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PHOSPHATING BATH AND PROCESS

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ABSTRACT OF THE DISCLOSURE

The invention provides for a composition to form a bath for the production of corrosion resistant phosphate coatings on ferrous zinc and aluminum parts. The bath comprises an aqueous solution of phosphoric and nitric acids, zinc and nickel salts and a small amount of a β-ketonic ester, e.g. methyl or ethyl acetoacetate.

This application is a continuation-in-part of our prior application Ser. No. 510,947 filed Dec. 1, 1965, now abandoned.

An object of the present invention is the provision of a bath and of a process for producing zinc phosphate coatings on steel and other ferrous metals which is extremely economical, has unusually low sludge and scale build-up, and is further characterized by reduced chemical consumption, wide latitude in solution concentration and extended bath life. A further object is the provision of a zinc phosphate coating bath which reduces the need for large and frequent additions of new chemicals, and which allows simpler and less frequent chemical control of the composition of the bath.

In accordance with the present invention the chemical bath of the present invention includes a chemical for complexing insoluble zinc and phosphates in the bath so that the zinc is returned to the operating bath in a usable form, thereby reducing sludge and scale formation, reducing consumption of chemicals, extending the bath-life and controlling the iron build-up of the bath.

The bath and process of the present invention produces excellent and superior zinc phosphate coatings on ferrous metals with coating weights of from 2000 to 3000 mg. per square foot being produced in 2 to 30 minutes at temperatures of from 160° to 210° F.

The phosphate coating process of the present invention is illustratively and preferably carried out in accordance with the following example:

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The cleaner recommended to remove oil, grease and dirt from the metal surface is any alkaline cleaner especially for steel, such as—

	Parts by weight
Trisodium phosphate, anhydrous	4
Sodium tripolyphosphate, anhydrous	4
Sodium metasilicate, anhydrous	30
Sodium carbonate, anhydrous	23
Sodium hydroxide	30
Anionic wetting agents, such as "Sterox DJ"	9
or—	
Trisodium phosphate, anhydrous	8
Sodium carbonate, anhydrous	23
Sodium hydroxide	30
Sodium metasilicate	30
Anionic wetting agent ("Sterox DJ")	9

The tank should be of low carbon steel and equipped with a steam coil at one end of the tank, or gas burners under the tank to operate at a slow boil. An overflow dam may be provided at the other end of the tank. From 4 to 8 ounces by weight of the cleaner is required per gallon of solution to start the tank and additions should be made in small amounts from time to time.

Processing time is generally about 5 minutes, but exceptionally dirty work may require longer. Vapor degreasing or solvent cleaning may be substituted for alkali cleaning.

SCALE OR RUST REMOVAL

Whenever the steel parts are coated with an oxide or scale it is desirable to pickle the metal prior to phosphating. For most parts a pickle in cold hydrochloric acid is satisfactory, although for exceptionally heavy scale, a hot sulfuric acid pickle may be required.

Where hydrochloric acid is used, a strength of 50% by volume concentrated acid and water is recommended and in most cases an inhibitor is desirable. The use of 4 oz. by weight of urea or thiourea, as an inhibitor, for every 10 gallons of acid will prevent any appreciable attack on this base metal and in addition will conserve the acid strength of the pickle.

While alkali cleaning and acid pickling are satisfactory for preparation of work for phosphating, abrasive treatments such as sand, grit or vapor blasting are very effective in cleaning and the phosphate film produced after such treatment is excellent.

WATER RINSING

Since it is desirable not to carry over any alkali into the acid tank or acid solution into the phosphating bath, it will be advantageous to provide water tanks in the processing line and the tanks may be constructed of steel.

ILLUSTRATIVE PROCESSING CYCLE

Tank	Concentration	Temperature, °F.	Time	Tank material
#1 Alkaline Cleaner	4–8 oz./gal	180–212	5–10 min	Mild steel.
#2 Cold Water Rinse		Ambient		Do.
#3 Acid Dip (optional):				
Hydrochloric Acid	18%	do	10–60 sec	Polyethylene, rubber-lined or fiberglass.
Sulfuric	10%	120–150	do	Lead-lined.
#4 Cold and Hot Water Rinse		Ambient to 180		Mild steel.
#5 Phosphate Dip	4%	160–210	2–30 min	Stainless steel Type 304 or 316.
#6 Cold Water Rinse		Ambient		Mild steel.
#7 Sealer	1 pint/100 gals	130–150	10–60 sec	Do.
#8 Supplementary finish, such as oil, wax or lacquer.				

PHOSPHATE DIP

The tank for holding the phosphating bath solution should be of stainless steel, type 304 or 316. Steam coils should preferably be of electropolished Type 316 stainless steel.

PHOSPHATE DIP SOLUTION MAKE-UP

The phosphating dip bath is very simple to make up and a minimum of control is required for operation. A new solution is made up using 4 gallons of concentrate and 96 gallons of water, plus 1 pint of the promoter-extender for each gallon of concentrate used.

A solution made up with 4 gallons concentrate per 100 gallons of solution will result in a 40 point bath. Additions of concentrate are required to maintain the strength of the processing bath at the rate of 1 pint per 100 gallons of solution to raise the total acid 1 point. Promoter-extender is again added in the ratio of 1 pint per gallon of concentrate used.

The preferred composition of the bath may be provided by mixing the following ingredients, which may be made up in concentrated form in the following proportions:

	Grams
Phosphoric acid 75%	27.2
Nitric acid 42° Bé.	9.6
Zinc oxide	9.4
Nickel nitrate (6 H_2O)	0.6
Water to make 80.0 ml.	

which concentrate is diluted with water to make 1 liter to form the working bath, to which is added from 2.5 to 25 ml. of undiluted commercial methyl acetoacetate or ethyl acetoacetate as a promoter-extender.

In place of the nickel nitrate, a cobalt salt such as cobalt carbonate may be used, and of course other soluble cobalt and nickel salts may be substituted for those specified in a similar molar ratio.

A slower working bath may be formed from zinc phosphate in water solution acidified by a slight excess of phosphoric acid.

Other excellent baths have the following compositions:

Phosphoric acid 75%—640 grams, 730 grams
Nitric acid 42° Bé.—252 grams, 214 grams
Zinc oxide—238 grams, 250 grams
Nickel nitrate (6 H_2O)—up to 5.0 grams
Cobalt carbonate—up to 6.0 grams
Water—400 ml., 426 ml.

and for the working bath, one part of either of the above is diluted with from 25 to 50 parts by volume of water. These working baths thus have compositions corresponding to:

	Grams per Liter			
Dilution	1:25	1:50	1:25	1:50
Phosphoric acid 75%	25.6	12.8	29.2	14.6
Nitric acid 42° Bé	10.8	5.4	8.56	4.28
Zinc oxide	9.5	4.75	10.0	5.0
Nickel nitrate (6 H_2O)	0.2	0.1		
Cobalt carbonate			0.24	0.12
Promoter-extender	2.5 to 25 ml.			

In place of methyl or ethyl acetoacetate, β-ketonic esters subject to substantial enolization in dilute aqueous solution may be used.

Methyl acetoacetate is preferred as the promoter-extender in the bath. Where some of the other β-ketonic esters are used as the promoter-extender for the bath, the effect of the β-ketonic ester may not be fully achieved until after a period of several hours or a day.

A new phosphating bath for use with the present invention should be operated for several hours with about 3½ pounds of scrap iron, iron chips or steel wool per 100 gallons, before regular production work is processed. This builds up some iron in the bath, which is required for proper operation.

The phosphating bath should be maintained in the temperature range of 140°–210° F. and frequent additions of water should be made to replace that lost through evaporating to maintain the solution within proper concentration limits.

The immersion time in the phosphating bath may vary from 2 to 30 minutes. The time is dependent upon coating weights required, type of processing equipment, operating temperature and strength of the bath as well as the chemical composition and surface condition of the ferrous metals to be treated. Coating weights of 2000 to 3000 milligrams/square foot are usually produced in 15 minutes at 200° F.

SOLUTION CONTROL

During the operation of the phosphating bath, it is advisable to control the total acid, free acid and iron content of the bath within specified limits. The following procedures may be used to determine the condition of the phosphating bath.

(A) Total acid

(1) Pipet a 10 ml. sample into a 250 ml. beaker. Add 100 ml. distilled water.
(2) Add 5 drops of Phenolphthalein Indicator.
(3) Titrate to a yellow endpoint with 0.1 Normal sodium hydroxide.
(4) The number of mls. of 0.1 Normal sodium hydroxide used equals the number of points free acid.

(C) Iron

(1) Pipet a 10 ml. sample into a 150 ml. beaker.
(2) Add 1 to 2 drops of concentrated sulfuric acid.
(3) Titrate with 0.18 Normal potassium permanganate until a faint pink color persists.
(4) Each ml. of 0.18 Normal potassium permanganate used is equal to 1 gr./liter of iron.

For optimum results, the phosphating bath should be maintained within the following limits:

Total acid	40–45
Free acid	4–6
TA/FA ratio	6/1–10/1
Iron (gr./liter)	3–5

Acid dipping prior to phosphate coating will cause larger phosphate crystals to form. Acid dips are preferably used only if necessary to remove rust or scale from parts to be treated.

The bath prepared from the above formula comprises a mixture of zinc phosphate and zinc nitrate in aqueous solution with orthophosphoric and nitric acids and with a minor amount of a nickel or cobalt salt, to which is added a minor amount of a β-ketonic ester subject to enolization.

The range of concentration of the various ions in the bath may vary between rather wide limits and in the working bath are:

Zinc (Zn^{++})—1.3 to 16 g./liter, preferably 3.8 g./l.
Nickel (Ni^{++}) or cobalt (Co^{++})—0 to 60 g./liter, preferably 0.06 g./l.
Phosphate (PO_4^{---})—7 to 250 g./liter, preferably 9.9 g./l.
Nitrate (NO_3^-) (optional)—0 to 35 g./liter, preferably 3.3 g./l.

The promoter-extender of the present invention is used in a concentration of from 2.5 to 25 grams per liter of working bath, preferably 5 grams per liter. While methyl acetoacetate and ethyl acetoacetate are preferred for use in the present invention, a similar amount of ethyl-C-methyl acetoacetate may be used.

In use, the baths of the present invention show great advantages over baths of the prior art as shown by the following table, showing the number of similar panels of steel sheet which can be treated by various baths and the sludge which accumulates during use.

The standard bath had the same composition as the preferred composition above, but with the addition of no promoter-extender.

Bath	No. of good panels	Sludge
Standard Bath, no addition	12	¼" to ⅜".
Standard Bath plys 0.5% methyl acetoacetate	40+	1/16" to ⅛".
Standard Bath plus 0.5% ethyl acetoacetate	40+	1/16" to ⅛".

What is claimed is:

1. A composition to be diluted with water to form a bath for the production of a corrosion resistant zinc phosphate coating on ferrous, zinc and aluminum parts consisting essentially of zinc and phosphate ions and methyl acetoacetate, ethyl acetoacetate or ethyl-C-methyl acetoacetate as a promoter extender to yield from 1.3 to 16 grams per liter zinc ions, 7 to 250 grams per liter phosphate ions and from 2.5 to 25 grams per liter of the promoter-extender.

2. A composition as in claim 1 including nickel or cobalt ions to yield up to 60 grams per liter.

3. A composition as in claim 1 including nitrate ions to yield up to 35 grams per liter.

4. A composition according to claim 1 to yield: zinc ions 3.8, phosphate ions 9.9, nitrate ions 3.3 grams per liter and 5 grams per liter of the promoter-extender.

5. A process for providing a corrosion resistant zinc phosphate coating on ferrous, zinc and aluminum parts comprising treating a part in a hot acidic solution consisting essentially of phosphate ions 7 to 250 grams per liter, zinc ions 1.3 to 16 grams per liter and 2.5 to 25 grams per liter of methyl acetoacetate, ethyl acetoacetate, or ethyl-C-methyl acetoacetate.

6. A process as claimed in claim 5 in which the bath also includes up to 60 grams per liter of nickel or cobalt ions.

7. A process as claimed in claim 5 which also includes up to 35 grams per liter of nitrate ions.

8. A process as claimed in claim 5 in which the bath consists of 3.8 grams per liter of zinc ions, 9.9 grams per liter phosphate ions, 3.3 grams per liter nitrate ions, 0.06 gram per liter of nickel or cobalt ions and 5 grams per liter of the promoter-extender.

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