

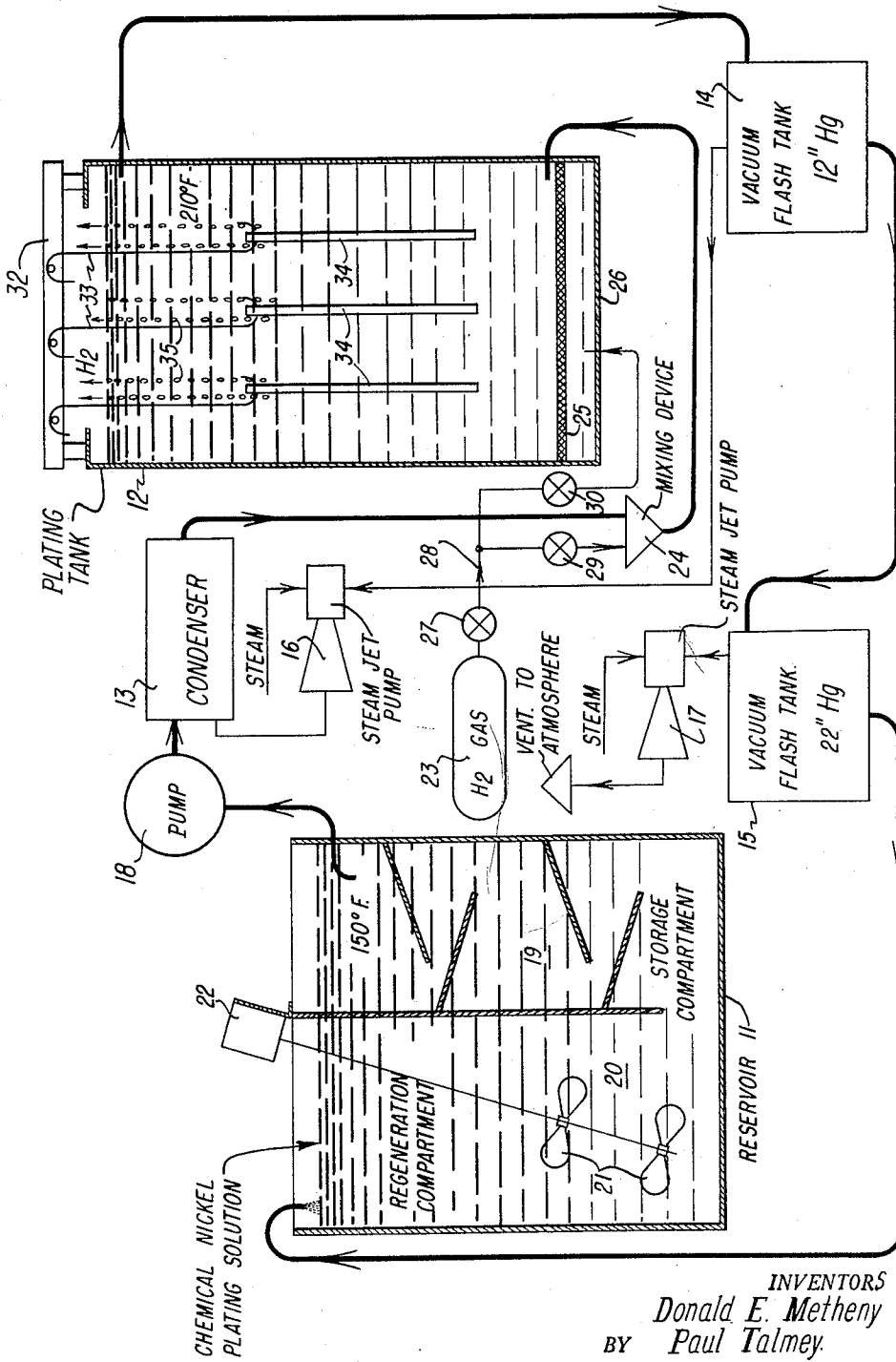
Jan. 7, 1958

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2,819,188

PROCESSES OF CHEMICAL NICKEL PLATING

Filed May 18, 1954



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PROCESSES OF CHEMICAL NICKEL PLATING

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Application May 18, 1954, Serial No. 430,604

11 Claims. (Cl. 117—130)

The present invention relates to processes of chemical nickel plating of catalytic materials; and it is the general object of the present invention to provide an improved process of this character, employing an aqueous chemical nickel plating solution of the nickel cation-hypophosphite anion type, which is productive of smoother and brighter and better adhering nickel deposits than have been obtained heretofore.

The chemical nickel plating of a catalytic material employing an aqueous chemical nickel plating bath of the type noted is based upon the catalytic reduction of nickel cations to metallic nickel and the corresponding oxidation of hypophosphite anions to phosphite anions with the evolution of hydrogen gas at the catalytic surface. The reactions take place when the body of catalytic material is immersed in the plating bath, and the exterior surface of the body of catalytic material is coated with nickel. The following elements are catalytic for the oxidation of hypophosphite anions and thus may be directly nickel plated: iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum. The following elements are examples of materials which may be nickel plated by virtue of an initial displacement deposit of nickel thereon either directly or through a galvanic effect: copper, silver, gold, beryllium, germanium, aluminum, carbon, vanadium, molybdenum, tungsten, chromium, selenium, tellurium and uranium. The following elements are examples of non-catalytic materials which ordinarily may not be nickel plated: bismuth, admium, tin, lead and zinc. The activity of the catalytic materials varies considerably and the following elements are particularly good catalysts in the chemical nickel plating bath: iron, cobalt, nickel and palladium. The chemical nickel plating process is auto-catalytic since both the original surface of the body being plated and the nickel metal that is deposited on the surface thereof are catalytic; and the reduction of the nickel cations to metallic nickel in the plating bath proceeds until all of the nickel cations have been reduced to metallic nickel, in the presence of an excess of hypophosphite anions, or until all of the hypophosphite anions have been oxidized to phosphite anions, in the presence of an excess of nickel cations.

A number of suitable aqueous chemical nickel plating baths of the nickel cation-hypophosphite anion type that may be employed in a chemical nickel plating process of the character noted are disclosed in U. S. Patent No. 2,658,841, granted on November 10, 1953, to Gregoire Gutzeit and Abraham Krieg, and in U. S. Patent No. 2,658,842, granted on November 10, 1953, to Gregoire Gutzeit and Ernest J. Ramirez, and in the copending application of Gregoire Gutzeit, Paul Talmey and Warren G. Lee, Serial No. 478,492, filed December 29, 1954. In carrying out a chemical nickel plating process of the character noted upon a commercial basis, the plating baths disclosed in the Gutzeit, Talmey and Lee application are preferred, both from the standpoint of economy

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and of performance; and three examples of such aqueous chemical nickel plating baths may be designated: the malic acid-lactic acid-succinate bath, the malic acid-glycine bath, and the malic acid-succinate bath.

A typical malic acid-lactic acid-succinate plating bath comprises: an absolute concentration of hypophosphite anions in the range 0.15 to 1.20 moles/liter; a ratio between nickel cations and hypophosphite anions in the range 0.25 to 1.60; an absolute concentration of malic acid anions in the range 0.04 to 0.20 mole/liter; an absolute concentration of lactic acid anions in the range 0.04 to 1.00 mole/liter; the total quantity of the malic acid anions and the lactic acid anions are sufficient to complex at least 100% of the nickel cations; an absolute concentration of succinate anions of at least 0.04 mole/liter; and a pH within the range 4.5 to 7.0.

A typical malic acid-glycine plating bath comprises: an absolute concentration of hypophosphite anions in the range 0.15 to 1.20 moles/liter; a ratio between nickel cations and hypophosphite anions in the range 0.25 to 1.60; an absolute concentration of malic acid anions sufficient to complex at least 100% of the nickel cations; and an absolute concentration of glycine anions of at least 0.04 mole/liter; and a pH within the range 4.5 to 9.5.

A typical malic acid-succinate plating bath comprises: an absolute concentration of hypophosphite anions in the range 0.15 to 1.20 moles/liter; a ratio between nickel cations and hypophosphite anions in the range 0.25 to 1.60; an absolute concentration of malic acid anions sufficient to complex at least 100% of the nickel cations; an absolute concentration of succinate anions of at least 0.04 mole/liter; and a pH within the range 4.5 to 6.0.

In the formulation of any one of these plating baths, an aqueous solution is prepared of the ingredients named; the nickel cations may be derived from nickel chloride, nickel sulfate, etc., or various combinations thereof; the hypophosphite anions may be derived from sodium, potassium, etc., hypophosphites, or various combinations thereof; the other additives are introduced into the bath normally as the acids, or as the soluble salts thereof, etc.; and the desired pH of the bath is established by the eventual introduction thereto of an acid or a base, as required, hydrochloric or sulfuric acid and sodium hydroxide being recommended, as a matter of economy and simplicity.

In the compositions of the various plating baths, the terms "cation," "anion" and "ion," as employed, include the total quantity of the corresponding elements that are present in the plating bath; i. e., both undissociated and dissociated material. In other words, 100% dissociation is assumed when the terms noted are used in connection with molar ratios and concentrations in the plating bath.

In carrying out a chemical nickel plating process of the character noted, a bath of the aqueous chemical nickel plating solution is held in a plating chamber at a temperature only slightly below the boiling point thereof, about 210° F., and the solid body of catalytic material is immersed therein; whereby the chemical nickel plating reaction takes place, the exterior surface of the catalytic body being coated with the nickel deposit. Subsequently, the catalytic body is withdrawn from the plating bath after a time interval corresponding to the thickness of the nickel plating upon the surface thereof that is desired.

In the carrying out of this chemical nickel plating process, the deposit of nickel that is produced upon the surface of the catalytic body is not always as bright and smooth as is desired, and occasionally in deposits or coatings having a thickness above 2 or 3 mils there is encountered pitting or roughness that is most objectionable.

Accordingly, it is another object of the invention to provide a chemical nickel plating process of the character described, that involves an improved step, which positively insures a smooth and bright nickel deposit, effectively eliminates the occasional pitting and roughness in a relatively thick deposit or coating, and improves the adhesion of the nickel deposit to the base metal.

The present invention is predicated upon the discovery that bright and smooth nickel deposits may always be obtained in the chemical nickel plating process, along with effective elimination of the occasional pitting and roughness in the relatively thick coatings, by contacting the surfaces of the catalytic bodies with a light gas in highly dispersed form in the aqueous nickel plating solution, the light gas being chemically inert with respect to the plating solution, exhibiting a low surface tension toward the plating solution, and having a molecular weight that is not greater than that of neon. The phenomenon involved is not understood, but it is important to note that the results obtained from the dispersion of the inert gases in the plating solution vary with the molecular weights thereof, as will be hereinafter demonstrated.

In any case, the cause or causes of the lack of brightness and smoothness in the nickel deposits or coatings, as well as the occasional pitting in the relatively thick deposits, is effectively reduced or eliminated by contacting the catalytic bodies undergoing the plating reaction with the light inert gas, and presumably the action of the light inert gas upon the surfaces of the catalytic bodies, and possibly with respect to some surface gases occluded thereon, is entirely mechanical, as no chemical reaction therebetween has been observed or detected; and preferably, the light inert gas that is dispersed in the aqueous chemical nickel plating solution comprises: hydrogen, helium, methane or neon, or mixtures thereof. Hydrogen, the lightest, is the most desirable; and neon, the heaviest, is the least desirable.

Further features of the invention pertain to the particular arrangement of the steps of the process, whereby the above-outlined and additional operating features thereof are attained.

The invention, both as to its organization and principle of operation, together with further objects and advantages thereof, will best be understood by reference to the following specification taken in connection with the accompanying drawing, in which the single figure is a diagrammatic illustration of a continuous nickel plating system in which the process of the present invention may be carried out.

Referring now to the drawing, the continuous nickel plating system there illustrated, and suitable for the carrying out of the present process, is essentially of the arrangement disclosed in the copending application of Paul Talmey and William J. Crehan, Serial No. 299,784, filed July 19, 1952, now Patent No. 2,717,218, granted on September 6, 1955. More particularly, the system fundamentally comprises an upstanding reservoir 11, an upstanding plating tank or chamber 12, a condenser 13, a primary vacuum flash tank 14, a secondary vacuum flash tank 15, a primary steam jet pump 16, a secondary steam jet pump 17, and a mechanical pump 18. The reservoir 11 includes a baffled storage compartment 19 and a communicating regeneration compartment 20, the regeneration compartment 20 being provided with agitator mechanism 21 driven by an associated electric motor 22. In the arrangement, the inlet of the pump 18 communicates with the upper portion of the storage compartment 19; and the outlet of the pump 18 communicates with the upper portion of the condenser 13. The lower portion of the condenser 13 communicates with the lower portion of the plating tank 12; and the upper portion of the plating tank 12 communicates with the upper portion of the primary vacuum flash tank 14. The lower portion of the primary vacuum flash tank 14 communicates with the upper portion of the secondary vacuum flash tank 15; and

the lower portion of the secondary vacuum flash tank 15 communicates with the upper portion of the regeneration compartment 20. Also, the upper portion of the primary vacuum flash tank 14 communicates with the primary steam jet pump 16, that is also connected to an associated source of high pressure steam, not shown; and the discharge from the primary steam jet pump 16 communicates with the upper portion of the condenser 13. Also, the upper portion of the secondary vacuum flash tank 15 communicates with the secondary steam jet pump 17, that is also connected to the associated source of high-pressure steam, not shown; and the discharge from the secondary steam jet pump 17 communicates with the atmosphere. The system contains an aqueous chemical nickel plating solution of the character previously described; whereby a first portion of the plating solution is stored in the reservoir 11 at a relatively low temperature well below the boiling point thereof and in a relatively concentrated form; while a second portion of the plating solution is held as a bath in the plating tank or chamber 12 at a relatively high temperature only slightly below the boiling point thereof and in a relatively dilute form. Preferably, the composition of the plating solution in the plating tank 12 is that previously set forth and disclosed in the previously-mentioned Gutzeit, Talmey and Lee application.

The system further comprises a bottle or tank 23 containing a light inert gas under relatively high gauge pressure (hydrogen gas for the purpose of the present description) and an arrangement for dispersing the hydrogen gas in the aqueous chemical nickel plating solution contained in the plating tank 12. In the system alternative arrangements are illustrated for achieving the dispersion of the hydrogen gas in the plating solution, the first arrangement including a mixing device 24 arranged in the communication between the condenser 13 and the lower portion of the plating chamber 12, and the second arrangement including a dispersion plate 25 arranged in the lower portion of the plating tank 12 in spaced relation slightly above the bottom wall 26 thereof. More particularly, the bottle 23 is provided with a throttling valve 27 that communicates with a header 28; and the header 28 is connected via a control valve 29 to the mixing device 24 and via a control valve 30 directly with the space between the diffusion plate 25 and the bottom wall 26. Finally, a rack 32 is carried by the top of the plating chamber 12 and receives a number of hooks 33 that are employed for the purpose of suspending or hanging a number of catalytic bodies 34 in plating position in the plating tank 12 above the dispersion plate 30.

In the operation of the system, the plating solution in the storage compartment 19 may have a temperature of about 150° F.; while the plating solution in the plating tank 12 may have a temperature of about 210° F. The plating solution is circulated from the upper portion of the storage compartment 19 by the pump 18 into the upper portion of the condenser 13, wherein it is both heated to the required temperature of about 210° F. and diluted to the required concentration by the discharge from the primary steam jet pump 16. The dilution of the plating solution in the condenser 13 is achieved not only by the introduction of steam thereto, but also by the introduction of the water vapor thereto that is withdrawn from the upper portion of the primary vacuum flash tank 14. The plating solution from the condenser 13 is conducted into the mixing device 24 and thence into the lower portion of the plating tank 12 above the dispersion plate 25.

When the first arrangement noted is employed for the purpose of dispersing the gaseous hydrogen into the plating solution, the control valve 29 is opened, and the control valve 30 is closed; whereby the gaseous hydrogen from the header 28 enters the mixing device 24 so that it is dispersed therein into the plating solution entering the lower portion of the plating tank 12. On the other hand, when the second arrangement noted is employed for the purpose of dispersing the gaseous hydrogen into the plat-

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ing solution, the control valve 29 is closed and the control valve 30 is opened, whereby the gaseous hydrogen from the header 28 is introduced into the space between the diffusion plate 25 and the bottom wall 26, while the plating solution is introduced through the mixing device 24 into the lower portion of the plating tank 12. In the last-mentioned case, the gaseous hydrogen admitted into the space between the dispersion plate 25 and the bottom wall 26 is dispersed into the plating solution contained in the plating tank 12 by virtue of the action of the dispersion plate 25, which, of course, is of perforated or porous structure. In any case, an adequate supply of gaseous hydrogen under the required gauge pressure is maintained in the header 28 from the bottle 23 by virtue of the pressure-reducing action of the throttling valve 25; and the gaseous hydrogen is thoroughly dispersed in the plating solution contained in the plating tank 12 employing one of the arrangements described above; whereby the plating solution in contact with the catalytic bodies 34 suspended upon the hooks 33 in the plating chamber 12 from the rack 32 has the gaseous hydrogen dispensed therein. Moreover, rising streams of bubbles of the gaseous hydrogen proceed upwardly, as indicated at 35, from the bodies 34 undergoing the plating reaction and escape from the open top of the plating tank 12; whereby the rising bubbles of the gaseous hydrogen 35 are in sweeping or scrubbing relationship with the surfaces of the bodies 34. The plating solution from the upper portion of the plating tank 12 is introduced into the upper portion of the primary vacuum flash tank 14, and is circulated therefrom into the upper portion of the secondary vacuum flash tank 15, and ultimately back into the upper portion of the regeneration compartment 20. In the primary vacuum flash tank 14, a vacuum of about 12" Hg is drawn by the primary steam jet pump 16; whereby water vapor is withdrawn from the contained plating solution, as previously noted, so that the plating solution in the primary vacuum flash tank 14 is both correspondingly concentrated and cooled prior to the introduction thereof into the secondary vacuum flash tank 15; and in the secondary vacuum flash tank 15, a vacuum of about 22" Hg is drawn by the secondary steam jet pump 17, whereby water vapor is withdrawn therefrom, so that the plating solution in the secondary flash tank 15 is both correspondingly concentrated and cooled prior to the return thereof into the regeneration compartment 20. The plating solution returned into the regeneration compartment 20 may have a temperature of about 150° F., as previously noted, as a consequence of the tandem cooling effects produced in the primary and secondary vacuum flash tanks 14 and 15. Also, the plating solution thus returned to the regeneration compartment 20 is in the relatively concentrated form as a consequence of the tandem concentrating effects produced in the primary and secondary vacuum flash tanks 14 and 15. Since the discharge of the secondary steam jet pump is to the atmosphere, the water vapor withdrawn from the plating solution in the upper portion of the secondary vacuum flash tank 15 prevents the build-up of water in the circulated plating solution; and preferably, the weight of steam introduced into the plating solution in the condenser 13 by the primary steam jet pump 16 substantially equals the weight of the water vapor withdrawn therefrom in the secondary vacuum flash tank 15 and discharged to the atmosphere by the secondary steam jet pump 17; thereby maintaining the desired balance of the water supplied to and extracted from the circulated plating solution.

The catalytic bodies 34 are immersed in the plating bath in the plating chamber 12; whereby the metallic nickel (actually an alloy of nickel and phosphorus having a composition of about 89% to 97% nickel and 11% to 3% phosphorus by weight) is deposited upon the surfaces thereof; the bodies 34 being withdrawn from the plating bath when the coatings thereon are of the desired thickness. In the plating of the catalytic bodies 34, the

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rising streams of bubbles of hydrogen gas, being dispersed in the plating solution, sweep the surfaces of the bodies 34, so that the nickel coatings produced thereon are smooth and bright and free from pits and blemishes, as explained more fully hereinafter.

Incident to the plating of the nickel upon the catalytic bodies 34, the initial composition of the plating bath is altered by the reduction of the nickel cations and the oxidation of the hypophosphite anions, as previously noted; and the initial pH of the bath is reduced, as previously explained; whereby it is necessary to regenerate the plating solution in the regeneration compartment 20 by the addition thereto of an alkalizing reagent to restore the initial pH thereof and of a nickel salt and a hypophosphite to restore the initial composition thereof; the ingredients thus supplied in the regeneration chamber 20 being thoroughly dissolved therein by operation of the agitator mechanism 21 from the electric motor 22. As a matter of convenience, the added alkalizing reagent may be derived from an aqueous sodium hydroxide stock solution; and assuming that the initial bath was formulated utilizing nickel chloride and sodium hypophosphite, the added nickel salt may be derived from an aqueous nickel chloride stock solution and the added hypophosphite may be derived from an aqueous sodium hypophosphite stock solution. Of course, the exact initial composition of the plating solution is not restored, as it is apparent that there is a gradual build-up therein of sodium cations and chlorine anions, as a result of the additions, as well as a gradual build-up of phosphite anions, as a result of the plating reactions. However, this build-up of the foreign cations and anions named is gradual and of small moment until the phosphite anion concentration builds-up to about 1 mole/liter; whereby the aqueous plating solution may be employed continuously in the plating system throughout the corresponding time interval, provided it is appropriately regenerated, either continuously or periodically, as explained above.

In connection with the continuous nickel plating process, it is noted that the articles 34 to be nickel plated, and normally having a catalytic surface, are first properly prepared by mechanical cleaning, degreasing and light pickling, substantially in accordance with standard practices in electroplating processes, prior to the immersion thereof in the plating bath in the plating tank 12. For example, in the nickel plating of a steel article, it is customary to clean the rust and mill scale from the article, to degrease the article, and then to pickle lightly the article in a suitable acid, such as hydrochloric acid. Subsequently, the steel article is removed from the plating tank 12 after an appropriate time interval corresponding to the required thickness of the nickel coating deposited thereon that is desired; and ultimately the steel article is rinsed off with water and is then ready for use.

In some cases when a nickel coating of two mils or more is sought there has been some tendency toward the formation of surface discontinuities in the nickel deposits. This effect results in lack of smoothness and brightness in the nickel deposits and is occasionally productive of pits in the relatively thick deposits. This deleterious effect may be readily reduced or eliminated by the introduction and dispersion into the plating solution of the light inert gas, and presumably the action of the light inert gas is entirely mechanical, as no chemical reaction therebetween has been observed or detected.

Specifically, the light gas is chemically inert with respect to the aqueous chemical nickel plating solution (thereby eliminating the use of such active or reactive gases as air, oxygen, ammonia, etc.), exhibits a low surface tension toward the plating solution, has a molecular weight that is greater than that of neon, and is present in a highly dispersed form in the plating solution; and preferably, the light inert gas comprises: hydrogen, helium, methane or neon, or mixtures thereof. Possibly,

the fundamental function of the light inert gas is two-fold; firstly, the plating bath becomes completely saturated therewith and, secondly, the interfacial tension between the gas and the plating solution is reduced. In any case, the effect is very dramatic in that smooth and bright nickel deposits are obtained, and the tendency toward pitting in the relatively thick deposits is greatly minimized, or eliminated altogether.

Offhand, one might anticipate that a great variety of light inert gases might be employed for the present purpose, but extensive experimentation has proved the facts to be to the contrary. More specifically, hydrogen and helium effect a remarkable increase in brightness and smoothness of the nickel deposits, along with the elimination of pitting in the relatively thick nickel deposits (hydrogen, the lighter in weight, being more effective); and methane and neon (being heavier) effect a lesser, but nevertheless substantial, increase in brightness and smoothness of the nickel deposits, without any noticeable tendency toward the elimination of pitting in the relatively thick deposits; whereas heavier gases, like nitrogen, argon and carbon dioxide, exhibit no substantial beneficial effects with regard to improving the character of the nickel deposits in either of the particulars noted, although with nitrogen, having a molecular weight of 28.02, there is a slightly discernible improvement in brightness and smoothness. Accordingly, while the action of the light inert gas is considered to be mechanical, it must have a molecular weight that is not greater than that of neon, so that it has a very high diffusion rate in the aqueous chemical nickel plating solution and exhibits a low surface tension with respect thereto, in order to achieve the desired beneficial effects explained above. Thus, while the useful group of light inert gases in the present process consists of hydrogen, helium, methane and neon, it will be appreciated that hydrogen and helium are by far the most useful, as these gases achieve both the effect of increasing the brightness and smoothness of the nickel deposits and the effect of substantially decreasing or preventing pitting in the relatively thick deposits.

Another advantage of the process is that the light inert gas sweeping the plating solution seems to act as a collecting agent to remove therefrom dust or other foreign particles, somewhat in the manner of the removal of particles in a conventional froth-flotation separation process. In any case, this process step is most beneficial in the production of nickel deposits upon the catalytic bodies that are smooth, bright and lustrous, along with a considerable reduction in pitting in the relatively thick deposits.

A further advantage in the process resides in the discovery that there is a dramatic improvement in the adhesion of the nickel coatings to the catalytic bodies. As an illustration, it can be readily shown in the laboratory that if a 1/4" x 1" x 6" cold rolled steel bar is given the standard preparation previously described, and then placed directly into a plating bath of the character noted, the pH of which is 5 or greater, the resulting adhesion of the nickel deposit to the steel bar will not be as great as desired, as demonstrated by the subsequent bending of this plated steel bar 180° around a 2" diameter mandrel; whereby some of the nickel coating will separate from the steel base material. Now if a similar piece of cold rolled steel bar is prepared in an identical manner, and then placed directly in an identical plating bath, through which hydrogen gas is being bubbled, the resulting coating will not only be smooth and bright, and substantially free from pits, as previously explained, but subsequently in an identical bending test the adhesion of the nickel deposit to the steel bar will be found to be excellent, there being no separation of the nickel coating from the steel base material incident to the bending of this plated steel bar in the manner noted. Whether

the improved adhesion results from the circumstance that the nickel coating is of smoother and brighter character, or from some other factor, has not been determined, but the adhesion characteristic is vastly improved, and may be otherwise demonstrated in the laboratory in other and conventional impact and scratch tests.

In a series of tests, the following relatively high pH plating baths were employed:

Bath No. 1.—Lactic acid-succinate

Nickel sulfate	m./l.	0.07
Sodium hypophosphite	m./l.	0.23
Succinic acid	m./l.	0.12
Lactic acid	m./l.	0.21
pH		5.5
Adjusted with NaOH and/or H ₂ SO ₄ .		

Bath No. 2.—Malic acid-glycine

Nickel sulfate	m./l.	0.07
Sodium hypophosphite	m./l.	0.23
Malic acid	m./l.	0.135
Glycine	m./l.	0.07
pH		6.3
Adjusted with NaOH and/or H ₂ SO ₄ .		

Bath No. 3.—Glycine

Nickel sulfate	m./l.	0.07
Sodium hypophosphite	m./l.	0.23
Glycine	m./l.	0.21
pH		6.3
Adjusted with NaOH and/or H ₂ SO ₄ .		

In another series of tests, the following relatively low pH plating baths were employed:

Bath No. 4.—Succinate

Nickel sulfate	m./l.	0.09
Sodium hypophosphite	m./l.	0.23
Sodium succinate	m./l.	0.06
pH		4.6
Adjusted with NaOH and/or H ₂ SO ₄ .		

Bath No. 5.—Lactic acid-succinate

Nickel sulfate	m./l.	0.09
Sodium hypophosphite	m./l.	0.23
Lactic acid	m./l.	0.30
Sodium succinate	m./l.	0.12
pH		4.7
Adjusted with NaOH and/or H ₂ SO ₄ .		

Bath No. 6.—Malic acid-lactic acid-succinic acid

Nickel sulfate	m./l.	0.07
Sodium hypophosphite	m./l.	0.23
Malic acid	m./l.	0.06
Lactic acid	m./l.	0.21
Succinic acid	m./l.	0.02
pH		4.5
Adjusted with NaOH and/or H ₂ SO ₄ .		

In comparative tests involving each of the Baths No. 1 to No. 6, inclusive, it was verified that the nickel deposits produced upon properly prepared steel objects were improved to a remarkable degree with respect to brightness and smoothness when the light inert gas was diffused through the plating solution in the plating chamber during the plating reaction; these tests involving each of the light inert gases: hydrogen, helium, neon and methane; and also in these comparative tests, it was verified that the utilization of the light inert gases: hydrogen and helium, considerably reduced, or eliminated altogether, pitting in the relatively thick deposits.

Another peculiarity was discovered in carrying out these comparative tests in conjunction with the utilization of tellurium as a stabilizing additive in the aqueous chemical nickel plating bath, in accordance with the

process disclosed in the copending application Paul Talmei and Gregoire Gutzeit, Serial No. 359,428, filed June 3, 1953, now Patent No. 2,762,723, granted on September 11, 1956. More particularly in the Talmei and Gutzeit application mentioned, there is disclosed a process of chemical nickel plating that involves an aqueous chemical nickel plating bath of the general character described, and further including as a stabilizing and brightening additive tellurium, either in the form Te^{+++} or in the form TeO_3^{--} , the tellurium being present in the plating bath in about 0.1 to 10.0 parts per million by weight. Specifically, it was discovered that the nickel deposits containing the tellurium additive possessed very high adhesion to the base metal objects when the platings were produced in the manner described above (utilizing hydrogen as the light inert gas) in conjunction with the low pH plating Baths Nos. 4, 5 and 6; whereas, on the other hand, the nickel deposits containing the tellurium additive possessed only moderate adhesion to the base metal objects when the platings were produced in the manner described above (utilizing hydrogen as the light inert gas) in conjunction with the high pH plating Baths Nos. 1 to 3, inclusive. Accordingly, the present process renders entirely feasible the utilization in the low pH plating Baths Nos. 4 to 6, inclusive, of tellurium, as a stabilizing and brightening agent; and moreover, in these cases, it appears that the utilization of hydrogen as the light inert gas seems to enhance stability with reference to the inhibiting of the spontaneous formation of black precipitate in the plating bath, the problem of inhibiting the spontaneous formation of black precipitate in the plating bath being discussed in greater detail in the Talmei and Gutzeit application mentioned.

The present process may be carried out in an exceedingly simple manner as the amount of the light inert gas that is required is not critical, as only gentle bubbling thereof through the plating bath, without turbulence, is required; and as a practical matter it has been discovered that for each liter of plating solution in the plating chamber the rate of flow of the light inert gas therethrough may be conveniently established at a value corresponding to the rate of flow within the approximate range 20 to 60 ml./min. under standard temperature and pressure conditions (0°C . and 760 mm. Hg). In any case, the diffusion of the light inert gas through the plating bath is at a very low rate and the streams of rising bubbles therein comprise a great number of small individual bubbles.

In view of the foregoing, it is apparent that there has been provided an improved chemical nickel plating process that is highly suitable for use on a commercial scale, since it involves only simple manipulative steps, and is positively productive of smooth and bright nickel coatings, along with a great reduction of pitting in the relatively thick coatings.

While there has been described what is at present considered to be the preferred embodiment of the invention, it will be understood that various modifications may be made therein, and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. The process of chemically plating with nickel a solid body of catalytic material, which comprises providing a hot aqueous chemical nickel plating bath of the nickel cation-hypophosphite anion type, injecting a light gas from an external source into said hot plating bath in order to maintain a substantial dispersion of said light gas in said hot plating bath, said light gas being chemically inert with respect to said hot plating bath and having a molecular weight that is not greater than that of neon so that it has a high diffusion rate in said hot plating bath and a low surface tension with respect thereto, and contacting said body with said hot plating bath having said substantial dispersion of said light inert gas therein,

whereby a bright smooth nickel plating is deposited upon the surface of said body.

2. The process of chemically plating with nickel a solid body of catalytic material, which comprises providing a hot aqueous chemical nickel plating bath of the nickel cation-hypophosphite anion type, injecting a light gas from an external source into said hot plating bath in order to maintain a substantial dispersion of said light gas in said hot plating bath, said light gas being chemically inert with respect to said hot plating bath and having a molecular weight that is not greater than that of neon so that it has a high diffusion rate in said hot plating bath and a low surface tension with respect thereto, and immersing said body in said hot plating bath having said substantial dispersion of said light inert gas therein, whereby the surface of said body is wetted by said hot plating bath and is swept by bubbles of said light inert gas dispersed in said hot plating bath so that a bright smooth nickel plating is deposited upon the surface of said body.

3. The process of chemically plating with nickel a solid body of catalytic material, which comprises providing a hot aqueous chemical nickel plating bath of the nickel cation-hypophosphite anion type, injecting a light gas from an external source into said hot plating bath in order to maintain a substantial dispersion of said light gas in said hot plating bath, said light gas being chemically inert with respect to said hot plating bath and having a molecular weight that is not greater than that of neon so that it has a high diffusion rate in said hot plating bath and a low surface tension with respect thereto, circulating said hot plating bath having said substantial dispersion of said light inert gas therein through a plating chamber by introducing the same into the lower portion of said plating chamber and by withdrawing the same from the upper portion of said plating chamber, and arranging said body in said plating chamber so that it is immersed in said hot plating bath having said substantial dispersion of said light inert gas therein, whereby the surface of said body is wetted by a rising current of said hot plating bath and is swept by a rising stream of bubbles of said light inert gas dispersed in said rising current of said hot plating bath so that a bright smooth nickel plating is deposited upon the surface of said body.

4. The process of chemically plating with nickel a solid body of catalytic material, which comprises providing a hot aqueous chemical nickel plating bath of the nickel cation-hypophosphite anion type, circulating said hot plating bath upwardly through a plating chamber by introducing the same into the lower portion of said plating chamber and by withdrawing the same from the upper portion of said plating chamber, injecting a light gas from an external source into the lower portion of said plating chamber and into said hot plating bath in order to maintain a rising stream of bubbles of said light gas in a rising current of said hot plating bath in said plating chamber, said light gas being chemically inert with respect to said hot plating bath and having a molecular weight that is not greater than that of neon so that it has a high diffusion rate in said hot plating bath and a low surface tension with respect thereto, and arranging said body in said plating chamber so that it is immersed in said rising current of said hot plating bath having said rising stream of bubbles of said light inert gas therein, whereby a bright smooth nickel plating is deposited upon the surface of said body.

5. The process set forth in claim 1, wherein said light inert gas is selected from the class consisting of hydrogen, helium, methane and neon.

6. The process set forth in claim 1, wherein said light inert gas is selected from the class consisting of hydrogen and helium.

7. The process set forth in claim 1, wherein said light inert gas consists essentially of hydrogen.

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8. The process set forth in claim 1, wherein said light inert gas consists essentially of helium.

9. The process of chemically plating with nickel a solid body of catalytic material, which comprises providing a hot aqueous chemical nickel plating bath of the nickel cation-hypophosphite anion type, circulating a current of said hot plating bath through a plating chamber, producing a thorough mixing and a substantial dispersion of a light gas in said current of said hot plating bath circulated through said plating chamber by injecting said light gas thereinto from an external source, said light gas being chemically inert with respect to said hot plating bath and having a molecular weight that is not greater than that of neon so that it has a high diffusion rate in said hot plating bath and a low surface tension with respect thereto, and placing said body in said plating chamber so that it is immersed in said current of said hot plating bath having said substantial dispersion of said light inert gas therein, whereby the surface of said body is wetted by said current of said hot plating bath and is swept by bubbles of said light inert gas dispersed in said current of said hot plating bath so that a bright smooth nickel plating is deposited upon the surface of said body.

10. The process set forth in claim 9, wherein said light inert gas is injected into said current of said hot plating

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bath circulated through said plating chamber at a rate in the approximate range 20 to 60 unit volumes thereof per minute per liter of said hot plating bath contained in said plating chamber, wherein a unit volume of said light inert gas comprises 0.001 liter thereof at a standard temperature of 0° C. and a standard pressure of 760 mm. Hg.

11. The process of chemically plating with nickel a steel body, which comprises providing a hot aqueous chemical nickel plating bath of the nickel cation-hypophosphite anion type, injecting hydrogen gas from an external source into said hot plating bath in order to maintain a substantial dispersion of said hydrogen gas in said hot plating bath, and contacting said steel body with said hot plating bath having said substantial dispersion of said hydrogen gas therein, whereby a bright smooth nickel plating is deposited upon the surface of said steel body.

References Cited in the file of this patent

UNITED STATES PATENTS

2,658,839	Talmey	Nov. 10, 1953
2,658,841	Gutzeit	Nov. 10, 1953
2,758,075	Swalheim	Aug. 7, 1956

FOREIGN PATENTS

370,626	Great Britain	Apr. 14, 1932
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