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ELECTROLESS NICKEL PLATING

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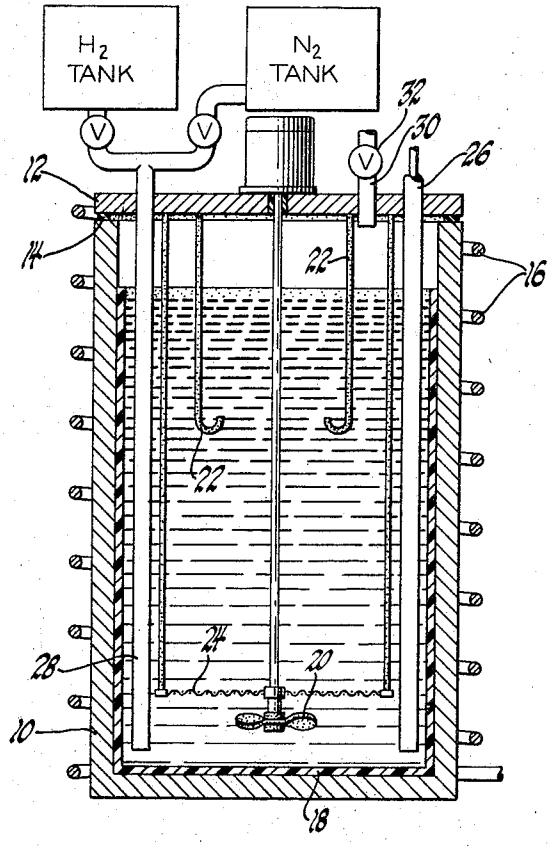


Fig. 1

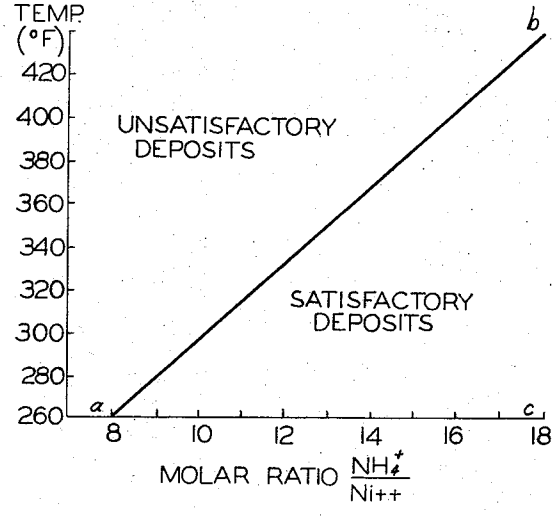


Fig. 2

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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 manner. I have now found an improvement by which one is allowed to use gaseous reduction to consistently produce such films, even under commercial production conditions.

It is, therefore, a principal object of my invention to provide a new process of electroless nickel deposition.

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 ammonium ion concentration to nickel ion concentration in the bath I use in my process and how this relationship varies with temperature.

Briefly, the invention comprehends forming a uniform, adherent, bright and smooth decorative nickel film by reducing an aqueous bath containing a nickel salt and ammonia and an ammonium salt in which the pH of the bath is maintained between approximately pH 2 and pH 9. A reducing gas is introduced into the bath while it is at an appropriate elevated temperature. The temperature of the bath is regulated during deposition to maintain the nickel ion to ammonium ion ratio within the area *abc* of FIGURE 2. A generally preferred mode of operation is to initially heat a bath of appropriate composition to a temperature of at least about 200° F. and then after plating commences, progressively increase the temperature during plating in accordance with the amount of nickel deposited so as to generally follow the line *ab* but within the area *abc* of FIGURE 2.

For convenience in describing the invention, reference is made herewith to FIGURE 1 which illustrates an 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 work 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. An open tube **28** projects through cover member **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 member **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 Teflon container **18** in sufficient volume to completely cover the workpiece to be plated:

Nickel chloride	moles per liter	.16
Ammonium hydroxide	do	.32
Ammonium chloride	do	1.9
Anthraquinone	milligrams per liter	200

A nickel workpiece was supported within the liner and the bath was placed in contact with it. The cover was placed on the autoclave, the exhaust valve **32** closed and the autoclave was then 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. This was repeated twice in immediate succession. Exhaust valve **32** was then closed and the introduction of nitrogen stopped. After purging the autoclave with nitrogen, the bath was then heated at a rate of approximately 2.8° F. per minute to a temperature of approximately 260° F. Hydrogen was then bubbled into the bath until a hydrogen partial pressure of about 600 p.s.i. was obtained in the autoclave. This temperature was maintained for approximately 36 minutes whereupon substantially all of the nickel in the bath was expended. The residual plating solution was about 0.001 molar with respect to nickel. A nickel film thickness of about 0.0005 inch was produced on the workpiece. Thereafter, the introduction of hydrogen into the autoclave was discontinued and the autoclave allowed to cool. When the autoclave had cooled to room temperature, the hydrogen pressure was released, the autoclave was opened, and the part was removed from the bath and rinsed.

While the present invention primarily involves an improvement in a process of nickel reduction, a discussion of the bath composition used is desirable to illustrate that a variety of bath compositions are useful in practicing this invention. Moreover, it serves to illustrate the intricate fundamental relationship I have discovered which exists between 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 bath composition, particularly as this composition varies during plating.

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

Analogously, virtually any ammonium 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 can be used. Substances, such as ammonium borate, ammonium iodide and the like, are generally satisfactory. However, I prefer to employ ammonium sulfate or ammonium chloride. The ammonium salt can be introduced directly into the bath or it can be formed in situ.

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 9 is generally to be avoided in order to preclude precipitation of nickel hydroxide in the bath. Nickel hydroxide ordinarily precipitates in an aqueous bath above a pH of about 7. However, my high ammonium ion concentration apparently prevents this precipitation up to about pH 9. Of course, it is conceivable that appropriate complexing agents may permit use of an even more alkaline bath. Since the bath increases in acidity as the nickel is reduced, it is usually desirable to formulate the bath so it has a relatively high pH within the operating range. Accordingly, I prefer to formulate the bath to have pH 6–8.

The nickel concentration can be varied to some extent while still permitting one to obtain the benefits of the invention. The nickel ion concentration which must be used to get an acceptable deposit is influenced by both the deposition temperature and the ammonium ion concentration. In general, the higher the nickel ion concentration is, the lower the plating temperature and the higher the ammonium ion concentration that must be used. If these factors are not in proper balance, a uniform, adherent, bright and smooth decorative film will not result. Moreover, while satisfactory plating rates can be obtained at about 5 grams per liter of nickel, a nickel ion concentration of at least about 10 grams per liter is preferred in order to obtain the film at a sufficiently rapid rate. On the other hand, while nickel concentrations above about 20 grams per liter can be used, the plating rate is not increased. Moreover, nickel concentrations in excess of 20 grams per liter require undesirably high corresponding ammonium ion concentrations which, as will be hereinafter amplified, cause a reduction in the plating rate. Accordingly, I prefer to employ nickel concentrations of about 10–20 grams per liter.

The ammonia, ammonium hydroxide, primarily serves as a buffer in the bath to maintain the pH in the bath within the desired operating range. Thus, the preferred minimum concentration of ammonia depends primarily upon the nickel ion concentration and secondarily upon the amount of nickel to be deposited. A molar ratio of at least about 2:1 of ammonia to nickel ion is needed to buffer the bath for deposition of substantially all the nickel in the bath. However, higher ammonia proportions can be used, even up to molar ratios of 6:1. It is generally economically undesirable to use ammonia to nickel ion molar ratios of less than 1:1.

The ammonium salt is used in the bath as a source of ammonium ions to expand the range of useful nickel ion concentration and permit use of higher plating temperatures. Due to its limited ionization, an ammonia solution has only a relatively negligible ammonium ion concentration and is, therefore, considered as undissociated. Hence, then ammonium salt is used, which is considered completely ionized for purposes of this discussion. The required concentration of ammonium ions from the salt is a direct function of both the nickel ion concentration and the plating temperature. The ammonium concentration must be increased if the nickel concentration is increased. Moreover, higher molar ratios of ammonium ions to nickel ions are required to get satisfactory deposits at high plating temperatures. FIGURE 2 illustrates how this molar ratio varies with temperature. In the graph in FIGURE 2, temperature is the ordinate and the molar ratio of ammonium ions to nickel ions is the abscissa. Within the area *abc*, uniform, adherent, bright and smooth decorative nickel films can be obtained. This graph, which is representative of baths having a 2:1 ammonia to nickel ion molar ratio, is characteristic of all baths within the scope of my invention. Slight shifts in this curve may be found in baths having different ammonia-nickel ion molar ratios, and the representative curve is intended, by way of illustration, to also include these other baths.

On the other hand, the preferred maximum concentration of ammonium ions from the salt used is governed by the acceptability of an associated corresponding decrease in plating rate. I have found that the higher the concentration of ammonium ions, the slower the plating rate. Hence, I prefer to use as low an ammonium ion concentration as is permissible to still attain the fruits of the invention. Accordingly, it is generally undesirable to employ an ammonium ion concentration which is appreciably in excess of that described as required in the graph shown in FIGURE 2. Hence, the initial ammonium ion to nickel ion ratio desired for the bath not only depends upon the initial nickel ion concentration and the initial deposition temperature to be used but also on the plating rate desired.

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 ion in the bath. 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. In such instance, particularly effective economy of the bath solution is obtained, since the plating process is over before the container starts to be coated. It appears that this cycle can be repeated and the container can be indefinitely reused 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 partial pressure of at least 50 p.s.i. is necessary to obtain an appreciable deposition rate. On the other hand, since the deposition rate is substantially constant between a pressure of approximately 150 p.s.i. and 800 p.s.i., at temperatures from about 200° F. to 370° F., I generally prefer to employ a hydrogen partial pressure in this range. Hydrogen partial pressures of about 200 to 400 p.s.i. provide a comfortable working margin and are, therefore, preferred for commercial production use. While partial pressures higher than approximately 800 p.s.i. may provide satisfactory results, they are generally not preferred since they do not provide an appreciable increase in plating rate.

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 ratio of the ammonium ion concentration to the nickel ion concentration. However, increased plating temperatures provide an increase in plating rate to make the process especially commercially practical. It is desirable to heat the bath solution to a temperature of at least about 200° F. in order to obtain adequate plating rate. Of course, the ammonium ion to nickel ion ratio necessarily must be sufficient to permit use of such an initial temperature. 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 in the bath solution. However, this increase in bath temperature must be such that the temperature-ammonium ion concentration-nickel ion concentration relationship is maintained within the area *abc* of FIGURE 2. This increase is allowable since the ammonium ion concentration to nickel ion concentration increases as nickel is deposited from the bath. 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 deposits. Accordingly, in practicing my process, particularly under commercial production conditions, I prefer to increase the bath temperature, but at a rate corresponding to the decrease in nickel ion concentration so as to maintain the desirable relationships described within the area *abc* of FIGURE 2.

In general, it is desirable to agitate the bath solution during the deposition to obtain deposition at the maximum rate. 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. This quantity can be readily calculated. 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, 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, an ammonium salt, the ratio of ammonium ion to nickel ion being at least about 8 to 1 when the temperature of said bath is in excess of about 260° F. and sufficient ammonia 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 induce deposition of said nickel on said workpiece, and concurrently increasing the temperature of said bath and ratio of ammonium ion concentration to nickel ion concentration therein 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 3–9, said bath containing nickel ion, an ammonium salt, the ratio of ammonium to nickel ion being at least about 8 to 1 when the temperature of said bath is in excess of about 260° F. and sufficient ammonia 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, maintaining said bath containing said workpiece below a powder producing temperature until deposition of a nickel coating commences on said workpiece, and thereafter increasing the temperature of said bath while increasing the ratio of the ammonium ion concentration to the nickel ion concentration thereof to more rapidly produce a smooth, bright, decorative nickel coating.

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, ammonia and a soluble ammonium salt, the ratio of ammonium ion to nickel ion being at least about 8 to 1 when the temperature of said bath is in excess of about 260° F., the ammonia 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 depositions of a smooth, bright nickel film on said workpiece, concurrently increasing temperature of said bath and the ratio of ammonium ion concentration to nickel ion concentration in said bath to accelerate the formation of a bright, decorative nickel coating without simultaneously appreciably increasing its surface roughness.

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 3–9, said bath containing nickel ion, an ammonium salt, the ratio of ammonium ion to nickel ion being at least about 8 to 1 when the temperature of said bath is in excess of about 260° F., and accelerator and sufficient ammonia 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 and the ammonium to nickel ion concentration ratio in said bath during deposition of said coating, and regulating the increasing temperature in relation to the increased ammonium ion to nickel ion concentration ratio 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, an ammonium salt, the ratio of ammonium ion to nickel ion being at least about 8 to 1 when the temperature of said bath is in excess of about 260° F. and sufficient ammonia 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 concurrently increasing the temperature of the bath

during the deposition of said coating yet regulating the temperature increase to maintain the ammonium ion concentration-nickel ion concentration-temperature relationship described within the area *abc* 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 10 grams per liter of nickel ion, an ammonium salt, an accelerator and ammonia 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 ratio of the ammonium ion concentration to the nickel ion concentration being at least 8 to 1 when the temperature of said bath is in excess of about 260° F., 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 and the ammonium to nickel ion concentration ratio of said bath during said deposition, and regulating the increasing temperature in relation to the increasing ammonium to nickel ion concentration ratio during said deposition to maintain the ammonium ion concentration-nickel ion concentration-temperature relationship described by the area *abc* 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 exces of 2, said bath containing a nickel ion, a soluble ammonium salt, the ratio of ammonium ion to nickel ion being at least about 8 to 1 when the temperature of said bath is in excess of about 260° F., an anthraquinoidal accelerator and ammonia, the ammonia 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 induce deposition of said nickel coating on said workpiece, and concurrently increasing the temperature of said bath and the ratio of ammonium ion concentration to nickel ion concentration therein to produce a smooth, bright, decorative nickel coating 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 10–20 grams per liter, an ammonium salt, the ratio of ammonium ion to nickel ion being at least about 8 to 1 when the temperature of said bath is in excess of about 260° F., and sufficient ammonia 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 induce deposition of said nickel coating on said workpiece, and concurrently increasing the temperature of said bath and the ratio of ammonium ion concentration to nickel ion concentration therein to produce a smooth, bright, decorative nickel coating on said workpiece.

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 which provides a nickel ion concentration of about 10–20 grams per liter, about 1.6–2.0 moles per liter of ammonium ion from a soluble ammonium salt and about 0.2–0.8 mole per liter of ammonium, the ratio of said ammonium ion concentration to nickel ion concentration in the bath being at least about 8 to 1, providing a pressurized gaseous reducing atmosphere for said bath containing said workpiece, heating said bath containing said workpiece to induce deposition of said nickel coating on said workpiece, and concurrently increasing the temperature of said bath and the ratio of ammonium ion concentration to nickel ion concentration therein to produce a smooth, bright, decorative nickel coating 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 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 10–20 grams per liter, a quinonoid accelerator, ammonia and an ammonium salt selected from the group consisting of ammonium acetate, ammonium sulfate and ammonium chloride, the ratio of said ammonium ion concentration to nickel ion concentration in the bath being at least about 8 to 1, providing a pressurized gaseous reducing atmosphere for said bath containing said workpiece, heating said bath containing said workpiece to induce deposition of said nickel coating on said workpiece, increasing the temperature and the ammonium to nickel ion concentration ratio of said bath during said deposition, and regulating said temperature increase to maintain the ammonium ion concentration-nickel ion concentration-temperature relationship within the area *abc* of 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, an ammonium salt, the ratio of ammonium ion to nickel ion being at least about 8 to 1 when the temperature of said bath is in excess of about 260° F., and sufficient ammonia 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 p.s.i.–800 p.s.i., heating said bath containing said workpiece initially to a temperature of at least about 200° F. to induce deposition of said nickel coating on said workpiece, and subsequently concurrently increasing the temperature of said bath to above said 260° F. and the ratio of the ammonium ion concentration to nickel ion concentration therein to above 8 but within the area defined by *abc* of FIGURE 2 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, an ammonium salt, the ratio of ammonium ion to nickel ion being at least about 8 to 1 when the temperature of said bath is in excess of about 260° F., an accelerator, and ammonia, said ammonia 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 p.s.i.–800 p.s.i., heating said bath containing said workpiece to an elevated temperature to induce deposition of nickel on said workpiece, and thereafter concurrently increasing the temperature of said bath to above 260° F. and said ammonium ion to nickel ion ratio to above 8 but within the area defined by *abc* of FIGURE 2 to more

rapidly produce said uniform, adherent, bright and smooth decorative nickel 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 10–20 grams per liter, an anthraquinoidal accelerator, about 1.6–2.0 moles per liter of ammonium ion from a soluble ammonium salt and about 0.2–0.8 mole per liter of ammonia, the ratio of said ammonium ion concentration to nickel ion concentration in the bath being at least about 8 to 1, 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 concurrently increasing the temperature of said bath and said ratio of ammonium ion concentration to nickel ion concentration therein 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 10–20 grams per liter, a quinonoid accelerator, ammonia and an ammonium salt selected from the group consisting of ammonium acetate, ammonium sulfate and ammonium chloride, the ratio of ammonium ion concentration to nickel ion concentration in the bath being at least about 8 to 1 when the temperature of said bath is in excess of about 260° F. 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 nickel coating from said bath as originally formulated until deposition of the nickel coating commences on said workpiece, and thereafter concurrently increasing the temperature and the ammonium ion to nickel ion ratio of said bath 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 cloride, nickel sulfate, nickel borate, nickel fluoborate, nickel sulfamate and nickel acetate, said salt providing a nickel ion concentration of about 10–20 grams per liter, an anthraquinoidal accelerator, ammonio and an ammonium salt selected from the group consisting of ammonium acetate, ammonium sulfate and ammonium chloride, the ratio of ammonium ion concentration to nickel ion concentration in the bath being at least about 8 to 1, providing a hydrogen atmosphere for said bath containing said workpiece, said hydrogen being at a pressure of approximately 150 p.s.i.–800 p.s.i., heating said bath containing said workpiece to a temperature of at least about 200° F., increasing the temperature and the ammonium to nickel ion concentration ratio of said bath during said deposition of said nickel coating, and regulating said temperature increase to maintain the ammonium ion concentration-nickel ion concentration-temperature relationship within the area *abc* of 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 10–20 grams per liter, an anthraquinoidal accelerator, ammonia and an ammonium salt selected from the group consisting of ammonium aceate, ammonium sulfate and ammonium chloride, the ratio of ammonium ion concentration to nickel ion concentration in the bath being at least about 8:1, providing a hydrogen atmosphere for said bath containing said workpiece, said hydrogen being at a pressure of approximately 150 p.s.i.–800 p.s.i., heating said bath containing said workpiece to a temperature of at least about 200° F., increasing the temperature and the ammonium to nickel ion concentraton ratio of said bath during said deposition of said nickel coating, and regulating said temperature increase to maintain the ammonium ion concentration-nickel ion concentration-temperature relationship along the line *ab* of FIGURE 2.

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