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METHOD AND COMPOSITION FOR THE FORMATION OF SMOOTH ZINC PHOSPHATE COATINGS ON STEEL

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This application is a continuation-in-part of my copending application Serial No. 635,130, filed January 22, 1957, now Patent No. 2,975,082, which was a continuation-in-part of Serial No. 587,939, filed May 29, 1956, but now abandoned; which was a continuation-in-part of Serial No. 274,839, filed March 4, 1952, but now abandoned; and which in turn was a continuation-in-part of Serial No. 193,290, filed October 31, 1950, and which issued as U.S. Patent No. 2,588,234 on March 4, 1952, and was re-issued June 7, 1955, as Reissue 24,017.

This invention relates to the phosphate coating of metals, and is particularly directed to the formation of smooth zinc phosphate coatings upon ferrous metals.

The principal object of this invention is to achieve low sludging and smooth coating zinc phosphate baths by means of highly soluble calcium salts of monovalent acids acting in conjunction with a nitrosyl accelerator.

It was shown in my Reissue Patent 24,017 that phosphate coating is brought about by a Wagner tarnish mechanism. The recognition that phosphate coating is a Wagner phenomenon is a great advantage, since it allows us to first write equations for the electrochemical reactions, and from these equations to derive a balanced formulation that will hold the desired bath composition for all the bath components when this balanced formulation is used to replenish the operating bath. The Wagner mechanism functions on a Faraday equivalent basis with the ferrous metal work piece acting as its own anode to furnish the electrochemical energy for the coating. A balanced bath will dissolve one mole of ferrous metal from the work surface, and evolve two moles of hydrogen as it coats out one mole of tertiary zinc phosphate mixed with iron phosphate as the conversion coating. The hydrogen can either be evolved or oxidized depending on the nature and composition of the bath. These events can be illustrated by the following equations. In these examples, the water of crystallization of the hydrated phosphates are not shown for the sake of simplicity. The concentrates shown after the equations are a 50% water solution of the bath ingredients in the proportions required by the accompanying equations.

(1) UNACCELERATED ZINC PHOSPHATE BATH

$$3Fe+3Zn(H_2PO_4)_2=Zn_3(PO_4)_2\cdot 2FeHPO_4+3H_2+Fe(H_2PO_4)_2$$

Concentrate —— Coating ——

A 50% water concentrate derived from this equation would have the following composition to hold the bath in balance as a replenisher.

Concentrate No. 1:	Percent
Zinc	10
(H_2PO_4)	33
Free H_3PO_4	6
Balance water.	

(2) LOW SODIUM NITRATE ACCELERATED ZINC PHOSPHATE BATH

$$3Fe+3Zn(H_2PO_4)_2=Zn_3(PO_4)_2\cdot 2FeHPO_4+3H_2+Fe(H_2PO_4)_2$$

Concentrate —— Coating ——

Depolarizer action.: $4H_2+HNO_3=NH_3+3H_2O3H_2$ requires ¾ $NaNO_3$.

A 50% water concentrate derived from this equation would have the following composition to hold the bath in balance as a replenisher.

Concentrate No. 2:	Percent
Zinc	10
(H_2PO_4)	30
Free H_3PO_4	6
$NaNO_3$	4
Water	50

(3) HIGH ZINC NITRATE ACCELERATED ZINC PHOSPHATE BATH

$$4Fe+Zn(H_2PO_4)_2\cdot 2H_3PO_4\cdot 2Zn(NO_3)_2=$$

Concentrate

$$Zn_3(PO_4)_2\cdot Fe_3(PO_4)_2+4H_2+2HNO_3+Fe(NO_3)$$

Coating

Depolarizer action: $4H_2+4NO_3=4H_2O+4NO_24H_2$ requires $4NaNO_3$.

A 50% water concentrate derived from this equation would have the following composition to hold the bath in balance as a replenisher.

Concentrate No. 3:	Percent
Zinc	13
Nitrate	17
Phosphate	20
Water	50

(4) NITROSYL ACCELERATED CALCIUM MODIFIED ZINC PHOSPHATE BATH

$$5Fe+3Zn(H_2PO_4)_2\cdot Ca(Cl)_2=$$

Concentrate

$$Zn_3(PO_4)_2\cdot Fe_3(PO_4)_2\cdot CaHPO_4+5H_2+Fe(Cl)_2+(H_2PO_4)$$

Coating

Depolarizer action: $5H_2+5NaNO_3=5H_2O+5NaNO_2$.

A 50% water concentrate derived from this equation would have the following composition in order to hold the bath in balance as a replenisher.

Concentrate No. 4:	Percent
Zinc	7.4
$(H_2PO_4)_2$	22.1
$Ca(Cl)_2$	4.3
$NaNO_3$	16.2
Water	50.0

Attention is called to the critical nature of the nitrate depolarizer concentration in the baths of this invention. At a low concentration, nitrate depolarizer in a zinc phosphate bath is largely reduced down to ammonia as shown in Equation 2 above, but does not produce the microcrystalline zinc phosphate in the presence of one-quarter molar calcium. On the other hand, a high concentration of nitrate is only reduced to nitrite, and such depolarization produces the smooth coatings of this invention in the presence of quarter molar calcium in relation to molar zinc. Without the high level nitrate, no nitrosyl type acceleration is obtained and the zinc phosphate coatings are crystalline even in the presence of quarter molar calcium. While it is difficult to prove by chemical analysis, we believe that the smoothing action of the nitrosyl acceleration is synergistic to the calcium action, and exerts its effect by giving a higher iron content to the coating, and

one in which the iron phosphate is a ferroso-ferric phosphate instead of a plain ferrous phosphate. It has been noted that zinc di-hydrogen phosphate baths that are accelerated by oxidizing agents like sodium nitrite, hydrogen peroxide, or sodium chlorate that oxidize ferrous to ferric give smoother coatings than low nitrate, which does not oxidize iron. Likewise, it was noted that a small amount of fluoride ion, which forms a soluble ferric complex, enhances the smoothing action of the calcium and nitrosyl modified zinc phosphate baths.

While the nitrate accelerator concentration is critical in these baths, it is simple to control by merely formulating the concentrate in the manner shown above, whereby there is at least one mole of nitrate per mole of evolved hydrogen. A very simple control is derived from the Tanner and Lodeesen patent, U.S. Patent 1,911,726 which taught that the oxidizing agent should oxidize the hydrogen given off by the acid phosphate attack of the iron base. A simple rule of thumb is to have sufficient nitrate in the bath to eliminate gassing from new work after about one minute immersion in the bath at the coating temperature. Table III, which follows, shows the gassing times of various nitrate levels in these baths and can be used as a guide. Another rule to assure adequate nitrate is to maintain the sodium nitrate in grams per liter equal to half the total bath points. If the zinc metal content is known, the sodium nitrate level should be held at about twice the zinc concentration. These nitrate strengths are merely the chemical equivalents required by the Wagner phenomena shown in Equations 3 and 4.

We believe that the smoothing action of the calcium ion and nitrosyl accelerator combination is brought about by nascent colloids adjacent to the work which interfere with the normal cubic crystal growth of tertiary zinc phosphate. As the iron neutralizes the free acid in the film of solution against the work, sparingly soluble calcium phosphate and ferric phosphate are precipitated and included at random in the deposit to prevent normal crystal growth.

While the nitrate concentration is critical, the calcium concentration is not, as long as at least 0.2 mole of calcium is present for each mole of zinc, and the nitrosyl acceleration is available. The calcium content can range from 0.2 up to 5.0 moles of calcium per mole of zinc. The coatings from baths having 2.0 or more moles of calcium per mole of zinc are even smoother and finer grained than the coatings from the preferred compositions of this invention in which the calcium is only 0.2 to 0.3 mole of calcium per mole of zinc. However, such high calcium baths have certain inherent defects. Since only about 0.25 mole of calcium are coated out per mole of zinc, a high calcium content gives a solution imbalance, and requires a special low calcium replenishing solution to thus complicate the operation and control of the process. In addition, a high calcium bath forms more of a sludge, and requires a correspondingly high nitrate concentration. Basically, calcium is a poison and inhibits the zinc phosphate coating mechanism. For example, the unaccelerated bath of Amundsen in U.S. Patent 2,540,314 shows a zinc di-hydrogen phosphate bath with an equimolar calcium chloride addition. This bath deposits only 60% as much coating and requires 35% more time than the identical zinc di-hydrogen phosphate bath without calcium chloride under identical conditions. It is therefore desirable to use only the minimum calcium required to give the smoothing action when coupled with the nitrosyl acceleration, and thus have a concentrate that can be used both for make-up and replenishment. Since these coatings are principally tertiary zinc phosphate, the high zinc and low calcium formulation will coat more surface than the high calcium formulations, and also produce less sludge. It is believed that the alkali metal ions of the sodium or potassium nitrate used as accelerators in this invention assist the smoothing action of the calcium to a slight extent since a bath in which all of the nitrate is furnished by zinc and calcium nitrate requires at least 0.5 mole of calcium to obtain the same finish as that obtained by 0.25 mole of calcium and all the nitrate furnished as alkali metal nitrate. For purposes of illustration, a typical high calcium type microcrystalline zinc phosphate bath can be obtained from the foregoing Equation 3 by the substitution of two moles of zinc nitrate with two moles of calcium nitrate to form a concentrate having one mole of zinc di-hydrogen phosphate to two of calcium nitrate, and having the following composition when made up into a 50% water solution.

Concentrate No. 5 (high calcium type):

	Percent
Zinc	4
Calcium	5
Nitrate	16
Phosphate	25
Water	50

Since the above has only one third of the zinc content of the original Concentrate No. 3 from which it is derived, it can coat out only a third as much tertiary zinc phosphate. If the No. 5 concentrate is used both for make-up and replenishment, the operating bath would soon have a serious imbalance, and would precipitate calcium sludge. The many advantages of the low calcium formulations of this invention are apparent.

Various attempts at calcium modified zinc phosphate baths were disclosed in the prior art. A discussion of these inoperative commercial failures will aid in pointing out the advantages of this invention.

In the prior art, three attempts were made to utilize an accelerated calcium containing zinc phosphate coating system.

The first attempt was that of Wilhelm Schmidding in German Patent No. 310,756, issued July 1, 1922. Schmidding used a highly acid mixture of calcium acid phosphate and zinc acid phosphate having a ratio of about one free acid to 2.3 total acid and using hydrogen peroxide for acceleration. Since such a solution is more of a pickle bath than a coating bath, it requires one to two hours to coat a ferrous article. Even when so laboriously coated out, such coatings have inferior rustproofing value because the underlaying steel is highly activated by the pickling action of the bath, and the work is readily corroded from underneath. Thompson and Tanner in U.S. Patent No. 1,869,121 pointed out and patented the fact that a balanced phosphate bath has a ratio of total acid to free acid of from 6 to 15 total to 1 free, and that any bath outside this range was inoperative. The "points" of free acid are the number of milliliters of 0.1 normal sodium hydroxide required to titrate a 10 ml. sample to the methyl orange end point while the total acid "points" are the milliliters of 0.1 normal sodium hydroxide required in the same sample to reach the phenolphthalein end point. Schmidding's bath could never attain the high acid ratio of Thompson and Tanner because as the ferrous metal from the work neutralizes the high free acid, the hydrogen peroxide would precipitate it from the bath as ferric phosphate and create more free acid in the following manner:

$$Fe(H_2PO_4)_2+H_2O_2=FePO_4+H_3PO_4+2H_2O$$

It was found by test that one mole of calcium acid phosphate requires 1.2 moles of phosphoric acid to dissolve it in water at the desired coating concentration, and that such a mixture has a ratio of less than 1.0 free acid to 3.0 total acid. Thus Schmidding was trapped with an acid ratio below 3.0 and with a slow coating pickle bath, since any higher ratio bath with less free acid would precipitate his calcium phosphate. Even the concentrate made according to Schmidding's directions precipitates

some calcium phosphate crystals on standing at room temperature over night.

Calcium phosphate cannot remain in solution at an acid ratio greater than 1 free acid to 3 total acid unless a calcium solubilizing anion is present. The use of a calcium solubilizing anion is the key to making a calcium modified zinc phosphate bath that is commercially operative, and is the main object of this invention. The preferred solubilizing anions are those of the monovalent acids whose calcium salt solubility exceeds the level of 400 parts per liter at room temperature, and may be selected from the following table:

Table I.—Highly soluble calcium salts of monovalent acids

Calcium acetate, $Ca(CH_3COO)_2H_2O$, 436 grs./lit., 0° C.
Calcium bromide, $CaBr_2$, 1250 grs./lit., 0° C.
Calcium chloride, $CaCl_2$, 595 grs./lit., 0° C.
Calcium iodide, CaI_2, 1920 grs./lit., 0° C.
Calcium propionate,
$Ca(CH_3CH_2COO)_2H_2O$, 490 grs./lit., 0° C.

Because of its extremely low cost and availability, calcium chloride is the preferred solubilizing salt of this invention. Calcium acetate is also cheap and available, and is as good a solubilizer as the chloride, and has the advantage of not making the coating any coarser or heavier as does the chloride. It is advantageous to use a mixture of the acetate and chloride salts of calcium. High price limits the use of the iodide and bromide, but they are fully equivalent to the chloride. While the propionate is expensive, it is an excellent mold and fungi inhibitor, and is preferred in mixtures where sugars are used as a nitrate reductant. The preferred formulations and the best use of these salts will be fully pointed out in the ensuing examples. By the addition of calcium as one of these infinitely soluble salts to a zinc di-hydrogen phosphate bath, it becomes possible to operate a mixed calcium and zinc phosphate bath at the necessary balanced ratio of more than five total acid to one free acid that is required for fast coating. Thus these highly soluble calcium salts make it possible for the first time to commercially operate a balanced and accelerated zinc phosphate bath containing calcium, and thus obtain a smooth microcrystalline coating.

After Schmidding, the next attempt to produce an accelerated calcium modified phosphate bath was made by G. L. Williams in U.S. Patent No. 1,514,494. Williams showed a rust removing composition based upon acid phosphates, Steffins waste liquor, and aqua regia. A reinvestigation of this early effort found this early bath to be more of a pickling composition than a coating bath; that his mixture could not be packaged and sold in commerce; and that his methods were without industrial value for true rustproofing. Nevertheless, it was found that by using some of his materials in a new manner, that very satisfactory results could be obtained and that a commercially valuable process could be evolved therefrom. Since the Steffins process utilizes lime to remove sucrose from beet sugar molasses as the calcium saccharate, the neutralizing of the alkalinity of the Steffins waste with aqua regia as practiced by Williams would form calcium chloride and some calcium nitrate. In addition, his mixture would contain nitrosyl chloride, nitro and nitroso betains and various nitrate reduction products from the sugars and proteins present. By the novel use of his calcium salts as smoothing agents and the reduced nitrates as depolarizers in a zinc phosphate bath, a modified Williams type material becomes operative, provided a low free acid is maintained.

The next effort to obtain an accelerated mixed calcium and zinc phosphate system was that of Waterfall in British Patent 440,215. Waterfall utilized a powdered mixture of about equal parts of calcium acid phosphate, zinc sulfate, and sodium nitrate. These proportions would give about equimolar calcium and zinc and have about three moles of sodium nitrate depolarizer. While this powder base was intended to form a zinc di-hydrogen phosphate bath by metathesis when dissolved in water, it actually forms a bath in which about half the zinc and calcium is dissolved to form a mixed phosphate bath, and half of the salts remain as undissolved sludge. This bath had the same defect that made the Schmidding bath inoperative, in that the calcium was furnished by sparingly soluble calcium phosphate and calcium sulfate instead of by the infinitely soluble calcium salts of this invention. Because of this, the coating from the Waterfall formula are marred by a serious roughness from the heavy sludges which comprise over half the original make-up and greatly increase as the bath is replenished. A second and fatal defect of the Waterfall composition is his lack of free acid. When made up according to his teachings, these baths have a supersaturated ratio of about 30 total acid to 1 free acid, well beyond the range of a balanced bath, and have too little free acid to dissolve the necessary iron to form a microcrystalline or amorphous zinc phosphate coating. It is only when the Waterfall bath is filtered free of all sludge and the clear filtrate boiled to create free acid by hydrolysis to drop the acid ratio from 30 to 1 down to about 6 to 1, that satisfactory amorphous type deposits are obtained. In the unfiltered bath the undissolved and precipitated salts keep the ratio at about 30 to 1 and the coating rough and crystalline. This lack of free acid prevents the solution of sufficient iron from the work and into the deposit as ferroso-ferric phosphate to render the coating amorphous. This prior art bath had another serious defect in the sulfate anion which is not only an undesirable calcium precipitant but which acts as a poison in zinc phosphate spray applications. Since ferric sulfate is water insoluble, the sulfate anion acts as a coating ion like phosphate, and has been patented as such both with and without added molybdate ion. The mechanism is such that a dilute sodium acid sulfate spray system will yield an iridescent iron oxide coating which will give a satisfactory rust inhibiting coating if chromic acid rinsed. When sulfate is added to a sodium acid phosphate system, it augments and improves the so-called "iron phosphate" coating mechanism which is principally an iron oxide coating system. When sulfate is added to a zinc phosphate spray coating bath, such as Waterfall's it produces bad patches of iron oxide that do not coat over with the tertiary zinc phosphate, and thus ruins the continuity of the intended zinc phosphate coating. It is thus most important that the sulfate ion be avoided in a calcium containing zinc phosphate bath. There must be a twofold aim of furnishing anions having infinitely soluble calcium salts, and of avoiding any ions other than phosphate that will precipitate the calcium, to obtain a commercial process.

It is an object of this invention to produce a successful industrial microscrystalline zinc phosphate coating process out of the workable elements of these early commercial failures. This is most effectively accomplished by adding a low level of the highly soluble calcium salt of a monovalent acid to a zinc di-hydrogen phosphate bath containing a high level of reduced nitrate accelerator. The best methods of achieving these results are illustrated in the examples which follow.

Zinc di-hydrogen phosphate baths are made by adding 1% to 5% of the concentrate to water and heating the solution up to the coating temperature. All commercial zinc phosphate concentrates are made by neutralizing diluted 75% phosphoric with zinc oxide. The neutralizing reaction results in a stable equilibrium product whether zinc oxide, zinc carbonate, or zinc dust is used as the neutralizer. This equilibrium product has an empirical formula of $Zn(H_2PO_4)_2H_3PO_4$, and the concentration is kept below 60% solids to avoid cold weather recrystal-

lization. Typical commercial concentrates are as follows:

Table II.—Typical zinc phosphate concentrates

No. 6—U.S. Pat. 2,132,883:
11% Zinc
40% H_3PO_4
49% Water
Specific gravity 1.53

No. 7—Highest feasible commercial:
13% Zinc
48% H_3PO_4
39% Water
Specific gravity 1.65

No. 6 is made by dissolving one and two-thirds pounds of commercial lead free zinc oxide in one-half gallon of 75% food grade phosphoric acid diluted with one-half gallon of water. No. 7 is made by dissolving three pounds of lead free commercial zinc oxide in one gallon of food grade 75% phosphoric acid diluted with one-half gallon of water. No. 7 has a convenient composition in that one milliliter contains exactly one gram of zinc di-hydrogen phosphate. The best use of these conientrates is shown in the ensuing examples.

A predominantly iron phosphate fifilm can be formed on ferrous stock by dipping it in solution of a diacidic phosphate such as sodium dihydrogen phosphate, potassium dihydrogen phosphate, ammonium dihydrogen phosphate, magnesium dihydrogen phosphate or calcium dihydrogen phosphate accelerated with an oxidizing or reducing agent. Suitable oxidizing agents are sodium chlorate, sodium nitrite, sodium nitrate, sodium nitroprusside, hydrogen peroxide, potassium persulfate, picric acid, quinone, and various other chlorates, bromates and iodates. Likewise, suitable reducing agents are sodium sulfite, sodium thiosulfate, and sodium phosphite.

EXAMPLE I.—IRON PHOSPHATE COATING

	Parts
$(NH_4)H_2PO_4$	75
$CaCl_2$	11
H_2O	14

This is made up 5 percent by volume into an iron phosphating solution. This bath could be accelerated by bubbling in gaseous nitrosyl chloride or by adding aqueous nitrobetaine, or NOCl amine complexes or Roussins' salts which are nitroso complexes of iron and sulfur. These are further described on page 678 of the Fritz Ephraim's Inorganic Chemistry, 4th edition, 1943. This is an improvement to the Glen L. Williams Patent No. 1,514,494 which disclosed phosphating solutions containing an unstable mixture of aqua regia and Steffan's sugar beet waste as accelerators. Zinc dihydrogen phosphate or manganese dihydrogen phosphate can be used in place of the monoammonium phosphate shown in the foregoing example if a heavier mixed zinc, or manganese, and iron phosphate is required.

The nitrosyl chloride, like the other oxidizing agents above mentioned, i.e. sodium nitrate and sodium nitrite, provides the nitrogen-oxide depolarizer for acceleration. The calcium ion in the above mix acts as an inhibitor to phosphating, but with nitrogen-oxide acceleration to cause coating, it serves as a grain refiner to decrease crystallinity and provide an amorphous-like coating. The amount may of course be varied in accordance with the acceleration present. The chloride ion serves to decrease the formation of sludge. The diacid phosphate materials, as may be seen, constitute the major proportion of the coating.

EXAMPLE II.—MICROCRYSTALLINE ZINC PHOSPHATE COATING

When zinc dihydrogen phosphate is substituted for ammonium dihydrogen phosphate in Example I above, the following bath is obtained:

	Parts
Zinc dihydrogen phosphate	75
Calcium chloride	11
Water	14

The concentrate has a specific gravity of 1.53 and is made up 5% by volume or 76.4 gms./liter. The amount of sodium nitrate which is added was that required to give an acceptable coating within five minutes, which in this case was found to be 26.2 gms./liter of sodium nitrate. With this addition, the subject bath had the following composition:

	Gms./liter
Zinc dihydrogen phosphate	57.3
Calcium chloride	8.4
Sodium nitrate	26.2

The ion percentages work out as follows:

	Percent
Zinc ion	1.27
Calcium ion	0.30
Phosphate ion	3.70
Nitrate ion	1.90

The weight ratio of calcium ion is substantially 0.25 and the weight ratio of nitrate ion to phosphate ion is 0.51. This bath gives a fine grey microcrystalline coating which is a mixture of zinc phosphate with small amounts of calcium and iron phosphates.

EXAMPLE III.—VARIABLE MICROCRYSTALLINE ZINC PHOSPHATE BATHS

The finest grained and thinnest possible microcrystalline zinc phosphate coating is usually preferred under paint to make the subsequent baked enamel highly lustrous and able to withstand reverse impact without chipping. However there are occasions when a heavy and more granular coating is preferred, as when the coating is to be used to hold a lubricant for cold extrusion, or when the work is to be phosphated and oiled for rustproofing. It is possible for a factory or job shop to have the versatility to produce both types of coatings from the same tank using the same concentrate. This is done by simply varying the sodium nitrate in relation to the calcium containing zinc phosphate concentrate. When the coating is too smooth, the calcium containing zinc phosphate concentrate is added to the bath in the proper proportion in relation to the sodium nitrate as shown in Table III, which follows. Likewise, if the coating is too coarse, it is simply brought to the desired smoothness by the proportioned addition of sodium nitrate, again using the Table III. The bath is first titrated for total points, and the bath adjusted to a sodium nitrate level equal to one-third of the total points for a coarser grained and heavier deposit; to two-thirds of the total points for a microcrystalline coating, and about equal to the total points for the thinnest amorphous type. The nitrate level can be determined by the gassing time on clean low carbon steel panels as shown in the table. Generally it is only necessary to add the calcium containing concentrate to coarsen the coating, or to dilute the bath and add sodium nitrate to make the coating amorphous. However, it may be advisable in large installations to analyze for the nitrate colorimetrically, and the calcium by ethylene diamine tetra acetate, in order to make a more accurate and economical conversion. The data in the following table are based upon the treatment of alkali cleaned and running water rinsed low carbon steel auto body stock. The phosphate bath was made up from 5% by volume of the No. 6 concentrate shown in Table II. This gave a zinc phosphate bath having a free acid of 7.5 and a total acid of 52.5

and which contained 38.5 gms./liter of zinc dihydrogen phosphate before the addition of either the calcium chloride or the sodium nitrate accelerator. The calcium chloride was added at 5 gms./liter $CaCl_2$ after running blanks in plain zinc dihydrogen phosphate, and the sodium nitrate added in gradual increments as shown in the table. The bath was held at 200° F. for these tests, and no agitation was used in order to carefully observe the hydrogen evolution. While the results would vary somewhat with different type steels and with different type cleaning, it is believed that the variation in the gassing times would always be of the same order of magnitude in relation to the nitrate depolarizer. An approximate classification of the average grain size of the coatings is shown in the table in order to differentiate the heavy from light type of microcrystalline zinc phosphate coatings.

Table III.—Effect of variable sodium nitrate additions in a 50 point zinc phosphate bath containing 5 g./l. $CaCl_2$

[Using alkali cleaned low carbon steel panels the bath at 200° F.]

Test No.	G./l. $CaCl_2$	G./l. $NaNO_3$	Gassing time in minutes	Approx. grain size	Remarks
1	None	None	57.0	1/16 inch	Prior art.
2	5	None	71.0	1/32 inch	Finer coat.
3	5	5	29.0	1/32 inch	Same as 2.
4	5	10	8.5	1/64 inch	Finer than 3.
5	5	17	4.2	Barely visible	Microcryst.
6	5	20	2.1	do	Do.
7	5	30	0.8	Amorphous	Preferred.
8	5	35	0.6	do	For paint.
9	5	40	0.5	do	Do.
10	5	50	0.3	Thin amorp	Do.
11	5	60	0.1	do	Too light.

The baths shown in 4 and 5 are the type that would be used as a drawing lubricant base, while the baths shown in 8 and 9 would be preferred under enamel for the highest lustre finish. The types shown in 6 and 7 would be used for the average or usual phosphate applications. In using this table, the bath total and free acid is determined, and then the gassing time to approximate the nitrate, and the bath adjusted to a coarser or smoother finish, as required. When a smoother amorphous coating is being sought, it is important that the total to free acid ratio fall below 8 total to 1 free acid, which may require an addition of the concentrate to obtain free acid. In cases where more concentrate is added to raise the free acid, the desired proportion of nitrate should also be added.

EXAMPLE IV.—MICROCRYSTALLINE ZINC PHOSPHATE SPRAY BATH

A spray phosphate concentrate was made from the No. 6 zinc phosphate concentrate in Table II by dissolving 7.3% by weight of $CaCl_2$ therein. This calcium chloride containing phosphate concentrate was used at 2% by volume to make up a spray bath that is accelerated by sodium nitrite in the manner disclosed by Romig in U.S. Pat. 2,132,883. The spray solution is maintained by a constant feed of the calcium containing zinc phosphate concentrate along with a constant feed at the same rate of a sodium nitrite solution containing one pound per gallon of $NaNO_2$. The bath is kept at a twenty point strength of calcium modified zinc phosphate and a 2 to 3 point strength of sodium nitrite measured by a titration with 0.042 normal permanganate, by constant feed proportioning pumps. The solution is held at 140 to 150° F. and continuously sprayed over the conveyorized work by a circulating pump at the tank. The resultant zinc phosphate coatings are of a smooth amorphous nature, and make an excellent paint base when water rinsed, dilute chromic acid rinsed, and dried in the usual manner. Such amorphous type coatings have a higher lustre when enameled and less tendency to chip under impact. Besides the improved smooth finish, this process has another advantage over the prior art of Romig, in that the chloride ion produces much less sludge in the bath than the prior art zinc phosphate baths without this addition.

It is apparent that the calcium modified zinc phosphate system when accelerated by the nitrosyl depolarizers of this invention can be used in both spray and dip type installations, and that the system can be modified to coat either heavier coatings for cold extrusion or very light coatings for under paint.

It is to be understood that in accordance with the provisions of the patent statutes, the particular form of product shown and described and the particular procedure set forth are presented for purposes of explanation and illustration and that various modifications of said products and procedure can be made without departing from my invention.

Having thus described my invention, I claim:

1. A smooth coating zinc di-hydrogen phosphate immersion coating bath made up from 1% to 5% by volume of a zinc phosphate coating concentrate that is substantially free of sulfate ion and that has an acid ratio above 1 free acid to 5 total acid to provide a bath strength of 10 to 50 points, and consisting essentially of from about 2 to 10 grams per liter of zinc, from about 7 to 35 grams per liter of phosphate and a highly soluble non-oxidizing salt of calcium that is about one quarter molar to the zinc, said bath being accelerated by an alkali metal nitrate equal numerically in grams per liter to at least one half of the total bath points.

2. A smooth coating zinc di-hydrogen phosphate spray coating bath made up from 1% to 5% by volume of a zinc phosphate coating concentrate that is substantially free of sulfate ion and that has an acid ratio above 1 free acid to 5 total acid to provide a bath strength of 10 to 50 points and consisting essentially of from about 2 to 10 grams per liter of zinc, from about 7 to 35 grams per liter of phosphate, and a highly soluble non-oxidizing salt of calcium that is about one quarter molar to the zinc, said bath being accelerated by the addition of a solution of alkali metal nitrite in sufficient amount to oxidize the dissolved iron from ferrous to ferric, to depolarize the evolved hydrogen and to titrate at least 2 points of 0.042 normal permanganate.

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