Feb. 20, 1968 C. DAVIDOFF ETAL 3,369,987

APPARATUS FOR PERIODICALLY SUPPLYING MAKE-UP MATERIAL TO AN ELECTROCHEMICAL BATH

Filed June 5, 1964

FIG. 1

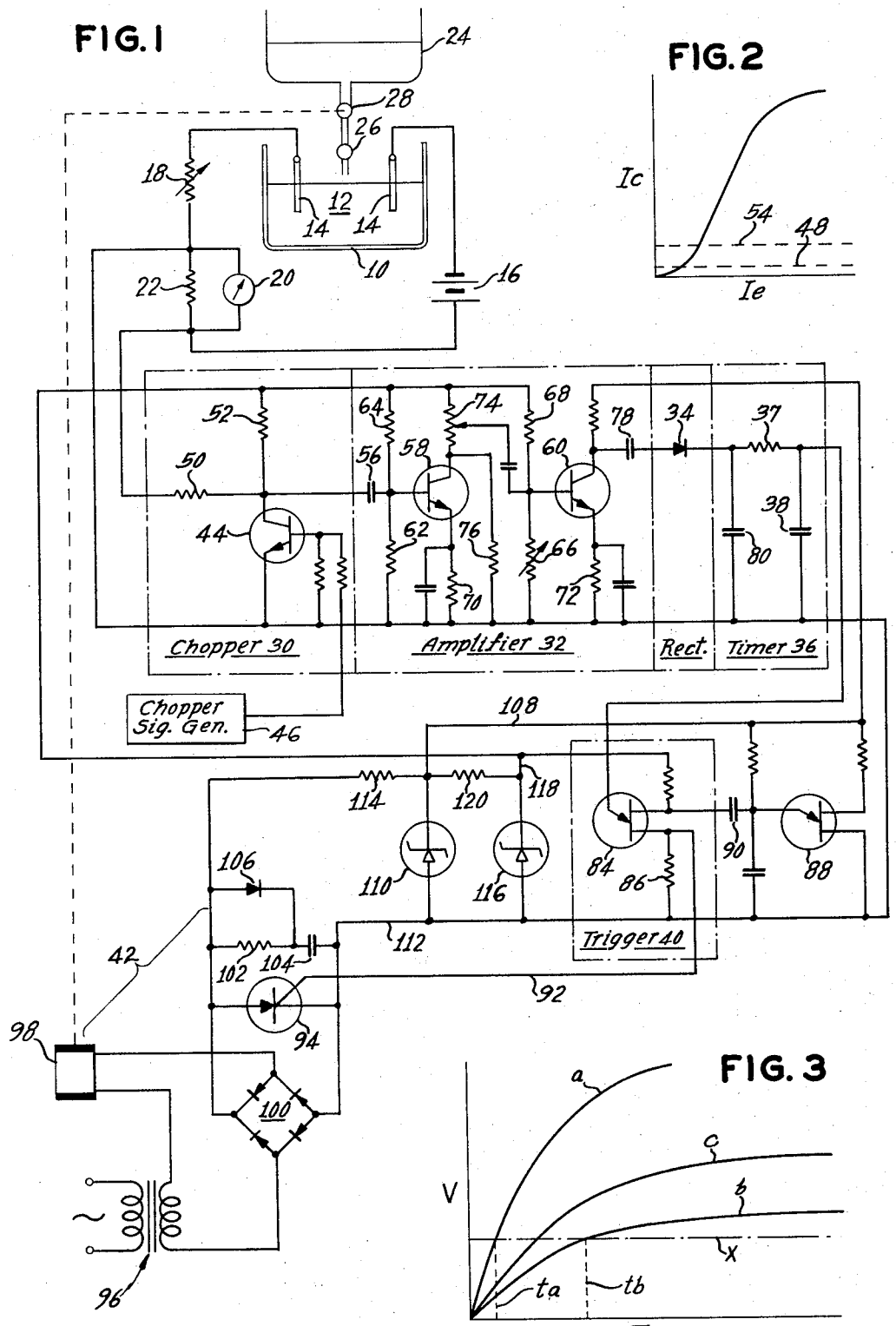


FIG. 2

FIG. 3

United States Patent Office 3,369,987 Patented Feb. 20, 1968

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APPARATUS FOR PERIODICALLY SUPPLYING MAKE-UP MATERIAL TO AN ELECTROCHEMICAL BATH

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Filed June 5, 1964, Ser. No. 372,911
7 Claims. (Cl. 204—275)

The present invention relates to electrochemical apparatus and in particular to apparatus for supplying quantities of make-up material to the solution used in an electrochemical process. While electroplating is discussed below, the invention is applicable generally to electrochemical processes.

It is well known that certain constituents of an electroplating solution are consumed in the course of the operation of electroplating apparatus. Examples of constituents of an electroplating bath that are depleted in the course of operation are the metal ion where an insoluble anode is used, and brighteners used in various electroplating processes. It is customary for such constituents to be added to the plating bath from time to time as are necessary to restore its desired composition.

The composition of a plating bath changes as a function of the level of plating current and the time during which such current flows. In a common procedure for keeping the plating tank continuously in operation, a record will be kept of the last time make-up material was added and of the plating current. Periodically a quantity of make-up material will be added, which is calculated and empirically verified in advance to be proper for restoring the desired composition of the bath. Where regular time intervals elapse, the added quantities will vary in linear proportion to the current level. This procedure has the disadvantage of requiring frequent attention of the supervisor to the electroplating unit, an expensive procedure that depends for success on the consistency of this attention. If long time intervals elapse between additions of make-up material, the composition of the plating solution departs significantly from the optimum composition, so that the quality of the plating must suffer.

An object of the present invention resides in the provision of apparatus which automatically and at frequent intervals delivers make-up material to an electrochemical bath. The term "make-up" material is used here to represent constituents that are consumed as the process continues. In electroplating, these could be metal ions, wetting agents, ductility agents, brightening agents, and so forth.

A more particular object of the invention resides in the provision of apparatus which monitors the current flowing in electrochemical equipment and delivers a measured charge of make-up material to the bath at various times so that the product of the current and the time during which such current flows is substantially a constant. A further object of the invention resides in the provision of the foregoing type of apparatus, which is of relatively low cost construction, yet of relatively high accuracy for the purpose involved. As will be seen from the disclosure below, the illustrative apparatus embodying the various features of the invention and which achieves the foregoing and other objects, includes a device that is adapted to deliver a measured quantity of liquid to a plating bath each time such device is operated; a plating-current monitoring device; a circuit responsive to the monitoring device and including a resistor-capacitor integrating circuit that acquires a charge representing the product of time and the plating current; and a trigger that operates the liquid-delivering device and discharges the integrating circuit each time the predetermined charge has been

reached. The plating-current circuit is of a design that responds nonlinearly to different currents, in such a manner that the trigger-operating level of charge is reached when the product of time and the plating current is a constant, to a close approximation, over a 5:1 range of different levels of plating current. When using this novel apparatus, it is no longer necessary to depend on the attentiveness of an attendant for adding the right amount of make-up reagents at the proper time. Further, it becomes practical to add the needed reagents frequently (rather than once or twice a day) so that the composition of the plating bath can be held virtually constant, with optimum proportions.

The nature of the invention and its further features and aspects of novelty will be more fully appreciated from the following detailed description of an illustrative embodiment which is shown in the annexed drawings forming part of this disclosure. In the drawings:

FIGURE 1 is an illustration of conventional electroplating equipment, together with the wiring diagram of an illustrative embodiment of the invention for adding reagents to the plating bath;

FIGURE 2 is a graphical representation of the operating characteristic of a transistor in the circuit of FIG. 1; and

FIGURE 3 is a graph including a number of curves representing the charging characteristic of the integrating network in FIG. 1 for different voltage input levels.

Electroplating equipment in FIG. 1 is diagrammatically illustrated as including a plating tank **10** containing solution or a bath **12** and electrodes **14**. One electrode is the anode and the other is the cathode that is largely formed by the objects to be electroplated. Plating current through the electrodes is provided by a direct-current supply, here diagrammatically represented by battery **16** and a variable resistor **18** for adjusting the current to the proper value. Different current levels are required for establishing the optimum current density at cathodes of different areas, the current density needed being different in various plating processes. The current is indicated on an ammeter **20** that normally has an internal or external shunt **22**. Conventionally, the ammeter and its shunt are related so as to produce a drop of the order of 0.050 volt for full-scale reading of the ammeter.

Suitably supported above the tank **10** is a container **24** for make-up reagent. The reagent is delivered through a discharge passage that includes a manually adjustable valve **26** and an electromechanical valve **28**. Valve **28** is opened automatically from time to time and remains open for a controlled time interval; and by proper adjustment of valve **26** in relation to the open time a desired quantity of reagent can be delivered to bath **12** each time valve **28** is opened.

For controlling valve **28**, the following apparatus is provided. The voltage drop appearing across ammeter shunt **22** is converted by chopper **30** to a train of interrupted pulses. These are greatly amplified by a two-stage amplifier **32** and converted once again to direct-current by a rectifier **34**. The rectified output is applied to a timer **36** which includes a capacitor **38** whose charge gradually increases over a period of time as a function of the current flowing through shunt **22**. A trigger **40** is connected to capacitor **38**, and fires when the charge reaches a predetermined level. This causes operation of a network **42** that opens valve **28** for a controlled time interval each time trigger **40** operates.

In operation of this apparatus, current flows from supply **16** through bath **12** via electrodes **14**. An electrical representation of the product of time and plating current is developed in capacitor **38**. Each time that this product reaches a predetermined level, trigger **40** and device **42**

operate valve 28 to deliver a measured quantity of make-up reagent.

Timer 36 includes a resistance-capacitance (R-C) network, here including resistor 37 and capacitor 38. The charging curves for capacitor 38 are shown in FIG. 3. It may be considered that a voltage is impressed at the input of network 36 that corresponds to the plating current level. For a full-scale current level on ammeter 20, the rise of charge voltage across capacitor 38 with time is represented by curve *a*, the rise of capacitor-charge voltage for a low level of plating current is represented by curve *b*, and curve *c* represents the charge corresponding to an intermediate plating current. Broken line X represents the charge level at which trigger 40 fires. This level is set low enough to provide a wide range of firing times *ta* to *tb*, where curves *a* and *b* cross line X.

The part of curve *a* below line X is virtually straight, but the part of curve *b* below line X has prominent curvature. Because of this variation in the R-C network charging characteristics for different input voltages, the firing time *ta* represents disproportionately long time for the firing level to be reached in response to low-level plating currents. For some purposes and for a limited range, the lack of proportionality may not be objectionable; but by properly relating the response characteristic of the circuits 30–32–34–36, it has been found possible to hold the product of plating current and time constant within 2% over a 5:1 range of currents.

A more detailed description of the illustrated embodiment follows, constituting relatively compact and low-cost apparatus for the purpose involved. The apparatus includes features through which the product of plating current and time to the firing point is held constant over a wide range of currents.

The voltage that develops across ammeter shunt 22 as a measure of the plating current is a relatively low level of direct-current voltage. For amplifying such a voltage it is common to use a chopper that converts an available low D-C voltage to a pulse train. Chopper 30 includes a transistor 44 having a grounded emitter and a base that is driven to cut-off by a chopper signal generator 46. As the cut-off half-waves of unit 46 disappear, transistor 44 gradually starts to conduct but it does not reach its linear stage until the so-called offset voltage is exceeded. The characteristic of a typical transistor is illustrated in FIG. 2. Above offset voltage level 48 the transistor characteristic is substantially linear. The chopper circuit includes a resistor 50 connected between one terminal of shunt 22 and to the collector of transistor 44. The opposite terminal of shunt 22 is connected to the emitter. A resistor 52 extends from the collector of transistor 44 to a positive direct-current line. Transistor 44 here is the NPN type. The resistance of shunt 22 is a small fraction of an ohm, 0.01 ohm, for example. The resistance of resistor 50 is made extremely large in comparison to that of ammeter shunt 22. Resistor 50 may be 1,000 ohms, for example. The current through resistor 50 may be adjusted to a voltage between the emitter and the collector, by proper selection of resistor 52, so that the offset voltage 48 will appear across the terminals of chopper transistor 44 in the absence of any voltage across ammeter shunt 22. The effect of the current in resistors 52 and 50 flowing through ammeter shunt 22 is of course negligible. Thereafter, upon appearance of any voltage across ammeter shunt 22 due to plating current flow, such voltage is added to the voltage developed in resistor 50 and impressed on the chopper.

It is advantageous to proportion resistors 50 and 52 so as to provide a higher bias voltage 54 (FIG. 2) across resistor 50 than offset voltage 48. This disproportionately increases low-voltage signals and corrects partially for the disproportionally long firing time *ta* (FIG. 3).

The output signal of chopper 30 is a train of pulses that is coupled via capacitor 56 to a first stage of amplifier 32. The amplifier includes transistor 58 in a first stage and transistor 60 in a second stage. This amplifier is of a design that incorporates features promoting gain stability over a normal variation in ambient temperature and against drift in the transistor characteristics. For this purpose, the base of transistor 58 has a stabilized operating bias developed by resistors 62 and 64 and the base of transistor 60 has a stabilized bias provided by resistors 66 and 68. Bypassed resistors 70 and 72 interposed between ground and the emitter of each transistor 58 and 60, respectively, provide temperature stabilization. Resistor 74 which forms the collector load of transistor 58 has a gain-adjusting slide tape for a linearity control, and resistor 66 is also adjustable for zero adjustment. A stabilizing resistor 76 is connected between the collector of transistor 58 and ground. Further promoting stable operation, a relatively low operating voltage is used for the first transistor amplifier stage 58, and for the base bias of transistor 60. A higher operating direct-current voltage is used for the second transistor 60 of the amplifier, the latter having a much higher level of signal input and being less sensitive to drift than transistor 58.

A small coupling capacitor 78 couples the output of amplifier 60 to rectifier 34 and timer 36. This timer includes an input capacitor 80 that is charged to the peak value of output pulses of rectifier 34. Resistor 37 and capacitor are proportioned to have a long time constant, of the order of the longest time interval desired between operations of valve 28. Capacitor 38 should have low leakage. A tantalum capacitor is desirable for this purpose.

The junction of resistor 37 and capacitor 38 is connected to the emitter or trigger of a unijunction transistor 84. Below its firing point, the trigger draws very little current, and this has only a negligible effect in retarding the build-up of charge on capacitor 38. When the charge on capacitor 38 rises to the firing point of unijunction transistor 84, firing occurs. Capacitor 38 discharges through the trigger and this produces a pulse across resistor 86.

As unijunction transistor 84 approaches its firing condition, the trigger starts to draw a certain amount of leakage current; and this could delay the build-up of charge an capacitor 38, in some conditions even making build-up of the charge to the firing point uncertain. To avoid this effect, a form of relaxation oscillator including unijunction transistor 88 is provided having a small output coupling condenser 90 to apply a small signal such as minus 0.1 volt to the anode of unijunction transistor 84.

It may be assumed that the charge on capacitor 38 is approaching the firing point of unijunction transistor 84, which may be 2.4 volts in an example. As the actual firing point is very closely approached, the emitter would start to draw leakage current. However, by virtue of the signal applied by coupling condenser 90 to unijunction transistor 84, what might otherwise be a marginal firing voltage on the emitter of the unijunction transistor constitutes a definite firing voltage during the time of pulse transmission from coupling condenser 90.

Firing of trigger 40 (including unijunction transistor 84) is effective to discharge capacitor 38 and to provide an output pulse along line 92 to the device 42 that operates valve 28. Device 42 includes an isolating transformer 96 whose secondary is connected to an electromagnet 98 and the alternating-current input terminals of a full-wave diode bridge 100. Electromagnet 98 when energized opens valve 28 to deliver make-up reagent to the plating bath. The direct-current terminals of bridge 100 extend to the anode and cathode of silicon controlled rectifier (SCR) 94, whose gate is connected to pulse input line 92. A timing circuit is connected across the direct-current terminals of bridge 100. This timing circuit becomes charged before firing of the SCR, and maintains SCR 94 conductive for a controlled time interval after it is initially fired, to hold valve 28 open for a definite interval and thereby deliver a definite amount of reagent. The timing circuit includes a resistor 102 in series with a capacitor 104. A diode 106

is connected as a shunt across resistor **102**, polarized to charge capacitor **104** to the peak value of voltage at the direct-current terminals of bridge **100** when SCR **94** is not conductive.

It may now be considered that a firing pulse has developed on line **92** and SCR **94** fires. As is well known, the SCR remains conductive so long as the anode-to-cathode voltage remains above the minimum value. During the first one-half alternating current cycle at the secondary of transformer **96**, current is passed through bridge **100** and SCR **94** to energize relay **98**. At the end of that half-wave of alternating current, there might be an end to the energization of electromagnet **98** but for the timing circuit **102, 104**. The latter maintains a minimum amount of current flow through the SCR to sustain conduction until the next half-wave of alternating current which sustains the fired condition of the SCR and continues the energization of electromagnet **98** during that second half-cycle. So long as SCR **94** remains conductive between half-waves, the voltage across the timing circuit remains relatively small and consequently capacitor **104** continues to discharge through resistor **102** and into the SCR. After a time interval which depends upon the time constant of resistor and capacitor **102, 104** and the extinction-current level of SCR **94**, the SCR becomes non-conductive. Electromagnet **98** is therefore deenergized and it remains deenergized until another firing pulse for the SCR appears on line **92**.

Direct-current operation potential for the entire circuit is supplied by bridge **100** when SCR **94** is non-conductive. A first relatively high-voltage direct-current output is developed on line **108** by virtue of the stabilizing action of zener diode **110**, which is connected between line **108** and the common negative line **112** of the entire system. Variable current is drawn by zener diode **110** through resistor **114**, with the result that a stabilized voltage appears on line **108**. Similarly, another zener diode **116** is connected between low-voltage D-C line **118** and common negative line **112**. A resistor **120** is connected between lines **108** and **118**, and this resistor together with zener diode **116** act to maintain a stabilized low voltage on line **118**, below that of line **108**. It will be recalled that a low level of voltage is supplied to certain portions of the chopper and amplifier circuits **30** and **32**.

This low voltage is supplied by line **118**. Low-voltage zener diode **116** is extremely stable, and consequently provides a stable voltage for the base bias and operation of transistor **58** and for the base bias of transistor **60**. The same low stable voltage supply is provided for developing offset and corrective voltage via resistors **50** and **52** in chopper **30**.

Various plating baths will draw various amounts of current, but in general the voltage developed across the ammeter shunt at full scale reading will ordinarily be of the order of 0.050 volt. Between full-scale reading and as low as perhaps 20 or 25% of scale reading, the same ammeter ordinarily will be used. However, when still lower currents are to be used in a given plating bath or on other plating baths, a different ammeter will ordinarily be used. As a result, it is intended that the present circuit shall respond to a range of current levels between approximately 20% and 100% of full-scale when the product of plating-current and time reaches a constant, within a permissible latitude. Ordinary transistor and chopper circuits are designed to respond linearly to a range of small input signals by providing proportionally amplified output signals. As noted above, it is of distinctive advantage in the described embodiment to impart non-linearity to the circuit that couples the plating ammeter to the R-C timing network **37, 38**. One circuit feature is the inclusion of greater-than-offset bias input to chopper **30**, for boosting over-all response of the circuit to plating currents at the low end of the range. Another design feature toward maintaining a constant product of plating current and time over a range of different currents is to make deliberate use of the non-linear top portion of the transistor characteristic, by ensuring its operation into the saturation region in response to high levels of plating current, at the top of the range of this apparatus. The same loss-of-gain at the high levels is promoted by using unusually high values of collector load resistance. The manner of imparting disproportionately large response to low-level signals and causing lower-than-linear response to high-level signals can no doubt be achieved in various ways; but it is a detailed feature of the present invention that the translating circuit between the plating-current measuring device and the R-C time-current product integrating network should not be linear. More particularly, the translating circuit should either have enhanced response to plating current levels near the lower end of the range or the response toward the high end of the range should fade or increase at a less-than-proportional rate, or both features of non-linearity may be used, where the R-C network illustrated is used for response to a wide range of plating currents and high accuracy is wanted.

The apparatus described is effective for supplying make-up constituents to the bath at frequent intervals. This avoids the wide variations in bath composition that occur where an attendant adds make-up constituents at widely spaced times. In an example, the times between operations of valve **28** may be adjusted to 1 to 5 minutes, the frequency of such valve operations depending on the planting current; and the duration of a valve opening being 5 seconds in an example.

It will be readily recognized that the illustrative embodiment of the invention shown and described will be subject to a latitude of modification and varied application, and therefore the invention should be broadly construed in accordance with its full spirit and scope.

What is claimed is:

1. Apparatus for periodically supplying make-up material to the bath of electrochemical equipment, where such equipment includes electrodes and electrode-current supply means, said apparatus including a feeding device effective when operated to deliver a predetermined amount of make-up material to the bath, an integrating network including a capacitor for storing a charge representing the integral with time of a voltage applied to the input terminals of the network, means for applying to the input terminals of said integrating network a voltage representing the electrode current so that the capacitor stores a charge approximately representing the product of said electrode current and time, and means responsive to said network when the stored charge attains a predetermined level for operating said feeding device.

2. Apparatus in accordance with claim **1**, including means for discharging said capacitor in coordination with the operation of said feeding device.

3. Apparatus in accordance with claim **1**, wherein said voltage applying means has a nonlinear characteristic in which the response to low-level input signals is relatively higher than that for higher level signals.

4. Apparatus in accordance with claim **1**, wherein said voltage applying means includes means for adding a biasing signal to the representation of the electrode current for enhancing the low-level part of the range thereof.

5. Apparatus in accordance with claim **1**, wherein said voltage applying means includes means providing less-than-proportional output at the upper portion of its voltage range.

6. Apparatus in accordance with claim **1**, wherein said voltage applying means includes means adding bias to the electrode-current representing signal for enhancing the output at the low part of the voltage range and means having less-than-proportional output at the upper part of its operating range.

7. Apparatus for supplying make-up material to the bath of electrochemical equipment, such equipment including electrodes, current supply means for the electrodes

and electrode-current measuring means, said apparatus including adjustable means for feeding make-up material to the bath at a constant rate, means for integrating a representation of the electrode current as a function of time, means for initiating operation of said feeding means when the integrated quantity reaches a certain level, and uniform timing means for maintaining operation of feeding means during a definite time period to effect delivery of a predetermied quantity of make-up material each time said feeding means is operated.

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