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ELECTROLESS NICKEL PLATING

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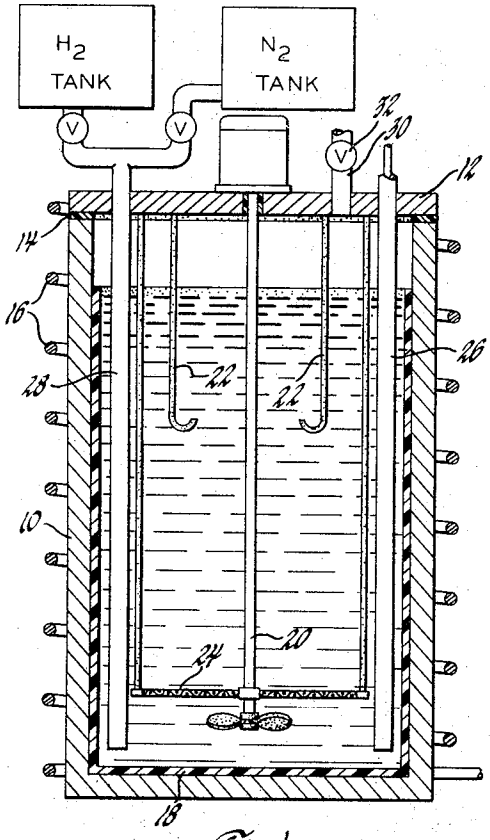


Fig. 1

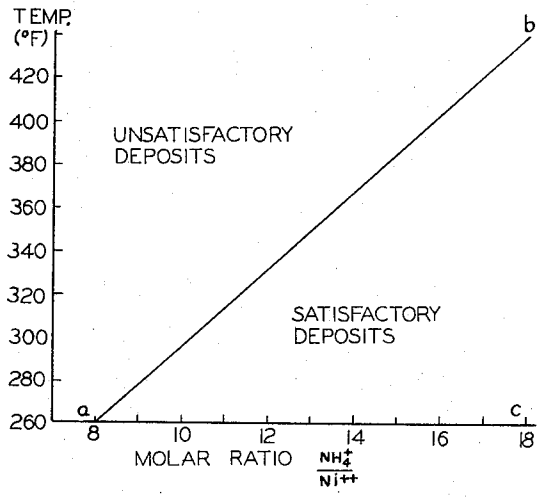


Fig. 2

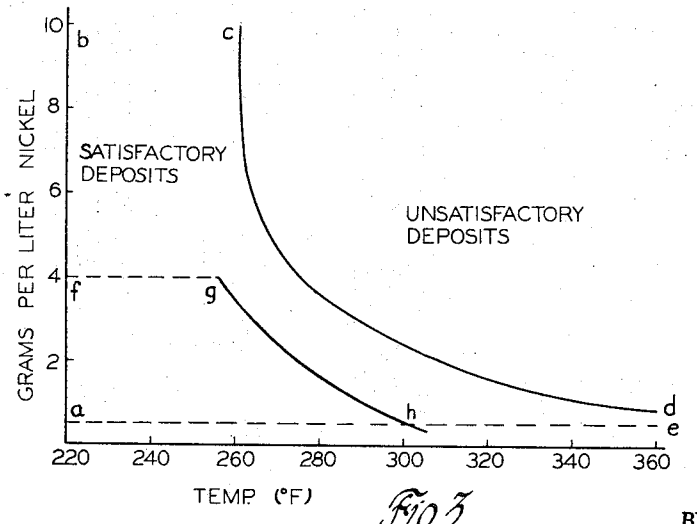


Fig. 3

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ELECTROLESS NICKEL PLATING

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

It has been known for many years that nickel could be precipitated from a salt solution by hydrogen reduction. However, it was not heretofore possible 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 films, even under commercial production conditions. It is, therefore, a principal object of my invention to provide a new process of electroless nickel deposition by hydrogen reduction.

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

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

FIGURE 2 shows a graph illustrating the relationship of the plating temperature for my process to the molar ratio of ammonium ion concentration to nickel ion concentration in one bath used in my process; and

FIGURE 3 shows a graph illustrating the relationship of plating temperature for my process to the nickel ion concentration in another bath used in my process.

Briefly, my invention encompases placing a workpiece in the presence of a buffered nickel salt solution, introducing a reducing gas into the salt solution and regulating the temperature of said bath solution with respect to the nickel concentration during nickel deposition. Temperature regulation with respect to nickel ion concentration is used to obtain an adherent, bright, smooth decorative nickel film. Preferably the nickel bath is initially heated to only a moderate temperature, about 200° F., to induce deposition of the nickel film. The temperature of the bath is then increased as the dissolved nickel concentration decreases, with the rate of temperature increase below that level which induces deleterious effects on the film being deposited.

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 holder **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----	1.0
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.

The following serves as another example of my process. 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 ----------moles per liter--	0.17
Sodium acetate ----------do----	0.12
Anthraquinone ----------grams 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 were 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.

In still a further example of the invention, the following aqueous bath composition was used to coat beryllium:

Nickel acetate	moles per liter	0.083
Sodium acetate	do	0.050
Anthraquinone	grams 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 40 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} 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 fluoborate, nickel borate and the like, may be useful, I prefer to employ a nickel salt, such as nickel acetate, nickel chloride or nickel sulfate.

Borate ion, acetate ion and ammonia (ammonium hydroxide) type buffers have provided good results, particularly the latter two. However, any buffer system can be used which will maintain the appropriate pH level without forming a nickel complex resistant to hydrogen reduction. Of course, combinations of buffer systems can be employed, for example, a bath solution formulated with nickel acetate and ammonium hydroxide. However, for simplicity of operation, it is generally preferred to use only one buffer in the bath.

In a bath formulated with an ammonia buffer, an ammonium salt is also used to expand the range of useful nickel ion concentration. Virtually any ammonium salt which is soluble in the bath solution and which does not objectionably complex 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 salt can be introduced directly into the bath or it can be formed in situ. The pH can also be reduced by additions of ammonium salts.

Analogously, in the bath formulated with an acetate buffer, 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. Moreover, if desired, a plurality of nickel salts and acetate salts can be simultaneously employed in the same bath. 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 in the acetate bath and above about 9 in the ammonia bath are 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, the higher ammonium ion concentration in the ammonia bath 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 is at least pH 3 and preferably a relatively high pH within the operating range. Generally, I prefer to formulate the acetate bath to have pH 5–6 and the ammonia bath to have pH 6–8.

The nickel ion concentration can vary from even small but effective amounts, e.g., about 0.01 gram per liter, up to saturation. However, for most purposes, a nickel ion concentration of at least 0.5 gram per liter is necessary in order to obtain a satisfactory plating rate. In the ammonia bath best plating rates are obtained at about 10–20 grams per liter. Concentrations in excess of 20 grams per liter require undesirably high ammonium ion concentrations which decrease plating rate. On the other hand, excesses of acetate ion do not appreciably affect the plating rate. Hence, in the latter type baths, large nickel ion concentrations can be used if one so desires.

However, as previously indicated, the nickel ion concentration to be used is related to the deposition temperature or, for a given nickel ion concentration, the temperature must not be alowed to exceed a certain critical limit. In general, the higher the nickel ion concentration is, the lower the plating temperature that must be used. Where the nickel ions are not complexed to any appreciable extent, such as in an acetate buffered bath, the maximum plating temperature is a function of the actual nickel ion concentration. By actual nickel ion concentration, I mean the total quantity of nickel per unit volume of the bath. On the other hand, if a portion of the nickel ions is complexed by additives in the bath, such as in my ammonia buffered bath, the maximum plating temperature is a function of the effective nickel ion concentration. By effective nickel ion concentration, I refer to that portion of the nickel ion in the solution which is not complexed. Hence, in the ammonia buffered bath, the plating temperature is also a function of the ammonium ion concentration as well as the nickel ion concentration. Thus, a higher plating temperature can be used for a given nickel ion concentration than in an acetate bath. For a better understanding of this, specific reference is now made to the ammonia buffered bath.

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 general-

ly 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, ammonia has only a relatively negligible ammonium ion concentration and is, therefore, considered as undissociated. Hence, the 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 higher 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.

FIGURE 3 shows a graph involving the acetate buffered bath in which temperature is the abscissa and the concentration of nickel ions is the ordinate. This graph, obtained form 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 saturation. 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 3.

If a plating temperature in excess of the maximum indicated by the graph in FIGURE 3 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 3 as providing satisfactory deposits. For higher concentrations, of course, it is preferred to use the temperature indicated by the curve *cd* in FIGURE 3. However, 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.

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 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 nistances 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, 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 due to the prohibitive cost of equipment operative at such 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 acetate buffered 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 *abcde* 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, smooth and bright 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 ion and sufficient buffers 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 regulating the temperature of said bath such that said temperature varies inversely with respect to the concentration of dissolved nickel ion therein to produce a smooth, bright decorative nickel coating on said workpiece.

2. The method of electroless plating workpieces with a uniform, adherent, smooth and bright decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH of about 2–9, said bath containing dissolved nickel ion and sufficient buffers to maintain the bath at 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 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, smoooth and bright 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 ion, an accelerator and sufficient buffers to maintain the bath at above about pH 2 during chemical reduction of at least a major proportion of the dissolved 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 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 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, smooth and bright 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 dissolved nickel ion, an accelerator and sufficient buffers to maintain the bath at above about pH 2 during reduction of at least a major proportion of the dissolved 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 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, smooth and bright 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 ion and sufficient buffers 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 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 nickel coating to maintain the ratio of temperature to dissolved nickel ion in the bath within the limit established by the curve *cd* in FIGURE 3.

6. The method of electroless plating workpieces with a uniform, adherent, smooth and bright 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 ion, an accelerator and sufficient buffers to maintain the bath at above about pH 2 during reduction of at least a major proportion of the dissolved 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 said deposition, and regulating the temperature of the bath during said deposition to maintain the ratio of temperature to dissolved nickel ion in the bath within the limit established by the curve *cd* in FIGURE 3.

7. The method of electroless plating workpieces with a uniform, adherent, smooth and bright 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 ion, an anthraquinoidal accelerator and sufficient buffers 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 on said workpiece, and increasing the temperature of said bath in such relation to the decreasing concentration of nickel therein that said bath never exceeds a nickel powder producing temperature to produce a smooth, bright decorative nickel coating on said workpiece.

8. The method of electroless plating workpieces with a uniform, adherent, smooth and bright 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 dissolved nickel ion concentration of at least about 10 grams per liter and sufficient buffers 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 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.

9. The method of electroless plating workpieces with a uniform, adherent, smooth and bright 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 dissolved nickel ion concentration of about 10–20 grams per liter and sufficient buffers 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 hydrogen atmosphere for said bath containing said workpiece, heating said bath containing said workpiece to induce deposition of said nickel 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.

10. The method of electroless plating workpieces with a uniform, adherent, smooth and bright 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 dissolved nickel ion concentration of at least 10 grams per liter, a quinonoid accelerator and sufficient buffers 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 atmosphere for said bath containing said workpiece, heating said bath containing said workpiece to induce deposition of said nickel 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.

11. The method of electroless plating workpieces with a uniform, adherent, smooth and bright 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 dissolved nickel ion concentration of at least 10 grams per liter, an accelerator and sufficient buffers 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 hydrogen environment for said bath containing said workpiece, heating said bath containing said workpiece to induce deposition of said nickel 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 bright decorative nickel coating on said workpiece.

12. The method of electroless plating workpieces with a uniform, adherent, smooth and bright 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 ion and sufficient buffers 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 of about 200° F.–400° F. to induce deposition of said nickel on said workpiece, and subsequently increasing the temperature of said bath in relation to the decreasing concentration of dissolved nickel ion therein such that said bath never exceeds a nickel powder producing temperature to produce a smooth, bright decorative nickel coating on said workpiece.

13. The method of electroless plating workpieces with a uniform, adherent, smooth and bright 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 ion and sufficient buffers 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 hydrogen atmosphere having a pressure of about 100–800 p.s.i. for said bath containing said workpiece, heating said bath containing said workpiece in said atmosphere to a temperature of about 200° F.–400° F. to induce deposition of said nickel on said workpiece, and increasing the temperature of said bath in relation to the decreasing concentration of dissolved nickel ion therein such that said bath never exceeds a nickel powder producing temperature to produce a smooth, bright decorative nickel coating on said workpiece.

14. The method of electroless plating workpieces with a uniform, adherent, smooth and bright 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 one nickel salt from the group consisting of nickel chloride, nickel sulfate, nickel acetate, nickel borate, nickel fluoborate and

nickel sulfamate, an anthraquinone accelerator and sufficient buffers to maintain said bath above about pH 2 during chemical reduction of a major proportion of the nickel in said solution, the dissolved nickel ion concentration in the bath being about 0.5–20 grams per liter, providing a pressurized reducing atmosphere containing hydrogen 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 during deposition of nickel on said workpiece to maintain the ratio of temperature to nickel ion concentration within the limit established by the curve *cd* of FIGURE 3.

15. The method of electroless plating workpieces with a uniform, adherent, smooth and bright decorative nickel coating, said method comprising the steps of placing at least one workpiece in an aqueous bath having a pH of at least about 3, 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 dissolved nickel ion concentration of at least 5 grams per liter, an accelerator and sufficient buffers to maintain the bath above about pH 2 during chemical reduction of a major proportion of the dissolved nickel in the bath, providing a reducing atmosphere containing hydrogen for said bath containing said workpiece, said hydrogen being at a pressure of about 100–800 p.s.i., heating said bath containing said workpiece to a temperature of approximately 200° F.–400° F. to induce deposition of a smooth, bright decorative 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 during deposition of said coating to increase its rate of formation without concurrently appreciably inducing coating roughness.

16. The method of electroless plating workpieces with a uniform, adherent, smooth and bright 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 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 dissolved nickel ion concentration of at least 0.5 gram per liter, an accelerator and sufficient buffers to maintain the bath above about pH 2 during chemical reduction of a major proportion of the dissolved nickel in the bath, providing a reducing atmosphere containing hydrogen for said bath containing said workpiece, said hydrogen being at a pressure of about 100–800 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 below a powder-producing temperature until deposition of a nickel coating commences on said workpiece, and thereafter increasing the temperature of said bath in a relation to the decreasing nickel content thereof such that said bath never exceeds a nickel powder producing temperature to more rapidly produce a smooth, bright decorative nickel coating without inducing coating roughness.

17. The method of electroless plating workpieces with a uniform, adherent, smooth and bright 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 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 dissolved nickel ion concentration of at least 5 grams per liter, an anthraquinoidal accelerator and sufficient buffers to maintain the bath above about pH 2 during chemical reduction of a major proportion of the dissolved nickel in the bath, providing a reducing atmosphere containing hydrogen for said bath containing said workpiece, said hydrogen being at a pressure of about 100–800 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 below a powder-producing temperature until deposition of a nickel coating commences on said workpiece, and thereafter increasing the temperature of said bath in relation to the decreasing nickel content thereof such that the ratio of temperature to dissolved nickel ion concentration is within the area *abc* shown in FIGURE 2.

18. The method of electroless plating workpieces with a uniform, adherent, smooth and bright 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 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 dissolved nickel ion concentration of at least 10 grams per liter, an accelerator and sufficient buffers to maintain the bath above about pH 2 during chemical reduction of a major proportion of the dissolved nickel in the bath, providing a reducing atmosphere containing hydrogen for said bath containing said workpiece, said hydrogen being at a pressure of about 100–800 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 below a powder-producing temperature until deposition of a nickel coating commences on said workpiece, and thereafter increasing the temperature of said bath in relation to the decreasing nickel content thereof such that the ratio of temperature to dissolved nickel ion concentration is within the area *abc* shown in FIGURE 2.

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