AMORPHOUS NICKEL PHOSPHORUS ALLOYS FOR OIL AND GAS

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ABSTRACT
There is disclosed a system and method for applying an amorphous NiP coating on pipes and rods, particularly for use in the oil and gas industries to inhibit corrosion. In an embodiment, the method comprises applying an amorphous nickel phosphorus or NiP alloy coating to pipes and rods for use in oil and gas industries, comprising: preparing a Watt's type nickel phosphorus (NiP) plating bath solution utilizing a Watt's type nickel electrolyte containing hypophosphorous acid; maintaining the plating bath solution temperature at between 120°F and 170°F, adjusted to regulate phosphorus content over 11%; regulating a pH level of the plating bath solution between 1.0 and 3.0 utilizing sulphuric acid; and controlling the cathode current density in the range of 10-100 amps/sq/ft. Significant cost savings may be realized by using an electroplated nickel-phosphorus alloy over regular carbon steel alloy components at sufficient thickness to be pore free replacing the use of more expensive components made of stainless steels or nickel base alloys.

Diagram:
[Diagram showing schematic of the system and method]
Prepare NiP electroplating solution based on Watt’s solution

Maintain bath temperature at between 130°F and 160°F and adjust to regulate phosphorous content over 11%.

Regulate pH level of electroplating solution between 1.0 and 3.0 with sulfuric acid.

Utilize electrolytic nickel anodes in titanium baskets and inert anodes to maintain nickel level.

Control cathode current density in the range of 10–100 amps/sq/ft.

Heat and cool bath chemistry as necessary to maintain a constant bath temperature.

FIG. 2
AMORPHOUS NICKEL PHOSPHORUS ALLOYS FOR OIL AND GAS

FIELD OF THE INVENTION

[0001] The present invention relates to the use of electrodeposited amorphous nickel phosphorus alloys for oil and gas equipment used in downhole applications such as tubulars, sucker rods, pump barrels/plungers, electric submersible pump (ESP) components, progressive cavity rotary pump components, completion tools, packer assemblies, and components of hydraulic fracturing systems.

BACKGROUND

[0002] Historically, hypophosphorous acid and its compounds were first observed in the reduction of nickel from solutions by A. Wurtz in 1844 and Francois Roux in 1913. Work by Brenner and Riddell in the 1940s resulted in the first commercial applications of electrolecstic nickel plating using sodium salt of hypophosphorous acid. Later work by R. Duncan and others in the 1970s recognized the excellent corrosion resistance of high phosphorus electrolecstic nickel deposits on pipes and rods used in oil and gas applications with exposure to carbon dioxide (CO₂), hydrogen sulphide (H₂S) containing brines. The presence of CO₂, H₂S and free water can cause severe corrosion problems in oil and gas pipelines and rods. According to NACE International, the total annual cost of corrosion in the oil and gas production industry is estimated to be over $1.3 billion, with over $460 million annually in downhole tubing expenses.

[0003] The amorphous metallic glass type structure of high phosphorus electrolecstic nickel deposits is thought to provide the basis for this outstanding corrosion resistance provided by the electrolecstic nickel plating. It has also been observed that high phosphorus electrolecstic nickel deposits develop a passive layer in sour service oil and gas environments containing H₂S which effectively inhibits corrosion of the coating. Thus, high phosphorus electrolecstic nickel deposits have been used successfully in many oil and gas applications involving corrosion caused by CO₂ and H₂S in brines (for example, as recommended in NACE Standard MR0175-2006).

[0004] Amorphous nickel-phosphorus deposits have been successfully plated from Wutt’s type nickel baths containing phosphorus acid and phosphoric acid, and from nickel chloride baths containing nickel chloride, phosphoric acid, phosphoric acid, and using nickel carbonate to maintain a nominal free acid content. In both baths the phosphorus acid acts as the phosphorus source while the phosphoric acid acts to brighten and level the deposits.

[0005] While the benefits of high phosphorus electrolecstic nickel deposits in inhibiting corrosion has been recognized, the cost of applying the required thickness (typically 50 microns or more) on the large surface areas of parts such as tubulars, rods, pump barrels, rotors, etc. can be very costly. What is needed is an improved system and method for applying amorphous nickel phosphorus (NiP) alloy coating on pipes and rods in a faster, more cost efficient way.

SUMMARY

[0006] The present invention relates to an improved system and method for applying an amorphous NiP alloy coating on oil and gas equipment used in downhole applications such as tubulars, sucker rods, pump barrels/plungers, ESP components, progressive cavity rotary pump components, completion tools, packer assemblies, and components of hydraulic fracturing systems to prevent corrosion and wear and to extend the service life of said parts.

[0007] In an embodiment, the method comprises applying an amorphous nickel phosphorus or NiP alloy coating to various components used in oil and gas industries, comprising: preparing an electrolytic nickel phosphorus (NiP) plating, bath solution utilizing a Watt’s type nickel electrolyte containing phosphorus acid and phosphoric acid, maintaining the plating bath solution temperature at between 120° F. and 170° F.; adjusting to regulate the phosphorus content over 11%; regulating a pH level of the bath solution between 1.0 and 3.0 using sulphuric acid or nickel carbonate; and controlling the cathode current density in the range of 10-100 amps/sq.ft.

[0008] In another method comprises preparing an electrolytic nickel phosphorus (NiP) plating bath by using nickel chloride, phosphorus acid, and phosphoric acid, maintaining the plating bath solution temperature at between 1511° F. and 170° F.; controlling the free acidity of the bath by using nickel carbonate; and controlling the cathode current density in the range of 50-100 amps/sq.ft.

[0009] Significant cost savings may be realized by using an electrolecstic nickel phosphorus alloy over regular carbon steel alloy components at sufficient thickness to be pore free replacing the use of more expensive components made of corrosion resistant alloys (CRA’s) such as stainless steels.

[0010] The cost savings is directly related to the mass of the components being fabricated out of the more costly alloy. For example coatings of S mils of high phosphorus electrolecstic nickel have been successfully used to coat large carbon steel ball valves for sour oil and gas service at a much lower overall cost than manufacturing the ball valve from a 300 series stainless steel. The electrolytic nickel-phosphorus coating of the present disclosure has an even greater potential for cost savings for specific oil and gas applications where CO₂ and H₂S are present.

[0011] In this respect, before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not limited in its application to the details of construction and to the arrangements of the components set forth in the following description or the examples provided therein, or illustrated in the drawings. The invention is capable of other embodiments and of being practiced and carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein are for the purpose of description and should not be regarded as limiting.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The present invention will be better understood and objects of the invention will become apparent when consideration is given to the following detailed description thereof. Such description makes reference to the annexed drawings wherein:

[0013] FIGS. 1A to 1D show a system for coating long production parts such as pipes and sucker rods with NiP alloy in accordance with an embodiment;

[0014] FIG. 2 shows an illustrative flow chart of a method in accordance with an embodiment;

[0015] In the drawings, embodiments of the invention are illustrated by way of example. It is to be expressly understood that the description and drawings are only for the purpose of
illustration and as an aid to understanding, and are not intended as a definition of the limits of the invention.

**DETAILED DESCRIPTION**

[0017] As noted above, the present invention relates to an improved system and method for applying an amorphous nickel phosphorus or NiP alloy coating on pipes and rods, particularly for use in the oil and gas industries to inhibit corrosion.

[0018] In many cases, there may be a significant benefit to using electroless nickel coated steel components when suitable, instead of using components made of nickel based alloys. However, several drawbacks to the wide scale use of high phosphorus electroless nickel for oil and gas applications exist. First, the cost to apply the required thickness over a given surface area of pipes or rod is significantly higher than with traditional electrolytic nickel plating baths for engineering applications such as sulphamate nickel, since the nickel is replenished via chemical salts and not by the dissolution of nickel anodes. Second, the special operating conditions for use of an electroless nickel plating bath mandate the need for expensive equipment to maintain a relatively high bath temperature of 190 °F, a high level of filtration, and a sufficient level of solution movement for solution stability. Finally the speed of deposition of the high phosphorus electroless nickel is limited by to approximately 10-15 micron/hr.

[0019] The inventor has realized the drawbacks of the current approach, and has developed a system and method for lower cost and faster plating of NiP coating onto oil and gas components such as pipes and rods. With the present system and method, the amorphous NiP deposits containing a phosphorus content (i.e. 11% or higher) can be applied rapidly on a wide variety of oil and gas components. The characteristics of these deposits (i.e. amorphous and with a phosphorus content over 11%) make them well suited for oil and gas applications with high exposure to brines containing high levels of CO₂ and H₂S. As will be explained in more detail below, the cost to produce these coatings for these applications is significantly less than high phosphorus electroless nickel coatings.

[0020] In an embodiment, the deposits can be heat treated to improve the hardness and wear resistance in the same way high phosphorus electroless nickel deposits: can be heat treated. As with electroless nickel, the heat treating of electrolytic NiP deposits results in the formation of crystalline nickel phosphides within the deposit structure. In some cases corrosion resistance may be reduced by heat treatment so other techniques can be employed to improve wear resistance. The electrolytic NiP deposit would also provide great benefits as a hard, corrosion resistant underlayer to other wear coatings used in oil and gas applications such as hard chromium at a much lower cost than electroless nickel coatings.

[0021] In another embodiment, electrolytic NiP deposits can be rapidly plated with the co-deposition of hard silicon carbide (SiC) particles to produce a composite coating with good wear resistance.

[0022] When heat treated, this composite alloy becomes very hard (e.g. in the 1500 HV range) and provides exceptional wear resistance. The NiP coatings can be rapidly plated with co-deposited particles of polytetrafluoroethylene (PTFE) or boron nitride (BN) to impart a reduced co-efficient of friction to the plated surface of pipes and rods for specific oil and gas applications.

[0023] The inventor has determined that, with the present system and method, both SiC and PTFE can be rapidly and effectively co-deposited at a much lower cost than electroless NiP/PTFE or electroless NiSiC or electroless nickel-PTFE-SiC coatings. The speed and cost savings of the present system and method are of particular benefit with larger sized pipes and rods, and significant volumes of such parts coated with NiP for oil and gas applications. he system and process will now be described in more detail with reference to the figures.

[0024] Referring to FIGS. 1A to 1D, shown is an apparatus 100 for coating long production parts such as oil and gas pipes and sucker rods with NiP alloy in accordance with an embodiment. FIG. 1A shows a front view 100A, FIG. 1B shows a top view 100B, and FIG. 1C shows an enlarged side view of the apparatus, FIG. 1D shows an enlarged view of the plating bath and overflow reservoir portion of the apparatus 100.

[0025] As shown, apparatus 100 includes a series of filtration pumps 110 for pumping a filtered plating bath solution from a reservoir tank 106 to an overflow plating cell 105. A heater 120 may be used to heat the plating bath to maintain a desired operating temperature. Cartridge filters 130 may be used to clean the bath by removing particulates that may accumulate over time during operation of the bath.

[0026] In an embodiment, overflow plating cell 105 includes an overflow compartment 140 which receives overflow from overflow plating cell 105 via an overflow section 142. Overflow compartment 140 directs the overflow plating bath solution to reservoir tank 106 to be filtered and pumped back to overflow plating cell 105. A system control 150 may be used to regulate filtration pumps 110 to control the continuous flow of the plate bath solution from reservoir tank 106 to overflow plating cell 105, and also to control the operating temperature of the plating bath solution being pumped to overflow plating cell 105.

[0027] In an embodiment, overflow plating cell 105 is lined on each side with nickel anode containing titanium baskets 160, and which may be hung from a pair of anode bus bars 170. The anode bus bars are connected to as rectifier (not shown) to convey current between anode bus bars 170 to the nickel anode containing titanium baskets, and a cathode part 190 to be plated.

[0028] System control 150 may be used to control the rotation of the cathode (i.e. part 190) in the overflow plating cell 105 at various speeds while maintaining electrical contact through the ends of the part 190 using copper extension pieces. System control 150 is also used to control the current via anode bus bars 170 to allow for a desired current flow from the plating rectifier based on the required current density range needed to yield a suitable alloy content in the coating.

[0029] Now referring to FIG. 2, shown is an illustrative flow chart of a method 200 in accordance with an embodiment. As shown, at block 210, a NiP electroplating solution is prepared based on a traditional. Watt’s solution (e.g. 1.1 M nickel sulphate hexahydrate, 0.2-0.4 M nickel chloride hexahydrate, 0.65 M boric acid) and 0.25 to 6.0 M of phosphorus acid. The nickel chloride hexahydrate, 0.65 M boric acid) and 1.0 to about 4.0 M of hypophosphorous acid (which contributes to the overall plating efficiency of the process). The nickel chloride hexahydrate serves to maintain a nominal level of chloride in the bath to prevent metal oxidation formation on the electrolytic nickel anodes.

[0030] In an embodiment, the nickel chloride level has a workable range of 5 to 90 preferred range of 10-45 g/L, and a most preferred range of 15-20 g/L. The boric acid has a
preferred range of 30-45 g/L and a most preferred range of 40-45 g/L. The bath phosphorus acid in the Watt’s based chemistry has a preferred range 10-410 g/L, and a most preferred range of 20-30 g/L.

[0031] In another embodiment i) the nickel chloride based nickel phosphorus (NiP) plating bath could be used. For example a solution containing 0.75-1.2 M of nickel chloride hexahydrate, of phosphorus acid, 0.1-0.6 M of phosphoric acid, with the free acidity being maintained by using nickel carbonate.

[0032] In alternative embodiments, the Watt’s solution could also contain some variants in the chemistry. For example: (1) the solution may contain about 0.50-2.0 M of hypophosphorous acid; (2) the solution may contain about 0.25-1.0 M of phosphorous acid; (3) the solution may contain about 0.25-0.50 hypophosphorous acid and 0.25-0.50 of phosphoric acid. Of these variants, it is believed that (1) and (3) may be preferred due to higher overall efficiency that may be obtained.

[0033] Next, at block 220, the temperature of the plating bath solution is preferably maintained between about 130°F and 160°F and more preferably between about 150°F and 160°F. A workable range is approximately 1.20°F and 170°F, and the temperature may be adjusted to help regulate phosphorus content into the desired range of over 11% depending on the current density of the parts being processed (cathode). Higher bath temperatures allow higher current densities to be used without burning.

[0034] At block 230, the of the electroplating solution is regulated and maintained between about 1.0-3.0 by the use of sulphuric acid to lower the bath pH, and nickel carbonate to raise the bath pH. A more preferred range for the pH is about 2.0-2.5.

[0035] In an embodiment, at block 240, electrolytic nickel, anodes (such as Vale R-rounds or squares) are used in titanium baskets and inert anodes are used as required to maintain the nickel at a suitable level. An optimum nickel level is about 75 g/L, and the preferred range for the nickel level is between 65-95 g/L. A workable range is approximately 60-130 g/L. Nickel metal levels in the bath will climb due to higher anode efficiency than cathode efficiency (as in most electrolytic nickel electrolytes) and inert anodes are used to prevent the nickel level from climbing too high.

[0036] At block 250, cathode current density in typically run the range of 10-100 amps/sq/ft and part movement and solution flow are utilized to obtain the highest cathode current densities.

[0037] As an illustrative example, tubular parts and rods are rotated in the plating bath when plated in an overflow plating cell. Cathode rod movement and air agitation would be used for smaller parts being rack plated similar to the methods used in traditional bright nickel plating.

[0038] Finally, at block 260, heating and cooling of the bath chemistry is required to maintain a relatively constant bath temperature. The high cathode current densities employed can result in a large amount of current flowing through the plating electrolyte which may lead to the bath temperature climbing above the desired range. To maintain the desired optimal alloy composition the temperature must be tightly regulated with heating and cooling.

[0039] The above illustrative example describes a practical system and method for the production of amorphous nickel phosphorus coatings on oil and gas components using a standard Watts nickel based electrolyte with the compound phosphorus acid. The use of electrolytic nickel phosphorus (NiP) has been documented and developed in detail for diamond turning and other applications, the scope this invention covers its significant practical use as a low cost alternative to high phosphorus electroless nickel for applications specific to the oil and gas industry.

[0040] The following examples represent typical applications of the present system and method. It will be understood that these examples are provided to illustrate the method only, and are not to limit the scope of the method described above.

Example 1

[0041] A 1" diameter sucker rod 25 feet in length composed of AISI 1536 or AISI 4142 steel is coated with a minimum thickness of 0.00" of electrolytic NiP using the described method. The part is rotated in specialized flooded cell plating tank to achieve an average cathode current density of 100 amps/sq/ft using busing connections to a large plating rectifier. The electroplating solution is maintained at 150°F and pumped into plating cell with overflow back to main tank (see FIGS. 1A-1C). The electroplating cell is lined with titanium baskets filled with nickel rounds. Time to obtain minimum coating thickness is approximately 60-70 minutes with an alloy content of 11-13% phosphorus. The resulting coating is pore free and provides excellent corrosion resistance in sour oil and gas service.

Example 2

[0042] A 2.88 inch outer diameter (OD) production tubing 31 feet in length and composed of J55 steel is coated on the outside with 0.003" inches of electrolytic nickel-phosphorus using the given process. It is also electroplated in a specialized tank with an overflow cell. The pipe is rotated during plating via copper couplers attached at each end that are connected via copper buss bars to a large plating rectifier. A coating containing minimum phosphorus content of 11% is obtained and the produced coating has minimal porosity and excellent resistance to brines containing CO₂ and H₂S at a fraction of the cost and time to deposit a similar thickness of high phosphorus electroless nickel.

Example 3

[0043] A 0.75" sucker rod 25 feet in length used in an erosive wear service application is coated first with 0.002" minimum thickness of electrolytic nickel-phosphorus as in example 1 above and then transferred to another bath containing 1.5 to 2.5 g/L of 0.1 to 0.5 micron silicon carbide particles to plate an addition 0.001" minimum of the composite coating. In this case an amorphous electrolytic NiP alloy containing 20-30% co-deposited SiC particles is produced. The particles are kept suspended in the plating solution by pump agitation and solution movement over the cathode surface. After coating the part is heat treated, for example, at 650°F for 4 hours. The resulting coating has excellent corrosion resistance to sour service conditions and very good erosive wear resistance suitable for severe erosive wear conditions encountered in certain pumping environments in the oil and gas industry.

Example 4

[0044] Progressive cavity pump rotors are routinely plated with hard chromium to improve service life in applications with severe wear occurs. In many cases the rotors are exposed
to severely corrosive environments in conjunction with high wear. Sulfamate nickel and electroless nickel have both been successfully used as undercoats to the hard chromium to improve overall corrosion resistance in environments with brines and sour gas (H2S). Electrolytic nickel-phosphorus offers the advantages of high phosphorus electroless nickel (harder underlayer than sulphamate nickel and exceptional resistance to brine, CO2, and H2S (sour environments)) at a significantly reduced cost per unit.

A 30 foot steel progressive cavity pump rotor is plated in the electrolytic nickel phosphorus (NiP) bath in a specially designed vertical tank at a current density of 75 amps/sq.ft with vigorous bath agitation to obtain a minimum thickness of 30 microns. The rotor is suspended inside a specially designed anode system utilizing a mixture of inert and nickel anodes. After plating the part is rinsed and transferred to a hard chromium plating bath.

The above examples are illustrative of the types of uses to which the present system and method may be put. However, it will be appreciated that various changes and modifications may be made to the above described system and method without departing from the scope of the invention which is defined by the following claims.

1. A method of applying an amorphous nickel phosphorus (NiP) alloy coating to oil and gas equipment used in down-hole applications, comprising:
   a. preparing a Watt’s type NiP plating bath solution utilizing a Watt’s type electrolyte containing phosphoric acid;
   b. maintaining the plating bath solution temperature at between about 120°F and 170°F, adjusted to regulate phosphorus content over 11%;
   c. regulating a pH level of the plating bath solution at between about 1.0 and 3.0 utilizing sulphuric acid and regulating the cathode current density in the range of about 10-100 amps/sq.ft.
   2. The method of claim 1, wherein the plating bath solution temperature is between about 150°F and 170°F.
   3. The method of claim 2, wherein the plating bath solution controls the pH level of the plating bath solution using nickel carbonate.
   4. The method of any one of claims 3, wherein the cathode current density in the range of about 50-100 amps/sq.ft.
   5. The method of any one of claims 5, wherein the plating bath solution comprises about 1.1 M nickel sulphate hexahydrate, 0.2-0.4 M nickel chloride hexahydrate, 0.65 M boric acid, and 0.25 to 6.0 M of phosphorous acid.
   6. The method of any one of claims 5, wherein the nickel chloride level has a preferred range of 10-45 g/L, and a more preferred range of 15-20 g/L.
   7. The method of any one of claims 6, wherein the boric acid has a preferred range of 30-45 g/L, and a more preferred range of 40-45 g/L.
   8. The method of any one of claims 7 wherein in the bath phosphoric acid has a preferred range 10-40 g/L, and a more preferred range of 20-30 g/L.

9. The method of claim 1, wherein the nickel chloride based nickel phosphorus plating bath comprises a solution containing 0.75-1.2 M of nickel chloride hexahydrate, 1.5-3.0 M of phosphorous acid, 0.1-0.6 M of phosphoric acid, and a level maintained by using nickel carbonate.
10. The method of claim 1, wherein the plating bath solution includes about 0.5-2.0 M of hypophosphoric acid; about 0.25-1.0 M of phosphorous acid.
11. The method of claim 1, wherein the plating bath solution includes about 0.25-0.50 hypophosphoric acid and 0.25-0.50 of phosphorous acid.
12. A system for applying an amorphous nickel phosphorus (NiP) alloy coating to oil and gas equipment used in down-hole applications, wherein the system is adapted to:
   a. preparing a Watt’s type NiP plating bath solution utilizing a Watt’s type electrolyte containing phosphoric acid;
   b. maintaining the plating bath solution temperature at between about 120°F and 170°F, adjusted to regulate phosphorus content over 11%;
   c. regulating a pH level of the plating bath solution at between about 1.0 and 3.0 utilizing sulphuric acid and controlling the cathode current density in the range of about 100-1,000 amps/sq.ft.
13. The system of claim 12, wherein the plating bath solution temperature is between about 150°F and 170°F.
14. The system of claim 13, wherein the plating bath solution controls the pH level of the plating bath solution using nickel carbonate.
15. The system of any one of claims 14, wherein the cathode current density is the range of about 50-100 amps/sq.ft.
16. The system of any one of claims 15, wherein the plating bath solution comprises about 1.1 M nickel sulphate hexahydrate, 0.2-0.4 M nickel chloride hexahydrate, 0.65 M boric acid, and 0.25 to 6.0 M of phosphorous acid.
17. The system of any one of claims 16, wherein the nickel chloride level has a preferred range of 10-45 g/L, and a more preferred range of 15-20 g/L.
18. The system of any one of claims 17, wherein the boric acid has a preferred range of 30-45 g/L, and a more preferred range of 40-45 g/L.
19. The system of any one of claims 18 wherein the bath phosphoric acid has a preferred range 10-40 g/L, and a more preferred range of 20-30 g/L.
20. The system of claim 12, wherein the nickel chloride based nickel phosphorus plating bath comprises a solution containing 0.75-1.2 M of nickel chloride hexahydrate, 1.5-3.0 M of phosphorous acid, 0.1-0.6 M of phosphoric acid, and a pH level maintained by using nickel carbonate.
21. The system of claim 12, wherein the plating bath solution includes about 0.25-2.0 M of hypophosphoric acid; about 0.25-1.0 M of phosphorous acid.
22. The system of claim 12, wherein the plating bath solution includes about 0.25-0.50 hypophosphoric acid and 0.25-0.50 of phosphorous acid.

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