

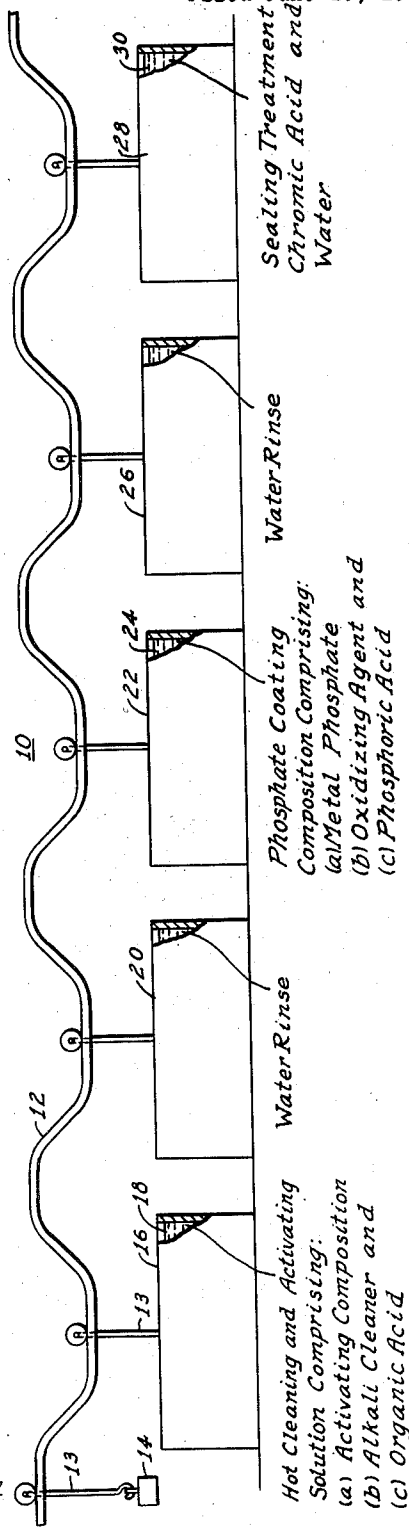
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2,516,008

COMPOSITION AND PROCESS FOR TREATING METAL SURFACES

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WITNESSES:

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COMPOSITION AND PROCESS FOR
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This invention relates to the art of producing corrosion resistant phosphate coatings on the surfaces of iron, zinc, cadmium, aluminum, and other metals and alloys.

It is a common and extensive practice at the present time to treat the surfaces of metals, such as iron, zinc, cadmium and aluminum and the like, with phosphate solutions that react with the metal surface to produce thereon a protective phosphate coating. Such phosphate coatings provide for a high corrosion resistance and form an excellent base for paints or other subsequently applied organic finishes.

It has been known that for a given metal the surfaces vary considerably in their degree of reactivity to the phosphate solutions so that non-uniform and widely varying phosphate coatings result. On some metals, such, for instance, as zinc the formation of a protective phosphate coating is usually difficult because of its inherent passivity, and the uniformity and protective characteristics of phosphate coatings on zinc is much poorer than secured with iron or steel. However, even between sheets of steel, which as a whole react more completely and more uniformly with phosphates than does zinc, there may be a considerable variation in the amount and protective quality of the applied phosphate coating not only between different sheets but with different areas on a single sheet. It has long been held desirable to be able to treat metal surfaces, regardless of their inherent characteristics, to produce a high quality phosphate coating that is relatively uniform at all times.

The prior art practices for producing protective phosphate coatings on metals, such, for example, as sheet steel comprised the following essential steps: first, the cleaning of the sheet in an alkaline solution consisting, for instance, of soda ash dissolved in water; secondly, the application of the phosphate coating composition to the sheet steel for a period of time of the order of one minute; and lastly, applying a dilute water solution of chromic acid to seal the phosphate coating previously produced.

It has been suggested that the cleaned sheet steel may be pretreated with an activating composition composed of an aqueous solution containing disodium orthophosphate and a small amount of an activating metal, such as titanium. The activating composition appears to render the entire metal surface much more active so that the phosphate coating composition reacts more rapidly and more completely with the metal in the subsequent step of the process.

In the co-pending applications, Serial Nos.

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569,274, filed December 21, 1944, now Patent 2,456,947, and 510,251, filed November 13, 1943, now abandoned, it has been further suggested that the activating composition be combined with the alkaline metal cleaner so that the metal surfaces may be simultaneously cleaned and activated. The advantages of such a combined operation are that the conventional processing equipment need not be changed and the time for complete treatment of a piece of metal is not increased over that required when no activating composition is produced.

However, it has been discovered that when the activating composition is combined with the alkaline cleaner, the activating composition deteriorates rapidly at temperatures above 140° F. whereas the alkali cleaner itself is most effective at temperatures of from 160° F. to 212° F. Thus, it has been found that the use of the alkaline cleaner containing the activating composition at a temperature of 200° F. results in the activating effect disappearing in about an hour. It is obviously both uneconomical and undesirable to replenish the activating composition frequently, particularly since the change in its effect becomes noticeable in less than an hour, and therefore erratic results may occur.

The object of this invention is to provide a composition containing both an alkaline cleaning component and an activating component, plus a stabilizer so that the composition has a long life at elevated temperatures.

A further object of the invention is to provide a process for effectively and reliably treating the surfaces of metal members, whereby to simultaneously clean and activate them at an elevated temperature.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

For a better understanding of the nature and objects of the invention, reference should be had to the following detailed description and drawing, in which the single figure is a view in elevation of an apparatus for carrying out the invention.

In accordance with this invention, there is produced a composition for simultaneously cleaning and activating metal surfaces that has a long life when employed at elevated temperatures. The composition is prepared by combining (a) from 0.1 to 10 parts by weight of an activating composition composed of disodium orthophosphate and an activating compound of a metal from the group consisting of titanium, zirconium, lead and tin, (b) from 0.002 to 5 parts by weight of a stabilizer comprising a water soluble organic acid

having a carboxyl group attached directly to an aliphatic group, the organic acid being added in an amount equal to from 2% to 50% of the weight of the activating composition, and (c) from 2 to 20 parts by weight of an alkaline cleaning composition suitable for cleaning metal surfaces in a short period of time while at temperatures as high as the boiling point of the composition.

The entire composition is dissolved in water to provide from 0.1% to 10% of the activating composition in solution and from 2 to 10 ounces per gallon of the alkali cleaner composition.

The alkaline composition may be any suitable alkali metal compound which, when in water solution, produces a pH of between 10 and 12.5, and is effective in removing surface dirt from metal surfaces. Suitable alkaline compounds are soda ash, sodium bicarbonate, sodium silicates, trisodium phosphate, sodium hydroxide, borax, and mixtures thereof. Also, there may be employed alkaline soaps of the alkali metals, and ammonia or amine soaps, such for instance, as the reaction product of ammonia or triethanolamine with oleic or stearic acid, palmitic acid or other fatty acids having 16 carbon atoms. The soaps may be employed in the form of an emulsion with a hydrocarbon solvent, such as kerosene.

The activating composition is prepared by dissolving in water from 0.005 to 20 parts by weight a water soluble compound of at least one metal of the group consisting of titanium, zirconium, lead or tin, all of these metals being in group IV of the periodic table, with from 80 to 100 parts by weight of disodium orthophosphate. The aqueous solution so prepared is evaporated to dryness and the dried residue possesses the characteristics of activating metal surfaces when dissolved in water or water containing an alkali that does not exceed a pH of 12.5, or water that is not acid.

Examples of water soluble compounds of titanium, zirconium, tin and lead, that have been found satisfactory for producing the activating composition are titanium carbide, titanium tetrachloride, titanium trichloride, titanium hydroxide, titanium nitride, titanium potassium oxalate, titanium dioxide, zirconium chloride, zirconium sulphate, lead acetate, tin tetrachloride and stannic sulphate. Since only relatively small amounts of any titanium, zirconium, lead and tin compound need be dissolved, the compounds selected need be only slightly soluble in water to be suitable. Since the weight proportion of the required metal present varies from compound to compound, the amount of metallic compound employed should be selected accordingly.

As an example of the preparation of the activating composition, in 150 pounds of water there was dissolved 100 pounds of disodium orthophosphate and 3 pounds titanium potassium oxalate. The solution was heated to about 75 C. and slowly evaporated to a dry residue. The dry residue was a powerful activator for metal surfaces and was ready for use for activating metals by simply dissolving it in water.

Suitable organic acids for stabilizing the activating compositions are water soluble organic carboxylic acids having a carboxyl radical attached directly to an aliphatic group. Examples of such acids are citric acid, tartaric acid, oxalic acid, acetic acid, propionic acid, succinic acid, maleic acid, lactic acid and glycolic acid. Acids in which the carboxyl group is directly attached to an aryl group such, for example, as benzoic

acid have been found to be ineffective. The amount of the acid should comprise at least 2% of the weight of the dried activating composition, and preferably be of the order of 10%. The organic acid may be present in an amount equal to 50% of the weight of the activating composition. The maximum amount of any particular organic acid usable may be limited by its relative solubility in the solution.

The compositions combining the alkaline cleaning composition, the activating composition and the organic acid stabilizer may be prepared, without any water or only a small amount of water, as a composite mixture which may be shipped and need only be dissolved in sufficient water to produce a relatively dilute solution capable of simultaneously cleaning and activating metal surfaces at elevated temperatures. If desired, the three components may be shipped as mixtures of any two or else may be combined at the time the aqueous solution is prepared at the time the metal is being treated.

The organic acid stabilizer cannot be incorporated with the activated composition when it is being made by evaporation to a dry residue since it has been found that the resulting dry residue containing the organic acid is useless for its intended purpose if so prepared.

The following typical examples of compositions whose aqueous solutions in the proportions of from 2 to 10 ounces of the alkaline cleaner per gallon of water will function extremely effectively to simultaneously clean and activate metal surfaces:

Example I

	Parts by weight
Activating composition (containing 5% titanium)	2
Soda ash	6
Citric acid	0.2

Example II

	Parts by weight
Activating composition (containing 1% titanium)	3
Sodium sesquisilicate	10
Tartaric acid	0.6

Example III

	Parts by weight
Activating composition (containing 10% titanium)	6
Trisodium phosphate	13
Oxalic acid	1.0

Example IV

	Parts by weight
Activating composition (containing 1% titanium)	0.2
Soda ash	5
Trisodium phosphate	5
Lactic acid	0.01

Example V

	Parts by weight
Activating composition (containing 1% titanium)	0.4
Emulsion cleaner composed of:	
Kerosene.....per cent... 59	} ----- 15
Oleic acid.....do..... 5	
Triethanolamine.....do..... 2.3	
Water.....do..... 33.7	
Acetic acid.....	0.1

The compositions in each of the above examples

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may be dissolved in water in the amount of from 2 to 10 ounces of the alkaline composition per gallon and providing a pH of from 10 to 12.5 may be employed at any desired temperature, preferably above 160° F. A composition similar to Example I was used for over a week at near boiling temperature without loss of activity. The same solution without the citric acid was incapable of activating metal surfaces shortly after one hour at 200° F.

The composition may be employed for treating sheet steel, iron castings, steel bars and rods, zinc die castings, galvanized sheets and electro-plated zinc base members, cadmium plated members, sheets of aluminum and aluminum alloys, and alloys in which these metals predominate. The time of application of the hot cleaning and activating solution need not be long. A few minutes is ordinarily sufficient to remove surface grease and loose oxides and dirt. The composition may be applied by spraying, if necessary, under high pressure to remove the more adherent particles of dirt. If the metal is badly rusted or oxidized or scaled, it may be necessary to wire brush or acid etch the metal before it is subjected to the activating alkaline solutions of this invention.

After the metal surface has been treated with the component alkaline cleaner and activating composition so that it is clean and in a highly active state, it may be subjected to an appropriate phosphate coating solution. A suitable solution for treating steel or other metals is the following:

Manganese phosphate	-----pounds--	1.75
Phosphoric acid (83%)	-----do-----	5
Sodium nitrate	-----do-----	0.5
Cupric nitrate	-----ounces--	.25
Water—to make one gallon.		

This forms a concentrated solution which may be diluted in the proportion of 1 part to about 33 parts of water to make a 3% solution which may be applied to the metal to produce a protective coating.

A solution suitable for treating zinc metal to produce a phosphate coating thereon comprises the following by weight:

Iron	-----per cent--	0.25
Zinc phosphate	-----do-----	0.04
Sodium nitrate	-----do-----	0.5
Phosphoric acid (85%)	-----do-----	1.0
Remainder ----- Water		

Numerous other solutions for producing phosphate coatings are known in the art and it is believed unnecessary to list them in detail. Essentially, such solutions comprise a phosphate, free phosphoric acid and an oxidizing agent, such as sodium or potassium nitrate or nitrite. They may be applied by spraying, brushing or dipping of the metal surfaces therein.

When applied to the activated and cleaned surfaces, such phosphate coating compositions will produce protective phosphate coatings thereon within a short period of time, about 15 seconds being sufficient. However, the greatest advantage derived from activation is the fact that metal surfaces acquire a highly uniform phosphate coating. In most cases the phosphate coatings are almost velvety in appearance. Under the microscope they exhibit a very fine crystalline structure. There are no bare spots, nor do they show a gross blotchy effect which often occurs with metal that has not been activated.

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Referring to the single figure of the drawing, there is illustrated an apparatus 10 for carrying out the complete process disclosed herein. The apparatus comprises a track 12 for supporting a plurality of roller mounted hangers 13 on which depend metal members 14 to be provided with a protective phosphate coating. The members initially are moved into position over a tank 16 and drop therein for immersion, or for spraying if desired, in a solution 18 having a pH of from 10 to 12.5, in which solution the members 14 are cleaned and activated simultaneously. The solution 18 comprises an alkaline cleaner, the activating composition and the organic stabilizer. The solution is used hot, that is between 160° F. and boiling, and, therefore, operates rapidly and effectively to remove any surface contamination, such as grease and dirt. It has been found that while being cleaned the metal is most responsive to activation so that the highest degree of activation of the metal takes place under these conditions.

After being treated with the solution 18 until clean, usually in a short period of time, the clean and activated metal member 14 is subjected to a water rinse in tank 20. The water rinse will remove any material whose presence is not desired in subsequently applied phosphate coating compositions. Immediately after rinsing or, in some cases dispensing with the water rinse, the member 14 is conveyed to a tank 22 containing a phosphate coating composition 24. The phosphate composition reacts rapidly and uniformly over the entire pretreated surface of the member 16 to produce thereon a smooth, fine, uniform protective phosphate coating. Thence, the coated member 14 may be moved along the conveyor 12 to a second water rinse tank 26. The last step in the process is to dip the member 14 in a tank 28 containing a hot aqueous solution 30 of chromic acid in the proportion of 7.5 ounces of chromic acid to 100 gallons of water. The chromic acid functions so that in a few seconds it seals the phosphate coating thereby improving its corrosion resistance. If the chromic acid solution is about 200° F., the heat imparted to the members 14 is ordinarily sufficient to dry them by simple exposure to the atmosphere. In some cases, however, the members may be conveyed to a drying oven wherein any water on the surface is completely evaporated leaving a dry sealed phosphate coating having the utmost protective value.

The apparatus shown in the figure corresponds to that conventionally employed at the present time for phosphate coating without the use of an activating pretreatment. It will be apparent that by being able to combine the cleaning and activating solution to effect a simultaneous cleaning and activation of metal in the single tank 16, no changes in the apparatus are required. Otherwise, the necessity for a separate tank for the solution for activating the metal surfaces would require extensive changes, such as rebuilding of a conveyor and shifting of tanks. Also the extra time required for an additional treating step is avoided by the present invention. Furthermore, the effectiveness of the combined cleaning and activating solution is greater than that processed by separate applications of a cleaning solution and an activating solution.

Both the alkaline cleaner and the activating composition may be replenished from time to time as they are used up. The proportion of activated composition to cleaner may be readily

determined from experience for metal of a given degree of cleanliness and a combined salt or the like may be added that replenishes both in the proportions in which they are used up.

Since certain changes may be in the above invention and different embodiments of the invention may be made without departing from the scope hereof, it is intended that all matter contained in the disclosure shall be interpreted as illustrative and not in a limiting sense.

I claim as my invention:

1. An aqueous composition suitable for hot treating the surface of a metal selected from the group consisting of iron, zinc, cadmium, aluminum and alloys in which these metals predominate to provide for simultaneously cleaning and activating the surface therein for expediting the subsequent formation of protective coatings thereon, consisting of (a) between 0.1% and 10% by weight of the dried residue of an activating composition derived by dissolving in water from 0.005% to 20% by weight of a water soluble compound of at least one of the group of metals consisting of titanium, zirconium, lead and tin and the balance being disodium orthophosphate, and evaporating the solution so produced to dryness, (b) from 2% to 50%, based on the weight of the dried residue, of a water soluble organic acid having a carboxyl radical attached directly to an aliphatic group to stabilize the activating composition, (c) an alkaline composition selected from the group consisting of alkaline alkali metal compounds, ammonia soaps and amine soaps suitable for cleaning metal surfaces in an amount to provide a pH of from 10 to 12.5 in the aqueous composition, and the balance being water.

2. An aqueous composition suitable for hot treating the surface of a metal selected from the group consisting of iron, zinc, cadmium, aluminum and alloys in which these metals predominate to provide for simultaneously cleaning and activating the surfaces therein for expediting the subsequent formation of protective coatings thereon, consisting of (a) between 0.1% and 10% by weight of the dried residue of an activating composition derived by dissolving in water from 0.005% to 20% by weight of a water soluble compound of at least one of the group of metals consisting of titanium, zirconium, lead and tin and the balance being disodium orthophosphate, and evaporating the solution so produced to dryness, (b) from 2% to 50%, based on the weight of the dried residue, of a water soluble organic acid having a carboxyl radical attached directly to an aliphatic group to stabilize the activating composition, (c) an alkaline composition including substantial amounts of at least one alkali metal compound from the group consisting of phosphates, silicates and carbonates, the alkaline composition being suitable for cleaning metal surfaces in an amount to provide a pH of from 10 to 12.5 in the aqueous composition, and the balance being water.

3. An aqueous composition suitable for hot treating the surface of a metal selected from the group consisting of iron, zinc, cadmium, aluminum and alloys in which these metals predominate to provide for simultaneously cleaning and activating the surfaces therein for expediting the subsequent formation of protective coatings thereon, consisting of (a) between 0.1% and 10% by weight of the dried residue of an activating composition derived by dissolving in water from 0.005% to 20% by weight of a water solu-

ble compound of at least one of the group of metals consisting of titanium, zirconium, lead and tin and the balance being disodium orthophosphate, and evaporating the solution so produced to dryness, (b) from 2% to 50%, based on the weight of the dried residue, of a water soluble organic acid having a carboxyl radical attached directly to an aliphatic group to stabilize the activating composition, (c) an alkaline composition, including a substantial proportion of an amine soap, the alkaline composition being suitable for cleaning metal surfaces in an amount to provide a pH of from 10 to 12.5 in the aqueous composition, and the balance being water.

4. A composition composed of (a) from 0.10 to 10 parts by weight of the activating composition derived by dissolving in water from 0.005% to 20% by weight of at least one water soluble compound of a metal from the group consisting of titanium, zirconium, lead and tin, and the balance being disodium orthophosphate, and evaporating the solution to dryness, (b) from 0.002 to 5 parts by weight of a water soluble organic acid having a carboxyl group attached directly to an aliphatic group, the amount of the organic acid being between 2% and 50% by weight of the activating composition, and (c) from 2 to 20 parts by weight of an alkaline composition selected from the group consisting of alkaline alkali metal compounds, ammonia soaps and amine soaps capable of cleaning metal when dissolved in water, the alkaline composition being present in an amount to produce a pH of from 10 to 12.5 when 4 to 10 ounces of the entire composition is dissolved in a gallon of water.

5. A composition composed of (a) from 0.10 to 10 parts by weight of the activating composition derived by dissolving in water from 0.005% to 20% by weight of at least one water soluble compound of a metal from the group consisting of titanium, zirconium, lead and tin, and the balance being disodium orthophosphate, and evaporating the solution to dryness, (b) from 0.002 to 5 parts by weight of a water soluble organic acid having a carboxyl group attached directly to an aliphatic group, the amount of the organic acid being between 2% and 50% by weight of the activating composition, and (c) from 2 to 20 parts by weight of an alkali composition including at least one alkali metal compound from the group consisting of the alkali metal phosphates, silicates and carbonates, the alkaline composition being capable of cleaning metal when dissolved in water, the alkaline composition being present in an amount to produce a pH of from 10 to 12.5 when 4 to 10 ounces of the entire composition is dissolved in a gallon of water.

6. A composition composed of (a) from 0.10 to 10 parts by weight of the activating composition derived by dissolving in water from 0.005% to 20% by weight of at least one water soluble compound of a metal from the group consisting of titanium, zirconium, lead and tin, and the balance being disodium orthophosphate, and evaporating the solution to dryness, (b) from 0.002 to 5 parts by weight of a water soluble organic acid having a carboxyl group attached directly to an aliphatic group, the amount of the organic acid being between 2% and 50% by weight of the activating composition, and (c) from 2 to 20 parts by weight of an alkaline composition including an amine soap, the alkaline composition being capable of cleaning metal when dissolved in water, the alkaline composition being

present in an amount to produce a pH of from 10 to 12.5 when 4 to 10 ounces of the entire composition is dissolved in a gallon of water.

7. In the process of applying phosphate coatings on metals, wherein simultaneous cleaning and activating of the surfaces of metals from the group consisting of iron, zinc, cadmium, aluminum and alloys in which these metals predominate is effected to enhance the subsequent formation of protective phosphate coatings thereon, the step comprising applying to the metal surface a hot aqueous solution consisting of (a) between 0.1% and 10% by weight of the dried residue of an activating composition derived by dissolving in water from 0.005% to 20% by weight of a water soluble compound of at least one of the group of metals consisting of titanium, zirconium, lead and tin and the balance being disodium orthophosphate, and evaporating the solution so produced to dryness, (b) from 2% to 50%, based on the weight of the dried residue, of a water soluble organic acid having a carboxyl radical attached directly to an aliphatic group to stabilize the activating composition, (c) an alkaline composition selected from the group consisting of alkaline alkali metal compounds, ammonia soaps and amine soaps suitable for cleaning metal surfaces, in an amount to provide a pH of from 10 to 12.5 in the aqueous composition, and the balance being water.

8. In the process of applying phosphate coatings on metals, wherein simultaneous cleaning and activating of the surfaces of metals from the group consisting of iron, zinc, cadmium, aluminum and alloys in which these metals predominate is effected to enhance the subsequent formation of protective phosphate coatings thereon, the step comprising applying to the metal surface a hot aqueous solution consisting of (a) between 0.1% and 10% by weight of the dried residue of an activating composition derived by dissolving in water from 0.005% to 20% by weight of a water soluble compound of at least one of the group of metals consisting of titanium, zirconium, lead and tin and the balance being disodium orthophosphate, and evaporating the solution so produced to dryness, (b) from 2% to 50%, based on the weight of the dried residue, of a water soluble organic acid having a carboxyl radical attached directly to an aliphatic group to stabilize the activating composition, (c) an alkaline composition selected from the group consisting of alkaline alkali metal compounds, am-

monia soaps and amine soaps suitable for cleaning metal surfaces, in an amount to provide a pH of from 10 to 12.5 in the aqueous composition, and the balance being water, the aqueous solution being at a temperature of between 160° F. and the boiling point, the organic acid enabling the activating composition to function at the high temperature for long periods of time.

9. The process of simultaneously cleaning and activating the surfaces of metals from the group consisting of iron, zinc, cadmium, aluminum and alloys in which these metals predominate, to enhance the subsequent formation of protective phosphate coatings thereon comprising applying to the metal surface a hot aqueous solution consisting of (a) between 0.1% and 10% by weight of the dried residue of an activating composition derived by dissolving in water from 0.005% to 20% by weight of a water soluble compound of at least one of the group of metals consisting of titanium, zirconium, lead and tin and the balance being disodium orthophosphate, and evaporating the solution so produced to dryness, (b) from 2% to 50%, based on the weight of the dried residue, of a water soluble organic acid having a carboxyl radical attached directly to an aliphatic group to stabilize the activating composition, (c) an alkaline composition selected from the group consisting of alkaline alkali metal compounds, ammonia soaps and amine soaps suitable for cleaning metal surfaces, in an amount to provide a pH of from 10 to 12.5 in the aqueous composition, and the balance being water, the aqueous solution being at a temperature between 160° F. and the boiling point, the organic acid enabling the activating composition to function at the high temperature for longer periods of time, and immediately thereafter applying to the cleaned and activated metal surfaces a phosphate coating composition comprising a solution of phosphoric acid, phosphates and an oxidizing agent to produce a protective phosphate coating thereon.

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