

METHOD AND APPARATUS FOR CONTROLLING
ELECTROLESS PLATING BATH

5 This invention relates to a method for controlling electroless plating baths, such as electroless nickel plating baths, and to apparatus used therefor.

Electroless plating baths are susceptible to considerable variation in their composition since metal salt, reducing agent and other ingredients are quickly consumed during plating. It is thus necessary frequently to replenish such consumed ingredients to keep the rate of deposition constant and the thickness and properties of deposits uniform. For such purposes, a variety of methods and apparatus for the automatic control or replenishment of electroless plating baths have been proposed as disclosed in Japanese Patent Application Laid-Open Nos. 53-44434, 53-45631 and 54-8123.

However, electroless plating baths such as electroless nickel plating baths and electroless copper plating baths have a short effective life. As electroless plating is continued for an extended period of time, reaction by-products accumulate in the plating solution. The reaction by-products, which are believed to be decomposition products of a reducing agent and neutralization salts resulting from plating reaction, adversely affect such factors as plating rate and properties of deposits. With reaction by-products accumulated, the replenishment of ingredients consumed by plating cannot prevent reduction.

of the plating rate and variation of the composition and properties of deposits. Accordingly, although electroless plating solution is replenished either by the above-mentioned automatic replenishing methods or manually when needed, plating baths age or become unusable within a relatively short period of time. The rate of deposition is greatly reduced and the properties of the resulting deposits vary considerably compared with those obtained from the initial plating solution, even when the metal ion and the reducing agent are replenished so as to increase their concentrations to the levels in the initial plating solution. Under such circumstances, the aged bath must be discarded and replaced by a fresh plating solution.

Even in the case where the above-mentioned automatic control of an electroless plating bath is employed to automatically replenish a plating solution, the degree of aging of the bath should always be separately monitored to accommodate such aging. Accordingly, plating baths must be discarded after a relatively short period of use in the prior art electroless plating processes combined with the above-mentioned automatic control method. The prior plating processes are also unsatisfactory with respect to bath maintenance.

It is therefore desirable to provide a method and apparatus for controlling an electroless plating bath whereby stable continuous electroless plating can be carried out for an extended period of time with substantial elimination of the need

for remaking the electroless plating bath, or at least with substantial reduction of plating bath remaking as compared with the prior art method, and hence with substantial advantages in waste disposal.

5 It is also desirable to provide a method and apparatus for controlling an electroless plating bath whereby the rate of desposition and the properties of deposits can be kept substantially constant and uniform for an extended period of time, and bath maintenance is easy and accurate.

10 It is further desirable to provide electroless plating control method and apparatus suitable for the practice of electroless plating of e.g. nickel, cobalt, nickel-cobalt alloy, copper, tin, gold and silver.

 According to one aspect of the present invention,
15 there is provided a method for controlling an electroless plating bath the method comprising the steps of:
 continuously or intermittently measuring the concentration of at least one consumable ingredient in the electroless plating bath, and automatically adding to the plating bath
20 a first replenishing composition comprising consumable ingredients after detecting that the measured concentration has reached a predetermined value while continuously or intermittently measuring, directly or indirectly, the amount of at least one consumable
25 ingredient of the electroless plating bath consumed over a period to determine the degree of aging of the bath, and automatically discharging a predetermined volume of the plating solution and automatically adding to the plating

bath a second replenishing composition containing unconsumable ingredients in an amount essentially corresponding to the amount lost by the discharging after detecting that the amount of the consumable ingredient
5 consumed during said period has reached a predetermined value.

According to another aspect of the present invention, there is provided apparatus for controlling an electroless plating bath, the apparatus comprising:

10 a mechanism for adding a first replenishing composition including:

means for automatically measuring the concentration of at least one consumable ingredient in the electroless plating bath,

15 concentration detecting means for generating a first signal when the measured concentration has reached a predetermined value and

means for automatically adding the first replenishing composition comprising consumable ingredients to
20 the electroless plating bath upon receipt of the first signal, and

a mechanism for discharging a predetermined volume of the electroless plating solution and adding a second replenishing composition including

25 means for measuring directly or indirectly the amount of at least one consumable ingredient of the electroless plating bath consumed during the current period upto the next discharging and

replenishment to determine the degree of aging
of the bath,

aging degree detecting means for generating a second
signal when the amount of the consumable

5 ingredient consumed during the current period
has reached a predetermined value,

means for discharging a predetermined volume of the
plating solution upon receipt of the second
signal, and

10 means for adding to the electroless plating bath the
second replenishing composition containing
unconsumable ingredients in an amount
essentially corresponding to the amount lost by
the discharging.

15 In the present invention, "consumable ingredients"
refers to ingredients consumed during electroless plating,
e.g. metal ion such as nickel ion and a reducing agent
such as sodium hypophosphite for nickel electroless
plating bath, and "unconsumable ingredients" refers to
20 ingredients not essentially consumed during electroless
plating except by drug-out, e.g. a chelating agent such as
sodium acetate, sodium citrate, etc.

In preferred embodiments of the present invention, the
concentration of the electroless plating bath is measured
25 in terms of the concentration of metal in the bath, while
the degree of aging of the electroless plating bath is
obtained by measuring the consumed amount of

metal ion in the bath. In this case, the amount of the metal ion consumed in the bath may be monitored by counting the number of replenishments of the first replenishing composition which in turn, is obtained by counting the number of command signals for commanding the automatic replenishment of the first replenishing composition.

Since the concentration of the electroless plating bath, for example, the metal concentration in the bath, is measured to determine the amount of the consumable ingredients consumed during plating, and the first replenishing composition essentially consisting of the consumable ingredients is automatically replenished in accordance with the measured value, while the consumed amount of a consumable ingredient (for example, a metal ion) in the bath is measured to determine the degree of aging of the bath and a predetermined volume of the plating solution is discharged, and the second replenishing composition containing the unconsumable ingredients essentially corresponding to the discharged portion is automatically replenished each time the given consumable ingredient has been consumed in a predetermined amount (that is, each time the degree of aging has reached a predetermined value), the bath is automatically refreshed, substantially eliminating the need for remaking the plating bath or at least substantially extending the effective life of the bath as compared with the prior art methods. Furthermore, since the consumable ingredients such as metal ions, reducing agents, etc. are maintained at substantially constant

concentrations and the amount of reaction by-products resulting from plating process is maintained within an allowable range, the rate of deposition and the properties of the resulting deposits are maintained
5 constant and uniform. Differently stated, the bath is maintained under highly stable conditions for an extended period of time. It is also possible to maintain the plating bath at a lower metal concentration than the prior art bath while retaining the rate of
10 deposition at substantially the same level as the prior art. These features are also advantageous from a point of view of waste disposal.

The present invention may advantageously be applied to electroless plating baths of nickel, cobalt,
15 nickel-cobalt alloy and copper.

The invention will become more apparent from the following description with reference to the
20 accompanying drawings, in which:

FIG. 1 is a block diagram schematically showing one embodiment of the electroless plating arrangement according to the present invention;

FIG. 2 is a block diagram of an example of the
25 concentration measuring device;

FIG. 3 is a block diagram of a spectrophotometer section of the concentration measuring device; and

FIG. 4 is a block diagram of a control section of the concentration measuring device.

Referring to FIG. 1, one embodiment of the arrangement for controlling an electroless nickel plating bath according to the present invention is schematically shown as including a plating tank 1 which is provided with the necessary attachments including a heating element for heating an electroless plating bath 2 to a desired temperature, for example, a heater or steam pipe, a cooling element for cooling the bath 2 to a approximately room temperature after the completion of plating, a filter, a stirrer and the like, although they are not shown in the figure.

In connection with the plating tank 1, the arrangement includes a concentration measuring/detecting device 3 for automatically measuring the concentration of the plating bath and transmitting signal A when the measured value has reached a predetermined concentration level and signal B when the number of command of signals A has reached a predetermined level, a fluid circulating pump 4 in the form of a microtube pump, for example, and a circulating line 5 connecting the tank 1, measuring/detecting device 3 and the pump 4. The plating solution 2 in the tank 1 is pumped from the inlet through the line 5 to the concentration measuring/detecting device 3 where the concentration of the plating solution 2, for example the nickel concentration, is measured before it is returned into the tank 1 from the outlet of the line 5.

FIGS. 2 to 4 illustrate an example of the concentration measuring/detecting device 3. As shown in FIG. 2, the line 5 is provided with a bypass conduit 6 which in

turn, is provided with a spectrophotometer unit 7 including a flow-through cell 7a. As the plating solution 2 flows through the bypass conduit 6 and then through the flow-through cell 7a of the spectro-
5 photometer unit 7, the optical transmittance of the solution is measured to determine the metal concentration in the solution. In this respect, it is preferable to measure the absorbance of a metal complex in the plating solution in order to follow the consump-
10 tion of the metal by plating in a more sensitive manner. The transmittance of the plating solution at the absorption wave length of the metal complex is transduced into a voltage signal by means of a suitable transducer. The concentration of the plating solution
15 2 is monitored in this manner.

The concentration measuring/detecting device 3 is described in detail by referring to FIGS. 3 and 4. As shown in FIG. 3, light L emitted by a light source 8 in the spectrophotometer unit 7 passes through a heat radiation-
20 absorbing filter 9, a wave length-selecting filter 10 and a condensing lens 11 in this order before it passes through the cell 7a through which the plating solution flows continuously. The absorption of light by the plating solution is detected by a photometer 12. Another cell
25 7b containing the standard solution is mounted adjacent the cell 7a so that the cells may be alternately placed in the light path. The measurement cell 7a and the standard cell 7b are movable in the direction shown by an arrow. The standard cell 7b may be moved in the light
30 path to replace the measurement cell 7a when needed,

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thereby measuring the absorbance of the standard solution. The spectrophotometer unit 7 is electrically connected to a control section 13. As shown in FIG. 4, a minute current flow output of the photometer 12 is fed to an input 14, amplified and converted into a voltage by an amplifier 15, and indicated by a voltmeter 16 in the form of a voltage corresponding to the absorbance. A comparator 17 compares the output of the amplifier 15 with a preset voltage and produces signal A at its output 18 when the amplifier output reaches the preset value. If the preset voltage value corresponds to the absorbance at a given concentration to which the metal ion in the plating solution is consumed, then signal A developing at the output 18 represents that the metal concentration has reached the given value. Signal A is transmitted to a first replenishing mechanism 19 which consists of a reservoir 20 containing a first replenishing composition, a supply conduit 21 connected to the reservoir 20 and opening in the plating tank 1, and an electromagnetic valve 22 in the conduit 21. Upon receipt of signal A, the valve 22 is opened for a given time to allow a given amount of the first replenishing composition to flow into the plating tank 1 through the conduit 21. Thus the given amount of the first replenishing composition essentially consisting of consumable ingredients, for example, a metal salt, a reducing agent, a pH regulating agent and other consumable components is added to the electroless plating bath corresponding to the consumption. It should be noted that although the single

reservoir 20 is depicted in FIG. 1, a plurality of reservoirs may be used. Each reservoir contains different one of the consumable ingredients (e.g., a metal salt, a reducing agent, a pH regulating agent and other components). Of course, each reservoir is provided with its own conduit and electromagnetic valve.

By analyzing the metal value, e.g. nickel value in an electroless nickel plating bath, in this manner, not only the amount of the metal consumed during plating is available, but also the amount of the reducing agent consumed and the variation of pH value are available at the same time.

As shown in FIG. 4, a counter 23 is connected to the control section 13. The counter 23 counts the number of command of signals A for instructing opening of the electromagnetic valve 22 of the first replenishing mechanism 19. The number of actuation of the electromagnetic valve 22 is the number of replenishment of the first replenishing composition. A detector 24 is also provided which detects that the number of command of signals A (that is, the number of replenishment of the first replenishing composition) reaches a predetermined number. At this point, the detector 24 transmits signal B from its output 25.

Referring to FIG. 1 again, numeral 26 is a discharge mechanism actuatable upon receipt of the above-mentioned signal B. This discharge mechanism 26 comprises a discharge pipe 27 having one end in fluid communication with the plating tank 1 and a control pump 28 disposed

in the pipe. Upon receipt of signal B from the output
25 of the detector 24, the pump 28 operates for a
given time to discharge a given volume of the plating
solution 2 out of the tank 1. Numeral 29 is a mechanism
5 for supplementing the second replenishing composition
containing essential ingredients which are to be lost
by the discharging. The replenishing mechanism 29
comprises a reservoir 30 containing the second replenish-
ing composition, a feed pipe 31 having one end connected
10 to the reservoir 30, and an electromagnetic valve 32
disposed in the pipe 31. The electromagnetic valve 32,
which receives signal B from the output 25 of the
detector 24, opens for a given time after the discharge
pump 28 has been interrupted, to thereby add the second
15 replenishing composition containing unconsumable in-
gredients in a volume essentially corresponding to the
discharged volume into the tank 1. In this regard, the
replenishing mechanism 29 may include a plurality of
reservoirs each for different one of the ingredients to
20 be replenished, each having an individual feed pipe and
valve.

In FIG. 1, a cooler 33 is provided in the measur-
ing line 5 to cool the flow of the plating solution
therethrough from the tank 1 to near room temperature.
25 Also provided in the line 5 is a filter 34 for filtering
out very fine insolubles out of the flow of the plating
solution therethrough. The location of the cooler 33
in the line 5 upstream of the concentration measuring/
detecting device 3 allows for measurement of concentra-
30 tion at room temperature because a flow of the plating

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solution through the bypass conduit 6 has been cooled
to room temperature. For the purpose of avoiding
temperature dependence of these measurements, any other
means may be employed as exemplified by the use of a
5 constant-temperature bath or a temperature probe ac-
companied with electrical compensation.

Described below is how to control an electroless
nickel plating bath using the above-constructed arrange-
ment.

10 A workpiece to be plated is first subjected to
well-known necessary pre-treatments in a conventional
manner before electroless nickel plating is carried out
by immersing the pre-treated workpiece in the plating
bath 2 in the tank 1 heated at a desired temperature,
15 for example, 90°C.

In the practice of plating in this manner, the
pump 4 is operated to introduce part of the plating
solution 2 from the tank 1 into the measuring line 5.
As the plating solution continuously passes through the
20 concentration measuring/detecting device 3 where the
concentration (nickel concentration in the case of the
concentration measuring/detecting device 3 shown in FIG.
2) of the solution is automatically measured.

The progress of plating results in a reduction
25 of the concentration of the plating solution, particular-
ly the concentrations of nickel ion and a reducing agent
(such as sodium hypophosphite) in the solution. In the
event a hypophosphite is used as a reducing agent for
electroless nickel plating, the plating solution also
30 shows a reduction of pH. As a result of such concentration

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reduction, when the nickel concentration measured by the spectrophotometer unit 7 reaches a predetermined concentration value in the case of the concentration measuring/detecting device 3 shown in FIG. 2, the control section 13 associated with the detecting device 3 produces signal A. In detail, prior to measurement of the absorbance of the actual plating solution, the standard solution cell 7b is moved in the light path to replace the cell 7a. The absorbance of nickel in the standard solution in the cell 7b is measured and the thus obtained absorbance value is set in the comparator 17 as a reference value. Then the flow-through cell 7a is moved in the light path. When the concentration (nickel concentration) of the solution which is given in terms of the absorbance of the plating solution measured by the spectrophotometer unit 7 reaches the predetermined concentration value or when the voltage detected reduces to or below the preset reference value, the comparator 17 transmits signal A to the electromagnetic valve 22 of the first replenishing mechanism 19 to open the valve 22 for a given time. Accordingly, a given amount of the first replenishing composition is fed from the reservoir 20 to the tank 1 to compensate for those ingredients consumed during the preceding plating such as nickel ion and reducing agent and to adjust the pH of the plating bath 2. It should be noted that the first replenishing composition mainly contains those ingredients consumable during plating including nickel salt, reducing agent and pH regulating agent such as sodium hydroxide and optionally, a minor

amount of complexing agent, stabilizer, brightener, etc. It is generally desired to keep the nickel salt, reducing agent and pH regulating agent separate from each other. In such separate storage, each optional agent
5 such as complexing agent, stabilizer, and brightener may preferably be mixed with the basic ingredient to which it is inert.

By adding the first replenishing composition in this manner, the concentration of the plating bath 2 (the
10 concentrations of nickel, reducing agent, etc.) is restored to the initial level so that the rate of plating or deposition is maintained substantially constant.

On the other hand, the counter 23 counts the number of command of signals A to the valve 22 of the first
15 replenishing mechanism 19, that is the number of actuation of the valve 22, and hence the number of replenishment of the first replenishing composition. When the detector 24 detects that the counted number reaches a predetermined number, for example, each time when one or
20 several signals A are generated, the detector 24 transmits signal B from its output 25 to the pump 28 of the discharge mechanism 26 to operate the pump 28 for a given time, thereby discharging a given volume of the plating solution 2 from the tank 1 through the discharge pipe 27.
25 It should be noted that the discharge liquid is desirably fed to a waste treatment device and essential ingredients contained therein may be circulated for reuse after the undesired by-products are removed. Upon interruption of the pump 28, the electromagnetic valve
30 31 of the second replenishing mechanism 29 is opened for

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a given time to supply a given volume of the second replenishing composition from the reservoir 30 to the tank 1. It should be noted that this second replenishing composition makes up for those ingredients to be lost by discharging and mainly contains a complexing agent. Generally, use may be made of a solution having the same composition as the initially made-up plating bath or its concentrate or those solutions mainly containing a complexing agent which is scarcely consumed by plating. If ingredients to be replenished, such as metal salt and reducing agent tend to react with each other, it is preferred that they are separately stored in different reservoirs.

The discharging of a given volume of the plating solution and the replenishing of an essentially corresponding volume of the second replenishing composition prevent reaction by-products from accumulating in the plating bath to an undesired extent, thereby controlling the amount of such reaction by-products within an allowable range. As a result, reduction of plating rate due to accumulation of reaction by-products is precluded. The plating bath is intermittently renewed in the continued operation for an extended period of time. For an extended operation of the plating bath, the plating rate is maintained substantially constant and deposits are maintained substantially uniform in every respect including the composition and properties, for example, Ni-P alloy composition for a hypophosphite reducing agent and the hardness of deposits.

in a plating bath as plating is continued for a period of time. The accumulated reaction by-products adversely affect the plating rate and the quality of deposits. These reaction by-products mainly consist of the products of a reducing agent decomposed when the metal ion in the plating bath is reduced into an elemental metal by the reducing agent and neutralization salts resulting from this reaction. In this respect, the amount of reducing agent required to reduce a certain amount of metal ion into an elemental metal is substantially constant and the amount of reaction by-products resulting from this reduction is also substantially constant. The consumption of a given amount of metal ion or reducing agent results in the formation of a corresponding amount of reaction by-products. Therefore, the consumed amount of a consumable ingredient in such a plating bath represents the degree of accumulation of reaction by-products in the bath. Accordingly, by detecting the consumed amount of at least one consumable ingredient in the bath (for example, the consumed amount of metal ion or reducing agent, more specifically, the consumed amount of nickel ion, or hypophosphite in the case of electroless nickel plating bath using a hypophosphite reducing agent, or in some cases the consumed amount of caustic alkali), the degree of accumulation of reaction by-products, that is, the degree of aging of the plating bath can be accurately detected. In this embodiment, the detection of the number of actuations of the valve 22 is equivalent to the detection of the number of replenishments of the first replenishing composition which

in turn, is equivalent to the detection of the consumed amount of the consumable ingredients during plating. Each time the number of actuations of the valve 22 reaches a predetermined value, a given volume of the plating solution 2 is discharged and an essentially corresponding volume of the second replenishing composition (mainly containing ingredients to be lost by the discharging) is replenished, thereby maintaining the amount of reaction by-products within an allowable range in the plating bath. As a result, the plating solution is effective semi-permanently or at least the effective life of the plating solution is remarkably extended as compared with the prior art methods. In addition, the plating rate and the properties of deposits are maintained substantially uniform for the prolonged operation of the bath.

According to the above-mentioned plating process, the plating bath is automatically controlled and maintained in an easy, but accurate manner. Especially important is the easiness of maintenance of electroless plating baths which are notoriously troublesome to handle as compared with usual electroplating. Furthermore, since the plating bath is always maintained at a substantially constant concentration by the replenishment, the nickel concentration of the bath may be set lower at the beginning unlike the prior art which needs to set the initial nickel concentration to a higher level in order to compensate for the reduction of plating or deposition rate due to reduction of nickel concentration in the progress of plating. In addition, the plating bath is automatically renewed little by little by means of the discharging

and replenishing mechanisms 26 and 29, minimizing the burden of waste treatment.

In the above embodiment, the absorbance of a plating solution is directly measured in order to
5 determine metal concentration such as nickel in the plating solution. However, the method for measuring metal concentration in the plating solution is not limited thereto, but any other suitable means may be used. For example, an indicator or other suitable re-
10 agents such as EDTA may be added to the plating solution to cause the plating solution to develop the corresponding color. The degree of color development is a measure for the metal concentration. In this case, however, those portions of the plating solution which have been
15 subjected to concentration measurement cannot be fed back to the line 5 via the bypass conduit 6 as in the case of FIG. 2. The plating solution after measurement should be separately fed to a suitable unit for waste disposal. Another example of concentration measurement
20 is to measure the potential difference between the initial and the subsequent portions of the solution. However, the above-described method of directly measuring the absorbance of the plating solution is most advantageous among others because it can be performed by means of
25 simple equipment and the plating solution subjected to measurement can be fed back to the plating tank 1 again. Furthermore, it is also possible to detect the varying concentration of a plating solution by measuring the varying pH value thereof. Additionally, the above-
30 mentioned nickel concentration measurement may be combined

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with the pH measurement so that the pH of the plating solution may be automatically and independently controlled in accordance with the value of pH measured.

The detection of the consumed amount of the consumable ingredients is carried out by the method of detecting the number of actuations of the valve 22 by counting the number of commands of signals A in the above embodiment. If a dispensing pump is used to replenish a metered amount of the first replenishing composition, the consumed amount of the consumable ingredient may be detected by counting the number of actuations of the dispensing pump. Any other suitable detecting methods may be employed for a particular way of replenishing. Furthermore, the consumed amount of the consumable ingredient may also be detected by measuring the amount of a metal deposited. If workpieces to be plated have a substantially equal surface area and the necessary plating time or necessary deposition thickness is equal for each plating cycle, then an equal amount of metal is reduced and deposited and an equal amount of metal ion is consumed in each plating cycle. Then the detection method may be to count the number of signals generated by a limit switch each time a plated workpiece is replaced by a new unplated workpiece in the plating bath. If workpieces to be plated have a substantially equal surface area, but the necessary plating time is not always equal, then the amount of metal deposited may be detected by measuring the plating time and the consumed amount of the consumable ingredients may be derived therefrom. After a certain total plating time, the above-

mentioned discharging and replenishing steps may be carried out.

In the above-mentioned embodiments, the concentration measuring device is incorporated in the bypass conduit, but it may be directly incorporated in the circulating line with omission of the bypass conduit. Also, the concentration measuring device may be provided within the plating tank.

In the above-mentioned embodiments, the second replenishing mechanism 29 acts after the discharge pump 28 of the discharge mechanism 26 has been interrupted. Alternatively, the replenishing mechanism 29 may act by the command of signal B when or before the discharge pump 28 operates. The first and second replenishing mechanisms 19 and 29 are not limited to the above-mentioned embodiments. For example, a dispensing pump may be used for the supplement of the first or second replenishing composition.

The discharge mechanism 26 may be replaced by an overflow pipe 35 as depicted by a dot-and-dash line in FIG. 1. In this case, signal B is transmitted from the control section 13 to the second replenishing mechanism 29 to feed a given volume of the second replenishing composition to the plating bath in the tank 1. An incremental volume of the plating solution due to the addition of the second replenishing composition is discharged through the overflow pipe 35. Although the above-mentioned embodiments refer to the control of electroless nickel plating, similar results may be obtained for other electroless plating including electro-

less cobalt plating and electroless cobalt-nickel plating as well as electroless copper plating using a formalin or hypophosphite reducing agent.

Other modifications and variations may be made within the scope and spirit of the invention.

The invention will be understood more readily with reference to the following examples, which are not to be construed to limit the scope of the invention.

Example 1

Plating was conducted in 100 liters of an electroless nickel plating bath having the following composition:

Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	18 g/l
(nickel ion	4 g/l)
Sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)	24 g/l
Sodium succinate	16 g/l
Malic acid	18 g/l
Stabilizer (Pb^{2+})	0.003 g/l
pH	5.6

at a temperature of 90°C in an apparatus as shown in FIGS. 1 to 4 while the nickel concentration was automatically and continuously measured (the nickel concentration measurement was effected by measuring the transmittance at 670 nm). It was assumed that the set level of nickel ion was 4 g/l. At the time the nickel concentration measured had decreased to the set level (4 g/l) or below, signal A was generated to add a first replenishing composition consisting of the below-mentioned three replenishing solutions I, II and III in equal amounts of 400 ml (equivalent to 0.2 g/l of Ni^{2+})

for each addition. These replenishing solution I, II and III were contained in three separate reservoirs each provided with a feed conduit and an electromagnetic valve. In response to signal A, the valves were simultaneously opened for a given time to feed equal amounts of the respective replenishing solutions to the plating bath. It was also assumed that when 1 g/l of nickel ion was consumed or a total amount of the replenishing solution I adding up to 1 g/l of nickel ion was replenished, signal B was generated to discharge 5 liters of the plating bath each time before 5 liters of a second replenishing composition consisting of the solution IV having the following composition was fed. (the invention method)

15 For the purpose of comparison, the above-mentioned plating procedure was repeated except that signal B was not generated, and hence, neither the discharge of the plating solution nor the replenishment of the second replenishing solution IV was conducted. That is, only
20 the nickel concentration was measured and the solutions I, II and III were added accordingly. (comparative method)

After plating was conducted a given number of turns (by "one turn" is meant the consumption of 4 g of
25 nickel ion per liter of plating bath in continuous plating, and hence an increased number of turns results in further aging of the bath), the rate of deposition and the composition of Ni-P alloy deposit were determined, obtaining the results shown in Table 1.

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The first replenishing composition:

Replenishing solution I

Nickel sulfate	225 g/l
Stabilizer (Pb^{2+})	0.075 g/l

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Replenishing solution II

Sodium hypophosphite	270 g/l
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Replenishing solution III

Sodium hydroxide	68 g/l
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10 The second replenishing solution (composition) IV:
the same composition as the initial plating solution

Sodium succinate	16 g/l
Malic acid	18 g/l
Nickel sulfate	18 g/l
Sodium hypophosphite	24 g/l
Stabilizer (Pb^{2+})	0.003 g/l

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Table 1

Number of turns	Rate of deposition ($\mu\text{m}/\text{hour}$)		P content in Ni-P deposit (% by weight)	
	Invention	Comparative	Invention	Comparative
2	20.5	20.0	7.8	7.8
4	20.0	17.0	8.0	8.4
6	19.8	13.5	8.1	9.2
8	19.7	10.0	8.2	9.8
10	19.5	8.5	8.3	10.4
12	19.3	unplated	8.3	-
14	19.1		8.4	
16	19.0		8.5	
18	18.9		8.6	
20	18.8		8.5	
22	18.6		8.7	
24	18.4		8.7	
26	18.5		8.8	
28	18.3		9.0	
30	18.0		8.9	
32	17.9		9.1	
34	17.7		9.3	
36	17.4		9.3	
38	17.2		9.5	
40	16.7		9.6	

Example 2

Plating was conducted in an electroless cobalt plating bath having the following composition:

	Cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$)	22.5 g/l
5	Sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)	22.5 g/l
	Sodium tartrate	115.0 g/l
	Boric acid	8.4 g/l
	Thiourea	0.01 g/l
	pH	9.0

10 at a temperature of 90°C in an apparatus as shown in
FIGS. 1 to 4 while the cobalt concentration of the
bath was automatically and continuously measured. It
was assumed that the set level of cobalt ion was 4 g/l.
At the time the cobalt concentration measured had
15 decreased to the set level (4 g/l) or below, signal A
was generated to add a first replenishing composition
consisting of the below-mentioned three replenishing
solutions V, VI and VII in equal amounts of 2 ml per liter
of the bath for each addition. These replenishing solu-
20 tions V, VI and VII were contained in three separate
reservoirs each provided with a feed conduit and an
electromagnetic valve. In response to signal A, the valves
were simultaneously opened for a given time to feed equal
amounts of the respective solutions V, VI and VII to the
25 plating bath. It was also assumed that when 1 g/l of
cobalt ion was consumed or a total amount of the replenish-
ing solution V adding up to 1 g/l of cobalt ion was re-
plenished, signal B was transmitted to discharge 10 - 50
ml/l of the plating bath each time before the corresponding
30 amount of a second replenishing composition consisting of

the solution VIII having the following composition was fed. (the invention method)

For the purpose of comparison, the above-mentioned plating procedure was repeated except that
5 signal B was not generated, and hence, neither discharge of the plating bath nor replenishment of the second replenishing solution VIII was conducted. That is, only the cobalt concentration was measured and the solutions V, VI and VII were added accordingly. (the
10 comparative method)

After plating was conducted a given number of turns (by "one turn" is meant the consumption of 4 g of cobalt ion per liter of plating bath in continuous plating), the rate of deposition and the composition of
15 Co-P alloy deposit were determined, obtaining the results shown in Table 2.

The first replenishing composition

Replenishing solution V

	Cobalt sulfate	240 g/l
20	Thiourea	0.11 g/l

Replenishing solution VI

	Sodium hypophosphite	270 g/l
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Replenishing solution VII

	Sodium hydroxide	68 g/l
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25 The second replenishing solution VIII

	Sodium tartrate	115 g/l
	Boric acid	8.4 g/l

Table 2

Number of turns	Rate of deposition ($\mu\text{m}/\text{hour}$)		P content in Co-P deposit (% by weight)	
	Invention	Comparative	Invention	Comparative
1	14.7	14.5	4.4	4.3
2	14.4	14.0	4.4	4.4
3	13.8	13.3	4.6	4.8
4	13.3	12.8	4.8	5.2
5	13.0	11.1	-	5.7
6	12.7	9.1	5.2	5.8
7	12.3	6.3	-	6.4
8	12.0	3.6	5.5	7.1
9	11.6	unplated	-	-
10	11.0		5.7	
11	10.4		-	
12	9.8		6.0	
13	9.6		-	
14	9.0		6.2	
15	8.4		-	
16	7.6		6.4	

As seen from the results of Tables 1 and 2, the present invention is advantageous in that the effective life of an electroless plating bath is substantially extended as compared with prior art methods. Furthermore, the rate of deposition and the physical properties of deposits are substantially uniform and consistent, and plating baths can be maintained highly stable for an extended period of time since metallic value, reducing agent and other ingredients are maintained at substantially constant concentrations and the amount of reaction by-products resulting from plating process is maintained within an allowable range.



CLAIMS:

1. A method for controlling an electroless plating bath, the method comprising the steps of continuously or intermittently measuring the concentration of at least one consumable ingredient in the electroless plating bath, and automatically adding to the plating bath a first replenishing composition comprising consumable ingredients after detecting that the measured concentration has reached a predetermined value while continuously or intermittently measuring, directly or indirectly, the amount of at least one consumable ingredient of the electroless plating bath consumed over a period to determine the degree of aging of the bath, and automatically discharging a predetermined volume of the plating solution and automatically adding to the plating bath a second replenishing composition containing unconsumable ingredients in an amount essentially corresponding to the amount lost by the discharging after detecting that the amount of the consumable ingredient consumed during said period has reached a predetermined value.
2. The method as set forth in claim 1 wherein at least one consumable ingredient in the bath is a metal, and the concentration of the electroless plating bath is measured in terms of the concentration of a metal in the bath.
3. The method as set forth in claim 1 or 2 wherein the consumable ingredient used for the measurement of the consumed amount is a metal ion.
4. The method as set forth in claim 3 wherein the consumed



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amount of the metal ion in the electroless plating bath is monitored by counting the number of replenishments of the first replenishing composition, and the predetermined volume of the plating solution is discharged after
5 detecting that the number of replenishments has reached a predetermined value.

5. The method as set forth in claim 4 wherein the number of replenishments of the first replenishing composition is obtained by counting the number of command signals for
10 commanding the automatic replenishment of the first replenishing composition.

6. The method as set forth in any one of claim 1 to 5 wherein the electroless plating is electroless nickel plating, electroless cobalt plating, electroless nickel-
15 cobalt alloy plating or electroless copper plating.

7. Apparatus for controlling an electroless plating bath, the apparatus comprising:

a mechanism for adding a first replenishing composition including:

20 means for automatically measuring the concentration of at least one consumable ingredient in the electroless plating bath,
concentration detecting means for generating a first signal when the measured concentration has
25 reached a predetermined value, and
means for automatically adding the first replenishing composition comprising consumable ingredients to the electroless plating bath



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upon receipt of the first signal,

and

a mechanism for discharging a predetermined volume of
the electroless plating solution and adding a second
5 replenishing composition including:

means for measuring, directly or indirectly, the
amount of at least one consumable ingredient of
the electroless plating bath consumed during
the current period up to the next discharging and
10 replenishment to determine the degree of aging
of the bath,

aging degree detecting means for generating a second
signal when the amount of the consumable
ingredient consumed during the current period
15 has reached a predetermined value,

means for discharging a predetermined volume of the
plating solution upon receipt of the second
signal, and

means for adding to the electroless plating bath the
20 second replenishing composition containing
unconsumable ingredients in an amount
essentially corresponding to the amount lost by
the discharging.

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8. The apparatus as set forth in claim 7 wherein the
25 concentration measuring means is so designed as to deter-
mine the optical absorption of a metal in the electroless
plating bath.

9. The apparatus as set forth in claim 7 or 8 wherein the



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aging degree measuring means is means for counting the number of replenishments of the first replenishing composition.

10. The apparatus as set forth in claim 9 wherein the
5 replenishment number counting means is so designed as to count the number of command signals for commanding the automatic replenishment of the first replenishing composition.

11. A method for controlling an electroless plating bath
10 substantially as described herein with reference to the drawings.

12. Apparatus for controlling an electroless plating bath substantially as described herein with reference to the drawings.

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