



- (51) **International Patent Classification:**  
C23C 18/16 (2006.01) C23C 18/36 (2006.01)
- (21) **International Application Number:**  
PCT/US2016/042271
- (22) **International Filing Date:**  
14 July 2016 (14.07.2016)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**  
62/193,728 17 July 2015 (17.07.2015) US
- (71) **Applicant:** COVENTYA, INC. [US/US]; 4639 Van Epps Rd, Brooklyn Heights, Ohio 44131 (US).
- (72) **Inventors:** RUFFINI, Alan J; 4639 Van Epps Rd, Brooklyn Heights, Ohio 44131 (US). WOJCIK, Matthew J; 4639 Van Epps Rd, Brooklyn Heights, Ohio 44131 (US). LAPLANTE, Jean; 4639 Van Epps Rd, Brooklyn Heights, Ohio 44131 (US). MISTY, Nilesh; 4639 Van Epps Rd, Brooklyn Heights, Ohio 44131 (US).
- (74) **Agent:** SUTKUS, Richard A.; 1300 E. 9th Street, Suite 1700, Cleveland, Ohio 44114 (US).

(81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report (Art. 21(3))

(54) **Title:** ELECTROLESS NICKEL-PHOSPHOROUS PLATING BATHS WITH REDUCED ION CONCENTRATION AND METHODS OF USE

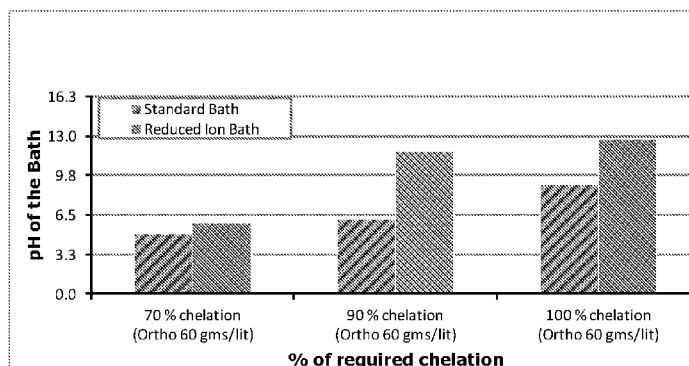


Fig. 1

(57) **Abstract:** An aqueous electroless nickel-phosphorous plating bath for forming an electroless nickel-phosphorous coating on an alkaline zincate coated substrate includes about 1.0 g/l to less than 5.0 g/l Ni, about 25 g/l to about 40 g/l hypophosphorous reducing agent; and 0 to about 120 g/l orthophosphite by-product. The electroless nickel-phosphorous bath with an orthophosphite concentration of up to about 120 g/l provides an electroless nickel-phosphorous deposit on the zincate coated substrate with an intrinsic stress that is more compressive than electroless nickel-phosphorous deposit provided using conventional electroless nickel-phosphorous baths.

**ELECTROLESS NICKEL-PHOSPHOROUS PLATING BATHS WITH REDUCED  
ION CONCENTRATION AND METHODS OF USE**

**RELATED APPLICATION**

[0001] This application claims priority from U.S. Provisional Application No. 62/193,728, filed July 17, 2015, the subject matter of which is incorporated herein by reference in its entirety.

**TECHNICAL FIELD**

[0002] This application relates to electroless nickel-phosphorous plating baths with reduced ion concentrations and methods for forming electroless nickel-phosphorous coatings on work pieces, such as alkaline zincate coated rigid data storage disks, using the baths.

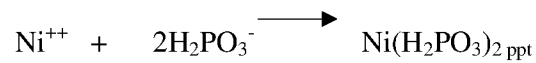
**BACKGROUND**

[0003] Electroless Nickel (EN) plating baths or plating solution, designed to provide high phosphorous deposits, are used to produce non-magnetic sublayers for rigid memory disks. The deposit should provide a uniform, hard and polishable plated surface to protect an aluminum substrate. Since the deposit serves as a base layer for a sputtered media film, it is desirable that it is free of asperities and microdefects, such as pits and nodules. Furthermore, there is a demand to increase the storage density of a data storage disk, which requires the EN deposit to be more corrosion resistant against corrosive polishing slurries and subsequent acid washing.

[0004] The reaction to deposit nickel and phosphorous is autocatalytic and requires the reduction of both nickel and phosphorous and the oxidation of hypophosphite (hypo). The formation of by-products, specifically orthophosphite (ortho), during the plating process prevents the EN plating bath from being used for prolonged periods of time because higher concentrations of ortho are responsible for the deterioration of deposit properties, specifically corrosion resistance and deposit stress. In fact, there have been attempts to control orthophosphite formation from aging EN plating solutions using precipitation methods. In practice the useful life of an EN plating process is described in terms of Metal Turnovers (MTO's), where one MTO is equivalent to the replenishment of the initial nickel concentration. In a typical EN plating bath containing 6.0 g/l Ni, for each MTO achieved, approximately 30 grams per liter of orthophosphite are generated, or for each gram of nickel deposited 5 grams of orthophosphite are formed. Consequently, the EN plating solution becomes highly concentrated with orthophosphite anions. This can become a problem if free nickel

-2-

ions are available as they can combine with the ortho anion to form an insoluble precipitate as shown below.



**[0005]** For the above precipitation (ppt) reaction to occur the concentrations of both Ni and ortho must be high enough to satisfy the solubility product constant (Ksp):

$$K_{\text{sp}} = [\text{Ni}^{++}] \times [\text{H}_2\text{PO}_3^-]^2$$

**[0006]** Furthermore at a given concentration of free Ni and ortho, the precipitation of  $\text{Ni}(\text{H}_2\text{PO}_3)_2$  is greatly affected by the pH of the bath and the chelation system. The chelation system is generally optimized to control the free Ni concentration to prevent the precipitation of  $\text{Ni}(\text{H}_2\text{PO}_3)_2$ , as well as to complex any extraneous metal ions introduced from the external environment, such as Zn, Fe and Al. However, even with the most efficient chelation system, precipitation can occur as the ortho concentration and pH of the working bath increase. For example, at an ortho concentration of 100 grams per liter, the onset of precipitation can occur at a pH around 5.0 at optimum chelation. Optimum chelation can be the amount of chelation required to complex 100% of the Ni ion.

**[0007]** In order to prepare an aluminum memory disk for EN plating, the pretreatment cycle requires the application of a dilute alloy zincate, which affords an immersion deposit of Zn and Fe and provides a barrier coating to prevent the aluminum substrate from oxidation. The process insures adequate adhesion of the EN film to the substrate. This is a well accepted practice for pretreating aluminum for hard disk applications and, in general, for plating electroless nickel on aluminum. The zincate solution is typically highly alkaline, with a pH greater than 14.

**[0008]** The highly alkaline zincate solution provides a zincate plated surface on the aluminum disk that has a high localized pH. Interaction of the EN plating bath with the highly alkaline zincate plated surface of the disk can result in *in situ* formation of colloids and submicron particles at the interface or diffusion zone of the bath and zincate surface. These colloids and submicron particles can potentially be adsorbed on the plating surface and disrupt uniform EN film growth. This can result in defects, such as micropits and nodules on the plated surface as well as increased deposit porosity of the EN plated film, which can decrease corrosion resistance of the EN plated film.

-3-

[0009] Additionally, during the plating operation, disks are arranged on plating mandrels that are closely spaced with average spacing between 6-10mm. The number of disks per load varies, but can range from 0.5-0.9 sq. ft. per gallon of operating EN plating bath. This close spacing and high loading not only restricts diffusion of reactants to and from the plating surface, but can also restrict the movement of EN plating solution. As a result, *in situ* particles generated at the interface between the substrate and EN plating solution are restricted from moving away from the plating surface, increasing the tendency of the particles/colloids to adsorb and negatively affect the plating film growth. While various additives, such as surfactants, can be used to improve this dynamic effect by helping to prevent the adsorption of particulates, the use of these additives can also have a deleterious impact on the plated film.

[0010] Once EN plating starts, orthophosphite anion is generated, and, as the plating progresses, this anion concentration increases. Typical orthophosphite levels obtained for hard disk platers can range from 30 grams per liter up to 100 grams per liter.

[0011] Data storage EN plating bath solutions can be controlled by a steady state “bleed and feed” mechanism to keep the concentration of ortho and other by-products at a constant level. This helps to keep the both the deposit properties and plating rate predictable as they change with the accumulation of by-products. This, however, does not resolve the issue of nickel orthophosphite insolubility and furthermore does not preclude the adsorption of *in situ* generated particles on the plating surface. Moreover, reduction of the bleed and feed orthophosphite or by-product set point of the bath can increase the cost of operation of the bath.

[0012] Defects from increasing orthophosphite concentration in the presence of free nickel ion include higher intrinsic stress in the plated EN film and an increase in deposit porosity, which can lead to poor corrosion resistance of the EN film in strongly acidic media. This is a condition that is highly unfavorable for advanced media production and further exaggerated by increasing pH, which is used to improve the speed of deposition.

### **SUMMARY**

[0013] Embodiments described herein relate to an improved electroless nickel-phosphorous plating bath with a reduced ion concentration that deposits an alloy of nickel-phosphorous (NiP) with improved corrosion resistance in acidic media and improved deposit

-4-

stress. Advantageously, the electroless nickel-phosphorous bath with reduced ion concentration can provide a uniform electroless nickel-phosphorous deposit on highly alkaline zincate coated substrates without the use of additives, which can produce plating defects.

**[0014]** The electroless nickel-phosphorous plating bath with a reduced ion concentration operates at a reduced specific gravity, providing the additional benefit of prevention of the co-deposition of inert particles into the deposit that can cause plating defects. The electroless nickel-phosphorous plating bath can better tolerate the by-product formation of orthophosphite while improving the critical deposit properties, such as smoother surface morphology and reduction of microdefects, during electroless nickel plating of alkaline zincate coated substrates, which are used for high storage density applications.

**[0015]** In some embodiments, the aqueous electroless nickel-phosphorous plating bath for forming an electroless nickel-phosphorous coating on an alkaline zincate coated substrate, such as zincate coated aluminum disk for data storage, can include about 1.0 g/l to less than 5.0 g/l Ni, about 25 g/l to about 40 g/l hypophosphorous reducing agent, and 0 to about 120 g/l orthophosphite by-products. The concentration of Ni in the bath relative to the concentration of orthophosphite is such that  $\text{Ni}(\text{H}_2\text{PO}_3)_2$  precipitation is inhibited during plating of the alkaline zincate coated substrate at orthophosphite by-product concentrations up to 120 g/l and bath pH of about 4.4 to about 4.8, which results in smoother surface morphology, reduction of microdefects, and enhanced corrosion resistance of the electroless nickel-phosphorous coating. The electroless nickel-phosphorous bath at orthophosphite concentrations of up to about 120 g/l can provide an electroless nickel-phosphorous deposit on the alkaline zincate coated substrate with an intrinsic stress that is more compressive than an electroless nickel-phosphorous deposit provided using similar electroless nickel-phosphorous baths containing greater than 5.0 g/l Ni.

**[0016]** In some embodiments, the bath can include at least one organic acid complexing agent. The amount of organic acid complexing agent provided in the bath can be substantially less than the amount of organic acid complexing agent employed in the similar electroless nickel-phosphorous baths containing greater than 5.0 g/l Ni. For example, the bath can include about 20 g/l to about 30 g/l of the at least one organic acid complexing agent compared to greater than about 40 g/l to about 60 g/l of organic acid complexing agent employed in similar electroless nickel-phosphorous baths containing greater than 5.0 g/l Ni. The organic

-5-

acid complexing agent can include, for example, at least one of malic acid, lactic acid, or succinic acid.

[0017] In some embodiments, the bath can consist essentially of water, about 2.0 g/l to about 4 g/l of Ni, about 25 g/l to about 40 g/l hypophosphorous reducing agent, 0 to about 120 g/l orthophosphite by-product, less than about 25 g/l of a combination of organic acid complexing agents selected from the group consisting of malic acid, lactic acid, and succinic acid, about 0.0004 to about 0.0007 g/l stabilizer, and at least one pH adjuster in an amount effective to provide the bath with a pH between about 4.4 and 4.8.

[0018] Other embodiments described herein relate to a method of forming an electroless nickel-phosphorous coating on an alkaline zincate coated substrate, such as a zincate coated aluminum disk for data storage. The method can include providing an alkaline zincate coated aluminum substrate. The alkaline zincate coated aluminum substrate can be provided by plating an aluminum substrate with an alkaline zincate solution. A surface of the zincate coated substrate is then contacted with an aqueous electroless nickel-phosphorous plating bath. The bath includes about 1.0 g/L to less than 5.0 g/l Ni, about 25 g/l to about 40 g/l hypophosphorous reducing agent, and 0 to about 120 g/l orthophosphite by-product.

The concentration of Ni in the bath relative to the concentration of orthophosphite is such that  $\text{Ni}(\text{H}_2\text{PO}_3)_2$  precipitation is inhibited during plating of the zincate coated substrate at orthophosphite by-product concentrations up to 120 g/l and bath pH of about 4.4 to about 4.8. The electroless nickel-phosphorous bath at an orthophosphite concentration of up to about 120 g/l can provide an electroless nickel-phosphorous deposit on the zincate coated substrate with an intrinsic stress that is more compressive than electroless nickel-phosphorous deposit provided using similar electroless-nickel-phosphorous baths containing greater than 5.0 g/l Ni.

### **BRIEF DESCRIPTION OF DRAWINGS**

[0019] Fig. 1 illustrates a graph showing maximum pH tolerance at 190°F for 70%, 90%, and 100% chelation of standard EN baths and reduced ion EN baths described herein.

[0020] Fig. 2 illustrates a graph showing pH of a reduced ion bath at which precipitate occurs with NaOH addition in the absence of chelation.

-6-

[0021] Fig. 3 illustrates a graph showing deposit weight loss/corrosion rate after exposure to 50% v/v nitric acid for 25 minutes with electroless nickel-phosphorous deposits formed using standard EN baths and reduced ion EN baths described herein.

[0022] Fig. 4 illustrates intrinsic stress profiles of electroless nickel-phosphorous deposits formed using standard EN baths and reduced ion EN baths described herein.

[0023] Fig. 5 illustrates a graph showing effect of increased pH on intrinsic stress profiles of electroless nickel-phosphorous deposits formed using standard EN baths and reduced ion EN baths described herein.

[0024] Fig. 6 illustrates a graph showing boiling stability of standard EN baths and reduced ion EN baths described herein.

[0025] Fig. 7 illustrates a graph showing specific gravity of standard EN baths and reduced ion EN baths described herein.

[0026] Fig. 8 illustrates a plot showing the Ra of electroless nickel-phosphorous deposits formed using standard EN baths and reduced ion EN baths described herein.

[0027] Fig. 9 illustrates a plot showing the Rp of electroless nickel-phosphorous deposits formed using standard EN baths and reduced ion EN baths described herein.

### **DETAILED DESCRIPTION**

[0028] In the specification and the claims, which follow, reference will be made to a number of terms, which shall be defined to have the following meanings.

[0029] The singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise.

[0030] "Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where the event occurs and instances where it does not.

[0031] Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as "about", is not to be limited to the precise value specified. In some instances, the approximating language may correspond to the precision of an instrument for measuring the value.

-7-

**[0032]** Embodiments described herein relate to an improved electroless nickel-phosphorous plating bath with a reduced ion concentration that deposits an alloy of nickel-phosphorous (NiP) with improved corrosion resistance in acidic media and improved deposit stress. Advantageously, the electroless nickel-phosphorous plating bath with reduced ion concentration can provide a uniform electroless nickel-phosphorous deposit on highly alkaline zincate coated substrates without the use of additives, which can produce plating defects.

**[0033]** The electroless nickel-phosphorous plating bath with a reduced ion concentration operates at a reduced specific gravity, providing the additional benefit of prevention of the co-deposition of inert particles into the deposit that can cause plating defects. The electroless nickel-phosphorous plating bath can better tolerate the by-product formation of orthophosphite while improving the critical deposit properties, such as smoother surface morphology and reduction of microdefects, during electroless nickel plating of alkaline zincate coated substrates, which are used for high storage density applications.

**[0034]** The electroless nickel-phosphorous plating bath formulations described herein can have a reduced ionic strength and, specifically, a reduced concentration of Ni ions compared to standard electroless nickel baths. In some embodiments, the electroless nickel-phosphorous plating bath can have a reduction in the concentration of Ni ions to levels ranging from about 1.0 to less than about 5.0 grams per liter, for example, about 2.0 g/l to about 4.0 g/l Ni, and, specifically, about 3 g/l Ni. The concentration of Ni in the bath relative to the concentration of orthophosphite is such that  $\text{Ni}(\text{H}_2\text{PO}_3)_2$  precipitation is inhibited during plating of the alkaline zincate coated substrate at orthophosphite by-product concentrations up to 120 g/l and bath pH of about 4.4 to about 4.8. Providing the Ni ions at reduced levels allows the electroless nickel-phosphorous plating bath to employ significantly less complexing agents compared to standard baths having Ni concentrations greater than 5.0 g/l (*e.g.*, about 6 g/l or more) and operate with an orthophosphite concentration of up to about 120 g/l to provide an electroless nickel-phosphorous deposit on the alkaline zincate coated substrate with an intrinsic stress that is more compressive than electroless nickel-phosphorous deposit provided using standard baths having Ni concentrations greater than 5.0 g/l. This allows the electroless nickel-phosphorous bath to be effectively used for a higher MTO set point as defined by the orthophosphite concentration, which can provide substantial cost savings for waste treatment. Moreover, electroless nickel-phosphorous deposit formed from electroless nickel baths that include 1.0 g/l to less than about 5.0 g/l Ni, for example, about 2.0 g/l to



about 4.0 g/l Ni, or about 3 g/l Ni, showed improved corrosion resistance in acidic media and have a smoother surface morphology and reduction of microdefects compared electroless nickel-phosphorous deposits formed using standard baths having Ni concentrations greater than 5.0 g/l.

**[0035]** In some embodiments, the electroless nickel-phosphorous plating bath used to form the electroless nickel-phosphorous coating includes Ni, a hypophosphorous reducing agent, orthophosphite by-product and optionally at least one of a complexing agent, chelating agent, stabilizer, and/or pH buffer.

**[0036]** The nickel can be provided in the bath in the form of a water soluble nickel salt. The water-soluble nickel salts can include those, which are soluble in the plating bath and which can yield an aqueous solution of a predetermined concentration. The nickel salt can be selected from the group consisting of nickel sulfate, nickel chloride, nickel bromide, nickel iodide, nickel acetate, nickel malate, a nickel hypophosphite and combinations thereof. The water-soluble nickel salts may be used alone or as a mixture.

**[0037]** The hypophosphorous reducing agent used in the bath can include any of a variety of hypophosphorous reducing agents used in known types of the electroless nickel plating baths. In some embodiments, the hypophosphorous reducing agent is selected from the group consisting of sodium hypophosphite, potassium hypophosphite, ammonium hypophosphite, and combinations thereof.

**[0038]** The concentration of the hypophosphorous reducing agent in the electroless nickel plating can differ with the respective types of hypophosphorous reducing agent and can be adjusted to vary the concentration of the phosphorous in the electroless nickel-phosphorous coating that is formed using the bath. In some embodiments, the concentration of the hypophosphorous reducing agent in the electroless nickel-phosphorous plating bath can be about 25 g/L to about 40 g/L, for example, about 30 g/l to about 35 g/l. In other embodiments, the concentration of the hypophosphorous reducing agent in the electroless nickel-phosphorous plating bath can be about 30 g/L.

**[0039]** In some embodiments, a complexing agent or a mixture of complexing agents may be included in the electroless nickel-phosphorous plating bath. Complexing agents as used herein can also include chelating agents. The complexing agents and/or chelating agents generally retard the precipitation of nickel ions from the plating solution as insoluble salts,

such as phosphites, by forming a more stable nickel complex with the nickel ions and provide for a moderate rate of the reaction of nickel precipitation.

**[0040]** The complexing agents and/or chelating agents can be included in the plating bath in amounts sufficient to complex the nickel ions present in the bath and to further solubilize the hypophosphite degradation products formed during the plating process. Advantageously, the amount of complexing agent is substantially less than the amount of complexing agent employed in the similar electroless nickel-phosphorous baths containing greater than 5.0 g/l nickel ions. In some embodiments, the complexing agents and/or chelating agents are provided in the electroless nickel-phosphorous plating bath at amounts from 20 g/l to about 30 g/l.

**[0041]** A variety of complexing agents, used in known electroless nickel plating solutions, may be used. Specific examples of the complexing agents may include monocarboxylic acids, such as glycolic acid, lactic acid, gluconic acid or propionic acid, dicarboxylic acids, such as malic acid, malonic acid, succinic acid, tartaric acid, oxalic acid or adipic acid, aminocarboxylic acids, such as glycine or alanine, ethylene diamine derivatives, such as ethylenediamine tetraacetate, versenol (N-hydroxyethyl ethylenediamine-N,N',N'-triacetic acid) or quadrol (N,N,N', N'-tetrahydroxyethyl ethylene diamine), phosphonic acids, such as 1-hydroxyethane-1,1-diphosphonic acid, ethylene diamine tetramethylene phosphonic acid and water-soluble salts thereof. The complexing agents may be used either alone or in combination.

**[0042]** Some complexing agents, such as acetic acid or succinic, for example, may also act as a pH buffering agent, and the appropriate concentration of such additive components can be optimized for any plating bath after consideration of their dual functionality.

**[0043]** In some embodiments, at least one pH buffer, complexing agent, or chelating agent can be selected from the group consisting of an acetic acid, formic acid, succinic acid, malonic acid, an ammonium salt, lactic acid, malic acid, citric acid, glycine, alanine, glycolic acid, lysine, aspartic acid, ethylene diamine tetraacetic acid (EDTA), and combinations thereof. In some embodiments, mixtures of 2 or more of the above pH buffers, complexing agents, and/or chelating agents can be used in the electroless nickel plating bath described herein.

**[0044]** In some embodiments, the electroless nickel-phosphorous plating bath can include about 20 g/l to about 30 g/l of a combination of organic acid complexing agents select-

ed from the group consisting of malic acid, lactic acid, and succinic acid. In other embodiments, the electroless nickel-phosphorous plating bath can include less than about 25 g/l of a combination of organic acid complexing agents selected from the group consisting of malic acid, lactic acid, and succinic acid.

**[0045]** The plating bath may also contain, in addition to the above components, additives with various kinds of purposes so long as the properties of the plating bath are not deteriorated. For example, the bath can include a stabilizer, such as lead acetate, at a concentration of about 0.0004 g/l to about 0.0007 g/l. Other stabilizers can also be used besides or in addition to lead acetate including those metal cations that act as catalytic poisons, such as Pb, Bi, Sn, In, salts or compounds thereof and combinations thereof.

**[0046]** In other embodiments, the electroless nickel-phosphorous plating bath can be free of or substantially free of additives, such as surfactants, which can have a negative effect on the corrosion resistance and surface morphology of the electroless nickel-phosphorous deposit. Surfactants including organic compounds from the class of fatty acids and water soluble salts thereof, amino compounds, and sulfates and sulfonates of fatty acids and fatty alcohols are typically employed in electroless nickel plating baths to modify the inherent properties of the plating bath itself or the quality of the nickel deposit. These additives, however, can potentially form colloids with other components of the bath, such as free Ni, Zn, Fe, and Al, ions, that can produce plating defects. Advantageously, the plating bath described herein can be free of or substantially free of such additives to minimize defects, such as micropitting and particle deposition, in the electroless nickel-phosphorous deposit.

**[0047]** The aqueous electroless nickel-phosphorous plating baths can be operated or maintained at a pH of about 4.4 to about 4.8 during electroless nickel-phosphorous plating of an alkaline zincate coated substrate. With this range of pH, the reducing reaction by the hypophosphorous reducing agent is allowed to occur efficiently to prevent decomposition of the hypophosphorous reducing agent as well as to prevent precipitation of nickel orthophosphite and the plating bath from decomposing. Moreover, with this range of pH, it is possible to prevent the plating bath from being lowered in stability as a result of the excessively high reducing potential of the reducing agent.

**[0048]** At least one pH adjustment agent can be used to adjust the pH to the above range. When the pH of the bath is too high, it can be adjusted by adding, for example, an ac-

id. When the pH of the bath is too low, it can be adjusted by adding, for example, ammonium hydroxide.

[0049] The stability of the operating pH of the plating bath can be controlled by the addition of various buffer compounds such as acetic acid, propionic acid, boric acid, or the like, in amounts up to about 30 g/l with amounts of from about 2 g/l to about 30 g/l being typical. As noted above, some of the buffering compounds such as acetic acid and succinic acid may also function as complexing agents.

[0050] In accordance with the methods described herein, a substrate can be plated with the electroless nickel-phosphorous plating bath to provide an electroless nickel-phosphorous deposit or coating on the substrate. In some embodiments, the substrate can be an aluminum substrate on which a zincate coating has been deposited using a highly alkaline zincate plating process. In some embodiments, the aluminum substrate can be an aluminum or aluminum alloy disc used for data storage applications, such as an aluminum hard disk for use in hard drive media. The alkaline zincate plating process can employ an alkaline zinc bath or solution having a high pH (*e.g.*, greater than pH 14).

[0051] The alkaline zincate coated aluminum substrate can be plated using the electroless nickel-phosphorous plating bath by contacting the substrate with or immersing the substrate in the plating bath for a duration time effective to form an electroless nickel-phosphorous coating or deposit on the zincate coated surface of the substrate. The zincate coated surface on the aluminum disk has a high localized pH than can potentially induce *in situ* formation of colloids and submicron particles at the interface or diffusion zone of the bath and zincate surface. Such colloids and submicron particles can disrupt uniform electroless nickel-phosphorous film growth and corrosion resistance of the nickel-phosphorous film. Advantageously, the reduced ion concentration of the electroless nickel-phosphorous plating bath is such that the bath has a reduced specific gravity and during plating of the alkaline zincate coated substrate  $\text{Ni}(\text{H}_2\text{PO}_3)_2$  precipitation is inhibited, thereby preventing co-deposition of inert particles into the electroless nickel-phosphorous deposit, enhancing uniform electroless nickel-phosphorous film growth, reducing microdefects in the electroless nickel-phosphorous film, and improving corrosion resistance of the electroless nickel-phosphorous film.

[0052] In some embodiment, the substrate can be cleaned or pre-processed prior to plating. During plating, the bath can be maintained at a bath temperature about 175°F to about

-12-

200°F, *e.g.*, about 188°F to about 194°F. The duration of contact of the electroless nickel-phosphorous plating bath with the substrate being plated will determine the thickness of the electroless nickel-phosphorous coating. Typically, a contact time can range from as little as about one minute to several hours or even several days, for example, about 60 to about 120 minutes.

**[0053]** During the deposition of the electroless nickel-phosphorous deposit or coating, mild to severe agitation can be employed. The mild agitation can be, for example, a mild air agitation, mechanical agitation, bath circulation by pumping, rotation of a barrel for barrel plating, rotation of mandrel for disk plating, etc. The electroless nickel-phosphorous plating bath also may be subjected to a periodic or continuous filtration treatment to reduce the level of contaminants therein. Replenishment of the constituents of the bath may also be performed, in some embodiments, on a periodic or continuous basis to maintain the concentration of constituents, and in particular, the concentration of nickel ions and hypophosphite ions, as well as the pH level within the desired limits.

**[0054]** Advantageously, the electroless nickel-phosphorous plating bath can be operated at orthophosphite concentrations of up to about 120 g/l and/or up to 4 MTOs (based on ortho generation per turnover) without a substantial reduction in the electroless nickel-phosphorous deposit properties or in plating bath efficiency. In some embodiments, the MTO of the plating bath can be between 2.0 and 4.5. Maintaining the MTO within these levels allows for an economic plating performance and consistently reproducible plating results.

**[0055]** The electroless nickel-phosphorous coated substrate so formed can be removed from the electroless nickel plating bath and rinsed, for example, with deionized water.

**[0056]** The electroless nickel coating formed on a surface of the substrate using the electroless nickel-phosphorous plating bath can have of relatively uniform thickness and be substantially free of asperities and micro defects, such as pits and nodules. The electroless nickel-phosphorous coating can also have an enhanced corrosion resistance and an intrinsic stress that is more compressive than electroless nickel-phosphorous coating provided using standard baths having Ni concentrations greater than 5.0 g/l.

**[0057]** In one embodiment, the electroless nickel-phosphorous coating can have an average thickness in a range from about 1 micron to about 250 microns. In another embodiment, the electroless nickel-phosphorous coating can have an average thickness in a range from about 1 micron to about 100 microns. The electroless nickel coating can be a high

phosphorous coating having a phosphorous content of about 10 to about 13% phosphorous. Actual thickness of an as plated disk can be about 250 to about 600 micro inches.

**[0058]** The following example illustrates the electroless nickel-phosphorous plating solutions of the invention. Unless otherwise indicated in the following examples, in the written description and in the claims, all parts and percentages are by weight, temperatures are in degrees centigrade and pressure is at or near atmospheric pressure.

Example 1

**[0059]** Reduced electroless nickel-phosphorous plating bath and a standard electroless nickel-phosphorous plating bath were prepared with the following formulations. The baths were operated under similar conditions noted below.

Table 1

	Reduced Ion Grams/Liter	Standard Bath Grams/Liter
Nickel Metal	3 (2-4)	6 (5-7)
Malic Acid	10	20
Lactic Acid	9	18
Succinic acid	4.5	4.5
Ammonium Hydroxide	to adjust pH	to adjust pH
Sodium Hypophosphite	30 (24-40)	30 (24-40)
Lead Acetate	0.00055	0.00055
pH	4.50 -4.55	4.50 -4.55
Temp (F)	188 – 194	188 - 194F
Deposition Rate microinches/min	3.6 – 4.0	3.6 - 4.0

**[0060]** Advantageously, the reduced ion electroless nickel-phosphorous plating bath formulation allowed for a significant reduction in the amount of organic acids needed for complexing to nearly half as compared standard formulations used in the data storage plating industry.

**[0061]** The main advantage of reduced ion formulation is the impact it has on the solubility of Ni orthophosphite.

-14-

$$K_{sp} = [Ni^{++}] \times [H_2PO_3^-]^2$$

**[0062]** Since the Ni concentration operates at approximately half the standard concentration of most commercial processes there is a profoundly positive impact on the concentration range of orthophosphite that is tolerated in the system. This process allows for higher levels of by-product formation while improving the corrosion resistance and intrinsic stress of the deposit. It is postulated that the primary reason for the system improvement is the change to the solubility product constant. The micro precipitation of Ni orthophosphite does not take place until higher by-product concentrations are reached due the equilibrium shift realized by the lower nickel concentration and further by the fact that the formulation can better tolerate the adverse affect of the pH neutralization that occurs during the introduction of the zincated aluminum into the working bath.

**[0063]** Fig. 1 illustrates the affect that chelation has on the impact of orthophosphite precipitation at 190°F. For example at 100% chelation, a titration of a working EN bath containing an orthophosphite concentration of 60 g/L with dilute sodium hydroxide reveals the Reduced Ion formulation can tolerate a pH of close to 13 while the standard formulation can only tolerate a pH of 9.2 before the onset of precipitation.

**[0064]** Fig. 2 further illustrates the tolerance of the Reduced Ion formulation to pH and precipitation and the impact the reduced nickel concentration alone (no chelation) has on the Nickel orthophosphite precipitation over a range of orthophosphite concentrations at room temperature.

**[0065]** As a result of the Reduced Ion's formulation tolerance to Ni orthophosphite formation the deposit corrosion resistance and intrinsic stress are improved significantly. Fig. 3 illustrates the weight loss results after exposure to 50% Nitric acid corrosion exposure at 74°F for 25 minutes. The Reduced Ion deposit, produced from a solution with a pH of 4.54 and 60 gpl orthophosphite afforded a 17% improvement in corrosion rate as compared to the standard process. This was reproducible at higher orthophosphite levels (90gpl) at pH 4.68. It is important to note that the plating rate for both processes was controlled at 3.8-4.3 microinches per minute.

**[0066]** It is well-known that as an electroless Nickel solution ages and by-products, particularly orthophosphite, increase in concentration, the intrinsic stress of the EN film will also increase. Furthermore it is generally accepted that a lower intrinsic stress of an EN deposit

-15-

will improve the fatigue life of the substrate and improve the overall adhesion of the plated film to the substrate. Stresses in the EN film that are tensile are unfavorable and will reduce the fatigue life of the substrate and result in deposits with inferior corrosion resistance. A given formulation with zero to low orthophosphite levels will have an intrinsic stress that is compressive, however as the orthophosphite concentration increases through the normal plating process, the intrinsic stress will become tensile. This fact is also further exaggerated by higher pH values.

**[0067]** Fig. 4 shows the impact that bath age (ortho level), pH, and formulation have on the resulting deposit stress. In all cases the Reduced Ion EN deposit afforded a compressive stress, even under the most severe plating condition of pH / ortho respectively 4.72 / 90 gpl. Increasing the pH to even higher levels at a 90 gpl ortho concentration has even a greater impact on intrinsic stress. Fig. 5 illustrates the improvement at a pH at 4.89.

**[0068]** An unexpected finding was an improvement in the bath stability during operation. Electroless nickel solutions are stabilized with certain additives such as Pb, Bi, and other inhibitors that act as catalytic poisons (such as Sn and In). They are very effective at very low concentrations and generally diffuse non linearly onto or near the plating surface. Concentration ranges from 0.2 ppm up to 2.0 ppm are typical. Even at this range of concentration the deposit performance can be impacted negatively and is a function of the plating process solution dynamics. In the data storage industry, it is favorable to improve the bath stability without the use of additional catalytic poisons, since other key performance factors like micro pitting and surface edge profiles/uniformity are impacted by higher stabilizer levels.

**[0069]** Fig. 6 shows the performance of the reduced ion chemistry against the standard formulation in a boiling stability evaluation. The boiling stability is a standard laboratory test and generally accepted for use to evaluate and predict the ability of an EN formulation to maintain stability under severe plating conditions. Although the time to seed out (nucleation of Nickel particles) was comparable for both the Reduced Ion chemistry (RI) and Standard chemistry the time to complete plate out was greatly improved. It is important to note that once seed out occurs the nucleation sites are present for further decomposition and the tolerance for the RI formulation to decompose is far greater than the standard chemistry. Additionally the improvement in bath stability can improve the overall surface smoothness of the EN deposit under more severe operating conditions such as higher temperatures above 194°F.



-16-

[0070] Another unexpected finding with the development of the Reduced Ion chemistry is the advantage of operating the chemistry with a reduced specific gravity. Fig. 7 illustrates the reduction in specific gravity of the reduced ion chemistry at three orthophosphite levels (30/60/90 g/L) correlating to bath ages of 1.0/2.5/3.8 MTO. Being able to operate at a low specific gravity may have an impact on particle adsorption and the subsequent encapsulation of particles during the plating operation. The particles may be generated in situ in the electroless nickel plating bath or can be introduced from the external environment. During the plating process the substrates are fixed on a rack system designed to continuously move in the plating bath, mainly to keep the solution velocity fast, keeping the diffusion zone free of any particles as disk spacing on the racks is very close making it difficult for those particles to escape before adsorption. During the plating process the disks are mechanically abrading the plastic racks (usually PVDF, PEEK, PP and PTFE) which introduce small plastic particles into the plating bath. It seems logical to add surfactants to the chemical formulation to prevent the adsorption of these particles, however the surfactant introduction itself can have a negative impact on other critical film properties such as corrosion resistance and micro pitting. As the requirement to increase areal density for data storage continues to increase the need for a defect free, EN plated and polished substrate, eliminating defects with sizes of less than 1 micron has been a primary focus of disk manufacturers. These small particles, even after filtration of the solution thru 0.1 micron filters, are present in sufficient quantity in the plating bath causing defects in processing for media. These small particles follow Brownian motion within the fluid boundary layer and in the diffusion zone near the plating surface. It seems logical that particles will be hindered from escaping due to the tight spacing between disks on the rack and will also be influenced by the specific gravity of the solution.

[0071] The settling velocity of a particle is given as follows:

$$\text{Settling Velocity} = \frac{(\text{diameter of particle})^2 \times (\text{particle density} - \text{liquid density})}{\text{viscosity of the liquid}}$$

[0072] Therefore to improve the settling velocity of a particle one can:

- increase the diameter of the particle
- reduce the viscosity of the plating bath or
- reduce the specific gravity between the particle and the plating bath.

**[0073]** The advantage of the reduced ion chemistry is further illustrated in the Table 2 below. The cost to operate and Electroless Nickel bath decreases as you operate at higher MTO's (higher ortho concentrations) so it is desirable to the disk manufacturer to plate at an MTO (ortho concentration) as high as possible without negatively impacting key deposit properties. As the orthophosphite levels required to keep the same specific gravity will vary between the standard chemistry and the reduced ion chemistry. As can be seen in the Table for a given MTO for the standard bath, the corresponding MTO for the Reduced Ion bath to maintain the same specific gravity of the plating solution is significantly higher, giving the disk manufacturer an opportunity to better control costs while improving the quality of the plated EN film.

Table 2 - Bath specific gravity differences

Operating Ortho levels to maintain equivalent specific gravity			
Standard Bath MTO	Reduced Ion Bath MTO	Ortho with Standard bath (gms/lit)	Ortho with Reduced Ion bath (gms/lit)
0	0.66	0	26
0.5	1.25	20	50
1	1.84	30	55
2	3.02	50	75
2.5	3.61	60	87
3	4.20	70	98
3.5	4.79	80	109
3.8	5.14	90	122

**[0074]** Disks produced using the reduced ion formulations have better surface morphology after corrosion testing in acid media than standard formulations. For example, disk substrates (95mm / alloy 5586D) were plated side by side under identical pH and temperature conditions in the respective formulations to 400 micro inches of NiP thickness.

**[0075]** The disks were polished using a Struers Tegramin -30 single sided polisher removing 40 micro inches, then subjected to a Nitric acid solution at 74 degrees for 60 minutes. The disk were measured (using a MicroXam 100 profilometer) before and after corrosion testing for Ra and Rp, indicating the degree of surface roughness and the degree of nodular height respectively. The results shown in Figs. 8 and 9 indicate that the polished surface analysis is statistically the same for both the reduced ion and standard chemistries, however after exposure to nitric acid the deposited NiP film from the reduced ion formulation showed a significant improvement in both Ra and Rp, indicating smoother surface morphology after exposure to strong acid. This test correlates well with the reduction of plated micro defects after polishing and after exposure to acid wash solutions associated with advanced data storage applications.

**[0076]** From the above description of the invention, those skilled in the art will perceive improvements, changes and modifications. Such improvements, changes, and modifications are within the skill of the art and are intended to be covered by the appended claims. All patent publications and references cited in the present application are herein incorporated by reference in their entirety.

-19-

Having described the invention the following is claimed:

1. An aqueous electroless nickel-phosphorous plating bath for forming an electroless nickel-phosphorous coating on an alkaline zincate coated substrate, the plating bath comprising:
  - about 1.0 g/l to less than 5.0 g/l Ni;
  - about 25 g/l to about 40 g/l hypophosphorous reducing agent; and
  - 0 to about 120 g/l orthophosphite by-product;wherein the electroless nickel-phosphorous bath with an orthophosphite concentration of up to about 120 g/l provides an electroless nickel-phosphorous deposit on the zincate coated substrate with an intrinsic stress that is more compressive than electroless nickel-phosphorous deposit provided using similar electroless-nickel-phosphorous baths containing greater than 5.0 g/l Ni.
2. The bath of claim 1, wherein the concentration of Ni in the bath relative to the concentration of orthophosphite is such that  $\text{Ni}(\text{H}_2\text{PO}_3)_2$  precipitation is inhibited during plating of the zincate coated substrate at orthophosphite concentrations up to 120 g/l at a bath pH of about 4.4 to about 4.8.
3. The bath of claim 2, having a pH of about 4.4 to about 4.8.
4. The bath of claim 1, comprising about 20 g/l to about 30 g/l of at least one organic acid complexing agent.
5. The bath of claim 4, wherein the organic acid complexing agent comprises at least one of malic acid, lactic acid, or succinic acid.
6. The bath of claim 4, further comprising at least one of a chelating agent, stabilizer, or pH buffer.
7. The bath of claim 4, being free of a surfactant.

-20-

8. The bath of claim 1, wherein the zincate coated substrate is an aluminum disk for data storage.

9. The bath of claim 1 consisting essentially of water, about 2 g/l to about 4 g/l of Ni, about 25 g/l to about 40 g/l hypophosphorous reducing agent, 0 to about 120 g/l orthophosphite by-product, less than about 25 g/l of a combination of organic acid complexing agents selected from the group consisting of malic acid, lactic acid, and succinic acid, about 0.0004 to about 0.0007 g/l stabilizer, and at least one pH adjuster in an amount effective to provide the bath with a pH between about 4.4 and 4.8.

10. The bath of claim 9, consisting essentially of nickel, malic acid, lactic acid, succinic acid, sodium hypophosphite, lead acetate, and ammonium hydroxide.

11. A method of form an electroless nickel-phosphorous coating on an alkaline zincate coated substrate, the method comprising:  
providing the alkaline zincate coated substrate;  
contacting surfaces of the zincate coated substrate with an aqueous electroless nickel-phosphorous plating bath, the bath including about 1.0 g/L to less than 5 g/l Ni; about 25 g/l to about 40 g/l hypophosphorous reducing agent; and 0 to about 120 g/l orthophosphite by-product; wherein the electroless nickel-phosphorous bath with an orthophosphite concentration of up to about 120 g/l provides an electroless nickel-phosphorous deposit on the zincate coated substrate with an intrinsic stress that is more compressive than electroless nickel-phosphorous deposit provided using similar electroless-nickel-phosphorous baths containing greater than 5 g/l Ni.

12. The method of claim 11, wherein the concentration of Ni in the bath relative to the concentration of orthophosphite is such that  $\text{Ni}(\text{H}_2\text{PO}_3)_2$  precipitation is inhibited during plating of the zincate coated substrate at orthophosphite concentrations up to 120 g/l at a bath pH of about 4.4 to about 4.8.

13. The method of claim 11, the bath is operated up to 4 (or up to orthophosphite levels of approximately 120 g/l) metal turnovers.

-21-

14. The method of claim 11, the bath having a pH of about 4.4 to about 4.8.
15. The method of claim 11, the bath comprising about 20 g/l to about 30 g/l of at least one organic acid complexing agent.
16. The method of claim 15, wherein the organic acid complexing agent comprises at least one of malic acid, lactic acid, or succinic acid.
17. The method of claim 15, the bath further comprising at least one of a chelating agent, stabilizer, or pH buffer.
18. The method of claim 15, the bath being free of a surfactant.
19. The method of claim 11, wherein the zincate coated substrate is an aluminum disk for data storage.
20. The method of claim 11, wherein the bath consists essentially of water, about 2 g/l to about 4 g/l of Ni, about 25 g/l to about 40 g/l hypophosphorous reducing agent, 0 to about 120 g/l orthophosphite by-product, less than about 25 g/l of a combination of organic acid complexing agents selected from the group consisting of malic acid, lactic acid, and succinic acid, about 0.0004 to about 0.0007 g/l stabilizer, and at least one pH adjuster in an amount effective to provide the bath with a pH between about 4.4 and 4.8.
21. A method of forming a disk for data storage, the method comprising:
  - providing an aluminum disk,
  - disposing an alkaline zincate coating over a surface of the aluminum disk; and
  - contacting a zincate coated surface of the disk with an aqueous electroless nickel-phosphorous plating bath, the bath including about 1.0 g/L to less than 5 g/l Ni; about 25 g/l to about 40 g/l hypophosphorous reducing agent; about 20 g/l to about 30 g/l of at least one organic acid complexing agent, 0 to about 120 g/l orthophosphite by-product; wherein the electroless nickel-phosphorous bath with an orthophosphite concentration of up to about 120 g/l provides an electroless nickel-phosphorous deposit on the zincate coated substrate

-22-

with an intrinsic stress that is more compressive than and a corrosion resistance that is superior in acidic media to electroless nickel-phosphorous deposit provided using similar electroless-nickel-phosphorous baths containing greater than 5.0 g/l Ni.

22. The method of claim 21, wherein the concentration of Ni in the bath relative to the concentration of orthophosphite is such that  $\text{Ni}(\text{H}_2\text{PO}_3)_2$  precipitation is inhibited during plating of the zincate coated substrate at orthophosphite concentrations up to 120 g/l at a bath pH of about 4.4 to about 4.8.

23. The method of claim 21, the bath is operated up to 4 (or up to orthophosphite levels of approximately 120 g/l) metal turnovers.

24. The method of claim 21, the bath having a pH of about 4.4 to about 4.8.

25. The method of claim 21, wherein the organic acid complexing agent comprises at least one of malic acid, lactic acid, or succinic acid.

26. The method of claim 21, the bath further comprising at least one of a chelating agent, stabilizer, or pH buffer.

27. The method of claim 21, the bath being free of a surfactant.

28. The method of claim 21, wherein the zincate coated substrate is an aluminum disk for data storage.

29. The method of claim 21, wherein the bath consists essentially of water, about 2.0 g/l to about 4 g/l of Ni, about 25 g/l to about 40 g/l hypophosphorous reducing agent, 0 to about 120 g/l orthophosphite by-product, less than about 25 g/l of a combination of organic acid complexing agents selected from the group consisting of malic acid, lactic acid, and succinic acid, about 0.0004 to about 0.0007 g/l stabilizer, and at least one pH adjuster in an amount effective to provide the bath with a pH between about 4.4 and 4.8.

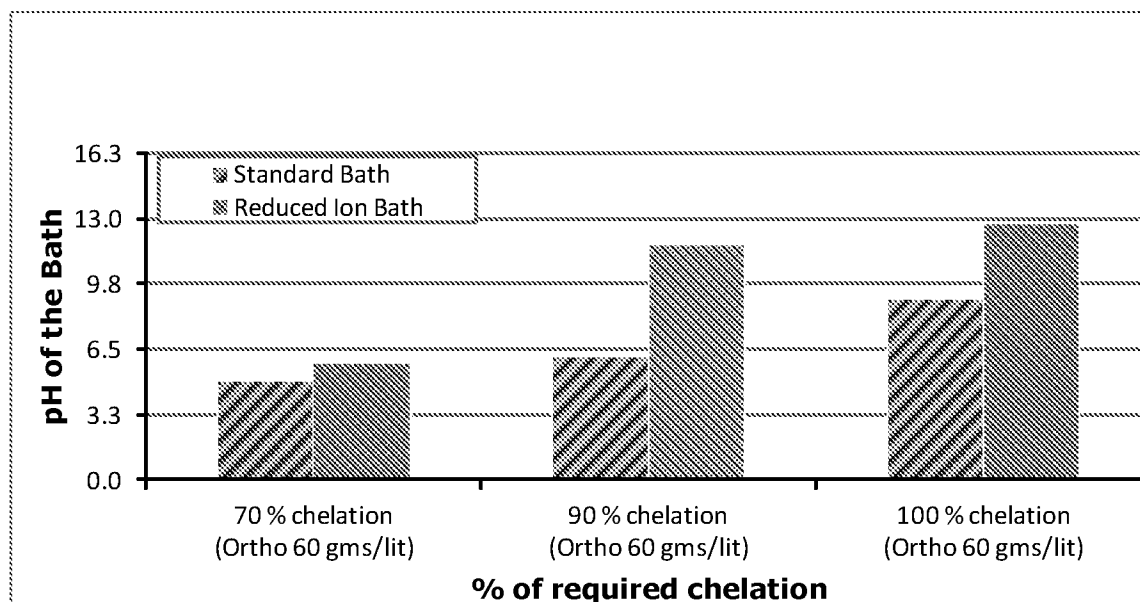


Fig. 1

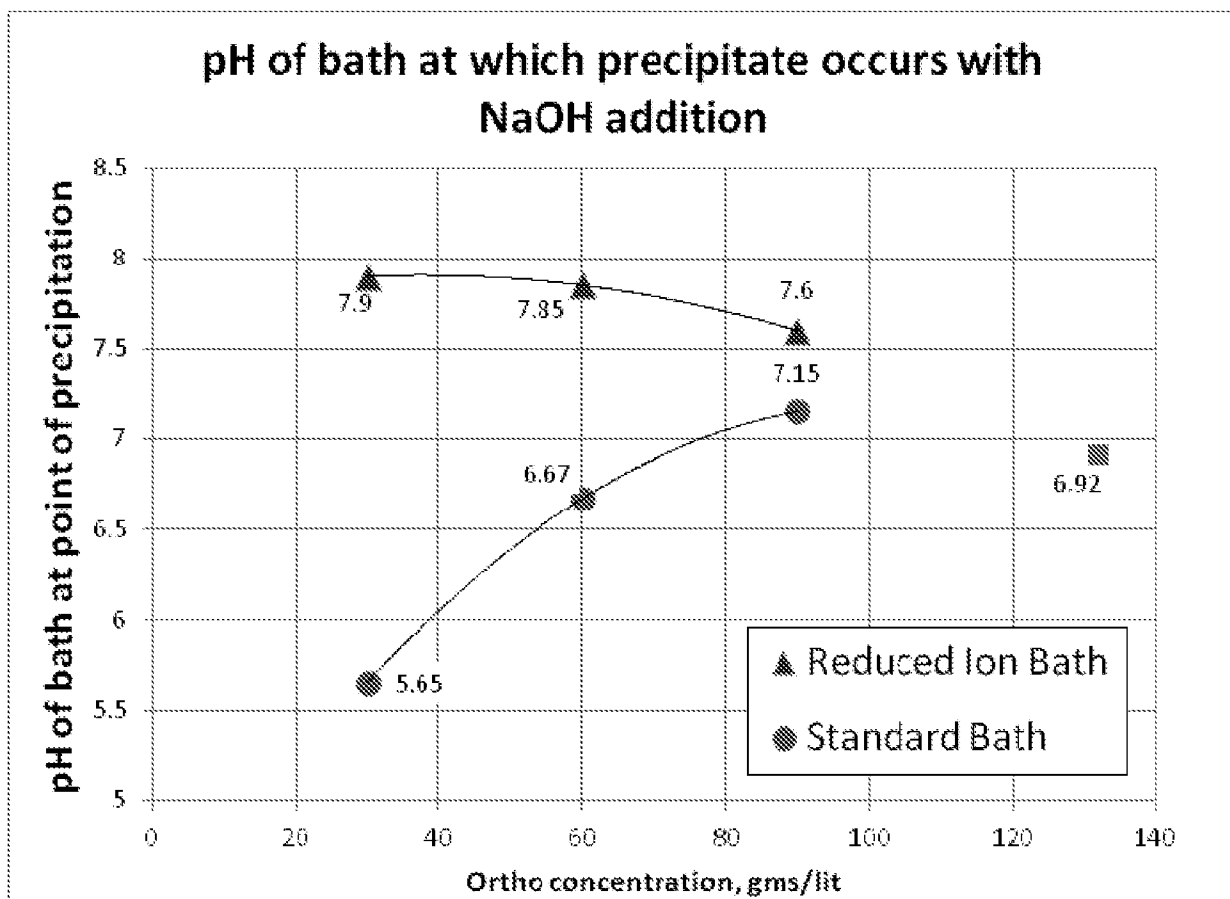


Fig. 2



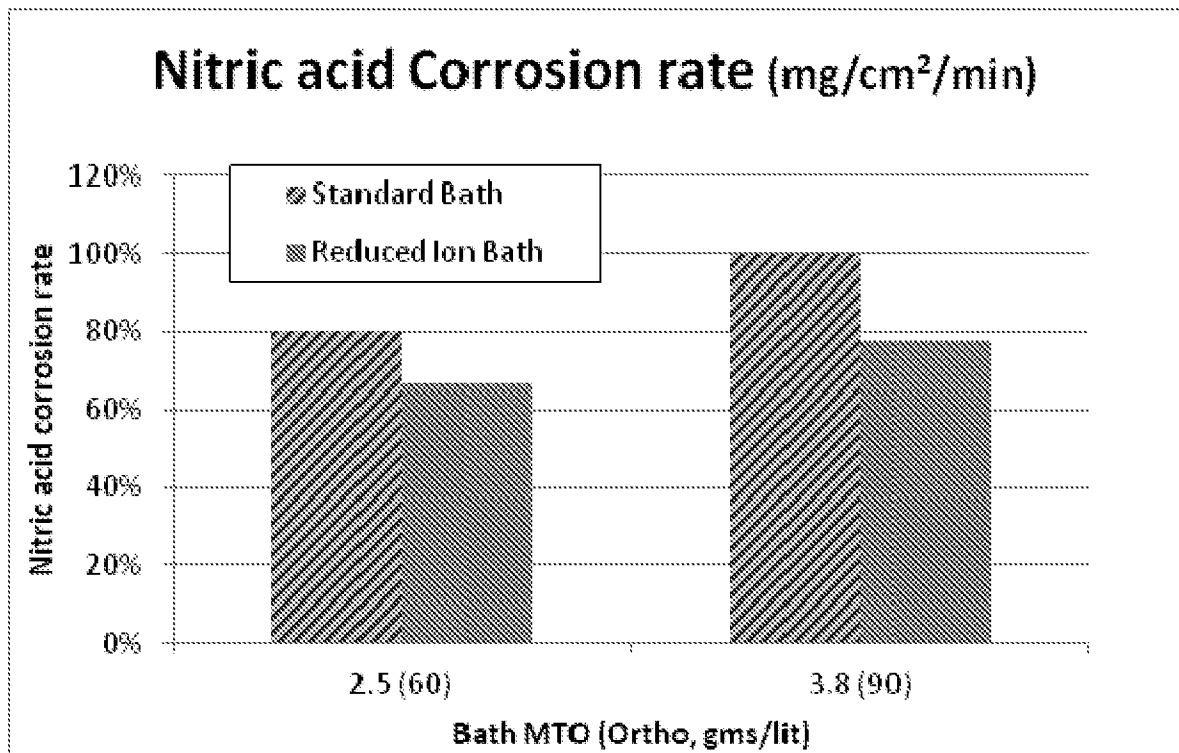


Fig. 3

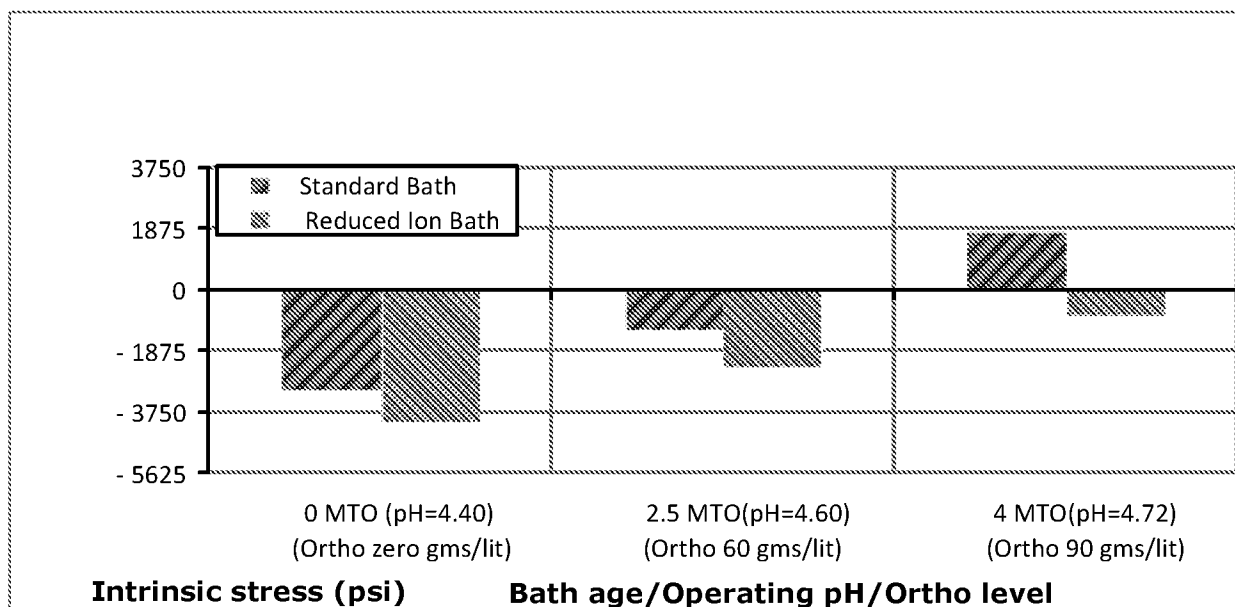


Fig. 4

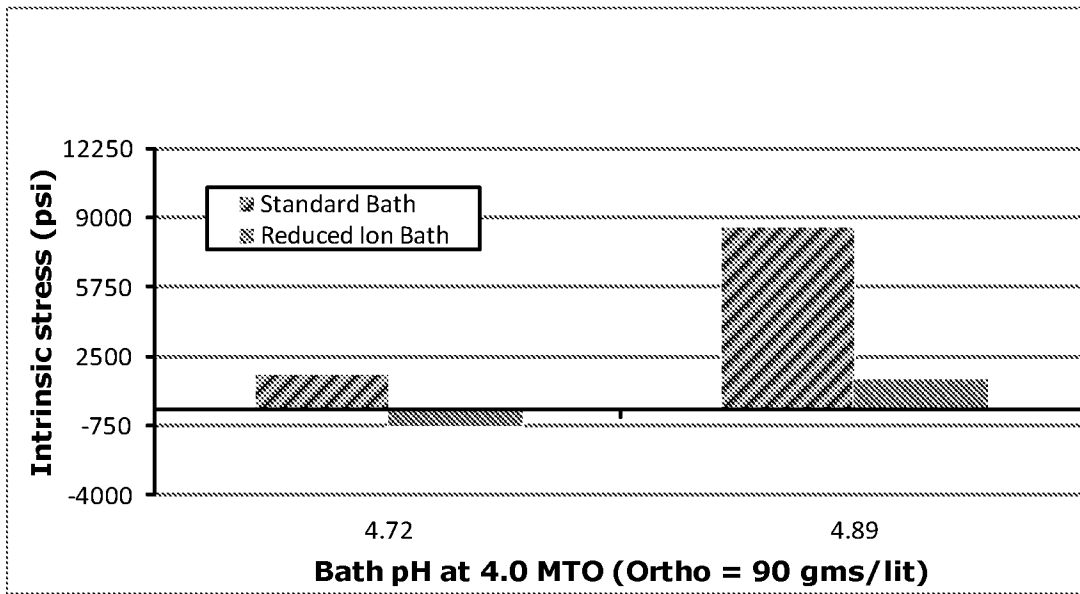


Fig. 5

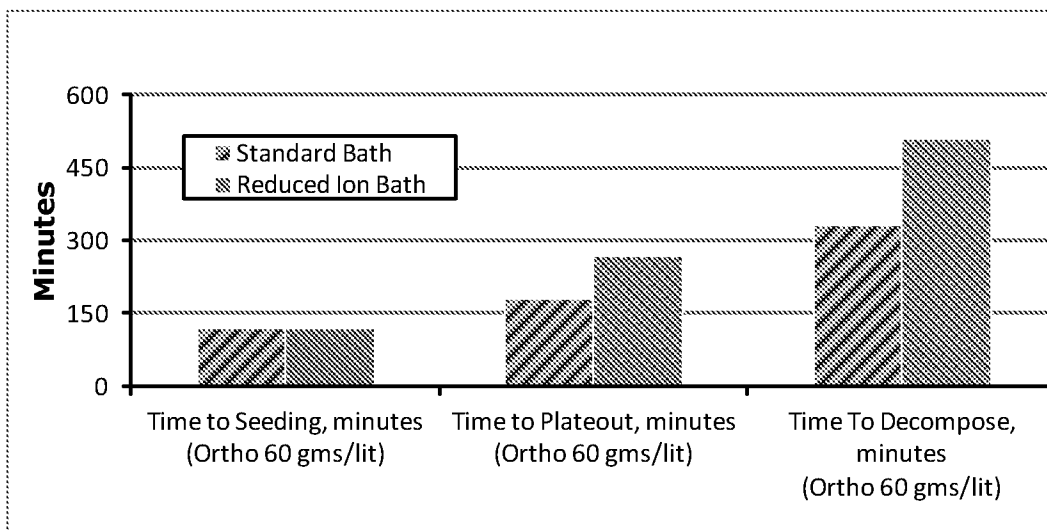


Fig. 6

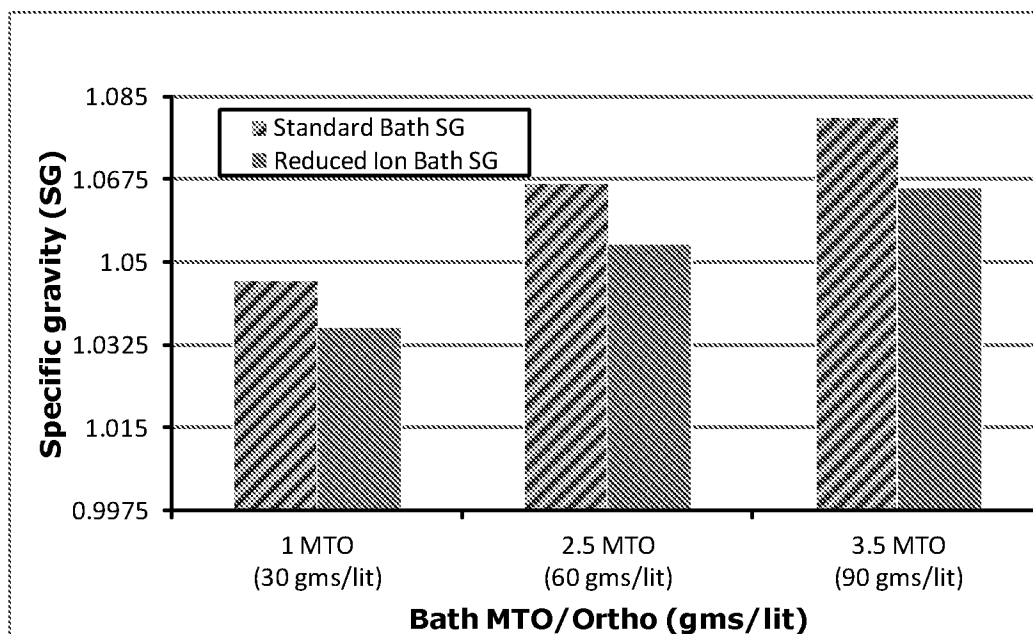


Fig. 7

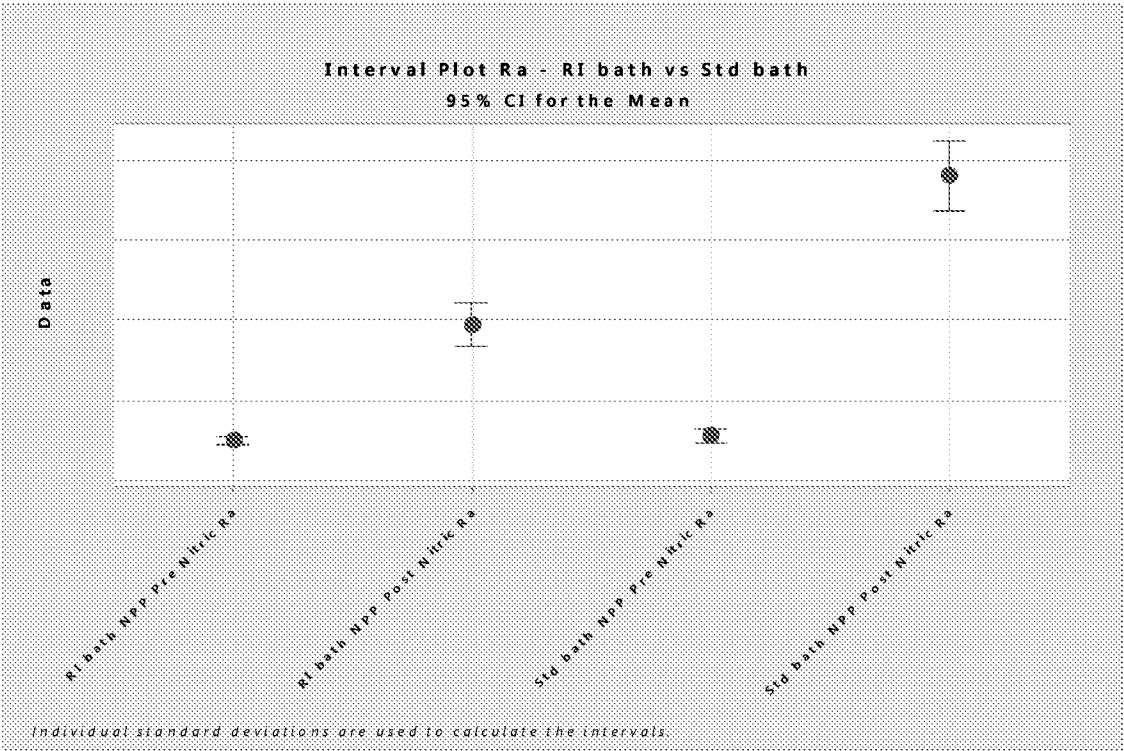


Fig. 8

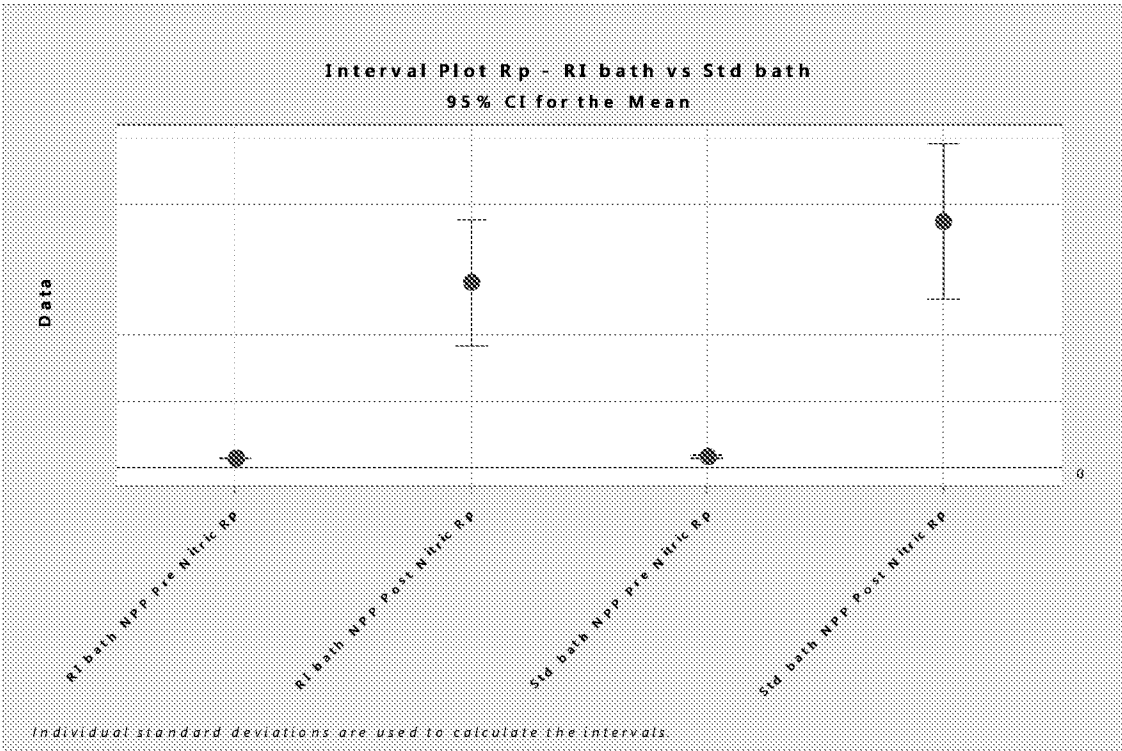


Fig. 9

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/42271

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C23C 18/16, C23C 18/36 (2016.01)

CPC - C23C 18/36, C23C 18/1655, C23C 18/1675

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - C23C 18/16, C23C 18/36 (2016.01)

CPC - C23C 18/36, C23C 18/1655, C23C 18/1675

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Patents and non-patent literature (classification, keyword; search terms below)Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
PatBase, Google Scholar (NPL), Google Patents; search terms: aqueous, electroless, nickel-phosphorous plating, bath, coating, alkaline zincate coated, orthophosphite, intrinsic stress, compressive, aluminum disk, memory, data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 2,177,646 A1 (Atotech Deutschland GMBH) 17 October 2008 (17.10.2008) para [0016]-[0019], [0021]-[0027], [0029], [0049]	1-20
Y	Engelhaupt et al., "Electrodeposition of Low Stress Nickel Phosphorous Alloys for Precision Component Fabrication", 01 January 2001 (01.01.01), pg 5 col 2 para 2, Document found under URL, <a href="http://ntrs.nasa.gov/search.jsp?R=20010038458">http://ntrs.nasa.gov/search.jsp?R=20010038458</a>	1-29
Y	US 6,524,642 B1 (Leibman et al.) 25 February 2003 (25.02.2003) abstract, col 3 ln 31-45, ln 58-63, col 4 ln 4-6, ln 9-19, ln 28-30, ln 41-43, Table 1	8, 13, 19, 21-29
A	US 4,511,614 A (Greeson et al.) 16 April 1985 (16.04.1985) entire document	1-29
A,P	WO 2016/083195 A1 (Atotech Deutschland GMBH) 02 June 2016 (02.06.2016) entire document	1-29

☐ Further documents are listed in the continuation of Box C.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

25 August 2016

Date of mailing of the international search report

30 SEP 2016

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents  
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300  
PCT OSP: 571-272-7774