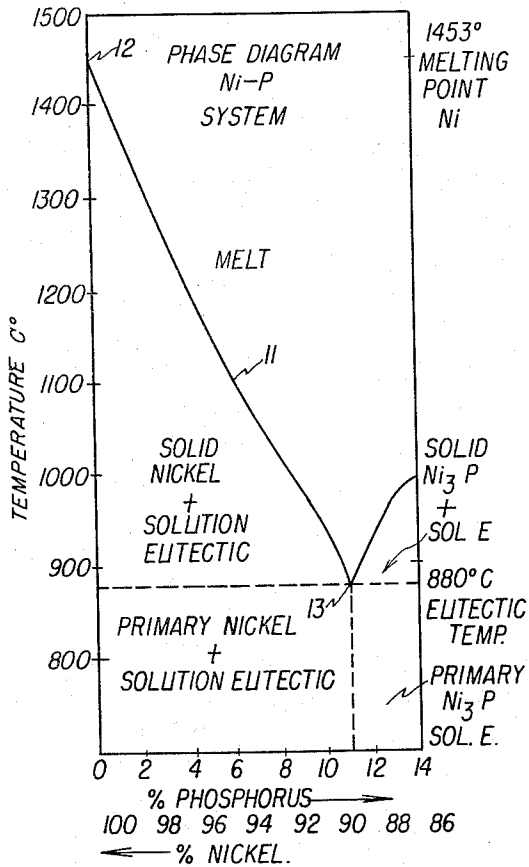


Aug. 29, 1961

W. J. CREHAN ET AL
METHODS OF APPLYING NICKEL PHOSPHORUS
COATINGS UPON BASE METAL BODIES
Original Filed June 10, 1955

2,997,783

FIG. 1



EUTECTIC COMPOSITION:
Ni = 89 % } BY WEIGHT.
P = 11 % }

FIG. 2

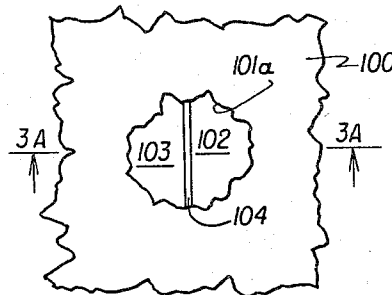


FIG. 3A

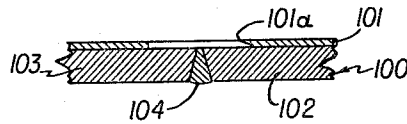
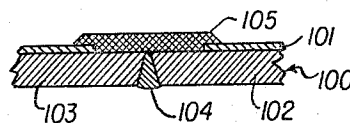


FIG. 3B



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2,997,783

METHODS OF APPLYING NICKEL PHOSPHORUS COATINGS UPON BASE METAL BODIES

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Original application June 10, 1955, Ser. No. 514,472, now Patent No. 2,908,568, dated Oct. 13, 1959. Divided and this application Aug. 22, 1957, Ser. No. 679,735 6 Claims. (Cl. 29—401)

The present invention relates to methods of applying nickel-phosphorus coatings upon base metal bodies, and more particularly to methods of repairing nickel-phosphorus coatings carried by base metal bodies. This application is a division of the copending application of William J. Crehan, Walter F. Klouse and Paul Talmey, Serial No. 514,472, filed June 10, 1955, now Patent No. 2,908,568, granted October 13, 1959.

It is an object of the invention to provide a method of repairing a hole or other rupture in a layer that has been chemically deposited on a metal support from a plating bath of the nickel cation-hypophosphite anion type.

Another object of the invention is to provide an improved method of making an article of manufacture comprising a base metal body carrying a composite nickel-phosphorus coating or lining, including two coating sections respectively intimately bonded to the body and also intimately bonded to each other, wherein one of the coating sections is of the nickel-phosphorus composition inherently produced by nickel plating from a chemical nickel plating bath of the nickel cation-hypophosphite anion type, and wherein the other of the coating sections is of the nickel-phosphorus composition of an alloy thereof that has been previously produced from a chemical nickel plating bath of the type noted.

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

The invention, both as to its organization and method 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:

FIGURE 1 is a phase diagram of the nickel-phosphorus system as far as it is pertinent to the nickel-phosphorus alloys that are employed in the repairing of chemically deposited nickel-phosphorus coatings, in accordance with the present invention, and illustrating the mutual relationships among phase and temperature and composition in these nickel-phosphorus alloys;

FIG. 2 is a fragmentary plan view of a metal wall provided with a chemically deposited nickel-phosphorus liner that has been broken;

FIG. 3A is a fragmentary vertical sectional view of the wall of FIG. 2, taken in the direction of the arrows along the line 3—3 in FIG. 2, therein; and

FIG. 3B is a fragmentary vertical sectional view of the wall of FIG. 3A, after the break in the liner thereof has been repaired or patched.

At the outset, it is noted that in the operation of a continuous chemical nickel plating system of the character of that disclosed in U.S. Patent No. 2,658,839, granted on November 10, 1953 to Paul Talmey and William J. Crehan, there is employed a plating bath of the nickel cation-hypophosphite anion type; and in the plating operation, nickel cations are reduced to metallic nickel and deposited upon the catalytic surface of the object undergoing the chemical nickel plating operation, and hypophosphite anions are correspondingly oxidized to phosphite anions and accumulate in the plating bath. In accord-

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ance with the method of Talmey and Crehan, the plating bath is continuously or periodically regenerated by the addition of nickel cations and hypophosphite ions, thereby to compensate the same for the depletion of these ions resulting from the plating reactions mentioned. Also, these plating reactions in the plating bath are productive of hydrogen ions, whereby hydroxyl ions are added in the regeneration to maintain the desired pH of the plating bath.

While this method greatly extends the useful life of the plating bath, it does not prevent the build-up of phosphite anions and alkali metal salts therein (assuming that the regeneration involves the addition of nickel sulfate, sodium hypophosphite and sodium hydroxide); whereby ultimately it is necessary to discard the plating bath, as a result of the build-up of high concentrations therein of phosphite anions, sulfate anions and sodium cations. Specifically, care must be exercised in this connection to prevent precipitation of nickel phosphite in the plating bath, since such precipitate serves as growth nuclei for the formation of "metallic precipitate" therein, with the resulting "random decomposition" of the plating bath. Specifically, the reactions involving the formation of the metallic precipitate in the plating bath are autocatalytic; whereby the formation of any substantial metallic precipitate therein effects the total decomposition of the plating bath very quickly and throughout the body thereof entirely at random and altogether independently of the catalytic surface of the body undergoing the plating operation.

Thus, a chemical nickel plating bath becomes "spent" when the phosphite anion concentration therein approaches the threshold of insolubility of nickel phosphite, and must be discarded, so as to prevent the possibility of random decomposition thereof in the plating system.

The spent chemical nickel plating bath contains valuable nickel, hypophosphite and phosphite, as well as sodium and sulfate; whereby it is ordinarily subjected to gross nickel salvage by treatment that induces random decomposition thereof, the residue of the plating bath comprising an aqueous liquid having the previously mentioned metallic precipitate suspended therein. The matter of the treatment of the chemical nickel plating bath to induce random decomposition thereof is exceedingly easy, as this phenomenon involves the previously mentioned reactions that are autocatalytic; whereby the reactions, once initiated, rapidly spread throughout the plating bath and proceed substantially on a quantitative basis with respect to the two ingredients (nickel cations and hypophosphite anions) with the formation therein of the metallic precipitate mentioned. Thus, all of the nickel cations in the plating bath are depleted in the presence of the normal slight excess of hypophosphite anions; whereby the subsequent recovery of the metallic precipitate from the aqueous liquid effects the complete recovery of the nickel cations from the residue of the spent chemical nickel plating bath.

The initiation of the reactions mentioned is also exceedingly simple, as it is noted that a chemical nickel plating bath is normally in a metastable state and is subject to "spontaneous decomposition." Specifically, the simplest procedure of initiating the reactions is to seed the spent chemical nickel plating bath with a small quantity of previously produced metallic precipitate or a small quantity of any catalytic material in finely divided form, such as iron, cobalt, nickel, palladium, etc. Palladium is highly catalytic and may be employed even in the form of an aqueous solution of a salt thereof, such as the chloride, sulfate, etc. Also, the reactions in the spent chemical plating bath may be initiated by appropriately increasing the pH thereof, by raising the temperature thereof to the boiling point, etc. Since the reactions are auto-

catalytic, as previously noted, it is very convenient, as a matter of manipulation, to initiate the same in a small quantity of the spent chemical nickel plating bath contained in a beaker, or the like, and then return the contents of the beaker into the vat or tank containing the bulk of the spent chemical nickel plating bath, thereby seeding the reactions in the bulk of the spent chemical nickel plating bath, in an obvious manner.

Heretofore, chemical nickel platers have returned the metallic precipitate thus salvaged from spent chemical nickel plating baths to initial nickel processors; whereby such processors, in turn, have recovered the nickel content of the metallic precipitate by smelting operations, involving reducing agents; whereby the crude metallic nickel thus recovered has been refined by electrolytic operations for further use. Although, these nickel processors have been informed of the fact that the metallic precipitate thus salvaged from a spent chemical nickel plating bath also contains substantial phosphorus, they have always treated this contained phosphorus as "just another impurity" encountered in the smelting of nickel ores; whereby the phosphorus content of the metallic precipitate has been totally wasted in these smelting operations.

Perhaps the primary reason for this gross salvage of only the nickel ingredient of this metallic precipitate by the nickel processors has been a total misconception of the fundamental character and composition thereof. Recently, this metallic precipitate has been discovered to be an amorphous solid comprising a metastable undercooled solution of phosphorus in nickel, and having no specific composition, but normally containing, as produced incident to the random decomposition of a chemical nickel plating bath of the nickel cation-hypophosphite anion type, constituents comprising about 88 to 94% nickel and 6 to 12% phosphorus by weight. The phosphorus content is affected by the excess of both hypophosphite anions and phosphite anions in the spent chemical nickel plating bath, but only within the narrow range mentioned. Specifically, a high phosphite anion content, or a high hypophosphite anion content, in the spent chemical nickel plating bath insures that incident to random decomposition thereof the metallic precipitate produced will have a high phosphorus content within this narrow range, but the presence of phosphite anions in the spent chemical nickel plating bath is by no means essential to the production of a high phosphorus content in the metallic precipitate. In fact, the metallic precipitate produced incident to the random decomposition of a pure simple freshly prepared standard aqueous solution of nickel sulfate and sodium hypophosphite always contains phosphorus in the range 6 to 12% by weight, frequently has a phosphorus content as high as 10% by weight, and occasionally has a phosphorus content as high as 12% by weight. This phenomenon is not really understood, as the random decomposition of the same standard solution in two separate batches is not necessarily productive of identical samples of metallic precipitate, as to phosphorus content. It is suggested that the average character of the ultimately produced metallic precipitate may be greatly influenced by the character of the first few nuclei of the metallic precipitate that form in the solution, since the reaction is autocatalytic, and the character of these first few nuclei may depend entirely upon probability, within a very narrow range of permissible character.

Next, it has been discovered that when this metallic precipitate is heated to a temperature of about 400° C. an irreversible structural change occurs therethrough in an exceedingly short time interval, whereby the phosphorus that was in solution in the nickel reacts with the nickel to produce nickel phosphide (Ni_3P), which latter compound is dispersed in the form of micro-crystals in a matrix of nickel in the resulting mass. As the temperature of this resulting mass is elevated, the Ni_3P crys-

tals grow in the nickel matrix until ultimately a melt is obtained in the temperature range 880° C. to 1100° C., depending upon composition; whereby the nickel and phosphorus constituents are in equilibrium.

These considerations will be best understood by reference to FIG. 1 of the drawings, wherein there is illustrated a portion of the nickel-phosphorus system that is pertinent to the nickel-phosphorus compositions produced by the melting of the metallic precipitate noted. Specifically, it was discovered that the eutectic composition comprises nickel and phosphorus constituents containing about 89% nickel and 11% phosphorus by weight, and that the eutectic temperature is about 880° C. On the curve 11, the melting point of nickel (1453° C.) is indicated at 12, and the eutectic point is indicated at 13. Also, from the curve 11, it will be observed that a composition containing about 5% phosphorus has a melting point of about 1150° C., a composition containing about 6% phosphorus has a melting point of about 1100° C., a composition containing about 10% phosphorus has a melting point of about 950° C., and a composition containing about 12% phosphorus has a melting point of about 950° C.

The eutectic composition of the system is not completely understood, since it appears that it involves fundamentally nickel and Ni_3P , and since the proportions by weight are not in strict accordance with Dalton's law; however, repeated and accurate analysis always yields this ratio of nickel and phosphorus by weight, and only nickel and Ni_3P have been detected in the alloy.

All of the compositions that are produced by melting of the metallic precipitate noted contain nickel and phosphorus in the previously mentioned range by weight (about 88–94% nickel and 6–12% phosphorus); and most of the compositions fall in the even more limited range containing about 90–93% nickel and 7–10% phosphorus by weight. Thus, it will be understood that when the metallic precipitate is heated to a temperature sufficiently high to melt the same, a melt is produced in which the nickel and phosphorus constituents are in equilibrium above the curve 61 of the phase diagram FIG. 1. Upon subsequent cooling, the melt becomes supersaturated with nickel in the event the phosphorus content of the composition is below 11%; whereas upon subsequent cooling, the melt becomes super-saturated with Ni_3P in the event the phosphorus content of the composition is above 11%. Specifically, in the event there is a deficiency of phosphorus the melt becomes supersaturated with nickel, upon subsequent cooling; whereby solid nickel is formed in the solution of the eutectic as the composition of the solution moves downwardly and toward the right along the curve 61 and toward the eutectic point 63; hence, when the cooling of the melt proceeds to the eutectic temperature of about 880° C. considerable solid nickel is present in the solution of the eutectic composition, so that upon further cooling of the mass, this solid nickel is productive of primary nickel crystals in the mass of the eutectic composition that appear as substantial nickel dendrites dispersed in the fine crystals of nickel and Ni_3P comprising the fundamental constituents of the eutectic composition. Specifically, in the event there is an excess of phosphorus, the melt becomes supersaturated with Ni_3P , upon subsequent cooling; whereby solid Ni_3P is formed in the solution of the eutectic as the composition of the solution moves downwardly and toward the left along the curve 61 and toward the eutectic point 63; hence, when the cooling of the melt proceeds to the eutectic temperature of about 880° C., considerable solid Ni_3P is present in the solution of the eutectic composition, so that upon further cooling of the mass, this solid Ni_3P is productive of primary Ni_3P crystals in the mass of the eutectic composition that appear as small crystals of Ni_3P dispersed in the fine crystals of nickel and Ni_3P comprising the fundamental constituents of the eutectic composition. Ac-

cordingly, it is the melting of the metallic precipitate noted, followed by the subsequent cooling and solidifying of the melt, that is productive of the nickel-phosphorus alloy characterized by the eutectic composition having dispersed therein the primary crystals mentioned. As previously noted, in this metallic precipitate, there is normally an excess of nickel in the composition, whereby the nickel-phosphorus alloys produced is normally characterized by the dispersion therein of nickel dendrites.

From a broad point of view, as a matter of definition, the original nickel-phosphorus material resulting directly from the nickel cation-hypophosphite anion reaction (the amorphous solid material described) may be termed as "alloy," although it is not characterized by the eutectic composition noted; however, it is preferably to apply the term "alloy" to the final nickel-phosphorus material that results from the melting and subsequent solidifying of the original material mentioned, since this final material is characterized by the eutectic composition noted. Thus, hereinafter the term "alloy" will be used only to refer to this final material.

Now this nickel-phosphorus alloy is substantially different, as to characteristics and structure, from the solid nickel-phosphorus material that is chemically plated from a plating bath of the nickel cation-hypophosphite anion type and from the solid nickel-phosphorus material of the metallic precipitate. For examples, this nickel-phosphorus alloy is substantially magnetic, whereas the nickel-phosphorus plating and the metallic precipitate are substantially non-magnetic; and the specific resistance of this nickel-phosphorus alloy is considerably less than that of the nickel-phosphorus plating or the metallic precipitate. There are also many other physical and structural differences between this nickel-phosphorus alloy and the nickel-phosphorus plating and the metallic precipitate that are not here discussed at length in the interest of brevity.

Moreover, it will be understood that while the metallic precipitate must be melted to effect the production of the nickel-phosphorus alloy described above, it is not necessary to maintain the condition of the melt for any particular time interval.

The method of making the nickel-phosphorus alloy, described above, from the spent chemical nickel plating bath not only provides an efficient scheme of salvaging valuable nickel and phosphorus therefrom, but provides an exceedingly valuable alloy having many important uses, as explained more fully hereinafter, and it is emphasized that the salvage method is applicable to a wide variety of chemical nickel plating baths, such, for example, as those disclosed in the following U.S. Patents: No. 2,532,283, Brenner and Riddell; No. 2,658,841, Gutzeit and Krieg; and No. 2,658,842, Gutzeit and Ramierz. Thus, the chemical nickel plater may select the chemical nickel plating bath that is best suited to his particular operation, and subsequently subject the spent chemical nickel plating bath to salvage in accordance with the present method, and regardless of the particular composition of the chemical nickel plating bath.

A preferred chemical nickel plating bath of extremely wide utility is disclosed in the copending application of Gregoire Gutzeit, Paul Talmey and Warren G. Lee, Serial No. 479,088, filed December 31, 1954, now Patent No. 2,822,293, granted February 4, 1958, this particular plating bath being admirably suited to the continuous plating process disclosed in the Talmey and Crehan patent. The chemical plating bath of the Gutzeit, Talmey and Lee application mentioned essentially comprises an aqueous solution of a nickel salt, a hypophosphite, a complexing agent selected from the group consisting of lactic acid and salts thereof, and an exalting additive selected from the group consisting of propionic acid and salts thereof. In this plating bath, the absolute concentration of hypophosphite is within the range 0.15 to 1.20 moles/liter, the ratio between nickel ions and hypophosphite ions is within the range 0.25 to 1.60, the absolute concentration of lactic

ions is within the range 0.25 to 0.60 mole/liter, the absolute concentration of propionic ions is within the range 0.025 to 0.060 mole/liter, and the pH is within the approximate range 4.0 to 5.6.

This particular chemical nickel plating bath is most satisfactory in carrying out a wide variety of nickel plating operations; and, of course, when it becomes spent, it may be subjected to the present salvage method to produce the nickel-phosphorus alloy previously described.

It has also been discovered that the "stray" plating that may occur in an undesirable manner in a chemical nickel plating system of the character of that of the Talmey and Crehan patent may also be employed in the production of the nickel-phosphorus alloy described in the general manner disclosed above. In other words, this stray plating that accumulates in the bottom of the tank in which the chemical nickel plating bath is stored, in the filters of the system, etc., may be accumulated and melted in the manner described above, either alone or with the metallic precipitate mentioned, in order to produce the nickel-phosphorus alloy described. In fact, it has recently been discovered that this stray plating is also an amorphous solid comprising a metastable undercooled solution of phosphorus in nickel, and having no specific composition, but normally containing, as produced, constituents comprising about 88 to 94% nickel and 6 to 12% phosphorus by weight. Since the metallic precipitate mentioned and the stray plating mentioned are substantially identical, as a matter of composition, they may be melted together in order to produce the nickel-phosphorus alloy described.

As a matter of convenience in handling, the molten nickel-phosphorus alloy described may be cast into rods, bars, or other commercial forms, for subsequent use; whereby, such forms of the alloy, within themselves, comprise useful articles of convenience.

This method of making the nickel-phosphorus alloy is disclosed and claimed in the previously mentioned application of Crehan, Klouse and Talmey, Serial No. 514,472, filed June 10, 1955.

Turning now to the utility of the nickel-phosphorus alloy that is produced by the present method, it is first noted that in a molten condition, it has very pronounced wetting and bonding characteristics; whereby it is generally useful as a coating material, and may be readily applied in a great variety of ways to a vast array of different base metal bodies after they have been subjected to standard degreasing, cleaning and pickling operations. Specifically, such an alloy coating may be applied to the cleaned surface of a base metal body by any one of the following groups of steps, in accordance with the present method:

(1) The cleaned base metal body is heated, and the alloy in molten condition is poured over the hot body in order to apply a "cast" coating of the alloy upon the body.

(2) The cleaned base metal body, at ambient temperature, is immersed in a molten mass of the alloy, and subsequently withdrawn with respect thereto, in order to apply a "hot-dipped" coating of the alloy upon the body.

(3) A mass of the alloy, at ambient temperature and in finely divided form, is sprinkled upon the cleaned surface of the base metal body, the body having been previously heated to a high temperature, in order to apply a "melted" coating of the alloy upon the body.

(4) A mass of the alloy, at ambient temperature and in finely divided form, is placed upon the cleaned surface of the base metal body, at ambient temperature, and the body and the carried alloy are transferred to a furnace or oven and heated, in order to apply an "oven melted" coating of the alloy upon the body.

(5) A portion of a bar of the alloy is melted with a torch, or the like, onto the heated and cleaned surface of the base metal body, in order to apply a "tinned coating" of the alloy upon the body.

(6) A mass of the metallic precipitate, or the stray plating in finely divided form, is sprinkled upon the

cleaned surface of the base metal body, the body having been previously heated to a high temperature, in order to melt the mass, whereby upon subsequent cooling and solidifying of the melt, the alloy coating is formed in situ upon the body.

(7) A mass of the metallic precipitate, or the stray plating in finely divided form, is placed upon the cleaned surface of the base metal body, at ambient temperature, and the body and the carried mass are transferred to a furnace or oven and heated in order to melt the mass, whereby upon subsequent cooling and solidifying of the melt, the alloy coating is formed in situ upon the body.

(8) A portion of a bar of the compressed metallic precipitate, or the stray plating, is melted with a torch, or the like, onto the heated and cleaned surface of the base metal body; whereby upon subsequent cooling and solidifying of the melt, the alloy coating is formed in situ upon the body.

The foregoing suggestions are merely illustrative of the many ways in which the previously prepared alloy may be applied as a coating upon a body and in which the alloy may be made in situ from the melted metallic precipitate, or the stray plating, applied as a coating upon a body; and many other modes of producing such coatings will be immediately apparent to those skilled in the tinning, soldering, brazing, galvanizing and other metal-coating arts.

Turning now to the character of the base metal of the body that may be coated with this alloy, it is noted that the only limitation that has been discovered is that it must have a melting point sufficiently high that it is not appreciably melted in contact with the molten alloy at a temperature in the general range 880° C. to 1100° C., as the molten alloy must be heated to a temperature in this general range to obtain the desired liquid condition thereof. Also, the alloy in molten condition must wet and bond with respect to the cleaned surface of the base metal, but this condition does not comprise a substantial limitation, as the wetting and bonding characteristics of the molten alloy are outstanding; whereby even chrome-alloys and aluminum alloys are readily wet and bonded thereby. These peculiar wetting and bonding characteristics of the molten alloy are believed to flow from the circumstance that the phosphorus constituents of the melt are capable of reducing chromic oxide, as well as the various oxides of aluminum. In any case and without reference to the exact mechanism involved, the wetting and bonding characteristics of this nickel-phosphorus alloy are unusual; whereby there is no difficulty in producing satisfactory coatings upon the cleaned surfaces of a great variety of bodies formed of base metals, precious metals, or alloys thereof; which coatings are useful either as final protective coatings for the bodies thus coated or as uniting layers employed in securing such bodies to still other such bodies.

As a matter of fact, the present method removes a limitation with respect to the conventional chemical nickel plating process and concerning the catalytic character of the base metal. More particularly, in order to obtain plating upon the cleaned surface of a base metal from a chemical nickel plating bath of the nickel cation-hypophosphite anion type, the surface of the base metal must be catalytic to the plating reactions involved, so as to bring about the chemical reduction of the nickel cations and the deposition of the resulting metallic nickel, and the companion oxidation of hypophosphite anions to phosphite anions; all as previously explained in the Talmey and Crehan patent. However, in accordance with the present method, the nickel-phosphorus alloy has been previously produced, or is produced in situ incident to the cooling and solidifying of the melted metallic precipitate, or the stray plating; whereby it is not critical that the cleaned surface of the base metal be catalytic in order to obtain a coating thereon with the previously produced alloy, or the alloy thus produced in situ.

This method of coating the base metal body with this nickel-phosphorus alloy is disclosed and claimed in the copending application of William J. Crehan, Walter F. Klouse and Paul Talmey, Serial, No. 678,683, filed August 16, 1957.

Referring now to FIGS. 2 and 3A, there is illustrated a fragmentary portion of a metal wall 100 that is provided with a coating 101 that has been chemically deposited thereon from a plating bath of the nickel cation-hypophosphite anion type previously described; which coating 101 is assumed to have a break or hole 101a therein. For example, the metal wall 100 may comprise two steel sheets 102 and 103 that have been butt-welded together, as indicated by the weld bead 104; and further, it is assumed that the hole 101a in the coating 101 occurs at a position therein disposed over a section of the weld bead 104. As previously explained, the coating or layer 101 comprises an amorphous solid material consisting essentially of a metastable undercooled solution of phosphorus in nickel, and including about 88 to 94% nickel and 6 to 12% phosphorus by weight; whereby heretofore it has been virtually impossible satisfactorily to repair holes in the layer 101 of the character described.

Now in the present example, it may be assumed that the hole 101a appears in the layer 101 by virtue of the circumstance that the corresponding portion of the surface of the composite steel plate 101 was not properly cleaned prior to the chemical plating step. On the other hand, it may be assumed that the hole 101a appears in the layer 101 by virtue of the fact that the associated portion of the layer 101 has been struck by a sharp instrument incident to the fabrication of some composite industrial article involving the metal wall 100. In any case, in order to achieve the repair utilizing the alloy of the present invention, the surface of the metal wall 101 disposed below the hole 101a in the layer 101 is first prepared by degreasing, cleaning and light pickling, employing a suitable acid, such as hydrochloric acid. Thereafter, as shown in FIG. 3B a patch or layer 105 of the alloy previously described is applied in molten condition to the cleaned surface of the metal wall 100 disposed below the hole 101a in the layer 101, whereby upon subsequent cooling and solidifying of the alloy, the patch 105 is intimately bonded to the surface of the metal wall 100 and to the adjacent surrounding surface of the layer 101. Specifically, in applying the patch 105 the prepared surface of the metal wall 100 should be heated, along with the bar of nickel-phosphorus alloy, so that as a portion of the alloy bar is melted, the melt is received upon the hot prepared surface of the metal wall 100; this step being virtually identical to that involved in a conventional soldering or brazing operation.

This arrangement is very advantageous, as it will be apparent that when the metal wall 100 is fabricated from the sheets 102 and 103 that have been previously provided with individual coating sections 101, there is always a seam between the meeting coating sections 101, since the heat involved in the production of the weld 104 invariably melts back the adjacent edges of the two coating sections 101; whereby the composite coat 101 carried by the resulting fabricated metal wall 100 is not continuous. In this case, the break or seam between the two coating sections 101 may be repaired, in the manner described above, so as to render entirely integral and of one-piece, the composite coating 101 carried by the metal wall 100. This arrangement permits of the ultimate production of the composite metal wall 100 carrying the unbroken integral and continuous layer or liner 101 of the character described.

Also in view of the foregoing description of the method of making the nickel-phosphorus alloy, it will be understood that the hole 101a in the layer 101 carried by the metal wall 100, as shown in FIGS. 2 and 3A, may be repaired employing the previously produced nickel-phosphorus alloy in finely divided form or employing the

metallic precipitate previously described or the stray plating previously described. In this case, a mass of the previously produced nickel-phosphorus alloy in finely divided form, a mass of the metallic precipitate, or a mass of the stray plating in finely divided form is placed directly in the hole 101a in the layer 101 and upon the exposed cleaned surface of the metal wall 100; and then the mass mentioned and the metal wall 100 are subjected to heat, employing a suitable flame, or the like, so as selectively to melt the mass mentioned in order that the resulting melt is flowed into wetting and bonding relation with the previously cleaned surfaces.

Subsequently, incident to cooling and solidifying of the melt, the patch 105 is produced, and of course comprises the previously described nickel-phosphorus alloy, regardless of the character of the initial material, as described above, in view of the considerations previously explained. This arrangement is also very advantageous, as it readily accommodates the patching of small holes or punctures 101a in the layer 101 in a simple and ready manner.

In conjunction with this utilization of the materials noted, in the repairing of holes or breaks in previously deposited layers of this type, it is recommended that when a flame is employed for heating purposes, that it be of the reducing type, such, for example, as is achieved by conventional atomic hydrogen welding equipment. Not only is the atomic hydrogen flame intensely hot, but it also exhibits a remarkable reducing effect upon any oxides that might remain upon the cleaned surface of the metal body that is exposed through the hole in the layer. This recommendation is particularly pertinent when the metal of the supporting wall contains substantial chromium that would otherwise tend substantially to interfere with wetting and bonding. The recommendation is equally applicable to making such repairs when the supporting metal wall is formed of aluminum and its alloys for this reason. As a matter of fact, it is a general recommendation that these repairs be made with an atomic hydrogen flame, as it is ideally suited to the production of the required intense localized heating effect, and the reducing effect thereof is always helpful in positively insuring the removal of oxides that have a general tendency to interfere with wetting and bonding.

The present method is applicable to the repairing of nickel-phosphorus coatings applied to bodies containing substantial chromium, notwithstanding the usual interference of the chromium with wetting and bonding by the formation of chromic oxide upon the surface of the body containing any substantial amount of chromium. It is believed that there is no difficulty in this regard in carrying out the present method due to the fact that the phosphorus constituents of the melt are capable of reducing chromic oxide, thereby accounting for the unusual wetting and bonding characteristics of the nickel-phosphorus alloy described. In any case and without reference to the exact mechanism involved, the wetting and bonding characteristics of this nickel-phosphorus alloy are unusual; whereby there is no difficulty in obtaining adhesion to a metal body having a high chromium content. These wetting and bonding characteristics are by no means peculiar to chromium, but are general characteristics; whereby aluminum and its alloys are readily wetted and bonded by the melt, notwithstanding the usual aluminum oxides on the surfaces of such aluminum alloy bodies.

Reconsidering the present method, since the nickel-phosphorus coating that is to be repaired is applied by chemical deposition from a chemical nickel plating bath of the type noted upon the base metal body, it is inherent in the arrangement that the surface of the body must be formed of catalytic material. Now while there are a great number of catalytic metals that are suitable, those that are more important industrially comprise: iron, cobalt, nickel, aluminum, copper, silver, gold, palladium and platinum, as well as the alloys of such elements.

However, the body may be formed of one of the following elements or alloys: iron, carbon-steel, chrome-steel, cobalt-steel, silicon-steel, manganese-steel, nickel-steel, molybdenum-steel, nickel-cobalt-steel, nickel-chrome-steel, chrome-manganese-steel, manganese-molybdenum-steel, chrome-copper-nickel-steel, copper, brass, bronze, silicon-bronze, phosphor-bronze, beryllium-copper, cadmium-copper, chromium-copper, nickel-copper, aluminum, aluminum-brass, aluminum-bronze, silver, palladium-silver, nickel-silver, copper-silver, zinc-copper-silver, zinc-cadmium-copper-silver, gold, copper-gold, copper-silver-platinum-gold, copper-silver-palladium-gold, platinum, gold-platinum, silver-platinum, iridium-platinum, rhodium-platinum, palladium-platinum, tungsten-platinum, nickel-platinum, ruthenium-platinum, gold-silver-platinum, palladium-gold-platinum, palladium, copper-gold-palladium, nickel, chromium-nickel, and cobalt.

In view of the foregoing, it is apparent that there has been provided an improved method of repairing with a patch a break or hole in a chemically deposited layer or liner carried by an associated supporting wall.

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 method of repairing a hole, or other break, in a coating that has been chemically deposited upon a metal support from a plating bath of the nickel cation-hypophosphite anion type; which method comprises cleaning both the surface of said metal support exposed through the hole in said coating and the adjacent surface of said coating surrounding the hole therein, and applying a melt of nickel-phosphorus material in the hole in said coating and upon said cleaned surfaces, said material comprising about 88 to 94% nickel and 6 to 12% phosphorus by weight, whereby upon subsequent cooling and solidifying of said melt a nickel-phosphorus alloy patch is provided that is intimately bonded to said cleaned surfaces, said alloy being characterized by an eutectic composition comprising constituents containing about 89% nickel and 11% phosphorus by weight and having an eutectic temperature of about 880° C.

2. The method set forth in claim 1, wherein the metal of said support contains sufficient chromium substantially to interfere with ready wetting and bonding.

3. The method of repairing a hole, or other break, in a coating that has been chemically deposited upon a metal support from a plating bath of the nickel cation-hypophosphite anion type; which method comprises cleaning both the surface of said metal support exposed through the hole in said coating and the adjacent surface of said coating surrounding the hole therein, arranging a mass of solid nickel-phosphorus material in the hole in said coating and upon said cleaned surfaces, said material comprising about 88 to 94% nickel and 6 to 12% phosphorus by weight, and then heating said mass in order to melt the same and to flow the resulting melt into wetting and bonding relation with said cleaned surfaces, whereby upon subsequent cooling and solidifying of said melt an alloy patch is provided that is intimately bonded to said cleaned surfaces, said alloy being characterized by an eutectic composition comprising constituents containing about 89% nickel and 11% phosphorus by weight and having an eutectic temperature of about 880° C.

4. The method set forth in claim 3, wherein said material as applied in the hole in said coating and upon said cleaned surfaces consists essentially of an amorphous solid undercooled solution of phosphorus in nickel.

5. The method set forth in claim 3, wherein said heating of said mass is effected with an atomic hydrogen flame.

6. The method set forth in claim 3, wherein said mass

as applied in the hole in said coating and upon said cleaned surfaces is in finely divided form.

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