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COMPOSITIONS AND METHODS FOR DEPOSITING AMORPHOUS METAL-PHOSPHATE COATINGS ON METAL SURFACES

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This invention relates to methods or processes of depositing coatings or films on metal surfaces to make them resistant to corrosion by applying chemical solutions to such metal surfaces, and to chemical compositions which may be employed in making up such chemical treating solutions.

An object of this invention is to provide a process whereby metal surfaces may be protected against the corrosive action of the atmosphere by wetting the surfaces to be protected with a solution containing a water soluble salt of a metal and a glassy or amorphous phosphate whereby an amorphous metal phosphate film or coating is deposited on the treated surfaces.

Another object of the invention is to provide a process of the character above set forth in which the chemical solution employed is operative in an unheated state, is rapid in its coating action, and which does not attack the metal or cause the metal itself to lose weight.

A further object of the invention is to provide a process of the character set forth above in which the treating solutions are capable of controlled replenishment so that they may be maintained in an active and operative condition, thereby making continuous processing of metals possible without wasteful use of chemicals.

A still further object of the invention is to provide a chemical composition containing certain chemical compounds so proportioned with respect to each other that treating baths or solutions suitable for the processes may be made up for use by operators unskilled in the chemical arts, and whereby, through the use of simple tests, the effectiveness of the solution may be readily determined and replenishment thereof effected by the addition of said composition to the solution in amounts indicated by the tests.

And a still further object of the invention is to provide a composition for, and a method of, treating metal surfaces to deposit thereon coatings which not only protect against corrosion, but also form desirable and useful bases for finish coatings, such as paints, lacquers, enamels, and which improve the bonds between the metals and such finish coatings, and in the case of organic coatings, gives the metals a high degree of protection against attack in corrosive atmospheres.

The chemical treatment of metals, particularly ferrous metals which are quite susceptible to corrosion, has been practiced for many years. Oeschger Patent No. 1,354,263 being one of the early patents teaching the treatment of metals with aqueous phosphate solutions discloses a process forming a protective coating by chemical

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reaction of the phosphate with an iron surface to be coated. Coslett Patent 1,007,069 and Heathcote, British Patent 29,504 both teach the use of phosphate solutions with attack ferrous metals to provide a corrosion resistant surface. Many subsequent patents have been issued which pertain to the use of processes involving the chemical reaction of the phosphate treating solution and the metal surface. In all of these processes, there is a visible etching or roughening of the metal and a loss of metal weight.

Roland application Serial No. 468,690 filed December 11, 1942, now abandoned, discloses the treatment of ferrous metals with solutions containing certain molecularly dehydrated phosphates and a minimum concentration of 100 p. p. m. of calcium, strontium, barium, zinc, or cadmium. In this process, an amorphous metal phosphate protective coating consisting of the reaction product of the molecularly dehydrated phosphate and the metallic element selected is deposited upon the metal surface, there being no visible attack of the metal by the phosphate treating solution.

The invention of this application involves improvements over the aforesaid application of Roland.

I have found that adequate protective phosphate coatings may be deposited on many metals other than the ferrous metals. For example, I may treat iron, steel, copper, zinc, silver, magnesium, and many alloys of these several metals. Although unalloyed ferrous metals are usually extremely susceptible to atmospheric corrosion, the other metals which may be treated by my process are also susceptible to corrosion in varying degrees.

When certain materials which function as oxidizing agents are employed in the coating solutions, a number of new and unexpected results and advantages are obtained. Notably, the treating solution deposits the desired amorphous metal phosphate coating without heating of the solution; the coating is deposited at a rapid rate; the solution may be made more concentrated by being capable of adjustment to lower pH values; the solutions are more stable and do not decompose to any material extent; the solutions may be replenished and restored to their initial condition by adding to the working solution the chemicals used in making up the solution initially in the same proportions as they were present in the original solution, and in the amounts required to restore the solution to its original or desired concentration; the ratio of coating metal

ion to phosphate does not change materially from that of the original solution even though a substantially large percentage of the total coating materials in the original solution have been removed thus making replenishment easy and subject to control: and lastly, the solutions are operative at relatively low pH values in the acid range without attacking the metal surfaces being treated.

Heretofore, the deposition of a commercially satisfactory protective amorphous metal phosphate coating was considered impracticable if not impossible at solution temperatures of about 25° C. (room temperature) unless the metal surfaces were in contact with the treating solutions for ten minutes or more. I have found that an acceptable coating may be deposited on metal surfaces in approximately ten seconds at 25° C. by using my preferred composition in accordance with the process of this invention. I have also found that such amorphous metal phosphate coatings may be applied in less than ten seconds if the solutions are maintained at slightly elevated temperatures or if relatively high concentrations of the chemical compositions are used in the solution. Operation of the coating process at room temperature has a two-fold advantage, a saving in heat and equipment costs and a prolongation of the effectiveness of the solutions. By adapting my process to the continuous production of sheet metals an amount of the protective phosphate coating can be applied in such a short period of time that the rate of output is not retarded.

In practicing the invention, the metallic surfaces to be coated are first cleaned to remove soil. I then apply the treating solution to the cleaned metal surfaces either by immersion of the metal in the treating solution or by spraying the solution on the metal. In many cases, spraying the treating solution on the metal is preferred.

While the treating solution is in contact with the metal, an amorphous metal phosphate film is deposited on the surface thereof. The rate at which the film is deposited at a given temperature of solution is dependent on a number of factors such as the concentration of and the particular kind of metal ion and phosphate employed in the solution and the ratio of the metal ion to phosphate, the pH of the solution and the amount and kind of oxidizing agent employed.

After the metal has been subjected to the treating solution, the excess solution may, if desired, be removed from the metal surfaces by rinsing. A preferred rinsing step if used is described more in detail elsewhere herein.

The treating solution may be made by adding to a known quantity of water at least one water-soluble salt of the metals of the group consisting of calcium, zinc, magnesium, cobalt, cadmium, iron, aluminum, barium, strontium, manganese, chromium, a molecularly dehydrated phosphate such as a glassy or amorphous alkali metal phosphate, for example, glassy sodium phosphate, an oxidizing agent, and if necessary a pH adjusting chemical which will establish the desired pH in the solution. The metal salts of the above group may for convenience be called coating metals.

The coating metals and phosphate are added to give a preferred weight ratio of metal ion to phosphates and in total amount to provide an optimum concentration at the pH selected, as set later herein in more detail.

By the term molecularly dehydrated phosphate glass, I means the glassy phosphates having the

ratio formula of $xM_2O:1P_2O_5$. A practical range of ratios of $M_2O:P_2O_5$ extends from about 0.4:1 to about 1.7:1 where M is an alkali metal or the ammonium radical. In the examples I have disclosed a specific sodium phosphate glass, also known commercially as sodium metaphosphate glass or a glass of the metaphosphate type, which has a ratio of $Na_2O:P_2O_5$ of about 1.1:1. The glassy phosphates in the range from 0.4:1 to about 1.1:1 are more or less acid, from the ratio of about 1.1:1 to about 1.7:1 the glasses range from about neutral to alkaline. The glass having a ratio of about 1.7:1 is most alkaline, having a pH in ¼% solution of about 9.5 to 9.8. The pH of a ¼% solution of a sodium phosphate glass of the ratio of about 0.4:1 is about 2 or less. The glasses in between these limits have intermediate pH values in ¼% solution depending on the particular ratio of $Na_2O:P_2O_5$ and the extent to which the glass is dehydrated.

The coating or film which deposits on metal surfaces from the treating solutions is an amorphous metal phosphate. The composition of the coating as determined by analysis is that of a metal phosphate. For example, the amorphous coating deposited from an aqueous solution made up from calcium chloride, sodium phosphate glass, and an oxidizing agent, has approximately the composition of $Ca(PO_3)_2$ and is amorphous.

The coating metals above mentioned may be in the form of chlorides, nitrates, sulfates, acetates, oxides, carbonates, or hydroxides. The sulfates and acetates are not as desirable as the chlorides and nitrates because the rate at which the amorphous metal phosphate coating is deposited is not as high as that attained with the chlorides and nitrates of these metals.

In the practice of the invention by industry, it is advantageous that a prepared composition be available from which coating solutions can be made by merely dissolving specified quantities of the composition in water in the proportions required for any particular or desired concentration of solution. Since the glassy phosphates suitable for these compositions are more or less hygroscopic, the coating metal salts, the pH adjusting materials, and the compounds which act as oxidizing agents should be relatively anhydrous to avoid caking of the composition during storage. The preferred metal salts are therefore chlorides. If the nitrates were readily obtainable in relatively anhydrous form, they would be more preferable for my purpose than the chlorides.

Of the various water soluble salts which react with the phosphate to deposit the amorphous metal phosphate coating on metal surfaces, calcium chloride is a desirable salt because it is relatively inexpensive, readily available in the market as a dry material, and is an effective compound for my purposes.

The water soluble salts which act as oxidizing agents and are suitable for purposes of this invention may be in the form of nitrates, nitrites, sulfites, permanganates, chromates, perborates, and ferricyanides. Of these, the sodium and potassium salts are preferable in that they are readily available at reasonable cost. In the practice of my invention I have found sodium nitrite, sodium nitrate, sodium sulfite, sodium perborate, potassium permanganate, potassium dichromate, potassium ferricyanide, and sodium hypochlorite, to be both practical and effective. However, any water soluble salt or substance which functions as an oxidizing agent may be employed.

In the prior art processes, where the orthophosphate coating solutions are employed, both oxidizing agents and reducing agents have been used to accelerate the rate at which coatings are formed. However, in these processes the solutions must be heated to temperatures ranging from 160°-200° F. In my process, furthermore, the reducing agents are not effective in that they deter the formation of the phosphate coating and in some cases prevent its formation. The relative effects of oxidizing agents and reducing agents on my coating solution are shown later herein by Table 1.

The effectiveness of my compositions and the solutions made therefrom or solutions made up from the individual components of the compositions, depends on the total concentration in solution of coating metal salt and phosphate glass, the ratio of the coating metal ion to phosphate in the solution and the oxidizing agent employed. The maximum concentration of metal ion and phosphate in the solution at a given temperature depends on the pH of the solution.

By effectiveness of my composition in solutions made from the components of the composition, I mean the quality of and the rate at which an amorphous metal phosphate coating will be deposited per unit area of metal surface per unit of time. The quality of the coating is a factor determinable by certain tests, for example, tests which indicate the ability of the coating or film to protect the metal against attack when (1) immersed in distilled water for a specified number of hours, (2) exposed to salt spray for a given number of hours, (3) exposed to atmospheric conditions at high or saturated humidities, and other well known tests. The ability of the coating to hold a paint or other finish when exposed as above, is also a measure of its quality. When metals which have been coated with the metal phosphate coatings in accordance with the invention are painted, and the painted surface is scratched through to the metal, the quality of the coating is measured by its ability to prevent the spread of corrosion beyond the area of the scratch, and by its ability to prevent the paint from lifting off the surface of the metal in the area contiguous with the scratch.

I have found that in order to obtain an effective amorphous metal phosphate coating on metal, the solution must contain not less than a certain minimum concentration of metal ion. Where calcium chloride is the coating metal salt employed, minimum effective concentration of calcium ion is about 100 p. p. m. by weight. While the solution to be effective must contain not less than a certain minimum of calcium ion, the weight ratio of molecularly dehydrated phosphate to metal ion must be held between certain limits, the maximum ratio being perhaps more critical than the minimum from the standpoint of ability of the solution to coat metal surfaces satisfactorily. I have also found that for a given total concentration of metal ion and molecularly dehydrated phosphate glass, and a given ratio of such phosphate to metal ion at that concentration, the solution will produce optimum coatings at a given pH value. In other words, there is an optimum pH value for a given solution at which optimum coating results are obtained. This is not to say, however, that effective coating results cannot be obtained at other pH values because effective coatings can be so obtained. By varying the concentration of metal ion and

proper adjustment of the pH of the solution to obtain optimum coating, the weight ratio of phosphate to calcium may vary between 0.05:1 to about 12:1. In this ratio range the optimum pH values will lie in the range from pH 3.0 to pH 8.0. For solutions containing 100 p. p. m. of calcium, the effective weight ratio of phosphate to calcium is in the range of about from 2:1 to about 8:1, that is, 200 p. p. m. of phosphate to 100 p. p. m. of calcium to 800 p. p. m. of phosphate to 100 p. p. m. of calcium. As the concentration of calcium is increased, the ratio range of phosphate to calcium is broadened. Thus, in a solution containing 5000 p. p. m. of calcium the effective ratio range of phosphate to calcium lies between values of about 0.05:1 and about 12:1.

So long as the proper ratio between calcium, or other coating metal employed, and molecularly dehydrated phosphate is maintained, and provided the solution is adjusted to the proper pH, there appears to be no real upper limit to the total concentration of metal salts such as calcium chloride, and molecularly dehydrated phosphate.

I have found that in the coating solutions a very orderly relationship exists between the following variables: pH value, total concentration of the sum of coating metal ion and molecularly dehydrated phosphate, and the ratio of coating metal ion to molecularly dehydrated phosphate. Thus, for a given time and temperature of treatment, I may prepare satisfactory treating solutions over a wide range of pH, concentration, and ratio of metal ion to phosphate. In order to adjust the pH of my coating solutions above pH about 5, a buffer must be employed. For example, if NaOH alone is used to adjust the pH of the coating solution from an initial pH of 5 to a final pH of 8, the properties of the solution are such that the pH will slowly return to near the original value. A buffer such as borax in conjunction with NaOH or other suitable alkaline material is satisfactory for adjusting the pH above 5. No special precautions need be observed when adjusting the solutions to pH values below about 5. I have found, for example, that at any given pH within the range above disclosed, I may prepare relatively more concentrated solutions merely by increasing the ratio of phosphate to metal ion. If, on the other hand, I choose to maintain a constant ratio of phosphate to metal ion, I may then prepare concentrated solutions by working in the lower range of pH values. When I prefer to employ solutions in the higher range of pH values, I may do so by using relatively lower total concentrations, keeping the ratio of metal ion to phosphate fixed; or, if I prefer to work both at a relatively higher value of pH and total concentration I may do so by increasing the ratio of phosphate to metal ion.

I have found that amorphous metal phosphate protective coatings can be deposited from treating solutions containing a metallic element in the solution, an oxidizing agent, and a soluble molecularly dehydrated phosphate over a rather broad range of pH values running from a minimum of 3 to a maximum of about 8. However, I have found that solutions containing a mixture of calcium and aluminum as metal ions in conjunction with the molecularly dehydrated phosphate glass in proper proportions and an oxidizing agent, will produce satisfactory amorphous phosphate coatings at pH values as low as 2.0, there being no visible attack on the metal even at this low pH value. When I employ a treat-

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ing solution having a total concentration of calcium and molecularly dehydrated phosphate of about 9000 p. p. m. by weight, the ratio of calcium to phosphate being 1:5, the most satisfactory pH range is from 3 to 5, whereas when I use a solution containing about 1800 p. p. m. of the sum of calcium and phosphate in the ratio of 1:5, the preferred pH range is from about 4 to about 8. I have found that at a concentration of 5.5% (33,300 p. p. m. of the combined calcium ion and phosphate) at a pH value of 3, a protective amorphous metal phosphate coating is very rapidly deposited on a ferrous metal surface. The pH value of these solutions may be controlled by adding the proper amount of either alkaline or acidic compound to the solutions or to the prepared compositions; or I may use a combination of metallic compounds and certain molecularly dehydrated phosphates which will produce the desired pH value without further adjustment.

I have prepared numerous compositions which may be dissolved in water to form effective treating solutions which may be used in accordance with this invention. By way of illustration, the following compositions are given which have proved to be very satisfactory for commercial use.

Chemical Components	Compositions	
	A	B
Sodium metaphosphate glass (ratio of Na ₂ O:P ₂ O ₅ =1.1:1)	Percent 49.2	Percent 54.6
Calcium chloride (78%)	34.7	38.6
Sodium nitrite	6.6	
Sodium acid sulfate	9.5	6.1
Sodium dichromate		0.7
	100.0	100.0

Chemical Components	Composition C
	Percent
CoCl ₂ ·6H ₂ O	66.5
Sodium metaphosphate glass (ratio of Na ₂ O:P ₂ O ₅ =1.1:1)	33.0
Na ₂ Cr ₂ O ₇ ·2H ₂ O	0.5

Sufficient amount of pH adjusting agent added to bring pH value to about 4.0 when this composition is dissolved in water to give a concentration of approximately 2%.

Chemical Components	Composition D
	Percent
CaCl ₂ (78%)	17.1
CoCl ₂ ·6H ₂ O	39.0
Sodium metaphosphate glass (ratio of Na ₂ O:P ₂ O ₅ =1.1:1)	43.2
Na ₂ Cr ₂ O ₇ ·2H ₂ O	0.7

Sufficient amount of pH adjusting agent is added to bring pH value to about 4.5 when this composition is dissolved in water to give a concentration of approximately 1.75%. In this example two coating metal salts (calcium chloride and cobalt chloride) are employed.

Chemical Components	Composition E
	Percent
Zn(NO ₃) ₂ ·3H ₂ O	61.7
Sodium metaphosphate glass (ratio of Na ₂ O:P ₂ O ₅ =1.1:1)	38.3

Sufficient amount of pH adjusting agent is

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added to bring the pH value to about 5.0 when this composition is dissolved in water to give a concentration of approximately 1.5%. This is an example of a compound in which the metal ion and oxidizing agent (NO₃) are supplied by one compound.

Chemical Components	Composition F
	Percent
CdCl ₂	59.5
Sodium metaphosphate glass (ratio of Na ₂ O:P ₂ O ₅ =1.1:1)	39.9
Na ₂ Cr ₂ O ₇ ·2H ₂ O	0.6

Sufficient amount of pH adjusting agent is added to bring the pH value to about 4.5 when this composition is dissolved in water to provide a concentration of about 1.9%.

Chemical Components	Composition G
	Percent
Mn(NO ₃) ₂ ·6H ₂ O	75.0
Sodium metaphosphate glass (ratio of Na ₂ O:P ₂ O ₅ =1.1:1)	23.0
NaNO ₃	2.0

Sufficient amount of pH adjusting agent is added to bring the pH value of the solution to about 4.0 when this composition is dissolved in water to provide a concentration of about 1.9%.

Chemical Components	Composition H
	Percent
SrCl ₂	43.7
Sodium metaphosphate glass (ratio of Na ₂ O:P ₂ O ₅ =1.1:1)	55.5
Na ₂ Cr ₂ O ₇ ·2H ₂ O	0.8

Sufficient amount of pH adjusting agent is added to bring the pH value to about 3.7 when this composition is dissolved in water to provide a concentration of about 1.5%.

Chemical Components	Composition J
	Percent
AlCl ₃	19.7
CaCl ₂ (78%)	81.60
Sodium metaphosphate glass (ratio of Na ₂ O:P ₂ O ₅ =1.1:1)	33.60
Na ₂ Cr ₂ O ₇	5.1

Sufficient amount of pH adjusting agent is added to bring the pH value of a solution of this composition to about 2.5 when the composition is dissolved in water to provide a concentration of about 2%.

Chemical Components	Composition K
	Percent
CaCl ₂	45.0
CdCl ₂ ·2½H ₂ O	24.5
Sodium metaphosphate glass (ratio of Na ₂ O:P ₂ O ₅ =1.1:1)	30.0
Na ₂ Cr ₂ O ₇	0.5

Sufficient amount of pH adjusting agent is added to bring the pH value of the solution to about 4.5 when this composition is dissolved in

Water to provide a concentration of about 2.5%.

Where the compositions above described are made up as a dry mixture and sold as such to be used for making coating solutions by adding the same to water in amounts required to give the desired concentration, the pH adjusting material, preferably in anhydrous form, is added to the mixture. Thus, in each of compositions A and B, I have included sodium acid sulfate in such amounts that when a solution of 1.4% by weight concentration is made up, the pH of the solution will be about 3.8. When preparing solutions of compositions A and B having either a greater or lesser concentration than 1.4%, the pH of the solution is automatically adjusted to the approximate optimum level. Thus, if I prepare more concentrated solutions, the concentration of sodium acid sulfate is likewise greater and the solution has a relatively lower pH. For example a 5½% solution of composition A or B will have a pH of about 3.2. Conversely, a solution more dilute than 1.4%, having a lesser amount of sodium acid sulfate, has a relatively higher pH. For example, the pH of a ¼% solution of composition B is 4.5. The concentration of oxidizing agent is likewise automatically present in these solutions in approximately the optimum amounts, because the amount is always proportional to the concentration of the solution.

If it is desired to make up coating solutions from the individual components of the composition above stated, a liquid rather than a solid acidifying or pH adjusting material may be employed. Thus, for example, instead of solid sodium acid sulfate, I may employ hydrochloric acid to adjust the solutions to the desired pH value.

I have found that a 1.4% solution of composition A containing sodium acid sulfate as the pH adjusting agent has a coating rate of about 36 mg./sq. ft./min. at room temperature, whereas a similar solution adjusted to the same pH with hydrochloric acid instead of sodium acid sulfate has a coating rate of 64 mg./sq. ft./min. at room temperature. The rate of coating of composition B containing sodium acid sulfate as the pH adjusting agent, is about 62 mg./sq. ft./min. Since it has been observed that almost 70% of the coating deposited in one minute is formed during the first 10 seconds of contact with the treating solution both compositions A and B are satisfactory for commercial application even though the sodium acid sulfate interferes to a certain extent with maximum deposition of the amorphous calcium phosphate film. I may overcome the slight inhibiting effect of the sulfate, however, by resorting to the use of another type of solid acidifying agent such as aluminum chloride, for example, if I desire to obtain maximum coating weight.

In practical applications, solutions prepared from compositions A or B, produce relatively uniform coatings during a treatment of a large area of metal surface and thus require only infrequent replenishment in order to maintain the solutions at uniform effective coating efficiency. I have found, for example, that when the time of contact between 1.4% solution of composition B and metal is one minute, the solution being at room temperature (about 25° C.) approximately 800 sq. ft. of metal per pound of composition may be effectively coated without making additions to the solutions. The weight of coating obtained during this period will not vary by more than ±20% of the average coating weight value of 50 mg./sq. ft. If I use a like concentration of

composition A under the same conditions I may treat approximately 800 sq. ft. of metal surface per pound of composition without making additions to the solution. In this instance, the coating weight will not vary by more than ±15% of the average value of 38 mg./sq. ft. I have found that in treating metals which are to be subsequently finished with an organic coating such as a paint or lacquer, a very short immersion time of the order of 5 to 60 seconds is adequate. For example, in the case of 2.5% solutions prepared from compositions A or B, the coating rate at room temperature is so rapid that a treating time of 5 seconds produces adequate coatings.

In composition A, 6.6% by weight of sodium nitrite is present. When composition A is dissolved in water to concentration of 1.4%, the amount of sodium nitrite present in the solution will be approximately 0.09% by weight. In composition B, 0.7% of sodium dichromate is present. When this composition is dissolved in water to a concentration of 1.4% by weight, there will be approximately 0.01% of sodium dichromate present in the solution. On a weight basis, sodium dichromate is considerably more effective for my purposes than sodium nitrite, consequently smaller amounts are required in the dry compositions.

As has been pointed out, one of the advantages of my compositions when dissolved is that the composition ratio of coating metal ion to phosphate remains substantially fixed even after long periods of use and the metal ion-phosphate concentration is depleted to the extent of about 35%. When depleted to this extent the solution should be restored to its original condition by merely adding the required amount of the composition and adding sufficient water to compensate for loss as carry-out or spray loss. In this respect the invention is a substantial improvement over the aforementioned Roland application.

In a typical treating solution such as is formed by preparing a 1.4% solution of composition B, the ratio of calcium to sodium metaphosphate glass is approximately 1:5. This ratio remains substantially constant up to a point where the concentration of the solution has been depleted to about 30-35%. In the course of reaching this point of depletion, the ratio will vary in narrow limits from 1:5 to about 1:4.74, but beyond this point the ratio decreases rapidly. Therefore, the proper time to add replacement material is before this point is reached. To determine this, the concentration of one of the components of the solution is determined. I may take samples of the solution and analyze for P₂O₅ content by any well known method, for example a colorimetric phosphate test, or I may analyze the sample for calcium content by one of several methods. I prefer to determine P₂O₅ concentration since this may be done quite rapidly with reasonable accuracy, whereas the determination of calcium is either less rapid, or less accurate, depending upon the method chosen. Having determined that the treating solution has reached a point requiring additional materials, I merely add the ready-mixed composition in sufficient amounts to restore the bath to its original concentration.

Although my new compositions and the various solutions I have developed will produce a corrosion resistant coating on many metal surfaces which will adequately protect the surfaces for reasonable periods of time if they are exposed

to atmospheric conditions, the primary application of my compositions and processes is in the field of processing metals which are to be subsequently coated with organic finishes or vitreous enamels.

When a metal such as hot or cold rolled steel is cleaned and dried and an organic finish is applied, the slightest break in the protective film will enable corrosion to set in thereby causing oxidization not only at the exact point of rupture but in the surrounding area as well. It is common knowledge that when the paint covering a steel surface is so scratched that the steel is exposed, corrosion will occur rapidly at the scratch and will soon cause a lifting of the paint from the surface adjacent the scratch. Eventually the corrosion extends from the scratch to a large surrounding area.

Light gauge steel sheet or strip which is painted or lithographed is frequently formed into various shapes in a later operation and in these forming operations quite frequently the protective coating is ruptured thereby enabling corrosion to set in. When the metal is treated in the usual orthophosphate type solution, the coating formed is crystalline, and consequently cannot withstand sharp bending to the degree tolerated by the amorphous phosphate coatings which are deposited from the solutions of my invention.

Since the solutions I employ do not visibly attack a metal surface but deposit a transparent glass-like film, the advantages are obvious if the surface is to be covered by a transparent varnish or lacquer. Not only is the surface protected against corrosion and the lacquer firmly bound to the amorphous phosphate, but the surface of the metal is visibly unimpaired. This means a great deal when decorative metals, possessing a natural lustre or a pleasing surface design are treated with my solutions and subsequently lacquered or varnished. The ordinary orthophosphate treatment would visibly etch the metal so that its desired appearance would be obliterated. The reflective power of metals treated by my process is affected but slightly whereas it is destroyed to a very large extent by the mat finish of the orthophosphate coating.

The amorphous phosphate coatings are perfectly smooth as contrasted with the uneven surface of the orthophosphate coatings and less paint or varnish is required to cover a given area of metal protected by my coatings than an equivalent area protected by the crystalline coatings.

As was mentioned previously, oxidizing agents have desirable and unexpected effects in the treating solutions made up from compositions used in accordance with this invention, whereas reducing agents either reduce materially the effectiveness of the solutions or in some cases nullify their effectiveness. The following table shows the relative effects of oxidizing and reducing agents on coating solutions of this invention.

Table I

Effect of oxidizing and reducing agents in treating solutions containing 1500 p. p. m. by weight of calcium (from calcium chloride) and 7500 p. p. m. by weight of sodium phosphate glass—ratio of $\text{Na}_2\text{O}:\text{P}_2\text{O}_5=1.1:1$.

Temperature of solution 49°C .; pH 3.5; time of immersion of cold rolled steel panels, 10 minutes. Weight of phosphate coating expressed in milligrams per square decimeter and per square foot.

Reagent	Concentration	Weight of Phosphate Coating		
		mg./dm. ²	mg./sq. ft.	
5 Oxidizing:	None	11.8±1.6	111±18.0	
	NaNO ₂	0.05	30.5	
		0.10	32.3	
		0.30	31.9	
		0.50	22.3	
		1.00	9.8	
	10 Na ₂ SO ₄	0.01	20.7	194
		0.10	33.5	314
		0.50	31.3	293
		NaNO ₂	0.17	17.1
		0.34	22.6	212
		0.47	28.5	266
15 KMnO ₄	0.84	31.1	291	
	0.001	11.0	103	
	K ₂ Cr ₂ O ₇	0.01	47.8	447
		0.01	48.2	451
		0.10	49.3	462
		0.10	36.5	342
20 Reducing:	NaOCl.....	0.01	19.5	182
		0.10	19.0	178
	None	11.8±1.6	111±18.0	
	Hydroquinone.....	0.01	9.5	89
		0.10	6.7	63
	"Elon".....	0.01	8.0	75
25 (p-methylaminophenol)	0.10	1.0	9.4	
	SnCl ₂	0.01	6.7	63
		0.10	5.8	54

In the following Table II, the effect of oxidizing agent on a coating solution at 25°C . is shown. The solution as made contained 7500 p. p. m. of sodium phosphate glass having a ratio of



of about 1.1:1, 3000 p. p. m. of calcium from calcium chloride, 2.46 grams of NaHSO_4 to adjust the pH of the solution to 3.8. The solution was divided into two equal parts. To the one, no oxidizing agent was added, to the other, 100 p. p. m. of $\text{Na}_2\text{Cr}_2\text{O}_7$ was added as oxidizing agent. A steel test panel was placed in each solution for one minute and the coating weight determined.

Table II

Solution Containing $\text{Na}_2\text{Cr}_2\text{O}_7$ in P. P. M.	Coating weight in mg./sq. ft./min.
0 (none).....	16.0
100.....	50.0

The solution containing 100 p. p. m. of $\text{Na}_2\text{Cr}_2\text{O}_7$ gave a coating weight over three times heavier than the solution without any $\text{Na}_2\text{Cr}_2\text{O}_7$ in one minute of contact with the solution.

I have found that if the treated metal is given a specially adjusted chromic acid rinse immediately after exposure to the coating solution, superior bond is obtained between an organic coating and the treated metal surface. If chromic acid itself is used, the results are not noticeably superior to those obtained when specimens are rinsed in plain water, but I have found that by adjusting the pH of the chromic acid rinse solution, extraordinary results are obtained. For example, chromic acid solution in a concentration of 0.05% has a pH of about 2.3, but if I adjust the pH of this solution so that its pH value is in the range of from about 3.9 to about 6.5, the adherence of the paint to the metal surface is markedly improved as is the salt spray resistance and the ability to withstand water immersion test. The optimum pH range I have found for the 0.05% chromic acid rinse solution is from about 3.9 to about 5.4. The rinse step may

be performed by immersing or rinsing the coated steel in the adjusted chromic acid solution for about one minute or less, the temperature of the solution being in the range of from about 40° C. to about 100° C. although I have found that superior results are obtained at the lower temperatures in this range.

A 0.1% solution of chromic acid has a pH of about 2.0 but if I adjust the pH value to within the range of from about 3 to about 5.5, the optimum range being about 3.5 to about 5.5, I again observe startling results in the adherence corrosion and water immersion resistance of the subsequently applied organic coatings. Although the use of a plain water rinse following the deposition of the phosphate coating on metallic surfaces produces satisfactory results, I prefer to employ the adjusted chromic acid rinse since there is a definite improvement over the use of water. I may also use dichromates or chromates, provided the pH of the solutions of these is adjusted to or falls within the range above stated. The metal undergoing treatment may be taken from the phosphate treating solution into the dilute adjusted chromic acid bath without an intermediate rinse in water or without an intermediate drying process. Following the chromic acid rinse the metal surface may be dried.

I have found that my metal phosphate coating solution may be applied to metallic surfaces by any means which brings the solution in contact with the surface, such as by immersion, by spraying, by brushing, or by roller coating. Tests have been conducted in a 4-tank spray washing and treating unit combined with a drying tunnel. In the first tank, an alkaline detergent maintained at a concentration of 1-oz./gallon at a temperature of about 140° F. (60° C.) was used. In the second tank, a hot water rinse was employed, the temperature of this rinse being in a range of 120° F. to 150° F. (49° to 66° C.) with the water being constantly replaced through a float controlled valve. In the third tank, a 1% concentration of my composition hereinbefore designated as composition B was employed at a temperature of about 90° F. (32° C.). Fresh water was added only to maintain working volume since there is a certain amount of carryover as the metal surfaces moves from this solution to the next stage in the process. The final operation was a hot water rinse maintained at a temperature of 120° F. to about 150° F. (49° C.-66° C.).

In the first two tanks the metal containers being processed were treated for about 40-50 seconds and in the last two stages, contact was maintained for about 20 seconds. The finished parts had a multi-colored iridescent sheen which is typical of the amorphous metal phosphate coating deposited on ferrous metals, and they were free from rust despite the fact that some moisture remained inside these container parts as the result of incomplete drying. The corrosion resistance of the subsequently painted containers as indicated by the standard salt spray test was excellent.

I have successfully treated large quantities of what is commercially known as bright annealed black plate by spraying the metal with a 1.5% solution of composition B. In this particular processing, the unit consisted of a series of rubber rolls which moved the metal sheets along in a horizontal plane between top and bottom spray

nozzles. The contact period between metal and treating solution was approximately 10 seconds followed by a hot water rinse for about 2 seconds and a forced hot air drying stage. The temperature of the phosphate coating solution was maintained in the range of from about 75-85° F. (24° C.-29.5° C.). The coating weight of the phosphate film as determined by the anodic stripping of the coating from small panels in a 10% caustic soda solution varied from an average of about 31 milligrams per sq. foot at the beginning of the run to about 30 milligrams per sq. foot at the end of the run.

A large quantity of steel sheets treated by the above mentioned method was stored in the mill atmosphere for observation on corrosion resistance in comparison with similar sheets treated in an orthophosphate bath which produced a crystalline phosphate coating. The amorphous metal-phosphate coating gave protection superior to both untreated sheets and to those which had been run through a treating process using orthophosphate baths.

A portion of the treated sheets was used in the formation of can ends. An observation of the phosphate coating by means of a binocular microscope showed the amorphous coating to be perfectly continuous even over sharp bends, whereas some of the can ends which were treated in orthophosphate solutions showed a rupture of the crystalline phosphate film at some points. Samples of both the amorphous metal-phosphate coated sheets and the crystalline phosphate coated sheets were given an organic finish by a roller coating process and the can ends were then stamped from the coated sheets and subjected to an adherence test, a humidity test, and an outdoor exposure test. Definite superiority in the amorphous metal-phosphate coated can ends was observed in each of these tests which would indicate that the flexibility of the amorphous coating has a definite relationship to the results obtained when coated metal surfaces are subjected to bending operations.

I have also employed my treating solution in conjunction with iron surfaces to be later coated with vitreous enamels. The adherence of vitreous enamel to the metal surfaces is of prime importance to the industry and one of the principal obstacles in the one-coat light enameling process suitable for refrigerators and other similar appliances, is the lack of adherence of the white enamel after it is fired. I have processed iron panels by a standard commercial cleaning and pickling procedure followed by the immersion of these panels in different phosphate treating solutions. I have found that the use of water-soluble nickel salts in conjunction with a molecularly dehydrated phosphate and the use of water-soluble cobalt salts in conjunction with the same type of phosphate improves the bond between the vitreous enamel and the iron surface. Visual comparison of the degrees of adherence is made by employing a ½ inch steel ball loosely held over the enamel surface and centered over a 1-inch hole in an anvil. The impact of a falling weight on the ball will cause the enamel to separate from the metal if the adherence is not satisfactory, whereas with good adherence qualities, the separation is very slight or almost negligible.

I have found that the amorphous protective phosphate coatings are also effective in the pre-

vention of high temperature oxidation of metals. For example, a steel strip coated with a phosphate film when exposed to a temperature of 600° C. for one hour will oxidize very slightly whereas an untreated strip is oxidized appreciably. Weight loss measurements indicate that oxidation is reduced appreciably, the reduction being of the order of 90% under the conditions described.

Having thus described the invention, what I claim as new and desire to secure by Letters Patent is:

I claim:

1. A water-soluble composition, solutions of which are capable of rapidly depositing coatings on surfaces of metals to prevent their corrosion, said composition containing approximately 54.6% by weight of a sodium phosphate glass having a ratio of $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ of about 1.1:1, about 38.6% by weight of 78% calcium chloride, 6.1% by weight of sodium acid sulfate and about 0.7% by weight of sodium dichromate, said composition being characterized by the fact that a protective amorphous calcium phosphate coating is deposited in approximately ten seconds from a solution containing approximately 2.5% by weight of said composition at a solution temperature of approximately 25° C.

2. A process for depositing an amorphous metal-phosphate coating on the surfaces of metals to prevent corrosion thereof which comprises subjecting a metallic surface composed of at least one of the metals of the group consisting of iron, copper, zinc, silver, and magnesium to the action of an aqueous solution having a pH value between about 3 and 8, and containing in solution at least 100 p. p. m. by weight of a metal ion of at least one element selected from the group consisting of calcium, zinc, cobalt, magnesium, cadmium, iron, aluminum, barium, strontium, manganese, chromium, and nickel, at least 200 p. p. m. by weight of a water-soluble alkali-metal phosphate glass and at least 10 p. p. m. of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfites, permanganates, chromates, ferricyanides, dichromates, and perborates, and maintaining the ratio of the phosphate glass concentration in said solution to the concentration of the metal ion therein between the values of about 0.05:1 and about 12:1.

3. A process for depositing an amorphous metal-phosphate coating on metal surfaces to prevent the corrosion thereof which comprises subjecting a metallic surface composed of at least one of the metals of the group consisting of iron, copper, zinc, silver, and magnesium, to the action of an aqueous solution having a pH value between 2.0 and 5 and containing in solution at least 100 p. p. m. by weight of the ions of calcium and aluminum, at least 200 p. p. m. by weight of a water-soluble alkali-metal phosphate glass and at least 10 p. p. m. of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfides, permanganates, chromates, ferricyanides, dichromates, and perborates.

4. The method as defined in claim 2 in which the alkali-metal phosphate glass has a molar ratio of alkali-metal oxide to P_2O_5 of from about 0.4:1 to about 1.7:1.

5. A process for depositing an amorphous metal-phosphate coating on metal surfaces to pre-

vent corrosion thereof which comprises subjecting a metallic surface composed of at least one of the metals of the group consisting of iron, copper, zinc, silver, and magnesium, to an aqueous solution having a pH value between 3 and 8, and containing from about 100 p. p. m. to about 10,000 p. p. m. by weight of a metal ion of at least one element selected from the group consisting of calcium, zinc, cobalt, magnesium, cadmium, manganese, chromium, iron, aluminum, barium, strontium, and nickel, at least 200 p. p. m. by weight of a water-soluble alkali-metal phosphate glass and at least 10 p. p. m. of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfites, permanganates, ferricyanides, chromates, dichromates, and perborates.

6. A process for depositing an amorphous metal-phosphate coating on metal surfaces to prevent the corrosion of metals which comprises subjecting a metallic surface composed of at least one of the metals of the group consisting of iron, copper, zinc, silver, and magnesium, to an aqueous solution having a pH value of from about 3 to about 8 and containing not less than about 100 p. p. m. of a metal ion of at least one element selected from the group consisting of calcium, strontium, chromium, manganese, barium, zinc, cadmium, cobalt, nickel, magnesium, aluminum, and iron, a water-soluble alkali-metal phosphate glass, and not less than about 10 p. p. m. of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfites, permanganates, ferricyanides, chromates, dichromates, and perborates for accelerating the rate of deposition by said solution of an adherent protective amorphous phosphate film on said metal surface, and maintaining a ratio between the concentration of the phosphate glass and the metal ion in the solution between the values of about 0.05:1 and about 12:1.

7. A process for depositing an amorphous metal-phosphate coating on metal surfaces to protect the same against corrosion which comprises subjecting a metallic surface composed of at least one of the metals of the group consisting of iron, copper, zinc, silver, and magnesium to the action of an aqueous solution having a pH value in the range of from about 3 to about 8 and containing from about 100 p. p. m. to about 10,000 p. p. m. by weight of a metal ion of at least one element selected from the group consisting of Ca, Zn, Co, Mg, Cd, Fe, Al, Ba, Sr, Cr, Mn, and Ni, a water-soluble alkali-metal phosphate glass in amount to give a weight ratio of said phosphate glass to the element of said group between about 0.05:1 and 12:1 and at least 10 p. p. m. of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfides, permanganates, ferricyanides, chromates, dichromates, and perborates.

8. A process for depositing an amorphous metal-phosphate coating on metal surfaces to protect the same against corrosion which comprises subjecting a metallic surface composed of at least one of the metals of the group consisting of iron, copper, zinc, silver, and magnesium, to the action of an aqueous solution containing at least 100 p. p. m. of a metal ion of at least one element selected from the group consisting of Ca, Zn, Co, Mg, Cd, Fe, Al, Ba, Cr, Sr, Mn, and Ni, and also containing a water-soluble alkali-metal phosphate glass in amount to give a weight ratio of said phosphate glass to the element of said

group between about 2:1 and about 12:1 and at least 10 p. p. m. of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfites, permanganates, ferricyanides, chromates, dichromates, and perborates, the pH value of said solution being between about 3 and 8.

9. A process for depositing an amorphous metal-phosphate coating on metal surfaces to protect the same against corrosion which comprises subjecting a metallic surface composed of at least one of the metals of the group consisting of iron, copper, zinc, silver, and magnesium to the action of an aqueous solution containing at least 100 p. p. m. of a metal ion of at least one element selected from the group consisting of Ca, Zn, Co, Mg, Cd, Fe, Al, Ba, Sr, Cr, Mn, and Ni, and containing an alkali-metal phosphate glass in which the molar ratio of alkali-metal oxide to P_2O_5 is from 0.4:1 to about 1.7:1, the amount of glass in said solution being such as to give a weight ratio of said glass to said metal ion of between about 0.05:1 to about 8:1, and the concentration of phosphate glass being not less than about 200 p. p. m. by weight, the treating solution also containing at least 10 p. p. m. by weight of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfites, permanganates, ferricyanides, chromates, dichromates, and perborates, the pH value of the solution being adjusted to a value between about 3 and about 8.

10. A process for treating metal surfaces composed of at least one of the metals of the group consisting of iron, silver, magnesium, copper, and zinc to withstand corrosion which comprises subjecting a metal of said group to an aqueous solution containing at least 10 p. p. m. by weight of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfites, permanganates, chromates, dichromates, ferricyanides, and perborates, a metal ion of at least one element selected from the group consisting of calcium, zinc, cobalt, magnesium, cadmium, iron, aluminum, barium, strontium, manganese, chromium, and nickel, and a water-soluble alkali-metal phosphate glass, the combined amount of said metal ion and said phosphate in the solution being from about 300 p. p. m. by weight to about 50,000 p. p. m. by weight and the ratio of alkali-metal phosphate glass to said metal ion being within the range of about 0.05:1 and about 12:1 so that an amorphous phosphate of said metal ion will deposit as a film upon the metal being treated, said film being sufficient to protect the metal from corrosion, the pH value of the solution being maintained at a value between about 3 and 8.

11. A method of rapidly forming a protective amorphous metal-phosphate coating on metal surfaces composed of at least one of the metals of the group consisting of silver, magnesium, copper, iron, and zinc which comprises treating said metals with an aqueous solution having a pH value of from 3 to 8, and at a temperature range of about 15° C. and not in excess of about 50° C., said solution containing a metal ion of at least one element selected from the group consisting of calcium, zinc, cobalt, magnesium, cadmium, iron, aluminum, barium, strontium, manganese, chromium and nickel, at least 10 p. p. m. by weight of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfites, permanganates, ferricyanides, 75

chromates, dichromates, and perborates and at least 200 p. p. m. of a water-soluble alkali-metal phosphate glass, the concentration of the metal ion being not less than 100 p. p. m. and the ratio of phosphate glass to metal ion in said solution being such that there is deposited upon the metal being treated an amorphous metal-phosphate protective coating exceeding one milligram per square decimeter in approximately ten seconds.

12. A method whereby metal surfaces composed of at least one metal of the group consisting of iron, silver, magnesium, copper, and zinc, may be treated to resist corrosion which comprises contacting a metal of said group for a relatively short period of time with a non-heated aqueous solution containing in solution at least 10 p. p. m. by weight of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfites, permanganates, chromates, dichromates, ferricyanides, and perborates, at least 200 p. p. m. of a water-soluble alkali-metal phosphate glass and a metal ion of at least one element of the group consisting of Ca, Zn, Co, Mg, Cd, Fe, Al, Ba, Sr, Mn, Cr, and Ni, the concentration by weight of such metal ion being maintained at such a value that the ratio of phosphate glass by weight to metal ion is within a range of not less than about 0.05:1 and not more than about 8:1.

13. In the treatment of the surfaces of metals composed of at least one of the metals of the group consisting of iron, zinc, copper, magnesium and silver, to produce a protective amorphous phosphate coating deposited by contacting the surfaces of such metals with an aqueous solution containing at least 100 p. p. m. of a metal ion of at least one element selected from the group consisting of calcium, zinc, cobalt, magnesium, cadmium, iron, aluminum, barium, strontium, manganese, chromium, and nickel, at least 10 p. p. m. of an oxidizing agent selected from the group consisting of inorganic water-soluble nitrates, nitrites, sulfites, permanganates, ferricyanides, chromates, dichromates, and perborates, and at least 200 p. p. m. of a water-soluble alkali-metal phosphate glass, that step which comprises rinsing said metal surface while wet with the amorphous metal coating solution with an aqueous solution of a salt of chromic acid having a concentration of CrO_3 of from about 0.05% to 0.5% and adjusted to a pH of from about 3 to about 5.5.

14. A process as defined in claim 13 characterized by the fact that the rinse solution is a chromic acid solution having a concentration of CrO_3 of from about 0.05% to about 0.5% and adjusted to a pH value of from about 3 to about 5.5.

15. An aqueous solution for depositing an amorphous metal-phosphate coating on the surfaces of metals composed of at least one of the metals of the group consisting of iron, zinc, copper, silver and magnesium, which solution contains as the major portion of its active chemical composition at least 100 p. p. m. of a metal ion of at least one element selected from the group consisting of calcium, zinc, cobalt, magnesium, cadmium, iron, aluminum, barium, strontium, chromium, manganese, and nickel, and at least 200 p. p. m. of a water-soluble alkali-metal phosphate glass and at least 10 p. p. m. of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfites, permanganates, chromates, ferricyanides, dichromates, and perborates, the ratio of

phosphate to metal ion in said solutions being within the range of about 2:1 to 8:1.

16. A water-soluble composition adapted for the preparation of solutions for forming amorphous metal phosphate coatings on metals at room temperature to prevent the corrosion of said metals, said composition containing approximately 49.2% by weight of a sodium phosphate glass having a ratio of $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ of about 1.1:1, 34.7% by weight of about 78% calcium chloride, about 6.6% by weight of sodium nitrite and about 9.5% by weight of sodium acid sulfate.

17. A dry, homogeneous composition which when dissolved in water will form a solution which is effective to deposit rapidly an amorphous protective coating on metal surfaces wetted by said solution so that said surfaces are protected by said film against corrosion, said composition containing approximately 49.2% by weight of a sodium phosphate glass having a ratio of $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ of about 1.1:1, 34.7% by weight of 78% calcium chloride, 6.6% by weight of sodium nitrite and 9.5% by weight of sodium acid sulfate, solutions containing about 2.5% by weight of said composition being such that a protective amorphous phosphate coating having a weight of about 44 milligrams per square foot is deposited on the metal surfaces in approximately ten seconds of contact with said solution at a temperature of about 24° C.

18. A dry, homogeneous water-soluble composition consisting essentially of an alkali-metal phosphate glass having a ratio of $\text{M}_2\text{O}:\text{P}_2\text{O}_5$ of about 0.4:1 to about 1.7:1 where M is an alkali metal or the ammonium radical, a water-soluble compound containing a metal selected from the group consisting of calcium, zinc, cobalt, magnesium, cadmium, iron, aluminum, barium, strontium, manganese, chromium and nickel, an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfites, permanganates, chromates, ferricyanides, dichromates, and perborates, and a water-soluble pH adjusting agent, the ratio by weight of the phosphate glass to the metal of the metal-containing compound being between about 0.05:1 and 12:1 so that when metals of the group consisting of silver, magnesium, copper, iron, and zinc are contacted with a solution containing about 2.5% by weight of said composition, said 2.5% solution containing not less than 10 p. p. m. of oxidizing agent and not less than 300 p. p. m. of phosphate glass, an amorphous phosphate coating will be deposited on the surface of said metals which is effective to protect the coated surface and provide a base for paints and enamels.

19. A composition whose water solutions are capable of depositing on metal surfaces in contact therewith an amorphous metal-phosphate coating, said composition consisting essentially of the following components:

- (a) at least one water-soluble salt of a coating metal selected from the group consisting of Ca, Zn, Co, Mg, Cd, Fe, Al, Ba, Sr, Mn, Cr, and Ni,
- (b) an alkali-metal phosphate glass,
- (c) an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfites, permanganates, chromates, ferricyanides, dichromates, and perborates,
- (d) a dry solid water-soluble pH adjusting compound,

the proportions of components (a) and (b) being such that when said composition is dissolved in water, the ratio of (b) to the metal ion of (a) in said solution is within the ratio range of 0.05:1 to 12:1, the amount of (d) is such as will produce a pH value within the range of about 3 to 8, the amount of (c) is such as to give a concentration of at least about 10 p. p. m. by weight, and the amount of (a) is such as will produce a concentration of metal ion in said solution of not less than about 100 p. p. m. by weight.

20. A composition according to claim 19 characterized by the fact that component (a) is a water-soluble calcium salt.

21. A process for depositing an amorphous metal-phosphate coating on metal surfaces to protect the same against corrosion which comprises subjecting a metallic surface composed of at least one metal of the group consisting of iron, copper, zinc, silver and magnesium to the action of an aqueous solution having a pH value in the range of from about 3 to 8 and containing at least 100 p. p. m. by weight of a metal ion of at least one element selected from the group consisting of Ca, Zn, Co, Mg, Cd, Fe, Al, Ba, Sr, Cr, Mn, and Ni, a water-soluble alkali-metal phosphate glass in amount to give a weight ratio of said phosphate glass to the metal ion of the element of said group between about 0.05:1 and 12:1 and at least 10 p. p. m. of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, ferricyanides, sulfites, permanganates, chromates, dichromates and perborates.

22. A process for depositing an amorphous metal-phosphate coating on metal surfaces to prevent the corrosion thereof which comprises subjecting a metallic surface composed of at least one of the metals of the group consisting of iron, copper, zinc, silver, and magnesium, to the action of an aqueous solution having a pH value between about 3 and about 8 and containing in solution not less than 100 p. p. m. of the ions of calcium and a water-soluble molecularly dehydrated alkali-metal phosphate having a ratio of alkali-metal oxide to P_2O_5 of about 0.4:1 to 1.7:1, the ratio of the concentration of alkali-metal phosphate to calcium ion being from about 2:1 to about 8:1, and at least 10 p. p. m. of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, sulfites, ferricyanides, permanganates, chromates, dichromates, and perborates.

23. A process for depositing an amorphous metal-phosphate coating on metal surfaces to prevent the corrosion thereof which comprises subjecting a metallic surface composed of at least one of the metals of the group consisting of iron, copper, zinc, silver, and magnesium, to the action of an aqueous solution having a pH value between about 2.0 and about 5.0 and containing in solution not less than 100 p. p. m. of calcium ion and also a water-soluble molecularly dehydrated alkali-metal phosphate having a ratio of alkali-metal oxide to P_2O_5 of about 0.4:1 to 1.7:1, the ratio between the concentration of phosphate and of calcium ion being within the range of 0.05:1 and 12:1, and at least 10 p. p. m. of an oxidizing agent selected from the group consisting of water-soluble inorganic nitrates, nitrites, ferricyanides, sulfites, permanganates, chromates, dichromates, and perborates.

24. A process for depositing an amorphous metal-phosphate coating on metal surfaces to prevent the corrosion thereof which comprises

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subjecting a metallic surface composed of at least one of the metals of the group consisting of iron, copper, zinc, silver, and magnesium, to the action of an aqueous solution having a pH value between about 3 and about 8 and containing in solution a concentration of not less than 100 p. p. m. of calcium ion and a water-soluble molecularly dehydrated alkali-metal phosphate having a ratio of alkali-metal oxide to P_2O_5 of from about 0.4:1 to 1.7:1, the ratio of alkali-metal phosphate to calcium ion being within the range of about 2:1 to about 8:1, and at least 10 p. p. m. of sodium dichromate.

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