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**ELECTROLYTIC TREATMENT OF BLACK
PLATE AND PRODUCT**

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This invention relates to an improved method of electrolytically treating black plate to improve corrosion resistance. In some of its more specific aspects, the present invention further relates to a novel electrolyte bath for electrolytically treating black plate and to the treated black plate product.

The present invention may be described hereinafter with specific reference to the treatment of black plate in the form of strip of indefinite length by a continuous process. However, it will be recognized by those skilled in the art that the present invention is not limited thereto, and that the principles of the process to be described hereinafter are applicable to other forms of black plate, or to other articles, in general, regardless of their form or shape provided they present a ferrous metal surface or an alloy surface that is predominately ferrous metal.

In recent years the container industry has become increasingly conscious of the critical shortages of tin which develop during periods of national emergency. As a result, manufacturers of "tin" cans and other "tin" containers have long sought a suitable substitute for tinplate for the manufacture of containers satisfactory for foods, beverages, and other products. One satisfactory substitute for certain relatively non-corrosive products such as coffee, tobacco, etc., has been found to be lacquered black plate. However, when black plate is utilized as a container material, it is necessary that it first be given some sort of chemical treatment for the purpose of inhibiting corrosion prior to applying a suitable protective coating such as a phenolic lacquer. It will be obvious to those skilled in the art that the nature of the chemical treatment designed to inhibit corrosion of the black plate must also provide a satisfactory treated surface for adhesion of the lacquer. In addition, it is necessary that the film formed thereon be non-poisonous.

Numerous processes for the treatment of black plate have been proposed which will inhibit corrosion. However, most of the prior art processes are concerned with the treatment of black plate in a chromate containing solution to deposit a film thereon containing considerable quantities of chromate. Although chromate containing films do inhibit corrosion to a considerable extent, such films are unsatisfactory in other respects. For example, the presence of the chromate in the deposited film is thought by some to bring about an undesirable catalytic effect on the drying properties of organic finishes, including phenolic lacquers, that are subsequently applied to the treated black plate surface in order to provide a suitable material for the container industry. Another disadvantage of prior art processes has been the relatively small amounts of corrosion inhibiting film deposited on the black plate in a satisfactory period of time. For example, in the electrolytic treatment of black plate by a continuous process wherein the black plate is in the form of strip moving at speeds of 1,000 to 2,000 feet per minute and higher, the period of time available for treatment of a given portion of the traveling black plate strip is severely limited. Thus, it is necessary that satis-

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factory amounts of corrosion inhibiting film be deposited on the moving black plate within short periods of time, such as within a very few seconds. In view of this, it will be appreciated that the provision of a process for depositing a corrosion inhibiting film on black plate in a minimum period of time is of great importance.

It is an object of the present invention to provide an improved method of electrolytically treating black plate for the purpose of improving its corrosion resistance and/or lacquer adhesion properties.

It is still a further object of the present invention to provide an improved process for electrolytically treating black plate in a minimum period of time to form a phosphate film thereon which satisfactorily inhibits corrosion of the black plate as well as improving lacquer adhesion properties.

It is still a further object of the present invention to provide a treated black plate product characterized by improved corrosion resistance and lacquer adhesion.

It is still a further object of the present invention to provide an improved bath for the electrolytic treatment of black plate in accordance with the invention.

Still other objects of the present invention and the advantages thereof will be apparent to those skilled in the art by reference to the following detailed description and the specific examples.

In accordance with the present invention, the corrosion resistance of black plate is improved by a process which comprises the step of anodically treating the black plate in an aqueous acidic bath containing at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate. When it is desired to deposit a phosphate film of a given weight on black plate in a minimum period of time, the process of the present invention further involves the electrolytic treatment of black plate in a bath of the aforesaid type which also contains a nitrate selected from the class consisting of sodium nitrate and potassium nitrate.

The present invention will be discussed hereinafter in connection with the use of sodium dihydrogen phosphate monohydrate and sodium nitrate in the aqueous acidic bath. However, it will be understood that the corresponding potassium salts, i.e., potassium dihydrogen phosphate and potassium nitrate, may be used to replace all or part of their corresponding sodium salts in the electrolytic bath. In instances where the corresponding potassium salt is substituted for the sodium salt, the quantity of the potassium salt should be so adjusted as to provide an equivalent amount of dihydrogen phosphate or nitrate, as the case may be, in the electrolytic bath. Therefore, when referring to quantities hereinafter in the specification and claims, unless otherwise stated the phosphate salt is calculated as $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and the nitrate is calculated as NaNO_3 , with all calculations being by weight. It will be noted that water of crystallization is included in calculating the amount by weight of phosphate to be added, while water of crystallization is not included in calculating the desired quantity of nitrate. Obviously, anhydrous phosphate salts may be substituted for the corresponding hydrated salts after making adjustments in quantities due to the absence of water of crystallization.

It is essential in accordance with the present invention that the aqueous acidic bath in which the black plate is treated include dihydrogen phosphate. However, the dihydrogen phosphate may be added as the free sodium salt or formed in situ in the desired amount. The amount of dihydrogen phosphate contained in the aqueous acidic bath may vary between about 1 to 15 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate. Lower concentrations are general-

ly unsatisfactory apparently due to phosphate being rapidly depleted from the solution. Higher concentrations, in addition to being uneconomical, do not offer any appreciable advantage and actually result in the deposition of a film which contains smaller amounts of phosphate than may be obtained under similar operating conditions employing lower concentrations. Even better results may be obtained when employing a concentration of sodium dihydrogen phosphate monohydrate of from 1 to 5 ounces per gallon of solution, with best results being obtained when the concentration of sodium dihydrogen phosphate monohydrate is about 3 ounces per gallon of solution.

The above described aqueous bath containing sodium dihydrogen phosphate will provide satisfactory phosphate films on black plate treated in accordance with the present invention provided the time element is not of importance. Where it is desirable to rapidly treat the black plate, such as when treating the black plate in the form of strip moving through a continuous electro-treating apparatus at high strip speeds of 1,000 feet per minute and higher, it is necessary to add sodium nitrate to the above described solution. For best results, the amount of sodium nitrate to be added should vary from 0.1 to 5.0 ounces per gallon of solution. The use of lower concentrations than 0.1 ounce per gallon do not generally accelerate the deposition of the phosphate film to a desired degree although some improvement is noted, while the use of concentrations above 5.0 ounces per gallon of solution do not appear to offer any practical advantage and may result in a decreased rate of film deposition. Better results can usually be obtained when employing a sodium nitrate concentration of 0.1 to 1.7 ounces per gallon of solution, while for best results, generally a sodium nitrate concentration of about 1 ounce per gallon of solution is preferred. The above mentioned ranges for the concentration of sodium nitrate in the bath of the invention are satisfactory from a general standpoint. However, when using a given concentration of sodium dihydrogen phosphate monohydrate, the ratio by weight of phosphate to nitrate should be from 1:1 to 30:1 when calculated on the basis of sodium dihydrogen phosphate monohydrate and sodium nitrate. In most instances optimum results will be obtained when employing a ratio by weight of sodium dihydrogen phosphate monohydrate to sodium nitrate of from 1:1 to 5:1 with even better results generally being obtained when the ratio is about 3:1.

It is essential in accordance with the present invention that the aqueous bath be acidic. The above described aqueous baths are acidic in nature and have a satisfactory pH due to the presence of the acid phosphate salts. It is not generally necessary to add a mineral acid for the purpose of adjusting the pH of the aqueous bath.

In accordance with the process of the present invention, the black plate is electrolytically treated in the above described aqueous acidic bath as an anode. The anodic current conditions are varied according to the weight of phosphate film it is desired to deposit on the black plate, which in turn will vary with the degree of corrosion inhibition it is desired to impart to the treated black plate. For this reason, it is not practical to set definite limits for the anodic current conditions which may be employed in practice since this is largely a matter of choice. However, it may be stated that anodic current conditions ranging from 6 to 60 ampere seconds per square foot of surface area treated are generally satisfactory and will produce phosphate containing films of desired weight for most commercial applications. When employing anodic current conditions ranging from 6 to 60 ampere seconds per square foot of surface area treated, the phosphate film deposited on the black plate is usually within the range of 2,000 to 5,000 micrograms of phosphate per square foot of surface area calculated as PO_4 , or higher under certain preferred conditions. If it is desirable to deposit smaller amounts of phosphate, this may be accomplished by decreasing the anodic current value to less than 6 ampere seconds per square foot of

surface area treated, while if higher weights of phosphate film are desired, they may be obtained by increasing the anodic current value to a value in excess of 60 ampere seconds per square foot of surface area treated.

It is possible to employ cathodic treatment of the black plate either before or after the anodic treatment. However, cathodic treatment does not appear to be of any particular advantage since the amount of phosphate in the surface film residue is not generally increased to an appreciable extent and in some instances the phosphate film may be actually decreased, as when the final treatment is cathodic. If a combination of anodic and cathodic current treatments should be employed, it is preferred that the cathodic treatment precede the anodic treatment where it is desired to deposit a maximum phosphate film on the black plate. In all instances cathodic treatment is not necessary and adequate films of phosphate may be obtained when employing only anodic treatment.

The presence of chromate in the aqueous acidic bath of the present invention greatly reduces the rate of deposition of phosphate film. In general, it may be stated that the presence of 1 to 3 ounces of chromate per gallon of solution (calculated as $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) will reduce the amount of phosphate film deposited under identical operating conditions to about one-half that obtained in the absence of chromate. Thus, the presence of chromate is not desirable if a maximum phosphate film is to be deposited in a minimum period of time. Similarly, aqueous baths containing sodium polyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) are ineffective in the formation of heavy phosphate films during minimum periods of treatment although small amounts of phosphate may be deposited.

Where the black plate is to be treated by a continuous treating operation, the black plate strip freshly scrubbed and cleaned by conventional procedure to remove oxides, grease, etc. from the surface is passed through an aqueous acidic bath of the present invention containing sodium dihydrogen phosphate and, preferably, sodium nitrate in proportions above specified. As the black plate is passed through the bath, it is connected to a source of direct current as the anode and moved between spaced insoluble grids which are connected to a source of direct current as the cathode, thereby anodically treating the black plate and depositing a phosphate film thereon. The current density in amperes per square foot may be varied according to variations in the line speed so as to obtain anodic current conditions such as from 6 to 60 ampere seconds per square foot of surface area treated, or otherwise varied to deposit the desired weight of phosphate film. The anodic treatment may be either preceded or followed by a suitable cathodic treatment in the same bath, if this should be desired. When a cathodic treatment is employed, the black plate strip is connected to a suitable source of direct current as a cathode and moved between additional spaced insoluble grids which are connected to a source of direct current as an anode. The current density in amperes per square foot during any cathodic treatment may also be varied according to variations in the line speed so as to obtain cathodic current conditions in ampere seconds per square foot of surface area treated within desired limits. Subsequent to the above described treatment, the treated black plate strip is then rinsed and dried.

The foregoing detailed description and following specific examples are for purposes of illustration only and are not intended as limiting to the spirit or scope of the appended claims.

EXAMPLE I

Samples of canmaking quality black plate 5 x 12 inches in size were cathodically cleaned at 20 ampere seconds per square foot for ten seconds in a warm solution containing 3.0 ounces per gallon of soda ash. After the

cleaning operation, each panel was washed in hot water, and then pickled by immersion for ten seconds at room temperature in a solution containing 10% HCl by volume. After pickling, each panel was washed with hot water and treated in the selected electrolyte at 12 ampere seconds per square foot for the desired period of time. Immediately after being treated, the panels were washed with hot tap water followed by a hot distilled water rinse, passed through wringer rolls and air dried.

The electrolyzing cell consisted of a cylindrical glass container 6 inches in diameter. This cell was fitted with two black plate grids each 4 inches in width and spaced approximately 4 inches apart.

The above described panels were then given an electrolytic treatment in experimental solutions represented by twelve different compositions. Each of the twelve different experimental solutions were also treated under eight different current-polarity combinations.

The compositions of the experimental solutions are given below in Table I, with each solution being identified in Table III by its respective identifying letter.

Table I.—Composition of experimental solutions

Solution No.	Oz./Gal. NaH ₂ PO ₄ ·H ₂ O	Oz./Gal. NaNO ₃	Oz./Gal. Na ₂ Cr ₂ O ₇ ·2H ₂ O	Oz./Gal. Na ₂ P ₂ O ₁₀
A	1.0	1.0	—	—
B	3.0	1.0	—	—
C	10.0	1.0	—	—
D	15.0	1.0	—	—
E	3.0	—	—	—
F	3.0	0.1	—	—
H	3.0	3.0	—	—
J	15.0	—	—	—
K	15.0	5.0	—	—
L	3.0	—	1.0	—
M	3.0	1.0	1.0	—
N	—	1.0	—	3.0

The eight different current-polarity combinations used in evaluation of each of the above experimental solutions are given below in Table II.

Table II

Electrolysis No.	Seconds Anodic at 12 amps./sq. ft.	Seconds Cathodic at 12 amps./sq. ft.	Seconds Anodic at 12 amps./ sq. ft.
1	0.5	—	—
2	1.0	—	—
3	5.0	—	—
4	—	1.0 followed by	1.0
5	—	1.0 followed by	5.0
6	—	5.0 followed by	1.0
7	1.0 followed by	1.0	—
8	5.0 followed by	1.0	—

Each of the treated panels was analyzed for phosphate content in the surface residue. The results of these analyses are tabulated below in Table III.

Table III.—Surface residues in micrograms
per square foot

Electrolysis No.	A	B	C	D	E	F	H	J	K	L		M		N
	PO ₄	PO ₄	PO ₄	PO ₄	PO ₄	PO ₄	PO ₄	PO ₄	PO ₄	PO ₄	Cr	PO ₄	Cr	PO ₄
1	1,368	2,258	1,542	550	990	360	2,196	984	1,884	876	10	588	10	38
2	2,350	2,490	1,560	434	930	756	2,040	696	1,776	910	10	960	22	48
3	3,900	3,748	1,950	2,364	1,710	2,970	2,256	1,596	3,000	588	12	1,076	12	36
4	3,300	4,012	900	516	576	2,178	2,256	481	2,712	516	12	948	19	72
5	6,240	5,596	696	2,732	798	2,778	2,172	1,788	1,692	804	10	906	22	149
6	2,172	2,508	612	2,508	1,808	2,526	1,830	360	792	696	19	1,536	22	125
7	2,256	1,116	1,020	624	355	498	1,782	250	1,920	984	31	672	34	34
8	5,860	4,672	2,748	1,440	1,284	2,658	1,782	564	1,920	564	26	1,128	5	31

It may be observed from the above tabulated data that the phosphate content in the surface residues is increased with an increase in the length of time of anodic treatment. Once electrolysis has started, the phosphate film is built up rapidly and, under preferred conditions, in less than a second the average phosphate content in the surface residue is over 1000 micrograms per square foot. Anodic electrolysis for five seconds increases the phosphate content in the surface residue up to 2000–5000 micrograms per square foot. Thus, a substantial phosphate film may be built up in no more than five seconds of anodic treatment.

When sodium dihydrogen phosphate monohydrate was used alone in the electrolyte, an increase in concentration from 3.0 to 15.0 ounces per gallon is of no particular advantage. In the presence of sodium nitrate, the amount of phosphate contained in the residue is increased by increasing the concentration of the phosphate salt from 1.0 to 3.0 ounces per gallon. Increasing the concentration of the phosphate salt from about 3.0 to 10.0, or up to 15.0 ounces per gallon in the presence of nitrate is of no particular advantage and in some instances caused a decrease in the amount of phosphate contained in the residue.

The addition of relatively small amounts of sodium nitrate to the phosphate solution, such as 0.1 ounce per gallon caused a marked increase in the rate of growth of the phosphate film during the anodic electrolysis. An increase in the sodium nitrate concentration from 0.1 to 1.0 ounce per gallon caused an additional increase in the rate of phosphate film formation. However, increasing the nitrate concentration from 1.0 to 3.0 ounces per gallon did not substantially increase the rate of phosphate film formation.

The use of 1.0 ounce per gallon of sodium dichromate generally reduced the rate of formation of the phosphate film by at least 50%. The solution containing sodium polyphosphate and sodium nitrate was ineffective in the formation of heavy phosphate films. This solution was alkaline in nature, having a pH of 8.82.

EXAMPLE II

14 x 26 inch panels of black plate of identical quality with that of Example I were anodically cleaned for 10 seconds at 12 amperes per square foot in a hot solution containing 1.0 ounce per gallon of orthosilicate and 1.0 ounce per gallon of soda ash. After cleaning, each panel was washed with water and anodically pickled at 40 amperes per square foot in 10% sulphuric acid solution maintained at room temperature. The pickled panels were then washed in water followed by immediate immersion in the solution to be tested and given various electrolytic treatments. Each treated panel was washed in water followed by a hot water rinse before being passed through rubber wringer rolls. The drying process was completed by the use of a bank of infra-red lamps.

Following the above described treatment, each of the panels was analyzed to determine the phosphate content of the corrosion inhibiting film deposited during the

various electrolytic treatments. The results are tabulated below in Table IV.

Table IV.—Surface residues in micrograms per square foot

Time and Polarity of Electrolysis at 6 amp./sq. ft.	Solutions, oz./gal.		
	A	B	
	3.0 NaH ₂ PO ₄ .H ₂ O 1.0 NaNO ₃	3.0 NaH ₂ PO ₄ .H ₂ O 1.0 NaNO ₃ 1.0 Na ₂ Cr ₂ O ₇ .2H ₂ O	
	PO ₄	PO ₄	Cr
Seconds:			
*1(—), 2(+)	2,059	529	22
2(+)	2,678	500	43
2(+), 1(—)	1,651	338	19
4(+), 1(—)	2,520		
6(+), 1(—)	2,448		

*(+) anodic; (—) cathodic.

The above tabulated data further illustrate that the phosphate residue builds up rapidly during anodic electrolysis in a phosphate-nitrate bath. After only two seconds of anodic treatment at the relatively low current density of 6 amperes per square foot, the phosphate content in the surface residue on the panels was within 2000 to 3000 micrograms per square foot. Cathodic electrolysis for one second following the anodic treatment reduces the phosphate residue considerably, while a cathodic treatment before the anodic treatment has much less effect on the surface residue. When only one ounce per gallon of sodium dichromate was added to the solution, the phosphate residue was reduced appreciably.

Phenolic lacquer adhesion tests (Scotch tape test) were made on each of the above treated panels. All of the panels had excellent laquer adhesion properties. Also, corrosion resistance was greatly improved.

What is claimed is:

1. A method of improving the corrosion resistance of black plate which comprises the step of anodically treating the black plate in an aqueous acidic bath consisting essentially of at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate, the amount of dihydrogen phosphate in the bath being from 1 to 15 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate.

2. A method of improving the corrosion resistance of black plate which comprises the step of anodically treating the black plate in an aqueous acidic bath consisting essentially of at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate, the anodic current value being from 6 to 60 ampere seconds per square foot of surface area treated, and the amount of dihydrogen phosphate in the bath being from 1 to 15 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate.

3. A method of improving the corrosion resistance of black plate which comprises the step of anodically treating the black plate in an aqueous acidic bath consisting essentially of at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate and at least one nitrate selected from the group consisting of sodium nitrate and potassium nitrate, the amount of dihydrogen phosphate in the bath being from 1 to 15 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate and the amount of nitrate in the bath being at least about 0.1 ounce per gallon of solution when calculated as sodium nitrate.

4. A method of improving the corrosion resistance of black plate which comprises the step of anodically treating the black plate in an aqueous acidic bath consisting essentially of at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate and at least one nitrate selected from the group consisting of sodium nitrate and potassium nitrate, the anodic current value being from 6 to 60 ampere seconds per square foot of surface area treated, the amount of dihydrogen phosphate in the bath being from 1 to 15 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate and the amount of nitrate in the bath being at least about 0.1 ounce per gallon of solution when calculated as sodium nitrate.

5. A method of improving the corrosion resistance of black plate which comprises the step of anodically treating the black plate in an aqueous acidic bath consisting essentially of at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate and at least one nitrate selected from the group consisting of sodium nitrate and potassium nitrate, the amount of dihydrogen phosphate in the bath being from 1 to 15 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate and the amount of nitrate in the bath being from 0.1 to 3 ounces per gallon of solution when calculated as sodium nitrate.

6. A method of improving the corrosion resistance of black plate which comprises the step of anodically treating the black plate in an aqueous acidic bath consisting essentially of at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate and at least one nitrate selected from the group consisting of sodium nitrate and potassium nitrate, the anodic current value being from 6 to 60 ampere seconds per square foot of surface area treated, the amount of dihydrogen phosphate in the bath being from 1 to 15 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate and the amount of nitrate in the bath being from 0.1 to 3 ounces per gallon of solution when calculated as sodium nitrate.

7. The method of claim 6 wherein the amount of dihydrogen phosphate in the bath is from 1 to 5 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate.

8. The method of claim 6 wherein the amount of dihydrogen phosphate in the bath is about 3 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate.

9. The method of claim 7 wherein the amount of nitrate in the bath is from 0.1 to 1.7 ounces per gallon of solution when calculated as sodium nitrate.

10. The method of claim 8 wherein the amount of nitrate in the bath is about 1 ounce per gallon of solution when calculated as sodium nitrate.

11. A method of improving the corrosion resistance of black plate which comprises the step of anodically treating the black plate in an aqueous acidic bath consisting essentially of at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate and at least one nitrate selected from the group consisting of sodium nitrate and potassium nitrate, the amount of dihydrogen phosphate in the bath being from 1 to 15 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate, and the ratio by weight of phosphate to nitrate being from 1:1 to 5:1 when calculated on the basis of sodium dihydrogen phosphate monohydrate and sodium nitrate.

12. A method of improving the corrosion resistance of black plate which comprises the step of anodically treating the black plate in an aqueous acidic bath consisting essentially of at least one phosphate selected from

the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate and at least one nitrate selected from the group consisting of sodium nitrate and potassium nitrate, the anodic current value being from 6 to 60 ampere seconds per square foot of surface area treated, the amount of dihydrogen phosphate in the bath being from 1 to 15 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate, and the ratio by weight of phosphate to nitrate being from 1:1 to 5:1 when calculated on the basis of sodium dihydrogen phosphate monohydrate and sodium nitrate.

13. The method of claim 12 wherein the ratio by weight of phosphate to nitrate is about 3:1 when calculated on the basis of sodium dihydrogen phosphate monohydrate and sodium nitrate.

14. The method of claim 12 wherein the amount of dihydrogen phosphate in the bath is from 1 to 5 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate.

15. The method of claim 12 wherein the amount of dihydrogen phosphate in the bath is about 3 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate.

16. The method of claim 14 wherein the ratio by weight of phosphate to nitrate is about 3:1 when calculated on the basis of sodium dihydrogen phosphate monohydrate and sodium nitrate.

17. The method of claim 15 wherein the ratio by weight of phosphate to nitrate is about 3:1 when calculated on the basis of sodium dihydrogen phosphate monohydrate and sodium nitrate.

18. The black plate product of improved corrosion resistance as produced by the method of claim 3.

19. The black plate product of improved corrosion resistance as produced by the method of claim 12.

20. An electrolyte bath consisting essentially of an aqueous acidic solution containing at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate and at least one nitrate selected from the group consisting of sodium nitrate and potassium nitrate, the amount of dihydrogen phosphate in the bath being from 1 to 15 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate and the amount of

nitrate in the bath being at least about 0.1 ounce per gallon of solution when calculated as sodium nitrate.

21. An electrolyte bath consisting essentially of an aqueous acidic solution containing at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate and at least one nitrate selected from the group consisting of sodium nitrate and potassium nitrate, the amount of dihydrogen phosphate in the bath being from 1 to 15 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate, and the ratio by weight of phosphate to nitrate being from 1:1 to 5:1 when calculated on the basis of sodium dihydrogen phosphate monohydrate and sodium nitrate.

22. An electrolyte bath consisting essentially of an aqueous acidic solution containing at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate and at least one nitrate selected from the group consisting of sodium nitrate and potassium nitrate, the amount of dihydrogen phosphate in the bath being from 1 to 15 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate, and the ratio by weight of phosphate to nitrate being from 1:1 to 30:1 when calculated on the basis of sodium dihydrogen phosphate monohydrate and sodium nitrate.

23. An electrolyte bath consisting essentially of an aqueous acidic solution containing as essential ingredients at least one phosphate selected from the group consisting of sodium dihydrogen phosphate and potassium dihydrogen phosphate and at least one nitrate selected from the group consisting of sodium nitrate and potassium nitrate, the amount of dihydrogen phosphate in the bath being about 3 ounces per gallon of solution when calculated as sodium dihydrogen phosphate monohydrate and the amount of nitrate in the bath being about 1 ounce per gallon of solution when calculated as sodium nitrate.

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