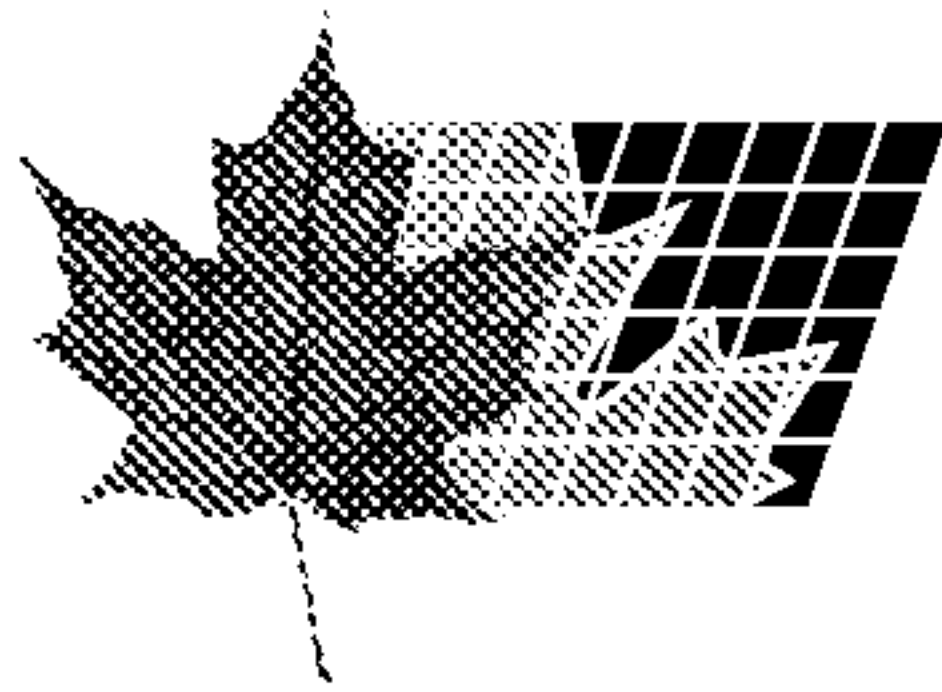




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(54) **REVETEMENTS DE CONVERSION A BASE DE PHOSPHATE
AU NICKEL-ZINC**

(54) **NICKEL-ZINC PHOSPHATE CONVERSION COATINGS**

(57) L'invention concerne un procédé permettant d'appliquer un revêtement sur une surface métallique, par conversion à base de phosphate. Ce procédé consiste a) à produire une solution aqueuse de traitement acide contenant des ions de phosphate, des cations de zinc, et des cations de nickel (II), ladite solution possédant entre environ 2,1 et 6,0 points d'acide libre; et b) à mettre en contact ladite surface métallique avec la solution de traitement pendant une durée et à une température suffisantes pour former un revêtement de conversion à base de phosphate sur la surface métallique. L'invention concerne également un objet métallique recouvert à l'aide de ce procédé, le pourcentage grammes/atomes de nickel par rapport à la quantité totale de nickel et de zinc contenue dans le revêtement étant environ entre 10 et 13.

(57) A method of applying a phosphate conversion coating to a metal surface, including the steps of: (a) providing an aqueous, acidic treatment solution comprising: phosphate ions; zinc cations; and nickel (II) cations; wherein the treatment solution has between about 2.1 and about 6.0 points of free acid; and (b) contacting the metal surface with the treatment solution for a time and at a temperature sufficient to form a phosphate conversion coating on the metal surface. A metal object coated in this manner is also provided, and the gram-atom percent of nickel to the total amount of nickel and zinc in the coating is between about 10 and about 13.

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(54) Title: NICKEL-ZINC PHOSPHATE CONVERSION COATINGS		
(57) Abstract A method of applying a phosphate conversion coating to a metal surface, including the steps of: (a) providing an aqueous, acidic treatment solution comprising: phosphate ions; zinc cations; and nickel (II) cations; wherein the treatment solution has between about 2.1 and about 6.0 points of free acid; and (b) contacting the metal surface with the treatment solution for a time and at a temperature sufficient to form a phosphate conversion coating on the metal surface. A metal object coated in this manner is also provided, and the gram-atom percent of nickel to the total amount of nickel and zinc in the coating is between about 10 and about 13.		

NICKEL-ZINC PHOSPHATE CONVERSION COATINGS

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BACKGROUND OF THE INVENTIONField of the Invention

10 The present invention relates to nickel-zinc phosphate conversion coatings. More particularly, the present invention provides a nickel-zinc phosphate conversion coating, metals having such coatings, and methods for applying a nickel-phosphate conversion coating to metal.

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Description of Related Art

Phosphate conversion coatings have been applied to metals for many years in order to improve corrosion resistance, as well as to improve the adhesion of organic coatings (particularly paint). These phosphate conversion
20 coatings are, in general, formed by a chemical interaction between the metal substrate and a treatment solution containing phosphate anions and divalent metal cations. Zinc is the most common metal cation employed, however other divalent metal cations are often used in combination with zinc, including nickel, cobalt, calcium, manganese, and magnesium. The treatment

compositions generally comprise an acidic, aqueous solution containing phosphate ions, one or more divalent cations (particularly zinc), and, optionally, oxidizing agents (such as nitrates), and other additives.

5 Phosphate conversion coatings, however, will dissolve in alkaline solutions, thereby reducing their effectiveness. While paint or other organic coatings applied over the phosphate conversion coating will generally prevent alkaline dissolution of the coating, the paint layer may become damaged (such as a scratch on the panel of an automobile), thereby exposing the phosphate
10 conversion coating. Alkaline environments, such as those created by the presence of sodium chloride, will dissolve the phosphate conversion coating in the region of paint damage. The result is a delamination of the paint from the metal surface in the area surrounding the initial damage (e.g. a scratch in the paint).

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As mentioned previously, phosphate conversion coatings, particularly those including zinc cations, have been used for many years. Exemplary coatings and treatment solutions are described in U. S. Patent Nos. 4,681,641, 5,236,565, 5,238,506, and 5,082,511. U. S. Patent No. 4,681,641 ("the '641
20 patent"), for example, describes a phosphate conversion coating which includes both zinc and nickel cations, with the molar ratio of these cations carefully controlled in a specific, narrow range. Many commercially-available products, however, generally require lengthy contact periods. In the '641 patent, the contact time (i.e., the time of immersion or spraying required to

achieve satisfactory results) is specified as being about 30-120 seconds, at a temperature of 100–140°F. In a commercial embodiment of the '641 patent, a contact time of 10–12 seconds has been recommended, however such increased processing speeds require a temperature of 160°F or above. The higher temperature of the treatment solution will provide for a faster reaction between the conversion coating and the metal substrate, which presumably allows for processing times which are shorter than that described in the '641 patent. Such higher temperatures, however, will obviously result in increased manufacturing costs. Any attempt to reduce the contact time below the minimum can result in incomplete and insufficient coating (i.e., void areas on the metal substrate wherein the conversion coating is not present).

Thus, there is a need for phosphate conversion coatings which provide corrosion resistance and paint (or other organic coating) adhesion, using more forgiving process conditions. Since the application of conversion coatings is merely one step in a generally lengthy process of manufacturing metal articles (such as steel panels of automobiles), the phosphate conversion coatings should provide corrosion resistance and paint adhesion while operating over a wide range of process conditions (e.g., lower temperatures and shorter contact times). Even more preferably, there is a need for phosphate conversion coatings which provide improved corrosion resistance and paint adhesion, even when the application time has been reduced and other cost-reducing adjustments in the process are employed (such as lower processing temperatures).

SUMMARY OF INVENTION

It is an object of the present invention to provide an improved phosphate conversion coating.

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It is another object of the present invention to provide an improved phosphate conversion coating which employs zinc and nickel cations.

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It is yet another object of the present invention to provide a method of preventing corrosion of metals, wherein a treatment composition comprising an acidified solution including phosphate ions, as well as nickel and zinc cations, is applied to the metal surface.

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The foregoing objects can be accomplished, in accordance with one aspect of the present invention, by providing a method of applying a phosphate conversion coating to a metal surface, comprising:

- (a) providing an aqueous, acidic treatment solution comprising:
 - phosphate ions;
 - zinc cations; and
 - nickel(II) cations;

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wherein the treatment solution has between about 2.1 and about 6.0 points of free acid; and

(b) contacting the metal surface with the treatment solution for a time and at a temperature sufficient to form a phosphate conversion coating on the metal surface.

Preferably, the total acid in the treatment solution is between about 30 and about 50 points, and the ratio of total acid to free acid is between about 5 and about 24. The gram-atom percent of nickel to the total amount of nickel and zinc in a preferred treatment solution is less than 83. A preferred embodiment of the treatment solution may also contain between about 3000 to about 8000 mg/l nickel (II) cations, and may further include nitrate and fluoride ions. Between about 8000 and about 20,000 mg/l nitrate anions, and between about 400 and about 2000 mg/l fluoride anions may be present in such preferred treatment solution.

The above method may be employed, for example, on a zinc-coated metal (such as steel). The treatment solution is preferably applied at a temperature of between about 135 and about 160 deg. F, for a period of between about 3 and about 20 seconds. A metal object having a nickel-zinc phosphate conversion coating thereon is also provided, wherein the gram-atom percent of nickel to the total amount of nickel and zinc in the coating is between about 10 and about 13. The phosphate conversion coating may be applied by the methods of the present invention. The metal object may also have a zinc coating beneath the conversion coating, and the object may be painted over top the conversion coating.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Applicants have surprisingly found that an improved zinc-phosphate conversion coating can be obtained by carefully controlling the amounts of total and free acid at unusual levels in the treatment solution, as well as the zinc and nickel concentrations. This new coating allows for faster processing times at reduced temperatures, as well as improved paint adhesion and corrosion resistance. Not only do the reductions in contact time and bath temperature result in significant cost savings and production increases for the end user, there is no sacrifice in paint adhesion or corrosion resistance. Surprisingly, paint adhesion and corrosion resistance are significantly improved, even though the resultant coating on the metal surface has a lower nickel content. The treatment solution of the present invention contains a higher level of free acid than certain prior art compositions, and these high acid levels are also directly contrary to conventional wisdom in the art.

The phosphating treatment solution of the present invention may be substituted for those currently used in preventing corrosion resistance on metals, particularly zinc-coated metals. More particularly, the treatment solution of the present invention provides superior results on steels having a zinc-containing coating, such as hot dip galvanized steel, electrogalvanized steel, and GALFAN®, the latter of which is a steel having a coating which includes zinc and aluminum, and is sold by Weirton Steel Corp., of Weirton, West Virginia. Applicants believe that substitution of the phosphating

treatment solution of the present invention in production lines currently employing other phosphate treatment solutions will provide unexpected and beneficial results, particularly with zinc-coated steel (e.g., galvanized steel). For example, the treatment solution of the present invention may replace those

5 described in the '641, which is incorporated herein by way of reference.

Use of the treatment solution of the present invention is straightforward. As is well known to those skilled in the art, metal surfaces to which a phosphate conversion coating is to be applied should be cleaned prior to

10 application of such coatings, preferably using a standard alkaline cleaner of the type formulated for application to mixed metal continuous coil steel. One such cleaner is sold under the name CHEM CLEAN 150G, by Brent America, Inc.

After, or even in conjunction with, such alkaline cleaning, and as well-

15 known to those skilled in the art, a titanium-conditioning compound should also be applied to the metal. For example, after alkaline cleaning, the metal to be coated should be rinsed in an aqueous suspension of a titanium-conditioning compound (also referred to a "grain refiner"). Numerous types of grain refiners are available and well known to those skilled in the art, and generally comprise

20 a colloidal suspension of titanium phosphate salts which help reduce the size of the ZnPO_4 crystals on the treated metal surface. The composition of the grain refiner can also be tailored to a specific application and/or process conditions present in a particular manufacturing facility. Although such grain refiners should be employed in conjunction with the methods and treatment

solution of the present invention, they form no part of Applicants' claimed invention. Two exemplary types of grain refiners which may be employed in conjunction with the treatment solutions of the present invention are CHEM ADD 6216, sold by Brent America, Inc., and Fixodine® AT, sold by Henkel
5 Surface Technologies. Such grain refiners can even be employed as part of the alkaline cleaning step.

After the conditioning rinse employing a titanium-based colloidal grain refiner, the zinc phosphate treatment solution of the present invention is
10 applied to the metal. Application of the phosphate treatment solution may be accomplished by any of a variety of well-known methods, including spraying or simple bath immersion. Additional details regarding the treatment solution application process are discussed further herein.

15 Following application of the phosphate treatment solution, the coated metal should be rinsed with water (typically at ambient temperature), and thereafter a final chromate rinse should be applied in order to provide additional corrosion protection. Such chromate rinses are well known to those skilled in the art, and generally comprise a dilute solution of chromic acid and
20 trivalent chromium compounds. It is believed that the final chromate rinse covers any pores present in the phosphate conversion coating, thereby improving corrosion resistance when painted. One suitable chromate rinse is CHEM SEAL 6900, which is sold by Brent America, Inc. After the final chromate rinse, the metal is dried, and may thereafter be coated with any of

a variety of organic layers, such as paint, PVC barrier coatings, and laminated plastic films.

Although the above-described procedures have been used for many years, Applicants have surprisingly found that by employing high levels of acid (both free and total acid) in the phosphating treatment solution unexpectedly superior results are obtained. In addition, higher levels of nickel are preferred, in conjunction with a gram-atom ratio of nickel to zinc in the treatment solution which is lower than that suggested in the '641 patent. Applicants believe that higher acid levels, particularly in combination with higher nickel levels and a lower gram-atom ratio of nickel to zinc, result in a treatment solution providing improved corrosion resistance and paint adhesion while allowing for a much wider range of processing conditions. In fact, application times can be reduced, without a need for a corresponding increase in application temperature. Although the ratio of nickel to zinc cations in the deposited coating is reduced as compared to the teachings of the '641 patent, for example, corrosion protection and paint adhesion is unexpectedly improved. In addition, the treatment solution of the present invention provides complete coating of the metal substrate with significantly reduced application times (as compared to a commercial embodiment of the '641 patent), thereby significantly increasing processing speeds.

As used herein and unless otherwise specified, all of the concentrations referred to are that of the actual phosphate treatment solution which is applied

to the metal surface. It will be recognized, however, that such treatment solutions are often formulated using various concentrates having higher levels of phosphate, metal cations, and other solution components, as compared to the actual treatment solution. In general, however, whether the treatment solution (or bath) is prepared from one or more concentrated solutions, or is formulated on site using raw solution components, it will have no effect upon the performance of the phosphate treatment solution. Concentrates, however, provide a convenient and economical means by which the treatment solution components may be supplied to end-users. In addition, the use of multiple concentrate solutions may simplify preparation of the treatment solution bath, as well as its replenishment.

Regardless of the manner in which the treatment solution bath is prepared (i.e. whether from concentrates or individual solution components), the treatment solution of the present invention will generally comprise an acidic, aqueous solution comprising at least the following components:

- a. phosphate; and
- b. zinc and nickel (II) cations

The treatment solution also preferably includes an oxidizing agent (or "accelerator"), such as nitrates, as well as fluoride anions (particularly when the metal being treated is a zinc-coated steel such as galvanized steel). It will be understood that while an oxidizing agent will generally be present, particularly since the metal cations will typically be provided in the treatment solution as a salt (such as a metal nitrate), the oxidizing agent merely

accelerates the formation of the coating on the metal surface. It is not deposited on the metal. Likewise, and as well-known in the art, fluoride ions facilitate the necessary dissolution of the metal surface, particularly zinc-coated steel.

5

While the treatment solution should be highly acidic, the required acidity may be provided by a variety of solution components such that the pH is between about 2.3 and about 3.5, more preferably about 2.9 to about 3.2. As further detailed below, however, the amount of total acid and free acid is of more significance than the actual pH of the treatment solution. In fact, Applicants believe that the use of free acid levels above that previously suggested significantly improves the properties of the deposited coating.

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As is well known to those skilled in the art, the phosphate ions of the treatment solution will complex with the divalent metal cations in order to form a phosphate conversion coating which is believed to primarily comprise $\text{Zn}_2\text{Ni}(\text{PO}_4)_2$. While it is generally believed that the nickel-zinc phosphate coating will principally comprise this species, it is also believed that various other nickel-zinc phosphate complexes are formed on the surface of the metal, depending upon the treatment solution composition and other process conditions. Regardless, the nickel-zinc phosphate coatings formed on the surface of the metal according to the procedures of the present invention will have reduced alkaline solubility as compared to other phosphate conversion coatings (such as hopeite, which is the conversion coating formed when only zinc cations are

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present in the treatment solution), as demonstrated by improvements in corrosion resistance and paint adhesion.

Phosphate is generally present in the treatment solution as salts of the divalent metal cations (i.e. nickel and zinc), as well as free orthophosphoric acid (H_3PO_4). As used herein, the amount of phosphate present in the treatment solution of the present invention refers to the total amount of phosphates present, and therefore includes all phosphorous containing anions resulting from the dissociation of phosphate salts, as well as any free phosphoric acid. The phosphate levels are reported herein as PO_4^{3-} . While the phosphate ions may be provided by a variety of starting materials (i.e., "raw ingredients"), it is preferred that phosphoric acid (H_3PO_4) be employed to prepare the treatment solution (either directly or by incorporation into various concentrates used to prepare the actual treatment solution). In this manner, not only are phosphates for the conversion coating provided, but also the necessary acidity.

The amount of phosphate present in the treatment solution is generally not critical, as long as there is enough present to form the dihydrogen phosphate salts with the metal cations ($\text{Zn}(\text{H}_2\text{PO}_4)_2$ and $\text{Ni}(\text{H}_2\text{PO}_4)_2$). It is preferred, however, that a stoichiometric excess of phosphates (as orthophosphoric acid) be employed in order to increase the acidity of the treatment solution bath. This acidity is necessary for reaction with the metal surface, as well as to maintain solubility of the metal dihydrogen phosphates.

It is preferred, therefore, that phosphate be present in the treatment solution bath in a range of about 16,000 to 26,000 mg/l, more preferably between about 18,000 and about 24,000 mg/l.

5 The zinc and nickel (II) cations of the treatment solution generally complex with the phosphates in order to form the conversion coating described above. By increasing the amount of nickel in the treatment solution, while reducing the gram-atom ratio of nickel to zinc in the coating produced on the metal surface (particularly as compared to the narrow ranges specified in the '641 patent), improved corrosion resistance, improved paint adhesion and
10 reduced application times will be achieved. In fact, a preferred embodiment of Applicants' present invention provides a significant increase in line speed (as high as 50%), with improved corrosion resistance and paint adhesion, as compared to a commercial embodiment of the '641 patent.

15 The zinc and nickel (II) cations of the treatment solution will generally be present as dihydrogen phosphates, namely $(\text{Zn}(\text{H}_2\text{PO}_4)_2$ and $\text{Ni}(\text{H}_2\text{PO}_4)_2$. However, as was the case with the phosphates, nickel and zinc cations may be provided by a variety of sources. Preferably, zinc is provided by zinc nitrate, while nickel (II) is provided by nickel nitrate. Use of the metal nitrates
20 has the added benefit of providing necessary nitrate anions. The concentration of zinc is preferably between about 800 and about 2000 mg/l, more preferably between about 1000 and about 1400 mg/l. Nickel should be present at level of between about 3000 and about 8000 mg/l, more preferably between about 4000 and about 6000 mg/l. Nickel is therefore present at a

significantly higher level than that previously suggested, and the beneficial results provided by the elevated amount of nickel level is contrary to what one skilled in the art would have expected.

5 Furthermore, reducing the gram-atom ratio of nickel to zinc cations in the treatment solution as compared to that required in the '641 patent provides improved results. Specifically, the gram-atom ratio of nickel cations to the total amount of divalent metal cations present (i.e., nickel and zinc) in the treatment solution should be less than 83, more preferably between about 70 and 83.

10 In fact, the beneficial and improved results of such treatment solutions is directly counter to the teachings of the '641 patent.

 The treatment solution of the present invention also includes one or more oxidizing agents, such as nitrate, which are a convenient source for

15 anions. Nitrate anions can be provided merely by an addition of nitric acid, which will also provide additional acidity to the treatment solution. Of course other nitrate salts can be employed, provided that the cation does not interfere with the coating process and reaction. The preferred level of nitrates in the treatment solution is between about 8000 and about 20,000 mg/l, more

20 preferably about 10,000 to about 17,000 mg/l.

 Since the treatment solution of the present invention is intended to be used primarily on zinc-coated metals (particularly galvanized steel), those skilled in the art will recognize that the phosphate treatment solution should

include fluoride anions. Fluoride, in an acidic environment, facilitates the initial corrosion step on the metal surface which is necessary for the formation of the conversion coating on the metal surface. Fluoride anions may be contributed by hydrofluoric acid, although other fluoride sources may be used. The preferred level of fluoride in the treatment solution is between about 400 and about 2000 mg/l, more preferably about 800 to about 1200 mg/l.

While the treatment solution of the present invention may include other additives known to those skilled in the art, the components described above are sufficient to provide the unexpected, beneficial results. The treatment solution should, however, contain little or no copper (preferably less than about 0.1 mg/l)

Controlling the acid levels within the treatment solution also provides unexpected improvements. Thus, the amount of total acid should be between about 30 and about 50 points (more preferably about 35 to about 45), and the amount of free acid should be between about 2.1 and about 6.0 points (more preferably about 2.5 to about 4.5). The ratio of total acid to free acid should be between about 5 and about 24, more preferably about 8 to about 12. It is believed that the higher levels of free acid facilitate faster reaction times. Acid levels (both free and total) may be controlled within the bath, for example, by additions of phosphoric acid (to raise acid levels), or sodium hydroxide (to lower acid levels).

As mentioned previously, the treatment solution of the present invention may be formed by simply mixing the various components in water (e.g., phosphoric acid, nickel nitrate, zinc nitrate, nitric acid, hydrofluoric acid, and, if needed, sodium hydroxide). Alternatively, and as preferred, one or more
5 concentrates containing the solution components may be combined in an aqueous solution. Regardless, the metal to be coated is cleaned and conditioned (with a grain refiner), and then either dipped into or sprayed with the treatment solution of the present invention. The treatment solution should be maintained at a temperature of between about 135 and 160 deg. F, more
10 preferably about 140 to about 150 deg. F. The treatment solution should be applied to the metal for a period of between about 3 and about 20 seconds, more preferably about 6 to about 10 seconds. The preferred application time will be the same for spraying or dipping application methods, provided that any dipping is performed in a counter flow cell. Of course it will be recognized that
15 the application time may be increased, if desired, by varying other treatment parameters such as temperature and acidity levels.

As is known to those skilled in the art, the temperature of the phosphate treatment solution will affect the amount of time necessary to ensure proper
20 coating. For example, it is known that higher temperatures will provide a quicker reaction time, which in turn allows for shorter contact time between the metal and the treatment solution. Since application of the phosphate treatment solution is generally accomplished as part of a multi-step process of converting raw metal (in either sheet or roll form) into final, painted components (such as

metal panels of an automobile), reductions in the time necessary for application of the phosphate conversion coating can be a critical factor in increasing factory throughput. Of course, any increase in required temperature for the treatment solution, however, will also increase operating costs and may adversely affect the quality of the resulting coating. Therefore, it is always desirable to provide for the fastest coating application while minimizing temperature requirements.

The treatment solution of the present invention also allows for a much broader range of operating conditions than commercially available products. For example, shorter contact times allow for increased line speed when needed. The acceptable temperature range for proper application is also both lower and broader. Likewise, the acceptable total and free acid ranges are broader and much more forgiving than commercially available products. The result is a faster process at lower temperatures, with a reduced need for precise control of the treatment conditions.

After the treatment solution has been applied, the metal is rinsed in water (preferably at ambient temperature), and thereafter chromate rinsed in the usual manner. Various types of chromate rinses well known to those skilled in the art may be used, particularly hexchrome/trichrome solutions or non-chromated equivalents. After standard drying, the coated metal surface is ready for painting.

Application of the treatment solution of the present invention, in the above-described manner, provides a phosphate conversion coating containing both nickel and zinc. Unlike the coating produced in the '641 patent, the treatment solution of the present invention provides a coating wherein about 5 10% to about 13% of the total amount of nickel and zinc in the coating comprises nickel (on a gram-atom basis). This can be alternatively characterized as a gram-atom percent of zinc to nickel in the phosphate conversion coatings according to the present invention of between about 6.7 and about 9.0. In the '641 patent, on the other hand, the coating comprises 10 15% to 43% nickel (on a gram-atom basis, as a percent of the total nickel and zinc in the coating). Applicants believe that the reduced levels of nickel in the conversion coating provide improved corrosion resistance and paint adhesion, and the modification of zinc/nickel ratios in the treatment solution likely varies the composition of the phosphate coating provided. In addition, the coating 15 provided by the present invention has a coating weight of between about 160 and about 240 mg/ft², which is heavier than that suggested in the '641 patent as well as that produced by commercial embodiments of the '641 patent. Applicants believe that the treatment solution of the present invention may be more reactive than those of the prior art, therefore resulting in a heavier 20 coating.

What we claim is:

1. A method of applying a phosphate conversion coating to a metal surface, comprising:

- (a) providing an aqueous, acidic treatment solution comprising-
- phosphate ions;
 - zinc cations; and
 - nickel(II) cations;

wherein said treatment solution has between about 2.1 and about 6.0 points of free acid; and

- (b) contacting said metal surface with said treatment solution for a time and at a temperature sufficient to form a phosphate conversion coating on said metal surface.

2. The method of claim 1, wherein the total acid in said treatment solution is between about 30 and about 50 points, and the ratio of total acid to free acid is between about 5 and about 24.

3. The method of claim 2, wherein said treatment solution has between about 3000 to about 8000 mg/l nickel (II) cations,

4. The method of claim 3, wherein said treatment solution further comprises nitrate ions.

5. The method of claim 4, wherein said treatment solution further comprises fluoride ions.
6. The method of claim 2, wherein said metal comprises a zinc-coated metal.
7. The method of claim 6, wherein said metal comprises zinc-coated steel.
8. The method of claim 2, wherein the gram-atom percent of nickel to the total amount of nickel and zinc in the treatment solution is less than 83.
9. The method of claim 2, wherein the temperature of said treatment solution is between about 135 and about 160 deg. F.
10. The method of claim 9, wherein said treatment solution is applied to said metal for a period of between about 3 and about 20 seconds.
11. The method of claim 5, wherein said treatment solution has between about 8000 and about 20,000 mg/l nitrate anions, and between about 400 and about 2000 mg/l fluoride anions.

12. A method of applying a phosphate conversion coating containing zinc and nickel (II) to a metal surface, comprising:

- (a) providing an aqueous, acidic treatment solution comprising-
- phosphate ions;
 - zinc cations;
 - nickel(II) cations; and
 - fluoride anions

said treatment solution having between about 3000 to about 8000 mg/l nickel (II) cations, and between about 800 and about 2000 mg/l zinc cations, wherein the gram-atom percent of nickel to the total amount of nickel and zinc in the treatment solution is less than 83; and

- (b) contacting said metal surface with said treatment solution for a time and at a temperature sufficient to form a phosphate conversion coating on said metal surface.

13. The method of claim 12, wherein the total acid in said treatment solution is between about 30 and about 50 points, the free acid is between about 2.1 and about 6.0 points, and the ratio of total acid to free acid is between about 5 and about 24.

14. The method of claim 13, wherein the temperature of said treatment solution is between about 135 and about 160 deg. F.

15. The method of claim 13, wherein said treatment solution further includes between about 8000 and about 20,000 mg/l nitrate anions, and wherein said treatment solution has between about 400 and about 2000 mg/l fluoride anions, and between about 16,000 and about 26,000 mg/l phosphates.

16. A metal object having a nickel-zinc phosphate conversion coating thereon, wherein the gram-atom percent of nickel to the total amount of nickel and zinc in the coating is between about 10 and about 13.

17. The object of claim 10, wherein said metal object has a zinc coating beneath said conversion coating.

18. The object of claim 11, wherein said object is painted over top said conversion coating.

19. A metal object having a phosphate conversion coating applied in accordance with the method of claim 12.

20. A metal object having a phosphate conversion coating applied in accordance with the method of claim 1.