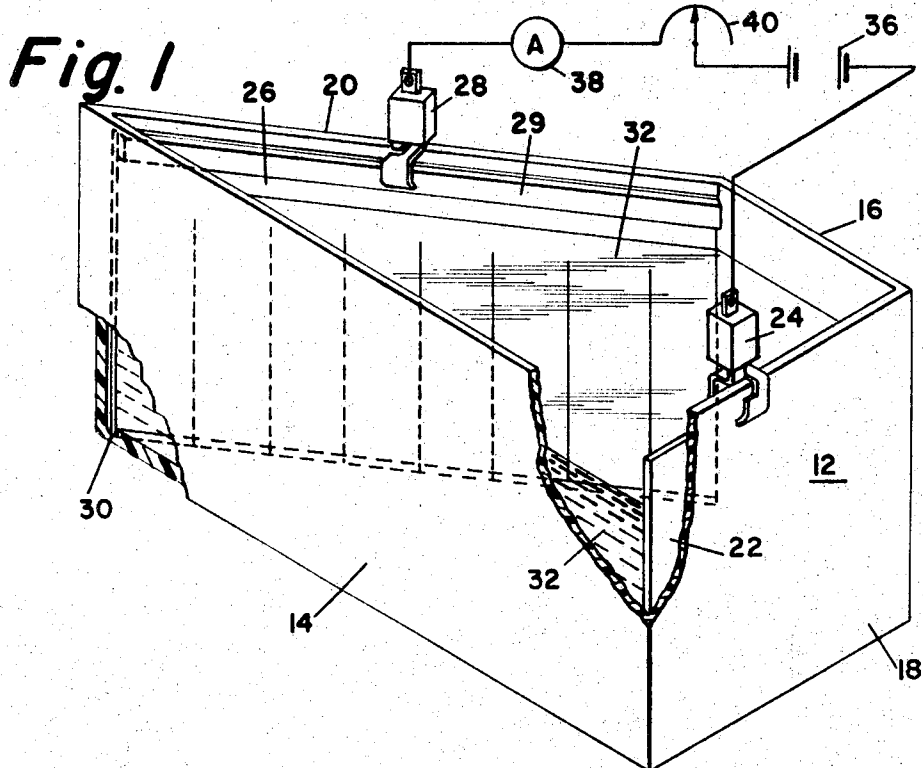


Fig. 2

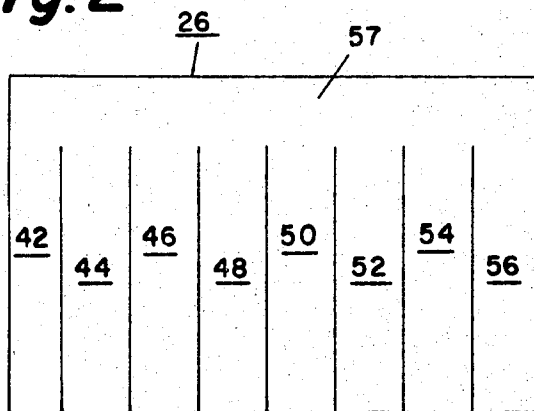
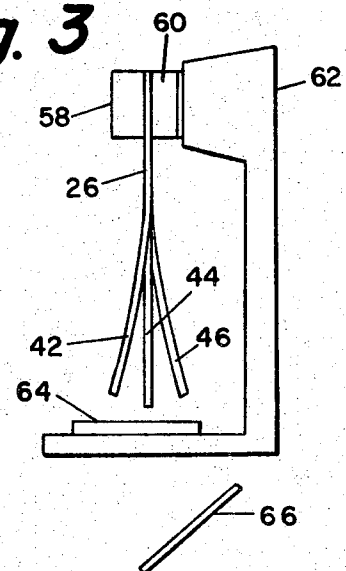


Fig. 3



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METHOD AND APPARATUS FOR MEASURING ELECTROFINISHING STRESSES

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Continuation of application Ser. No. 246,743, Dec. 24, 1962. This application Feb. 18, 1965, Ser. No. 437,623
4 Claims. (Cl. 204-1)

This application for United States Letters Patent is a continuation of my application Serial Number 246,743, filed December 24, 1962, bearing the same title, now abandoned.

This invention relates to electrochemical operations, including the surface electrofinishing operation, and more particularly to apparatus useful for determining the stresses in electrodeposited coatings as a function of the current density with which such coatings are deposited.

The art of electroplating, despite the well-known scientific foundations on which it depends, is dependent for its practical results upon a large number of variables of which it is not feasible to measure all even when their effect upon the result may be predicted. Bath compositions and the presence of additives either deliberately introduced or produced by decomposition of impurities or of chemicals deliberately added, and a vast number of unknowns which some in the trade refer to as "aging" of the bath, all tend to affect the plating obtained in various ways. Fortunately there is one variable which is readily controlled and fairly exactly determined; this is the current density. Since the current density may be altered in any commercial operation by the mere twist of a knob, it is to the variation of the current density that the practical electroplater first turns to compensate for minor variations in the performance of the bath. It is shown by Hull in United States Patent 2,149,344, with further elaboration in United States Patent 2,801,963, how the current density over a simple cathode may be caused to vary continuously from point to point in order to determine the variation in appearance of the electrodeposit with current density. This invention has come into wide use. It has the advantage that the effect of varying some other parameter, such as bath composition or temperature, may be studied for a wide range of current densities in a single operation. Once a reasonably stable initial bath composition, temperatures and other parameters have been chosen, Hull's method may be used when the passage of time causes the resulting deposits to change their appearance, to determine whether and, if so, what, change in current density will restore the desired original results.

Electrodeposited metal coatings frequently are in compression or tension with respect to the substrate upon which they are deposited. This effect may be sufficiently slight so that the effects of stress in the coating are never identified as such, appearing, if at all, only in such recalcitrant guises as a difference in corrosion resistance, fine cracks in the deposit, or some other effects not obviously related to coating stress. There is, however, one particular field in which any large stress remaining in the electrodeposit is highly undesirable. This is the field of electrotyping or electroforming in which the electrodeposit (formed upon an electrode whose shape is the inverse or negative of the desired shape) is itself a desired product. Since electroforming is frequently used to form intricate parts which it would be difficult to form with the required accuracy by any other process, any residual stress in the electrodeposit is more undesirable because it tends to cause the electrodeposited piece to distort itself upon its removal from the master electrode upon which it is formed. Brenner, in United States Patent 2,568,713, discloses a method for measuring stress in an electrodeposit

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by electroplating upon one side only of a helical cathode strip which is twisted, as a bimetal element is twisted by temperature change, because the electrodeposited metal is itself under stress. Brenner's method, while useful, has the disadvantage that it makes only one test at a time for all parameters, including the particular value of current density employed. This may be a rather serious difficulty in those cases where the object is really not to determine what stress is produced by plating at a given current density, but rather at what current density one must plate in order to minimize or avoid completely the production of stress in the electrodeposited coating.

I have invented apparatus and a method for the determination of the effect of current density upon residual stress in an electrodeposit. This method uses the basic technique of Hull to obtain variations in current density on a single cathode; but I have applied novel means to determine the varying compressive or tensile stresses produced in the deposit by the varying current densities existing at different parts of the cathode. To this end, I divide the cathode into strips upon which I plate at the various current densities given the other parameters under which I desire to conduct the tests. This procedure would ordinarily cause the strips of the cathode to curl up, displacing the cathode, and also impairing the required current distribution over the cathode surface. I avoid this and also avoid the non-uniform current density resulting ordinarily from the so-called edge effect by the particular electrode design I employ in the cathode and by the method of supporting the cathode.

Thus, the basic general objective of my invention is to provide means for determining simultaneously the effect of electrochemical operations such as electrodeposition at a plurality of different current densities upon a plurality of substantially identical mechanically separated portions of an electrode, particularly while maintaining a uniform shape among the cathode portions, despite results of the operation tending to change such shape. More specifically, I teach an embodiment comprising means and method for plating simultaneously but at different current densities a number of strips of identical material, employing the interaction of electrical flow to the various cathode strips to avoid the distortion of current density commonly known as edge effect. From the practice of my teaching there also result the achievement of certain other secondary objectives which will be apparent to those skilled in the art.

For the better understanding of my invention, I have provided figures of drawing in which

FIG. 1 represents an embodiment of the means for the practice of my invention, showing particularly the manner of use of a novel design of sample electrode which forms a part of my invention;

FIG. 2 represents in detail an embodiment of a sample electrode particularly suited to the practice of my invention, and

FIG. 3 represents a means and method of determining the quantitative results obtained by the use of my invention.

Referring to FIG. 1, there is represented a tank of insulating material which may conveniently be of transparent organic plastic, of which many are known commercially at this time, tank 12 having a bottom and separately identified walls 14, 16, 18, and 20. In the tank, and against wall 18, there is represented a flat plate of metal 22 held against wall 18 by the pressure of a conventional electrical clip 24. Plate 22 is intended to serve as the counter-electrode or anode in the electrodeposition of whatever metal is under consideration, and will be of material appropriate to that purpose. Sample electrode or cathode 26 (represented in more detail in FIG. 2) is represented held against wall 20 of cell 12 by clip 28 whose

pressure is applied through a batten 29 which presses against the top of 26; the lower edges of all portions of 26 rest in a slot 30 in the bottom of tank 12 immediately adjacent to the bottom of wall 20.

Cell or tank 12 contains an electrolyte 32. A battery 36, an ammeter 38 and a rheostat 40 are connected in series with each other to clips 24 and 28 in conventional fashion for electroplating, the polarity of battery 36 in this example being such that clip 24 is made positive, clip 28 is made negative, so that electrode 22 will serve as anode and electrode 26 will serve as cathode.

It is now informative to refer to FIG. 2 which represents in detail the embodiment 26. In a convenient embodiment, electrode 26 is made of beryllium copper sheet 2.5 mills thick, 4 inches long, and 2½ inches high. It is divided, in the embodiment under consideration, into 8 elongated portions, vertical strips or tongues extending from the bottom of the strip upwards for 2 inches, and a half inch in width, numbered respectively, in this figure, 42, 44, 46, 48, 50, 52, 54 and 56. These tongues are connected for the final one-half inch of height of the strip by the unslit portion 57, of 26, which extends one-half inch from the edge of each slit between tongues to the top of the piece, serving as a header strip. It is thus evident that each of the tongues, 42 through 56, inclusive, is itself one-half inch wide and 2 inches high.

When the process of electroplating is carried on as represented in FIG. 1, the current density across the face of cathode 26 will vary because cathode 26 is inclined at an angle to anode 22, so that the portion of cathode 26, which in FIG. 1 is represented at the viewer's left will be plated at the lowest current density, and the portion at the extreme right of the figure, being closest to anode 18, will be plated at the highest current density. A convenient shape of cell 12, to provide a satisfactory range of current densities over cathode 26 is that used in an embodiment of the cell disclosed by Hull in United States Patent 2,149,344. The internal dimensions of this may be as follows:

Wall 14 is 5 inches long; wall 16 is parallel to wall 14, and both 14 and 16 are perpendicular to the plane of wall 18, which is 2¼ inches long. Wall 20 is 4½ inches long, forming an acute angle at its intersection with wall 14 and an obtuse angle at its intersection with wall 16. It is evident from these dimensions that the plan view of the cell is that of a wedge-shaped quadrilateral. In a more or less conventional embodiment of the cell, the interior portion is 2½ inches deep, and the electrolyte 32 is inserted in it to a level of at least 2 inches, usually 2¼ inches. It is essential that the electrolyte cover the separate strips or tongues of cathode 26 to insure that deposition takes place over the entire length of each tongue. In a conventional copper plating operation, it was found that plating for 10 minutes at a total current of 3 amperes from the follow copper electroforming bath gave a satisfactory result:

Copper sulphate, ounces/gallon	28
Sulphuric acid, ounces/gallon	8
Molasses, ml./gallon	1
Thiourea, ml./gallon	0.1

Obviously, the method is applicable to any bath of interest; the above formulation is pro forma for completeness.

If the stress of the electrodeposit is a function of the current density at which the deposition occurs, a deposit which is in compression will tend, when released from the restraints imposed by clamp 28 and groove 30, to bend backwards the tongue on which its has been applied. Alternatively, a deposit in tension will, when released from constraints, tend to contract and cause its substrate to bend outward—into the tank in the present case. It is evident that the absence of tension or compression in the electrodeposit will leave it with no inclination to bend its substrate in either direction, even when released from

constraints. For determining the presence or absence of such bending, or for determining the magnitude of the bending, from which the stress may be determined, recourse may conveniently be had to the apparatus represented schematically in FIG. 3.

In FIG. 3, there is represented a cathode 26 whose unslit upper portion is held securely between rectangular prismatic blocks 58 and 60, the back face of 60 being, as represented, in contact with a reference surface of a stand or support 62. At the bottom of 62, there is represented a scale 64. In actual practice, blocks 58 and 60 may be clamped together by any of the numerous conventional means known; or, if non-magnetic metals exclusively are to be tested, blocks 58 and 60 may conveniently be ferromagnetic, as may the reference surface of stand 62. In this case, magnetic flux produced by remanence in block 58 or block 60 or stand 62 may be relied upon to provide the clamping force. Scale 64 is mounted in such fashion that a completely undistorted embodiment of cathode 26 mounted between blocks 58 and 60 will extend downward to a reference or zero mark on scale 64. Tongue 44 is so represented in the figure. Tongues 42 and 46 are represented curved in opposite directions. The magnitude of their curvature may be read by observing the displacement of their ends with respect to the position of tongue 44, on scale 64. A convenient way of making this observation is to provide scale 64 of transparent material mounted over a gap in stand 62 so that an observer may look into a plane mirror 66 which is mounted beneath scale 64 and look upward through transparent scale 64 at the distal ends of tongues 42, 44, and 46.

It is, of course, apparent that any suitable means for measuring the displacement of the tips of the tongues will be useful in the practice of this invention. Thus, a micrometer head may be mounted upon the upright portion of stand 62 so that its tip can be protruded to touch the end of tongues such as 42, 44 or 46. The relation between the displacement of the tongue end, the plating stress, and various other parameters is given by the following formulas:

Stress in plating=

Young's modulus of substrate (Substrate thickness + plating thickness)³

6 (Substrate thickness × plating thickness) Radius of curvature of tongue

Radius of curvature of tongue=

$$\frac{(\text{Tongue length})^2 + (\text{Displacement of tongue end})^2}{2 (\text{Displacement of tongue end})}$$

An information reference on the general subject of "Stress in Electrodeposited Metals" is an article of that title by I. Laird Newell in "Metal Finishing" for October 1960, page 56.

The advantages of employing a sample electrode, such as I have disclosed, in the particular fashion disclosed may not be obvious. The geometry of the cell employed is such that very little deposition will occur upon the back of the cathode 26 when it is mounted as represented in FIG. 1 since there will be essentially no electrolyte behind the cathode and any path through the electrolyte from the cell to the rear of the cathode would be of extremely small cross-section and thus of very high resistance. Current flow to the back of the cathode will therefore be negligible. This has the desirable advantage that there will be negligible deposition on the back of the cathode and therefore it will be unnecessary to mask the back or the cathode. This is an important advantage because any masking material which might be applied would be likely to produce a bending movement on its own account if it expanded or contracted with respect to the cathode material; and on the other hand, removal of such a mask would be very difficult without danger of deforming the thin cathode in such a way as to alter the apparent curvature of the fingers. It is well-known in the art that the ex-

posure of a finite plate in an electroplating bath tends to cause a concentration of field lines and thus of current density around the edges. The design of sample electrode which I employ and my teaching of clamping the individual tongues in such a fashion that they cannot move with respect to one another during the plating operation causes the entire electrode to present essentially a single plane to the electrolyte, each individual tongue being served by the tongues on either side as guide electrodes which prevent field distortion at the edges of the individual tongue. It is true that tongues 42 and 56 of electrode 26 will not be guarded on their outer edges. However, the structure of the cell tends to avoid excessive field distortion at these outer edges, and it is also true that normal good procedure would lead one to adjust his test parameters in such fashion that the results of major interest would appear on one of the inner tongues such as 48 or 50. Thus, if minimum distortion were the objective, one would plate at such current densities and for long enough time so that some of the fingers would bend forward and some backward, upon release from the constraint imposed by the slot 30. (This is comparable with the normal practice of choosing such an instrument scale that the readings obtained fall somewhere in the central part of the scale.) It should be observed that insofar as the cell structure tends to reduce edge effects, this operates only on those portions of the cathode which are close to the boundaries of wall 20. If an individual tongue such as 50 of cathode 26 were permitted to move forward into the path out of the plane of the other tongues as a result of stresses produced during electrodeposition, the cell structure would not prevent the concentration of field lines around the edges of the protruding tongue. It is, therefore, important to preserve the flatness of electrode 26 as a whole during the deposition operation in order that these benefits of my invention may be achieved. Materials which are hardenable by precipitation after slitting, such as beryllium copper, are particularly useful for this reason, since such hardening may be effected with minimal distortion.

The previously given formulas relate displacement of the substrate tongue end, the tongue length, its thickness, its Young's modulus of elasticity, and the plating thickness, to stress in the plating. Since the thickness of plating produced in a given bath by application of a given current density is readily determinable, all the parameters in these formulas are obviously ascertainable. However, the application of these formulas, even when all parameters are known, is somewhat laborious mathematically. For general use it is clearly convenient to provide standardized electrodes which may be used in connection with some simplified data reduction means. Thus, families of curves may be prepared which relate the displacement of a tongue end with the stress to be determined, a curve being provided for each given thickness of plating. Alternatively, nomograms may be provided which express the relation. All of these artifices, however, depend for easy use upon the electrodes successively used in successive tests having a known calibrated relation between tongue end displacement and the stress in a plating of given thickness applied to one side of the tongue.

If one considers a tongue, e.g. 46, of unit width, it is evident that a given plating of thickness T , having a unit stress of magnitude S , will apply to the tongue 46 a total force, parallel to the surface and to the length of tongue 46, which is equal to $T \times S \times \text{unit width}$, in tension or compression, as the case may be. If the tongue 46 were only half a unit wide, the total force upon it would be only $T \times S \times \text{half unit width}$; but this would be applied to a tongue of only half unit width, and the resulting tongue end displacement would be the same. Thus, what is required is that the electrode be precalibrated to have a known calibrated characteristic relating the displacement of the end of a tongue such as 46 with the magnitude of a force per unit of tongue width applied parallel to the

surface of and to the length of the tongue. The tongues, obviously, need not be all of the same width.

For maximum convenience in use of my invention a measuring electrode whose tongues are precalibrated as described is desirable. Provision of such an electrode relieves the user of it from the need for measuring the dimensions of the electrode, or determining its elastic modulus; and, most conveniently, it permits him to use simplified data reduction means to determine plating stress directly from the displacement of the distal end of the substrate tongue coated at the current density of interest.

It is apparent that my invention is not inherently confined to the electroplating of metals, but can be applied to an electrolytic operation in which a distorting effect upon the substrate is a function of current density. Thus if electropolishing produced distortion, an electrode of the material to be electropolished, shaped like anode 26, and restrained during electropolishing, would give a measure of the effect of current density upon this effect. While it is desirable, where the measurements are to be quantitative, that the sample electrode 26 be of well-controlled elastic characteristics, as is easily achievable with beryllium-copper, if the effect to be investigated is sensitive to the material of the substrate, the sample electrode should be of the material of interest. While in the example cited, the sample electrode 26 has sometimes been referred to as the cathode, appropriately to the example, it is clear that in electropolishing and possibly in electrophoresis the same electrode may be the anode. It is thus evident that the scope of my invention is best defined by the claims presented.

The appended claims are written in subparagraph form, in compliance with a recommendation of the Commissioner of Patents, to render them easier to read. This particular manner of division into subparagraphs is not necessarily indicative of a particular relative importance or necessary subdivision of the physical embodiment of the invention.

What is claimed is:

1. Test apparatus for the electrochemical art comprising:
 - (a) a first electrode;
 - (b) a container adapted to maintain a quantity of bath in contact with the said first electrode and with a sample electrode;
 - (c) a sample electrode comprising a plurality of commonly connected separate relatively thin, flat portions of the same material and of identical thickness, presenting a substantially continuous plane surface so oriented with respect to the said first electrode that application of electrical potential between the said first electrode and the said sample electrode when both are immersed in a bath will cause current flow of different densities at different ones of the said commonly connected separate portions;
 - the dimensions of each said separate portion being sufficiently small in the direction in which current density varies that the current density at each said separate portion will be substantially uniform;
 - the faces of all said separate portions being exposed without insulating obstructions which would impair the uniformity of current flow at the said separate portions, except at the outer periphery of the entire said plurality;
 - (d) releasable means for restraining said sample electrode portions against movement from stresses produced during electrodeposition thereon.
2. The method of measuring the dependence of stress in electrodeposited coatings upon the current density employed in the deposition of the said coatings which comprises:
 - (a) providing a plurality of elongated electrode portions having plane faces lying in one common plane, the said electrode portions being flat, relatively thin,

- of the same material and of identical thickness, and alike in mechanical properties, each said electrode portion having one end connected to a header strip common to all said portions;
- (b) immersing the said plurality of elongated electrode portions in an electrolytic bath, together with counterelectrode located non-parallel to the said common plane;
- (c) restraining the said electrode portions from motion relative to said header strip;
- (d) passing electric current between the said counter electrode and the said plurality of electrode portions in such polarity as to produce an electrodeposit upon the said plurality of electrode portions;
- (e) removing the restraint from said electrode portions, releasing them for motion relative to said header strip;
- (f) measuring the displacements of the said electrode portions from their initial positions relative to the said header strip.
3. The method of determining the effect of current density upon the mechanically distorting results of electrolytic operations which comprises:
- (a) providing a sample electrode comprising a plurality of separate but coplanar closely adjacent relatively thin and flat electrode portions of identical thickness and material mechanically connected to a common header strip and free at their distal ends;
- (b) providing temporary restraining means to prevent motion of the said distal ends with respect to said common header strip;
- (c) surrounding said sample electrode portions with an electrochemical bath;
- (d) immersing a counterelectrode in said bath in such orientation that electric current flowing between said counterelectrode and said sample electrode will flow in differing densities to each said sample electrode portion;
- (e) passing electric current between said counterelectrode and said sample electrode in the proper direction to cause the said electrolytic operation to occur at the sample electrode;
- (f) releasing the restraints of the said temporary restraining means;

- (g) determining the distortion of the various said sample electrode portions.
4. The method of determining the effect of current density upon the mechanically distorting results of electrolytic operations which comprises:
- (a) providing a sample electrode comprising a plurality of separate but coplanar closely adjacent flat, relatively thin electrode portions of the same material and of identical thickness mechanically connected to a common header strip and free at their distal ends;
- (b) providing temporary restraining means to prevent motion of the said distal ends with respect to said common header strip;
- (c) surrounding said sample electrode portions with an electrochemical bath;
- (d) immersing a counterelectrode in said bath in such orientation that electric current flowing between said counterelectrode and said sample electrode portions will flow in differing densities to each said sample electrode portions;
- (e) passing electric current between said counterelectrode and said sample electrode in the proper direction to cause the said electrolytic operation to occur at the sample electrode until some of said sample electrode portions are stressed in a first direction and other sample electrode portions are stressed in a second direction opposite to said first direction;
- (f) releasing the restraints of the said temporary restraining means;
- (g) determining the distortion of the various said sample electrode portions.

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