

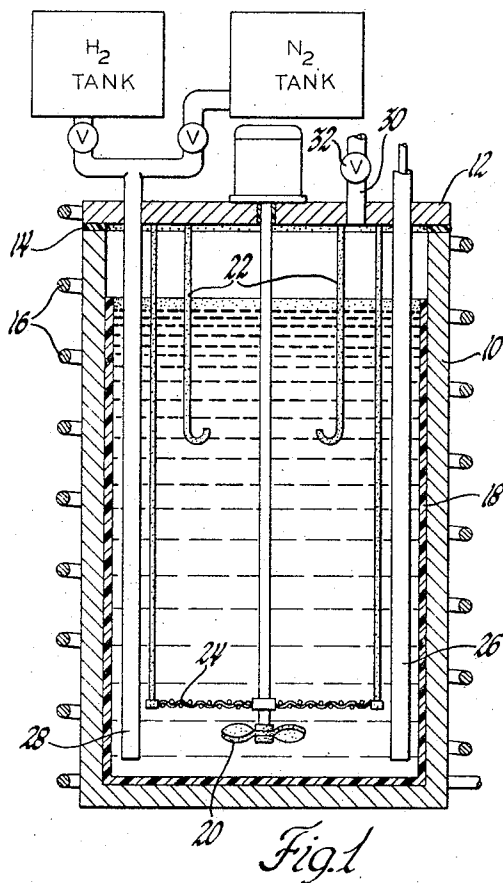
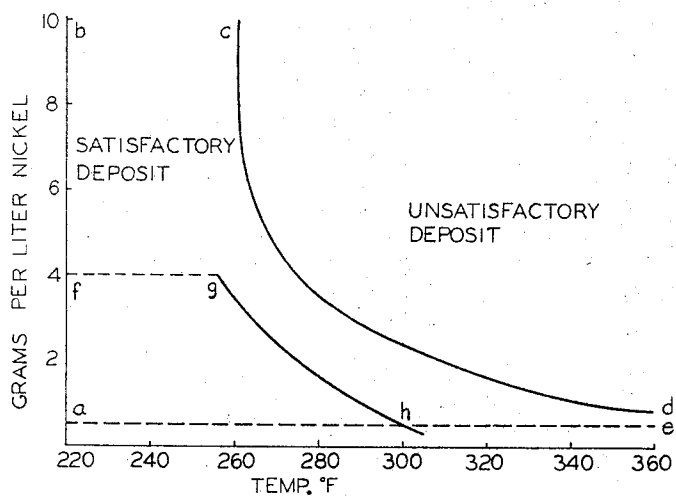
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ELECTROLESS NICKEL PLATING

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ELECTROLESS NICKEL PLATING

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This invention relates to electroless nickel plating and more particularly to a process for producing uniform, adherent, bright and smooth decorative nickel films by gaseous reduction of a nickel salt solution.

It has been known for many years that nickel could be precipitated from a nickel salt solution by hydrogen reduction. However, it was not heretofore known how to deposit the nickel in this manner to produce uniform, adherent, bright and smooth decorative nickel films, particularly in a commercially practicable process. I have now found an improvement which allows one to use gaseous reduction to consistently produce such nickel films, even under commercial production conditions.

It is, therefore, a principal object of my invention to provide a new process of electroless nickel deposition and a plating bath to be used in that process.

Other objects, features and advantages of the invention will become more apparent from the following description of a preferred embodiment thereof and from the drawings, in which:

FIGURE 1 shows a schematic diagram of an apparatus which can be used to practice the invention; and

FIGURE 2 shows a graph illustrating the relationship of the plating temperature for my process to the nickel ion concentration in the plating bath used.

Briefly, the invention comprehends forming an adherent, bright and smooth decorative nickel film by reducing an aqueous bath containing a nickel salt and an acetate ion buffer in which the pH of the bath is maintained between approximately pH 2 and pH 7. The temperature of the bath is regulated to maintain the temperature-nickel ion concentration relationship indicated by FIGURE 2. A reducing gas is circulated through the hot bath to deposit the nickel film. A generally preferred mode of operation is to initially heat a bath of appropriate composition to a suitable temperature and then, after plating commences, progressively increase the temperature during deposition in accordance with the amount of nickel deposited so as to maintain the temperature-nickel ion concentration within the limit indicated by the curve *cd* in FIGURE 2.

For convenience in describing the invention, reference is made herewith to FIGURE 1 which illustrates the apparatus useful in practicing the invention.

FIGURE 1 shows an autoclave that includes a steel cup-shaped container portion 10 having a steel cover member 12 for closing its open end. An O-ring 14 is used to seal the cover member 12 to the container 10. A heater 16 surrounds the container 10. Suitable means (not shown) are provided to control the heater to regulate the temperature within container 10. A Teflon liner 18 containing a plating bath is disposed within the container 10. The liner may be a separate cup-shaped member which is removable from the container 10, or it may be a coating which is applied to the inner wall of container 10. A Teflon propeller-type stirrer 20 depends into the liner 18 through cover member 12. Teflon hook-type holders 22 and tray-type work holders 24 are suspended within the liner 18 from the cover member 12. A closed-ended tube 26 depends into the liner 18 from the cover member 12. The tube 26 serves as a well for receiving temperature measuring devices (not shown) to monitor the temperature of the bath solution within the apparatus.

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An open tube 28 projects through cover 12 down almost to the bottom of liner 18. This tube is connected through appropriate valves to a hydrogen tank and to a nitrogen tank to permit introduction of either, or both, nitrogen and hydrogen gases into the interior of the apparatus after it has been closed. Tube 30 serves as a gas exhaust opening in cover 12. It has a valve 32 therein to seal this cover opening to maintain a positive pressure within the apparatus, as is desired.

In plating a workpiece in accordance with my process, an apparatus, such as shown in FIGURE 1, was used. A quantity of an aqueous nickel bath formulated as follows was placed in the container in sufficient volume to completely cover the workpiece to be plated:

Nickel acetate	-----mole per liter---	0.17
Sodium acetate	-----do-----	0.12
Anthraquinone	-----gram per liter---	0.2

In this example no Teflon liner was used, and the inside of container 10 was previously nickel plated. The bath was substantially neutral. An alumina tube was suspended in the bath within the autoclave. The autoclave cover was secured and the exhaust valve 32 closed. The autoclave was purged with nitrogen. It was pressurized to about 400 pounds per square inch (p.s.i.) with nitrogen. The exhaust valve 32 was then opened and the nitrogen discharged. The pressurization and discharge was repeated twice in immediate succession. Exhaust valve 32 was then closed and the introduction of nitrogen terminated. After purging the autoclave with nitrogen, hydrogen was bubbled into the bath until a hydrogen partial pressure of about 370 p.s.i. was obtained in the autoclave. The bath was then heated at a rate of approximately 4.9° F. per minute to a temperature of approximately 270° F. This temperature was maintained for approximately two hours, whereupon substantially all of the nickel in the bath was expended. The introduction of hydrogen into the autoclave was then discontinued and the autoclave allowed to cool. When the autoclave had cooled to room temperature, the exhaust valve was opened, the autoclave cover removed, and the part taken from the bath and rinsed. The resulting plate thickness on the alumina tube was about 3×10^{-4} inch.

The following aqueous bath composition was used to coat beryllium:

Nickel acetate	-----mole per liter---	0.083
Sodium acetate	-----do-----	0.050
Anthraquinone	-----gram per liter---	0.2

A sufficient quantity of the bath was placed in the Teflon liner 18 to cover the workpiece and the liner placed in container 10. A beryllium bar was then supported in the bath and the cover 12 placed on the container. The cover 12 was secured, the exhaust valve 32 closed and the autoclave then purged with nitrogen. Purging was effected as described in the preceding example. After purging, the exhaust valve was closed, the flow of nitrogen stopped and hydrogen introduced. When a hydrogen partial pressure of about 400 p.s.i. was obtained, the bath was heated at a rate of about 1.7° F. per minute to a temperature of about 270° F. A temperature of about 270° F.-290° F. was then maintained for about two hours. The heating and hydrogen introduction were then terminated. When the autoclave had substantially cooled, the exhaust valve was opened, the autoclave cover was removed, and the part taken from the bath and rinsed. A nickel film having a thickness of about 2×10^{-4} inch was produced on the beryllium bar.

A discussion of the bath composition used in practicing my process is desirable to illustrate the various nickel-acetate combinations that are useful. Moreover, it serves to illustrate the intricate relationship I have discovered

which exists between the bath composition and the temperature at which satisfactory plating can be achieved. It will also aid in understanding the principle of regulating temperature prior to and during plating with respect to the nickel ion concentration, particularly as this concentration varies during plating.

In general, any soluble nickel salt can be used in the preparation of my bath to use in practicing my process. While nickel salts, such as nickel sulfamate, nickel fluoroborate, nickel borate and the like, may be used, I prefer to employ a nickel salt, such as nickel acetate, nickel chloride or nickel sulfate.

Analogously, the acetate ion-producing substance can be acetic acid and/or virtually any acetate salt which is soluble in the bath solution and which does not objectionably complex with the nickel to deleteriously interfere with the proposed nickel deposition. Acetate salts, such as nickel acetate, sodium acetate, potassium acetate, lithium acetate and ammonium acetate, are generally satisfactory. Hence, it can be seen that nickel acetate can be used alone in the bath. However, it is generally desirable to also include another acetate ion-producing substance to the bath, for reasons which are subsequently clearer.

Accordingly, the following bath formulations are encompassed by the invention:

- Bath I: Nickel acetate and sodium acetate.
- Bath II: Nickel acetate and potassium acetate.
- Bath III: Nickel acetate and lithium acetate.
- Bath IV: Nickel chloride and sodium acetate.
- Bath V: Nickel sulfate and sodium acetate.
- Bath VI: Nickel chloride and potassium acetate.
- Bath VII: Nickel acetate.

Moreover, if desired, a plurality of nickel salts and acetate salts can be concurrently employed in the same bath as follows:

- Bath VIII: Nickel chloride, nickel sulfate, sodium acetate and potassium acetate.

The preferred concentration of salts in the aqueous bath is dependent upon the desired nickel ion and acetate ion concentrations, as is hereinafter described.

The pH of the bath solution must be at least about 2. If the bath becomes more acid than about pH 2, deposition ceases. On the other hand, a pH above about 7 is generally to be avoided in order to preclude precipitation of nickel hydroxide in the bath. Of course, incorporation of appropriate complexing agents may permit use of a more alkaline bath. Since the bath increases in acidity as the nickel is reduced, it is usually desirable to formulate the bath so it at least has an initial acidity above about pH 3 and preferably about pH 5–pH 6.

The nickel concentration can be varied while still permitting one to obtain the benefits of the invention. However, as previously indicated, the nickel ion concentration to be used is related to the deposition temperature. In general, the higher the nickel ion concentration is, the lower the plating temperature that must be used. For a better understanding of this, reference is now made to FIGURE 2.

FIGURE 2 shows a graph in which temperature is the abscissa and the concentration of nickel ions is the ordinate. This graph, obtained from an aqueous nickel acetate solution, is representative of those exhibited by various nickel baths which can be used in my plating process. Slight shifts in this curve are found with some baths and the representative curve is intended, by way of illustration, to also include these other baths, which also exhibit the similar criticalities in nickel ion concentration and temperature. The area to the left and under the curve *cd* indicates the temperature-nickel ion concentration relationship where uniform, adherent, bright and smooth decorative nickel films can be obtained. Test results show the curve *cd* approaches an asymptote at about 260° F. for increasing nickel concentrations up to satu-

ration. This higher concentration portion of the curve is not shown. Where exceptionally satisfactory deposits are desired, it is preferred to maintain the temperature-nickel ion relationship within the area *afgh* of FIGURE 2.

The more dilute bath solutions described in this area are particularly satisfactory for high quality, thin nickel coatings, such as are especially useful in the preparation of silicon diodes and the like.

If a plating temperature in excess of the maximum indicated by the graph in FIGURE 2 is employed, the deposit is adversely affected. It becomes rough, dull, etc. If the temperature is appreciably in excess of this maximum, a uniform, adherent, bright and smooth film will not form at all. On the other hand, the plating rate increases with temperature. Accordingly, for bath concentrations less than about 10 grams per liter, it is desirable to use as high a temperature as permissible within the area *abcde* indicated by FIGURE 2 as providing satisfactory deposits. For higher concentrations, of course, it is preferred to use the temperature indicated by the curve *cd* in FIGURE 2. In some instances it may be preferred to use a lower nickel ion concentration so that a higher temperature can be used to obtain a higher plating rate. This is a particularly useful advantage where only thin nickel coatings are desired.

Nickel ion concentrations from as low as about 0.5 gram per liter to as high as saturation can be used. Even small but effective amounts (e.g., 0.01 gram per liter) of nickel in solution can be used. However, the rate of deposition below about 0.5 gram per liter is usually too slow for most purposes. Hence, there is ordinarily little advantage in using such dilute solutions. On the other hand, larger concentrations, about 10–20 grams per liter of nickel, or even up to saturation, can be used. As previously indicated, though, a lower plating temperature must be used with such solutions until nickel precipitation reduces this concentration below about 10 grams per liter.

The acetate ions in the bath essentially serve in buffering the bath to maintain it within the operating pH range. Thus, the preferred minimum concentration of acetate ions depends upon the nickel ion concentration and amount of nickel which is to be deposited from the bath. Thus, the minimum concentration of acetate ion which is to be used is best described in terms of its relationship to the nickel ion concentration and that proportion of it which is to be reduced in practicing my process. On the other hand, the bath can accommodate appreciable excesses over this minimum without any significant effect on either the deposit or plating rate. Hence, I generally prefer to use enough acetate ion to buffer the bath for reduction of substantially all the nickel therein. By way of illustration, about 0.4 mole per liter of acetate ion is enough to buffer a 10 gram per liter nickel ion solution for substantially complete reduction of the nickel therein.

In some instances I may prefer to include only enough acetate ion to buffer the bath for reduction of only a major proportion of the nickel. For this, the acetate ion in the bath should be at least of the same molar concentration as the nickel. However, greatest economy of operation is achieved by reducing substantially all of the nickel in the bath. For this the acetate ion concentration should be at least twice the molarity of the nickel ion concentration. It is preferred to use a slight excess of 0.1–0.2 mole per liter of acetate ion to insure that an excess is present. An alkali metal acetate salt is best used for the excess, or even the whole buffer, since it inherently tends to raise the pH of the resulting solution to permit one to use a higher initial pH.

In addition, I have discovered that my process will not immediately form a deposit on many substances. A period of induction at operating conditions is initially required before this deposit is obtained. This induction period may vary from only a few seconds (e.g., a nickel substrate) to as much as about one hour, or more (e.g., Teflon).

In some instances I prefer to employ an accelerator, particularly one of the quinoid type, such as anthraquinone. Even small but effective amounts of the accelerator are useful. Significant accelerative effects are noted for accelerator concentrations of about 0.1 gram per liter for about each 10 grams of nickel in solution. However, I prefer to use about 0.2 gram of accelerator to insure the consistent attainment of best results with all baths.

The difference in induction period between two materials can be advantageously used. For example, the container for the bath solution can be formed of a material having a relatively long induction period, such as Teflon, so that deposition of the film takes place exclusively on the workpiece if it has a relatively short induction period, e.g., brass, nickel, silicon, iron. In such instance, particularly effective economy of the bath solution is obtained, since the plating process is completed before the container starts to be coated. It appears that this cycle can be repeated, and the container can be reused indefinitely in this manner without ever being coated.

Various reducing gases can be used in practicing the invention. While reducing gases, such as industrial reducing gas mixtures, carbon monoxide and the like, may be satisfactory in some instances, I prefer to use hydrogen gas as the reducing gas. In general, I have found that a hydrogen pressure of at least 50 p.s.i. is necessary to obtain an appreciable deposition rate. On the other hand, any higher pressure can be used. I generally prefer to employ a hydrogen pressure of approximately 150 p.s.i. to 800 p.s.i. Hydrogen pressures of about 200 p.s.i. to 400 p.s.i. are preferred for commercial production use. While pressures higher than approximately 800 p.s.i. may provide satisfactory results, they are generally not preferred because of the prohibitive cost of equipment operative at these pressures.

As previously pointed out, acquisition of the acceptable nickel deposit is determined by regulation of the temperature at which I practice my process with respect to the nickel ion concentration. However, increased plating temperatures provide an increase in plating rate to make the process especially commercially practical. It is, therefore, desirable to heat the bath solution to a temperature of at least about 200° F. in order to obtain adequate plating rates. However, the plating rate of approximately 200° F. is still not fast enough to be generally practical for commercial applications. I have found that the uniform, adherent, bright and smooth decorative film can be formed at a much faster rate by increasing the bath temperature as the nickel ion concentration decreases below about 10 grams per liter. Fastest satisfactory plating is realized when this increase closely follows the line *cd* within the area *abcd* of FIGURE 2. Thus, the rate of temperature increase is limited by the rate of nickel deposition. If the temperature is allowed to increase too rapidly, roughness in the film develops. Extensive coprecipitation of particulate matter forms loose, spongy, porous, dull deposits.

Of course, agitation of the bath during deposition is generally preferred. Agitation can be produced in any suitable manner, and any of the usual techniques, including mechanical stirring or the like, can be used.

The reducing gas can be introduced into the bath in a variety of techniques. It can be bubbled into the bath solution merely by immersing a tube into the bath. Similarly, a fritted glass end closure for the tube can be employed. Alternatively, the gas can be injected through a hollow propeller agitator stem into the vortex induced in the bath by the propeller agitator.

Deposition of the nickel film can be discontinued in a plurality of ways. Since it is ordinarily not convenient to merely remove the part from the bath in order to discontinue deposition, other means must be used. The hydrogen gas introduction can be stopped and/or the temperature can be reduced. However, I have found that a very effective means for regulating the thickness of

the film formed is to employ a bath solution which, when substantially exhausted of nickel, will provide a film thickness, such as is desired. On the other hand, the quantity of buffer in the bath can be regulated so that the acidity of the bath increases to such an extent when the desired quantity of nickel has been deposited that plating discontinues. In general, I prefer to substantially exhaust the bath solution of nickel. The concentration of the nickel in the bath, as well as the quantity of bath to be employed to get any coating thickness per unit area, are readily determinable.

It is to be understood that while I have described my invention in connection with certain specific examples thereof, no limitation is intended thereby except as defined in the appended claims.

I claim:

1. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in excess of 2, said bath containing dissolved nickel and sufficient acetate ion buffer to maintain the bath above about pH 2 during chemical reduction of at least a major proportion of the nickel in the bath, providing a pressurized gaseous reducing environment for said bath containing said workpiece, heating said bath containing said workpiece to induce deposition of said nickel on said workpiece, and regulating the temperature of said bath such that said temperature varies inversely with respect to the concentration of nickel therein but within the area of *abcd* of FIGURE 2 to produce a smooth, bright, decorative nickel coating on said workpiece.

2. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH of about 3-7, said bath containing nickel ion and sufficient acetate ion buffer to maintain the bath at above about pH 2 during chemical reduction of at least a major proportion of the nickel in the bath, providing a pressurized gaseous reducing atmosphere for said bath containing said workpiece, heating said bath containing said workpiece to an elevated temperature to induce deposition of nickel on said workpiece, said elevated temperature being below the nickel powder producing temperature of said bath, maintaining said bath containing said workpiece below said powder-producing temperature until deposition of a nickel coating commences on said workpiece, and thereafter increasing the temperature of said bath in such relation to the decreasing nickel content thereof that no new powder producing temperature is exceeded whereby smooth, bright, decorative nickel coatings are more rapidly produced.

3. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in excess of 2, said bath containing nickel ion, an accelerator, acetic acid and a soluble acetate salt, the acetate ion content in said bath being sufficient to maintain the bath at above about pH 2 during chemical reduction of at least a major proportion of the nickel in the bath, providing a pressurized hydrogen atmosphere for said bath containing said workpiece, heating said bath containing said workpiece to an elevated temperature in said atmosphere to induce deposition of a smooth, bright nickel film on said workpiece, said temperature being below the nickel powder producing temperature of said bath, and increasing the temperature of said bath in such relation to the decreasing nickel content thereof that no new powder producing temperature is exceeded whereby the formation of a bright, decorative nickel coating is accelerated without its surface roughness being appreciably increased.

4. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel

coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH of about 3-7, said bath containing nickel ion, an accelerator and sufficient acetate salt to maintain the bath at above about pH 2 during reduction of at least a major proportion of the nickel in the bath, providing a pressurized gaseous reducing environment in said bath containing said workpiece, heating said bath containing said workpiece to induce deposition of a smooth, bright, decorative nickel coating on said workpiece, progressively increasing the temperature of said bath during deposition of said coating, and regulating the increase in temperature of the bath in relation to the decrease in the nickel content thereof such that said bath never exceeds a nickel powder producing temperature to more rapidly form said coating without concurrently appreciably increasing surface finish of said coating.

5. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in excess of 2, said bath containing nickel ion and sufficient acetate ion buffer to maintain the bath above about pH 2 during chemical reduction of at least a major proportion of the nickel in the bath, providing a pressurized gaseous reducing atmosphere for said bath containing said workpiece, heating said bath containing said workpiece to induce deposition of a smooth, bright nickel coating on said workpiece, and regulating the temperature of the bath during the deposition of said coating to maintain the nickel ion concentration-temperature relationship indicated by the curve *cd* shown in FIGURE 2.

6. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in excess of 2, said bath containing at least about 0.5 gram per liter of nickel ion, an accelerator and an acetate ion buffer sufficient to maintain the bath at above about pH 2 during reduction of at least a major proportion of the nickel in the bath, the molar ratio of the acetate ion concentration to the nickel ion concentration being at least 1:1, providing a pressurized gaseous reducing environment in said bath containing said workpiece, heating said bath containing said workpiece to induce deposition of a smooth, bright, decorative nickel coating on said workpiece, progressively increasing the temperature of said bath during said deposition, and regulating said increasing bath temperature during said deposition to maintain the desirable nickel ion concentration-temperature relationship indicated by the area *abcde* of FIGURE 2.

7. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in excess of 2, said bath containing a nickel ion, an anthraquinoidal accelerator, acetic acid and a soluble acetate salt, the acetate ion concentration in said bath being sufficient to maintain said bath above about pH 2 during chemical reduction of at least a major proportion of the dissolved nickel in the bath, providing a pressurized gaseous reducing environment for said bath containing said workpiece, heating said bath containing said workpiece to an elevated temperature to induce deposition of said nickel on said workpiece, said elevated temperature being below the nickel powder producing temperature of said bath, and increasing the temperature of said bath in such relation to the decreasing nickel content therein that no new powder producing temperature is exceeded whereby a smooth, bright, decorative nickel coating is produced on said workpiece.

8. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in

excess of 2, said bath containing a nickel salt, providing a nickel ion concentration of about 0.5 gram per liter to saturation and sufficient acetate ion buffer to maintain the bath above about pH 2 during chemical reduction of at least a major proportion of the dissolved nickel in the bath, providing a pressurized gaseous reducing environment for said bath containing said workpiece, heating said bath containing said workpiece to a temperature sufficient to induce deposition of said nickel coating on said workpiece but below the powder producing temperature of said bath and subsequently increasing the temperature of said bath in relation to the increasing nickel content therein whereby the formation of a smooth, bright, decorative nickel coating is accelerated without its surface roughness being appreciably increased.

9. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in excess of 2, said bath containing a nickel salt, providing a nickel ion concentration of about 0.5-20 grams per liter, at least about 2 moles per liter of acetate ion from at least one soluble acetate salt for each mole of nickel ion in said bath, providing a pressurized gaseous reducing atmosphere for said bath containing said workpiece, heating said bath containing said workpiece to an elevated temperature below about 260° F. to induce deposition of said nickel coating on said workpiece, and subsequently increasing the temperature of said bath in such relation to the decreasing nickel content therein that no powder producing temperature of said bath is ever exceeded whereby a smooth, bright, decorative nickel coating is more rapidly produced on said workpiece.

10. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in excess of 2, said bath containing a nickel salt from the group consisting of nickel chloride, nickel sulfate, nickel borate, nickel fluoborate, nickel sulfamate and nickel acetate, said salt providing a nickel ion concentration of about 0.5-10 grams per liter, a quinonoid accelerator, acetic acid and an acetate salt from the group consisting of nickel acetate, ammonium acetate, sodium acetate, lithium acetate and potassium acetate, the acetate ion concentration being sufficient to maintain said bath above about pH 2 during deposition of substantially all of the nickel in said bath, providing a pressurized gaseous reducing atmosphere for said bath containing said workpiece, initially heating said bath containing said workpiece to induce deposition of said nickel coating on said workpiece, subsequently increasing the temperature of said bath in relation to the decreasing concentration of nickel therein during said deposition of said nickel, and regulating said temperature increase to maintain the nickel ion concentration-temperature relationship within the limit indicated by the curve *cd* in FIGURE 2.

11. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in excess of 2, said bath containing dissolved nickel and sufficient acetate ion to maintain the bath above about pH 2 during chemical reduction of at least a major proportion of dissolved nickel in the bath, providing a hydrogen atmosphere for said bath containing said workpiece, said hydrogen being at a pressure of about 150-800 p.s.i., heating said bath containing said workpiece to a temperature of at least about 200° F. to induce deposition of said nickel coating on said workpiece, and increasing the temperature of said bath in relation to the decreasing concentration of nickel therein such that said bath never exceeds a nickel powder producing temperature to produce a smooth, bright, decorative nickel coating on said workpiece.

12. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH of about 3-7, said bath containing nickel ion, acetate ion and an accelerator, said acetate ion being sufficient to maintain the bath at above about pH 2 during chemical reduction of at least a major proportion of the nickel in the bath, providing a hydrogen atmosphere for said bath containing said workpiece, said hydrogen being at a pressure of about 150-800 p.s.i., heating said bath containing said workpiece to an elevated temperature to induce deposition of nickel on said workpiece, maintaining said bath containing said workpiece at an appropriate temperature to produce said uniform, adherent, bright and smooth decorative nickel coating for the bath as initially formulated until deposition of a nickel coating commences on said workpiece, and thereafter increasing the temperature of said bath as the nickel content thereof decreases such that said bath never exceeds a nickel powder producing temperature to more rapidly produce said coating.

13. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in excess of 2, said bath containing a nickel salt which provides a nickel ion concentration of about 0.5-20 grams per liter, an anthraquinoidal accelerator and about at least one mole per liter of acetate ion from a soluble acetate salt for each mole per liter of nickel ion, providing a pressurized hydrogen atmosphere for said bath containing said workpiece, heating said bath containing said workpiece to induce deposition of said nickel coating on said workpiece, and increasing the temperature of said bath in relation to the decreasing concentration of nickel therein such that said bath never exceeds a nickel powder producing temperature to produce a uniform, adherent, bright and smooth decorative nickel coating on said workpiece.

14. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in excess of 2, said bath containing a nickel salt selected from the group consisting of nickel chloride, nickel sulfate, nickel borate, nickel fluoborate, nickel sulfamate and nickel acetate, said salt providing a nickel ion concentration of about 0.5 gram per liter to saturation, a quinonoid accelerator, acetic acid and an acetate salt selected from the group consisting of nickel acetate, sodium acetate, potassium acetate, lithium acetate and ammonium acetate, providing a pressurized gaseous reducing atmosphere for said bath containing said workpiece, heating said bath containing said workpiece to an elevated temperature to induce deposition of nickel on said workpiece, maintaining said bath containing said workpiece at a temperature for producing a uniform, adherent, bright and smooth decorative nickel coating from the bath as originally formulated until deposition of a nickel coating commences on said workpiece, and thereafter increasing the temperature of said bath as the nickel con-

tent thereof decreases such that said bath never exceeds a nickel powder producing temperature to more rapidly produce said coating.

15. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in excess of 2, said bath containing a nickel salt selected from the group consisting of nickel chloride, nickel sulfate, nickel borate, nickel fluoborate, nickel sulfamate and nickel acetate, said salt providing a nickel ion concentration of about 0.5 gram per liter to saturation, an anthraquinoidal accelerator, acetic acid and an acetate salt selected from the group consisting of nickel acetate, sodium acetate, potassium acetate, lithium acetate and ammonium acetate, the molar ratio of acetate ion concentration to nickel ion concentration in the bath being at least about 1:1, providing a hydrogen atmosphere for said bath containing said workpiece, said hydrogen being at a pressure of approximately 150-800 p.s.i., initially heating said bath containing said workpiece to a temperature of at least about 200° F. to induce deposition, subsequently increasing the temperature of said bath with respect to the decreasing concentration of nickel therein during said deposition of said nickel coating, and regulating said temperature increase to maintain the nickel ion concentration-temperature relationship within the limit indicated by the curve *cd* in FIGURE 2.

16. The method of electroless plating workpieces with a uniform, adherent, bright and smooth decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH in excess of 2, said bath containing a nickel salt selected from the group consisting of nickel chloride, nickel sulfate, nickel borate, nickel fluoborate, nickel sulfamate and nickel acetate, said salt providing a nickel ion concentration of about 0.5-4 grams per liter, an anthraquinoidal accelerator, acetic acid and an acetate salt selected from the group consisting of nickel acetate, sodium acetate, potassium acetate, lithium acetate and ammonium acetate, providing a hydrogen atmosphere for said bath containing said workpiece, said hydrogen being at a pressure of approximately 150-800 p.s.i., heating said bath containing said workpiece to a temperature of at least about 200° F., to induce deposition, subsequently increasing the temperature of said bath with respect to the decreasing concentration of nickel therein during said deposition of said nickel coating, and regulating said temperature increase to maintain the nickel ion concentration-temperature relationship within the area *afgh* of FIGURE 2.

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