

1

3,667,972

CHEMICAL NICKEL PLATING BATHS

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8 Claims

ABSTRACT OF THE DISCLOSURE

Acidic electroless plating solution comprising nickel ions, hypophosphite ions, and an ion of the group of sulfamate, fluoroborate and mixtures thereof for improved solution stability and providing electroless plates characterized by lower internal stresses so as to provide improved adhesion. Stability is further improved by the addition of glycolate ions and acetate ions. Boric acid is used to further improve characteristics of the plating bath.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a streamlined continuation of application Ser. No. 687,470 filed Dec. 4, 1967.

The present invention relates to the deposition of nickel plate by chemical reduction or "electrolessly" as opposed to electrolytic deposition, and more particularly to the processes and chemical solutions necessary to effect such plating on catalytic and non-catalytic base materials.

The process of depositing metallic nickel plate by chemical reduction is well known. Basically, the plating process includes the steps of immersing a base having a catalytically active surface into a plating bath containing nickel ions in a reducible ionic form and a reducing agent, such as, sodium hypophosphite. The nickel is reduced to free metal at the catalytically active surface to form the desired nickel plate and the hypophosphite is oxidized to orthophosphite. While, in theory, the mechanism of electroless plating is relatively uncomplicated, it has been found that extensive modifications of the basic electroless plating solution are necessary in order to adapt the electroless plating process to commercial use. Plating solutions which contain only nickel salts (nickel ions) and sodium hypophosphite exhibit stability problems in that the solutions tend to autocatalytically decompose after slight use; plating rates are too low to be commercially competitive to other metallizing techniques; appearance (brightness) of the plate is of poor quality; and adhesion of the plate to the base is generally poor. Much work has been done in an attempt to overcome these problems and various directives have been set forth. The various teachings and directives of the prior art are well summarized in two publications:

(1) Physicochemical Principles of Nickel Plating by: K. M. Gorbunova and A. A. Nikiforova, 1960, Academy of Sciences, U.S.S.R.—Institute of Physical Chemistry (English translation published 1963 by National Science Foundation available from Office of Technical Services, Document No. OTS63-11003, U.S. Department of Commerce, Washington, D.C.; and

2

(2) Electroless Nickel Plating Symposium: American Society for Testing Materials, Special Technical Publication No. 265, published 1959.

As stated in these references, the major factors requiring control for electroless plating solution stability are pH, hypophosphite ion concentration, nickel ion concentration and orthophosphite ion concentration. Instability generally occurs upon a buildup of orthophosphite ions in the plating solution, which ions have limited solubility and which may precipitate out of the plating solution as nickel orthophosphite. Nickel orthophosphite can act as a catalytic nuclei for the reduction of the nickel ion to free nickel and can, thus, cause spontaneous decomposition of the plating solution. The quality of the nickel plate obtained is also affected in that, in the presence of nickel orthophosphite, rough plates are obtained. The major factors involved in the control of solution stability are the pH, hypophosphite ion concentration and the nickel ion concentration. In acidic plating solutions (to which this invention is particularly directed), the solubility of the orthophosphite increases as the acidity increases, e.g., as the pH number decreases from 7. However, plating rates generally decrease with increasing acidity and plating usually ceases at a pH of about 3.0. Plating rates are optimum at pH's between 6 and 7. While pH's ranging from 4 to 7 have been used experimentally, commercial processes are generally conducted at pH's ranging from 4.0 to 5.5 to obtain an optimum balance between plating rate and solution stability. However, this selection of pH's is at the sacrifice of optimum plating rates. Another projected method of overcoming this problem of stability is the utilization of a specific ratio range of nickel ions to hypophosphite ions and which ratio is further based on a specific range of absolute hypophosphite ion concentration. It is theorized by the art that a balance of ionic components is set up in the solution which lowers the tendency of nickel orthophosphite to precipitate so as to thereby lower the tendency of nickel ion to be reduced by any precipitated nickel orthophosphite. While this method contributes to improved bath stability, it introduces the problem of low nickel salt concentration in the bath which requires replacement or replenishment of the plating solutions after relative short use. This is economically disadvantageous because of the long down times involved in changing solutions or in the complicated processing equipment necessary to effect replenishment, the cost of either being a major factor in the overall economics of the process. Also, it is known that higher nickel ion concentrations can improve the plating rate, and this is an important factor in relating labor costs per item plated. Due to high labor costs, greater plating rates mean less cost per item. As a further disadvantage, the plating rates of the presently known electroless plating solutions are rather slow at low temperatures and effective plating rates require the use of elevated temperatures within the range of 70 to 100° C. As would be obvious, the cost of processing at elevated temperatures adds an increased cost to the metallizing and makes the electroless plating system unattractive in relation to other metallizing systems. Also, and in relation to the growing field of nickel plating plastics electrolessly, high temperatures are disadvantageous to most of the plastics which are presently being metallized so that slower plating rates at lower temperatures must

be utilized in order to avoid the degradation of the plastic material being plate. Also, high plating temperatures can promote the high evolution of hydrogen from the solution to the detriment of the plate. The chemical reduction of nickel ions by hypophosphite ions produces, as a by-product, hydrogen gas. The rate of evolution of hydrogen gas from the vicinity of the object to be plated can be definitely correlated to the quality of plate obtained. If the rate of hydrogen evolution is too high, the plate suffers from hydrogen embrittlement and is also spongy in character rather than a good continuous film. High plating temperatures promote high hydrogen evolution rates to the detriment of the plate.

The present invention overcomes these prior art problems by providing an improved acidic electroless plating solution of the hypophosphite type which contains high quantities of reducible nickel ions and which remains stable for extensive periods of time in use, which solution provides effective plating rates at low temperatures; and which solution can provide nickel plates characterized by good adhesion to the plated base.

In accordance with the present invention, there is provided an improved electroless plating solution for nickel plating by chemical reduction comprising nickel ions, hypophosphite ions, and fluoborate and/or sulfamate ions, the pH of the solution being within the range of about 4.0 to about 7.0. It has been found that the presence of the fluoborate and/or sulfamate ions in the solution contributes to the formation of a more adherent plate. It has also been found that a solution having high nickel ion concentrations can be formulated by the addition of glycolate and acetate ions to the plating solution even at pH's above 5.5. The pH of the solution is preferably maintained above 5.5 by the use of a borate buffer for improved plating rates. Overall efficiency of the solution is increased by the addition of ammonium fluoride and thiourea to the plating solution as plating rate accelerators. It has also been found that the electroless plating solution formulated in accordance with the invention can be utilized in an electroless-electrolytic plating process wherein a first layer of nickel is deposited electrolessly and, upon the application of an electric current, a second layer is deposited electrolytically.

The chemical nickel plating process is a catalytically induced oxidation-reduction reaction which requires that the surface to be plated be catalytic to the oxidation-reduction reaction.

The following elements are catalytic for oxidation of hypophosphite and thus may be directly nickel plated: iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, silver and platinum. The activity of the catalytic materials varies considerably and iron, cobalt, nickel, silver, osmium and palladium have been found to be particularly good catalysts in the chemical nickel plating baths. Metallic bases such as bismuth, cadmium, tin, lead and zinc, and, other bases which are non-metallic, such as plastics, glass, wood, and the like can also be electrolessly plated when the surface of the base is treated in such a manner as to provide catalytic particles of one of the metals mentioned above as induction sites for the nickel plating on the surface of the base. As described in the prior art, a catalytic surface can be provided by effecting the reduction of palladium chloride on the surface of the base to be plated by first treating the base with stannous chloride followed by immersing the base in palladium chloride. The provision of a catalytic surface on the base is essential to effecting electroless plating and, as used herein, the term "plating a catalytic surface of a base" is intended to include both bases of metal which are catalytic in and of themselves and also bases which have been treated in some manner to deposit thereon catalytic nuclei which can induce the reduction of the nickel cations to metallic nickel.

The base to be plated also requires other pretreatments prior to the initiation of the plating operations. These

include the standard practice of cleaning and degreasing of the surface to eliminate any foreign matter which might detract from the adhesion of the metal plate to the base. Also, the base can be abraded, roughened, or in some manner treated to provide a slightly roughened or porous surface to which the metal plate can adhere. According to one theory, the adhesion of the metal plate to the base is mechanical in nature which is accomplished by the filling in of tortuously shaped holes on the surface of the base. Other methods of effecting this are by the use of the inclusion of a catalytic material in the base itself as disclosed in U.S. Pat. 2,690,401, by the etching or chemical treatment of the surface as is necessary with bases such as glass, and by the extraction of a filler substance included in such bases as plastic prior to plating as is disclosed and described in copending application of Coll-Palagos, Ser. No. 687,494 filed Dec. 4, 1967.

The provision of an adherent nickel plate is not totally dependent on the preparation of the base. The nickel plate itself and its method of formation also contributes in providing an adherent plate. It has been found that the presence of sulfamate and/or fluoborate ions within the plating solution provides nickel plates having adhesion greater than plates formed from plating solutions which do not contain such ions, particularly those containing chloride ions and sulfate ions. Chloride ions and sulfate ions are generally introduced into the plating solution as the anionic moiety of the nickel salt, e.g., nickel chloride or nickel sulfate. The sulfamate and/or fluoborate ions can be introduced into the solution by means of salts of fluoboric acid or the fluoborate ion can be formed in situ in the solution by the use of boric acid and hydrofluoric acid in the presence of a nickel salt such as nickel carbonate. Preferably, the fluoborate and/or sulfamate ions are added as the anionic moiety of the nickel salt. This avoids the introduction of extraneous sulfate and chloride ions as nickel chloride and nickel sulfate are the nickel salts generally used in electroless plating solutions. While small quantities of the nickel sulfate and chloride salts can be used in the plating solution, it is preferred that these salts be substantially absent to obtain the total advantage of the effect provided by the nickel fluoborate and/or sulfamate salts.

The present invention also relates to the provision of an electroless plating solution which contains high quantities of nickel ions and hypophosphite ions, which solution is characterized by improved stability over an extended period of time and use. It has been found that fluoborate ions, sulfamate ions, and combinations thereof increase the solubility of the nickel salt in the solution and that the presence thereof allows for the preparation of electroless plating baths having increased quantities of nickel salts in solution. In this area, ionic moieties such as chloride and sulfate can be included within the solution if the function of the solution is only to effect the increase of the nickel ion concentration. As would be obvious, the total absence of these aforementioned ions is desirable in order to not only provide a solution having increased nickel ion concentration but also to provide a nickel plate having improved lower internal stresses. While this is a primary preferable form of the present invention, it is to be understood that the invention is not limited to the absence of other ions, such as chloride and sulfate.

The nickel ions which are used in the present invention can be provided by the use of nickel salts, such as nickel chloride, nickel sulfate, nickel carbonate, nickel sulfamate, nickel fluoborate, and mixtures thereof. It is preferred that nickel fluoborate, nickel sulfamate and combinations thereof be utilized as the sources of nickel ion in the solution. As an alternative, and in line with the idea of eliminating the presence of chloride and sulfate ions in the solution, nickel carbonate or nickel acetate can be used as the nickel ion source and utilize fluoboric acid or sulfamic acid as the source of the fluoborate ion or the sulfamate ion.

The quantity of nickel ion can be anywhere in the range of from 1 gram/liter to 40 grams/liter, preferably from 4.0 grams/liter to 40 grams/liter and more preferably in the area of about 7.5 grams/liter to about 20 grams/liter. In contrast, known electroless plating solutions containing nickel chloride are generally limited to a maximum of approximately 7.5 grams/liter nickel ion.

As stated hereinbefore, the solution of the present invention can be utilized in an electroless/electrolyte plating system. Effective electrolytic plating requires high concentrations of nickel ion to provide good plating rates and good nickel plates. Electroless plating solutions having less than 10 grams/liter nickel ion are generally unsuitable for efficient electroless/electrolytic plating. Preferably, the nickel ion concentration of my solution for electroless/electrolytic plating is in the range of 7.5 to 40 grams/liter and more preferably from 15 to 40 grams/liter.

The electroless plating solution contains hypophosphite anions which act as reducing agents. The hypophosphite anions may be derived from sodium hypophosphite, potassium, ammonium, etc., hypophosphites or various combinations thereof. Preferably, and in order to prevent the introduction of sodium ions into the solution, which ions also appear to effect the adhesive quality of the nickel plate, the use of ammonium hypophosphite instead of the sodium hypophosphite is recommended.

The amount of hypophosphite ion in the solution is that amount necessary to effectively reduce the nickel. This amount generally relates to the amount of nickel in solution. Preferably, the amount of hypophosphite ion in grams per liter of the initial solution is between about 50 grams per liter and about 150 grams per liter. An increase of the hypophosphite content over about 150 grams/liter decreases the plating rate and also adversely affects the quality of the nickel plate. More preferably, the hypophosphite ion concentration of the initial solution is within the range of about 50 to about 100 grams per liter.

The use of slightly acidic conditions have also been found to be advantageous. The solution is maintained within the pH range of about 4 to about 7 and preferably within the range of about 5.3 to 7.0, and more preferably within the range of about 5.5 to about 6.5. The pH range of from about 5.3 to about 7 facilitates plating and improves adhesion, especially on glass substrates.

It is well known that an acid electroless plating bath becomes more acidic as the bath is used and this is disadvantageous in that changes in pH effect changes in the plating rate. In order to maintain the bath at the desired pH, a buffer material is desirably included in the plating solution. Any buffering agent which can maintain the pH with the desired pH range is operable as long as the buffer does not interfere with the plating operation. Many such buffers are known to those skilled artisans in the electroless plating field. A preferred buffering agent for use in the solution of the present invention is boric acid or borate ion which is effective in maintaining the pH within the desired 5.5 to 6.5 range. As used herein the terms boric acid and borate ion are intended to be synonymous.

Boric acid and borate ion, while useful as a buffering agent, also provides a second advantage of providing a brighter electroless nickel plate. A solution containing boric acid has been found to give a brighter plate than a solution containing some other buffering agent. Electroless plates formed from solutions which do not contain boric acid tend to haze and lose their brightness and the boric acid prevents this hazing. In theory, it is believed that the haze is an oxidized nickel salt and boric acid prevents this oxidation.

Boric acid has a further advantage in electroless/electrolytic process in providing good electrolytic nickel plates over those solutions which do not contain the boric acid.

The amount of boric acid utilized is dependent on the

amount of nickel salt present in the solution. As the concentration of nickel salt increases, so must the boric acid concentration for effective results. It has been found that from about 15 grams/liter to about 50 grams/liter boric acid are required for nickel solutions containing from 1 to 40 grams/liter nickel ion.

While the overall solution containing fluoborate and/or sulfamate ions is more stable than a solution not containing such ions, the use of these ions is not a per se panacea for all stability problems. In order to provide a substantially stable solution, a nickel chelating agent is used. This reduces the number of free nickel ions in the solution so as to decrease the chance of nickel orthophosphite formation. The chelating agent is again not a panacea for stability problems but only a contributory factor.

The use of chelating agents in nickel electroless plating baths are well known and many are numerated in the prior art. One of these agents is acetic acid or acetate ion.

The amount of acetic acid to be utilized is dependent on the nickel ion concentration up to a limiting point where the acetic acid tends to decrease plating rate. As the nickel ion concentration increases, the acetic acid concentration must also be increased. The limiting point appears at about 25 grams acetic acid per liter of plating solution. Acetic acid also performs the function of increasing the plating rate when used in proper amounts. The acetic acid is used in amounts of from 10 to about 25 grams acetic acid per liter of plating solution (weight based on acetate ions) and preferably between about 10 grams to about 20 grams per liter of solution. As used herein acetic acid and acetate ion are intended to be synonymous. The acetate ion can be added to the solution in the form of the pure acid or salts thereof such as sodium acetate. The use of the pure acid is preferred in that it avoids the introduction of extraneous ions into the solution.

The problem of stability relates to the formation of nickel orthophosphite by the combination of nickel ions with orthophosphite ions which are a by-product of the oxidation-reduction reaction. Chelation or sequestration of nickel ions contributes to stability as it removes one of the ions necessary for the formation of the product, e.g., as by the use of the acetate ions. It has also been found particularly effective to utilize, in combination with the fluoborate and/or sulfamate ion containing electroless plating solution, glycolate ions as a chelating or sequestering agent, especially when the electroless plating solution has a pH in the range of 5.3 to 7. The glycolate ion can be added to the solution by the use of glycolic acid or by the use of salts of the acid such as sodium glycolate, potassium glycolate, and the like. It is preferred to use the pure glycolic acid so as to avoid the introduction of any extraneous ions which might affect the quality of the nickel plate such as sodium ions. The amount of glycolate ions used is that amount needed to maintain solution stability. It has been found that the solutions of the present invention can be effectively stabilized with from about 7 to about 21 grams per liter of glycolic acid.

It has also been unexpectedly found that an electroless plating solution, which after having been used and which begins to precipitate nickel orthophosphite, can be regenerated by the addition of glycolic acid. The additional glycolic acid appears to interact with components of the solution so as to change the solubility rate of the formed nickel orthophosphite and thereby allow it to go back into solution. The use of this procedure effectively allows for the purification in a simple manner of an electroless plating solution which has not been completely depleted of nickel ions thereby allowing its use to the fullest extent of the nickel salt therein. This regeneration method can be utilized with any acidic electroless plating solution but is particularly effective when used to regenerate the solution of the present invention.

Plating rate accelerators can also be included in the solution of the present invention. Sulfides and mercaptan

compounds such as thiourea provide a marked increase in plating rate if used in small amounts. In larger amounts, a compound such as thiourea acts as a catalytic poison and stops the plating reaction. Thiourea is used in an amount of from 0.2 to 0.8 part per million parts of solution and preferably about 0.3 part per million. Thiourea, in amounts above 0.8 part per million parts of solution, reduces the plating rate. Thiourea is given as illustrative of the class of sulfur-containing plating rate accelerators and this discussion is not intended to be limited to thiourea though this is the preferred material. Other plating rate accelerators such as those providing free fluoride ion can also be used. Illustrative are compounds such as ammonium fluoride which is used in a quantity of about 2 grams per liter to about 10 grams per liter. Preferably, the ammonium fluoride is used in an amount of about 4 grams per liter in a solution containing about 10 grams per liter nickel ion and 75 grams per liter hypophosphite ion. Other fluoride accelerators such as sodium, potassium and ammonium bifluoride can also be used but ammonium fluoride is preferred.

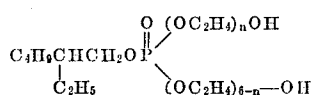
It is preferred that both types of the above mentioned accelerators be present in the preferred plating solution. Thus, the plating rate accelerator desirably comprises a combination of 0.3 p.p.m. thiourea and 4 grams per liter ammonium fluoride.

To effect an electroless/electrolytic plating procedure, fixed anodes of either the inert or dissolve type may be used. Preferably, dissolvable anodes of nickel are used to prevent depletion of nickel ions in the solution. However, nickel anodes do not easily dissolve in acid baths and the fluoride ion in the electroless/electrolytic plating bath provides the further advantage of assisting in the dissolving of the nickel anode.

In order to insure that the base is completely wetted with the plating solution, a wetting agent is preferably included in the plating solution. Any of the known cationic, anionic and non-ionic wetting agents which will perform this function are useable though the non-ionic type is preferred. Illustrative of these agents are:

Non-Ionic

- (1) sodium lauryl sulfate
- (2) sodium tridecylbenzenesulfonate
- (3) poly oxyethylene 2-ethylhexyl phosphate of the formula:



Cationic

- (1) trimethyl lauryl ammonium chloride
- (2) dimethyl distearyl ammonium chloride

Anionic

- (1) lauryl polyethoxyethanol
- (2) p-octylphenoxypolyethoxyethanol

Nonionic wetting agent No. 3 identified by the name poly oxyethylene 2-ethylhexyl phosphate is preferred for the solutions of the present invention as solutions containing this wetting agent provide better results as compared with solutions containing other wetting agents.

The wetting agent is generally included in an amount sufficient to provide the desired wetting action. This is dependent on its surface active qualities and molecular weight. This amount can be easily determined by a skilled artisan.

The plating time is dependent on the temperature of the plating bath, the plating rate of the solution and the thickness of the plate desired. Generally, the plating rate at room temperature, e.g., 25° C. is 15 millionths of an inch per hour of nickel. At 40° C. the plating rate increases to 0.1 mil, and at 60° C. to 0.4 mil, and at 65° C.

to 0.47 mil per hour. Known commercially available acidic solutions require 60° C. to 80° C. to obtain 0.1 mil/hr. plating rate. Selection of time and temperature are within the purview of one skilled in the art.

- 5 Plating solutions when prepared generally need pH adjustment prior to use. Since sodium ions appear to be detrimental to plate adhesion, it is preferred to utilize ammonium hydroxide instead of sodium hydroxide for pH adjustment.

- 10 The invention will be further illustrated in the examples which follow.

- 15 Example 1.—Plaques of electroless plating grade acrylonitrile-butadiene-styrene (ABS) having a flat surface on one side and various indicia and roughen areas on the other are pretreated under the following conditions:

TABLE I

	Temp. (° C.)	Time (min.)	Cold water rinses ¹
Cleaner, mild non-silicated alkaline.....	65	5	1 CWR
Neutralization, 15% H ₂ SO ₄	R.T.	1/2	1 CWR
Etch, CrO ₃ -H ₂ SO ₄	65	10	2 CWR
Etch, CrO ₃ -H ₂ SO ₄ -H ₃ PO ₄	R.T.	2	2 CWR
Neutralization, 15% HCl.....	R.T.	2	2 CWR
Sensitizing SnCl ₂	R.T.	1 1/4	2 CWR
Activation PdCl ₂	R.T.	1/4	2 CWR

¹ Integer=number of rinses.

- 30 Following pretreatment, the plaques are immersed in an electroless plating solution of the following composition:

SOLUTION A

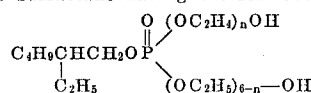
- Nickel fluoborate—42 grams/liter
- Sodium hypophosphite—100 grams/liter
- Boric acid—20 grams/liter
- Acetic acid—16 grams/liter
- Glycolic acid—14 grams/liter
- Ammonium fluoride—4 grams/liter
- 40 Thiourea—0.3 part per million parts of solution
- Wetting agent¹—0.4 gram/liter

- 45 The pH of the solution is adjusted to a range within 5.3–6.0 with ammonia. Plating times range from 3 to 8 minutes and the temperatures of the plating solution are varied from 30 to 45° C. The results are presented in Table II along with the results obtained from 2 commercially available acidic and 2 commercially available alkaline electroless plating solutions. All plates are bright in final appearance.

TABLE II

	Time (min.)	Temp. (° C.)	pH
55 Sample:			
1-A.....	8	30	5.6
1-B.....	8	35	5.3
1-C.....	10	35	5.3
1-D.....	12	35	5.3
1-E.....	14	35	5.3
1-F.....	16	35	5.3
1-G.....	3	40	5.5
1-H.....	6	45	5.5
1-I.....	8	45	5.4
1-J.....	6	55	5.35
1-K.....	2	60	5.5
1-L.....	4	60	5.5
Commercial solution:			
1.....	8	65	4.6
2.....	8	80	5.35
3.....	5	43	7.2
4.....	6	30	8.8

¹ A nonionic surfactant having the formula:



- 75 sold under the name of Victawet-12.

As can be seen, the solution of the present invention provides good plates electrolessly at temperatures well below those required in the commercially available acid solutions 1 and 2.

Electrolessly deposited nickel plate on plastics is generally not utilized as the final surface covering but as an electroconductive intermediate layer for further deposition of metals by normal electrolytic techniques. In general, a bright copper layer is applied, electrolytically over the electroless nickel, a bright nickel over the copper and a chrome plate over the bright nickel. Normal surface activation steps which are used in electrolytic plating,

TABLE III

	Temp. (° C.)	Time (min.)	Water rinses ¹
Activation 10% H ₂ SO ₄ +1% HCl.....	45	1½	2 CWR
Electrolytic copper, 54 amp/sq. ft.....	25	40	2 CWR
Activation 10% H ₂ SO ₄ +1% HCl.....	45	1½	2 CWR
Electrolytic bright nickel, 60 amp/sq. ft.....	50	10	2 CWR
Activation 10% H ₂ SO ₄ +1% HCl.....	45	1½	2 CWR
Electrolytic chrome, 226 amp/sq. ft.....	45	3	2 CWR
(Low concentration bath—325 grams/liter CrO ₃ +H ₂ SO ₄ cat.).			

¹ CWR=cold water rinse; Integer=number of rinses.

The following results of the thermal cycle and adhesion tests were obtained:

TABLE IV

Example	Planting conditions			Peel strength in pounds/in.	
	Time	Temp., ° C.	pH	Thermal cycle (before)	Thermal cycle (after)
1-I.....	8	45	5.5	Passed.....	7.7
Commercial solution 1.....	8	65	4.6	do.....	8.8
Commercial solution 2.....	8	80	5.35	Failed ¹	7.3
Commercial solution 3.....	5	43	7.2	Passed.....	9.9
Commercial solution 4.....	6	30	8.8	Failed.....	8.4
1-B.....	8	35	5.3	Passed.....	8.1
1-I.....	8	45	5.4	do.....	(?)
Commercial solution 1.....	8	65	4.62	do.....	0.9
Commercial solution 2.....	8	80	5.00	Failed.....	0.6
Commercial solution 3.....	5	43	8.45	do.....	
Commercial solution 4.....	6	30	8.7	Passed.....	

¹ Separation between electroless Ni and Cu.

² No adhesion Cu to electroless Ni.

such as acid treatments, before each plate are utilized. The bright nickel can be preceded by a semi-bright nickel plate to form what is called duplex nickel plate. In accordance with the invention, the electrolessly plated article can be immediately plated electrolytically with nickel by the application of sufficient electric current to the electroless plating bath. Following this, the plated article can be chrome plated electrolytically. By this procedure, the copper plating step and its attendant pretreatment and post treatment steps can be eliminated thereby simplifying the procedure of preparing a chrome plated plastic article and make such procedure more economical.

Electrolessly plated plastic articles which have been overplated electrolytically are generally subjected to two standard tests to determine the quality and adherence of the final composite plate to the base. The first is the thermal cycle test which is intended to determine the maximum temperature range within which a metal-plated plastic test plaque can be alternately heated and cooled without suffering visible damage such as blistering or warping, or losing metal to plastic adhesion (delaminating). The general method is as follows:

A metal-plated specimen is exposed to three cycles of alternately high and low temperatures and inspected for visible damage and loss of adhesion. The upper test temperature is +200° F., and the lower test temperature is -20° F. This procedure is repeated for three cycles or until damage or loss of metal-plastic cohesion is detected.

The procedure and the above method is generally set forth at page 542 of the June, 1967 Trans. Journal Plastic Institute, Great Britain. The second test is intended to measure the strength of the adhesive bond between the metal plating and the plastic substrate. Basically, a tensometer is used to measure the tensile load, acting at approximately 90° to the plastic surface and at a constant rate, which will peel a strip of metal plating, one inch wide, from its plastic substrate. Specific details of this test are given at page 541 of the aforementioned Journal.

Samples electroless plated with nickel are overplated with copper, bright nickel and chrome for the above tests by the following procedure:

As can be seen from Table IV, the solution of the present invention provides markedly improved adhesion results over the commercially available alkaline solutions and the commercially available acid solution No. 2. Further, the solution of the present invention provides adhesion equally as good as commercially available acid solution No. 1 even though plating was effected at temperatures at 20-25° C. lower than those required for commercial solution 1.

Example 2.—Glass plates of approximately 1 inch x 3 inches x 1/16 inch are pretreated under the following conditions:

TABLE V

	Temp., ° C.	Time, sec.	Water rinse
Cleaner mild non-silicated alkaline.....	65	(1)	2 CWR
Etch 5% HF solution.....	RT	15	1 CWR
Do.....	RT	15	2 CWR
Sensitizing—SnCl ₂	RT	45	2 CWR
Activation—Pd Cl ₂	RT	30	2 CWR

¹ 5 minutes.

Following pretreatment, the glass plates are immersed in one of the electroless plating solutions tabulated below. The pH of each solution is adjusted to a pH range of between 5.3 and 6.5 with ammonia. Good nickel plates are obtained from each solution.

TABLE VI

Components	Solution			
	B	C	D	E
Nickel fluoroborate, g./l.....	22	26	63	84
Nickel sulfamate, g./l.....	62	20	150	100
Sodium hypophosphite, g./l.....	100	100	30	40
Boric acid, g./l.....	20	16	16.8	35
Acetic acid (glacial), g./l.....	16	14	9	6
Glycolic acid, g./l.....	4	0.3	0.6	0.2
Ammonium fluoride, g./l.....	0.3	0.4		
Thiourea, p.p.m.....	0.4			
Wetting agent ¹ , g./l.....				

¹ Vietawet 12.

Example 3.—Glass plates of approximately 1 inch x 3 inches x 1/16 inch are pretreated using the procedure set forth in Table V hereinbefore.

Following pretreatment, the plates are immersed in an electroless plating solution. Various times and plating temperatures are utilized. Condition of the electrolessly deposited nickel plate during plating is noted. A post plating adhesion test is also conducted wherein the plated

glass samples are subjected to the force of flowing tap water (50 to 70 pounds per sq. in.) to determine if the nickel plate has sufficient adherence to the glass. Adhesion test is passed if plate does not delaminate under the pressure of the flowing water. The results are reported in Table VII following:

TABLE VII
Plating at 25 °C.

	30 sec.	1 min.	5 min.	Adhesion test
Solution A.....	Faint.....	Slight.....	Normal.....	Passed.
Solution B.....	No plating.....	Faint.....	do.....	Do.
Solution C.....	Faint.....	Slight.....	do.....	Do.
Commercial solution 1.....	No plating.....	No plating.....	No plating.....	
Commercial solution 2.....	do.....	do.....	do.....	

Plating at 50 °C.

Solution A.....	Normal.....	Normal.....	Normal.....	Passed.
Solution B.....	No plating.....	Faint plating.....	do.....	Do.
Solution C.....	Normal.....	Normal.....	do.....	Do.
Commercial solution 1.....	Faint plating.....	Spotty plating.....	Flaking at 3½.....	
Commercial solution 2.....	No plating.....	No plating.....	No plating.....	
Commercial solution 3.....	Plates (flaking).....	Plates (flaking).....	Plates (flaking).....	

Plating at 80 °C.

Solution A.....	Normal.....	Normal.....	Normal.....	Passed.
Solution B.....	do.....	do.....	Slight flaking.....	Do.
Solution C.....	do.....	do.....	do.....	
Commercial solution 1.....	do.....	Flaked.....	Flaked.....	
Commercial solution 2.....	do.....	Normal.....	Normal.....	Failed.
Commercial solution 3.....	Flaked.....			

Plating at 84 °C.

Solution A.....	Normal.....	Normal.....	Slight blistering.....	Passed.
Solution B.....	do.....	do.....	Normal.....	Do.
Solution C.....	do.....	do.....	do.....	
Commercial solution 2.....	do.....	do.....	Normal.....	Failed.

As can be seen from the results, effective plating of glass is accomplished at room temperature in contrast to the commercially available solutions which provide no plating; at 50° C. good non-flaked plates are obtained with good adhesion; and at 80° C. and 84° C. solutions A and B provide good plates and good adhesion.

Example 4.—Plates of aluminum are prepared and plated with electroless nickel as follows:

PRETREATMENT

	Temp., °C.	Time	Water rinses
Immerse in 2% NaOH solution containing 4 grams/liter sodium gluconate.....	60	30 sec.	1 CWR
Repeat step 1.....	60	30 sec.	2 CWR
Immerse in 5% HF solution.....	RT	1 min.	2 CWR
Activation—PdCl ₂ (0.05 g./l.).....	RT	2 min.	2 CWR

Following pretreatment the aluminum is electrolessly plated by immersing in electroless nickel solution A as described in Example 1 for 10 minutes at 60° C. Aluminum alloys 3003, 5052, 5252, 5357, 5457, 5557 and 6063 are effectively plated with a uniform and adherent nickel plate.

Equally good plates can be obtained by omitting the activation step (No. 4) in the pretreatment of the aluminum.

Example 5.—An electroless plating solution of the type denoted Solution A in Example 1 after extensive use turned cloudy. The cloudiness was determined to be caused by the precipitation of nickel orthophosphite from the solution. To this solution was incrementally added glycolate ion in the form of glycolic acid with stirring until the cloudiness disappeared. The pH of the solution was readjusted to within the range of 5.3–6.5 with ammonia and effectively used to deposit further nickel plate electrolessly.

The invention is defined in the claims which follow. What is claimed is:

1. An acidic electroless plating solution comprising:

Amount in grams/liter
from about

Nickel ion 1 to 40
Hypophosphite ion 50 to 150

Fluoborate ion 2 per Nickel ion
Borate ion 15 to 50
Glycolate ion 7 to 21
Acetate ion 10 to 25
Ammonium fluoride 2 to 10
Thiourea 0.2 to 0.8 p.p.m.

plus sufficient ions to complement the aforelisted ions to ionically complete the invention.

2. An acidic electroless plating solution as recited in claim 1 wherein said nickel ions and said fluoborate ions are provided by the addition of nickel fluoborate to said solution.

3. An acidic electroless plating solution as recited in claim 1 which further includes a non-ionic wetting agent.

4. An acidic electroless plating solution as recited in claim 3 wherein said wetting agent is poly oxyethylene 2-ethylhexyl phosphate.

5. An acidic electroless plating solution as recited in claim 1 wherein the pH of the solution is maintained within the range of about 5.3 to about 7.

6. An acidic electroless plating solution as recited in claim 1 wherein the pH of the solution is maintained within the range of about 5.5 to about 6.5.

7. In a method for regenerating an electroless plating solution comprising nickel ions and hypophosphite ions wherein said solution has become unstable due to the precipitation of nickel orthophosphite, the improvement which comprises adding glycolate ions to said solution until said precipitate redissolves and readjusting the pH to an operable plating range with an aqueous solution of a basic compound which yields hydroxyl ions in aqueous solution.

8. A method for regenerating an electroless plating solution as recited in claim 7 wherein said basic compound is ammonia.

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