June 22, 1943. G. W. JERNSTEDT 2,322,349

CORROSION RESISTANT COATINGS FOR METAL SURFACES

Original Filed Oct. 25, 1941 3 Sheets-Sheet 1

Fig. 1.

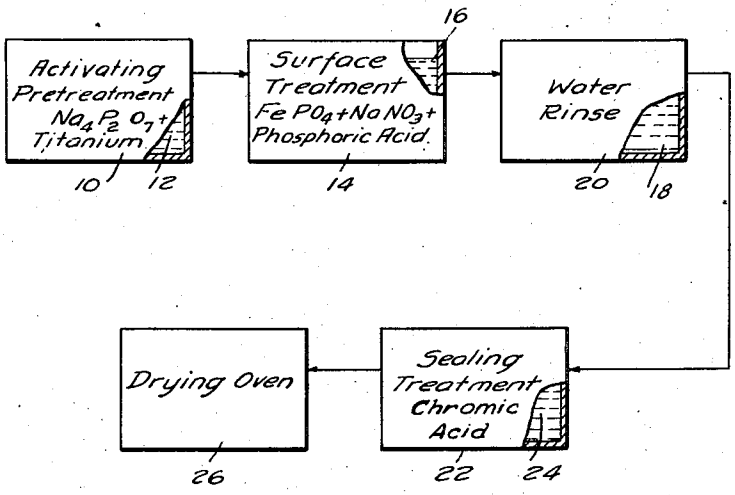
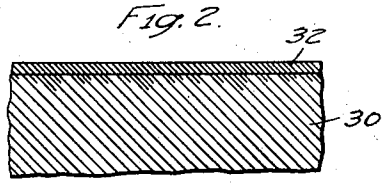


Fig. 2.



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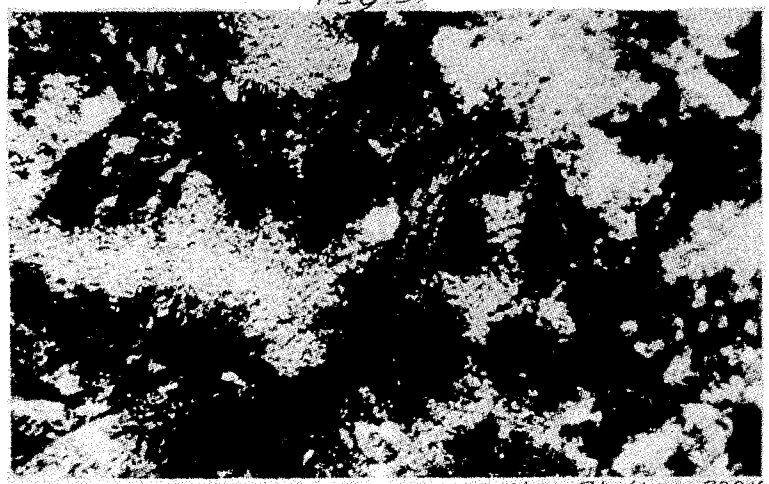
CORROSION RESISTANT COATINGS FOR METAL SURFACES

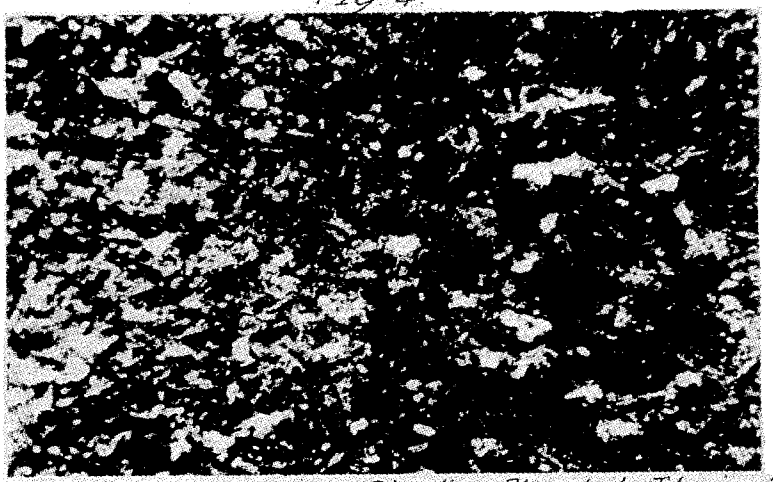
Original Filed Oct. 25, 1941 3 Sheets-Sheet 2

Fig 3.



Phosphate Coating on Non-Activated Zinc Plating 300X

Fig 4.



Phosphate Coating on Disodium Phosphate Titanium 300X
Preactivated Zinc Plating

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CORROSION RESISTANT COATINGS FOR METAL SURFACES

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Fig. 5



Phosphate Coating on Non Activated Steel Plating 300X

Fig. 6



Phosphate Coating on Disodium Phosphate-Titanium 300X
Preactivated Steel Plating

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2,322,349

CORROSION RESISTANT COATING FOR METAL SURFACES

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Original application October 25, 1941, Serial No. 416,552. Divided and this application November 11, 1942, Serial No. 465,259

6 Claims. (Cl. 148—6)

This invention relates to the art of producing corrosion resistant coatings on the surfaces of iron, zinc and other metals and alloys.

This application is a division of my copending patent application Serial No. 416,552, filed October 25, 1941.

This invention relates more particularly to the production of phosphate coatings upon the surfaces of metals. Such phosphate coatings are of great economical importance in the preparation of the metal surfaces for the reception of an organic finish.

The object of this invention is to provide a preliminary treatment for metal surfaces to accelerate the formation of corrosion resisting coatings thereon.

Another object of this invention is to provide a composition capable of activating metal surfaces to improve the process of forming corrosion resisting coatings thereon.

A further object of the invention is to provide a treatment for metal surfaces to produce protective phosphate coatings in a rapid and economical manner.

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

For a fuller understanding of the nature and objects of the invention, reference may be had to the following detailed description taken in conjunction with the accompanying drawings, in which:

Figure 1 is a schematic view of one form of process for accomplishing the invention;

Fig. 2 is a fragmentary sectional view of a metallic member carrying a protective coating produced by the treatment described herein.

Fig. 3 is a photomicrograph at 300X of zinc plated steel with ordinary phosphate treated surface;

Fig. 4 is a photomicrograph at 300X of zinc plated steel treated according to the invention;

Fig. 5 is a photomicrograph at 300X of steel with ordinary phosphate surface treatment; and

Fig. 6 is a photomicrograph at 300X of steel treated according to the invention.

The treatment of metallic surfaces with solutions or compositions which, under appropriate conditions, will deposit or form upon the metallic surface a protective phosphate coating is practiced extensively. These phosphate coatings protect the underlying metal from corrosion. Furthermore, the phosphate coatings are desirable since they constitute excellent surfaces for the successful application of organic finishes. The phosphate coatings occur as crystalline deposits to which organic finishes will bond and adhere more tenaciously than to the bare metal surface.

In the prior art, phosphate coatings have been produced by simply subjecting the metal surface to a solution containing phosphoric acid and phosphates. The time involved in treating the metal surface in order to secure a satisfactory protective coating usually has been reckoned in hours, but within recent years the time of treatment, has been reduced to a fraction of an hour, for example, 15 minutes.

According to the invention, it has been discovered that the time necessary for the reaction between the metal surface and a composition capable of developing the phosphate coating thereon depends to a great extent upon the relative activity of the metal surface to the composition. When treated with an activating solution as will be described herein, the bare metal surface has imparted to it improved characteristics whereby it is activated so that the normal or modified phosphate coating compositions will form a phosphate film or coating thereon with great rapidity, for example, in a minute or less.

Another advantage obtained by the activation of metal surfaces is that metal surfaces which previously did not form satisfactory phosphate coatings, successfully acquire phosphate good corrosion inhibiting coatings upon activation. As is well known, zinc does not form good protective phosphate coatings when coating compositions are applied, but with activation zinc will acquire coatings capable of meeting extreme corrosion requirements.

When metal surfaces are activated by a pretreatment, as disclosed in this invention, the surface may be subsequently treated with a phosphate coating composition to produce thereon a highly satisfactory and complete protective coating in a matter of one minute or less contact. Furthermore, it has been noted that such activated metal surface acquires a much better protected phosphate coating than the same solution would produce on unactivated surfaces. The improved coatings are characterized by a finely crystalline layer whose individual grains cannot be distinguished with the naked eye. The corrosion resistance of phosphate coatings as produced on activated surfaces is greatly superior to that secured on unactivated surfaces.

It is well known to those skilled in the art that zinc, galvanized iron and electroplated zinc can-

not be treated with uniformly satisfactory and consistent results with conventional phosphate solutions. Numerous attempts to modify the phosphate solutions in order to produce an adequate protective phosphate coating on zinc have been unsuccessful from a commercial standpoint. In contrast to the prior art difficulties with zinc, zinc surfaces after activation may be subjected to the phosphate coating solutions with phenomenally rapid production of crystalline deposits of highest quality.

In the practice of this invention, metal surfaces to be subsequently subjected to a treatment capable of producing crystalline phosphate coatings are activated by pretreatment with an activating solution. The pretreatment comprises the application of a solution of disodium phosphate containing additions of small quantities of titanium as a compound. In the absence of titanium, the disodium phosphate has negligible activating effect.

In preparing a satisfactory disodium phosphate and titanium pretreatment, the following process has been found to be successful. The titanium compound is added to ortho-disodium phosphate in water solution. Preferably soluble titanium compounds are employed for additions to the disodium phosphate. Titanium tetrachloride, titanium trichloride, titanium hydroxide, titanium nitride and titanium potassium oxalate have been employed for this purpose with highly satisfactory results. Less soluble compounds of titanium such as titanium carbide, titanium dioxide and titanium potassium fluoride however, have been added to disodium phosphate and all have rendered the disodium phosphate capable of activating metal surfaces. The solution of disodium phosphate with the titanium compound addition is preferably evaporated to dryness at temperatures above 60° C.

It has been found that disodium ortho-phosphate and sodium pyrophosphate are the only materials which are satisfactory in producing the desired activation of metal surfaces. Dipotassium phosphate and both monosodium phosphate and trisodium phosphate, for example, were substantially useless for this purpose. In the examples given hereinafter, sodium pyrophosphate may be substituted for the disodium phosphate with due allowances for differences in weight due to water of hydration and molecular weights.

The dried disodium phosphate titanium compound composition as prepared above may contain from 0.005% up to 20% by weight of titanium radical. The dried composition is dissolved in water to produce a solution suitable for use in activating treatment, having from 0.1% to 2% of disodium phosphate and generally from 0.005% to 0.05% of titanium ions in solution. Titanium may be present in larger amounts with beneficial results. However, it has been found that from 0.1% to a saturated solution of disodium phosphate will activate metal surfaces. A 1% aqueous solution of disodium phosphate with 0.01% titanium radical appears to be the optimum concentration. The pH at this concentration is from 8.0 to 8.5.

Referring to Fig. 1 of the drawings, there is shown a schematic process which may be followed in applying the activating pretreatment to metal surfaces including the subsequent treatment in producing the coated metal surface. Metal whose surface has been cleaned thoroughly is introduced into tank **10**. At **10** is an apparatus, either a tank in which the metal is to be dipped in the activating solution **12**, or a booth in which the activating solution is sprayed upon the members being treated. The disodium phosphate and titanium solution **12** need be applied for only 10 seconds to the metal surface to confer a satisfactory degree of activation. Applications of the activating solution of 45 seconds or longer are successful. Examination of the metal surface shows that there is no formation of protective coating during this stage of the process.

The member is taken from the activating solution and transferred to a receptacle **14** containing a conventional type of aqueous solution **16** of a phosphate composition capable of producing protective phosphate coatings. A typical solution **16** for use with zinc metal is of the following analysis:

	Per cent
Iron	0.03 to 0.30
Zinc phosphate	0.04
Sodium nitrate	0.2 to 1

Phosphoric acid to produce a 20 point solution and comprising 1:8 of total phosphate content.
Remainder water.

In 30 seconds or less a highly effective phosphate coating will be deposited on the zinc surface. Longer applications of the phosphate solution are also successful.

In the prior art, unactivated metal surfaces required treatment with a phosphate solution for 15 to 20 minutes. For example, in applying phosphate coatings to automobile bodies, several thousand gallons of solution were sprayed upon the metal before an adequate amount of phosphate coating was formed. In addition, the coatings were non-uniform and it was desirable to paint such coatings as soon as possible. When preactivated, metal surfaces may be sprayed or dipped in the phosphate solution **16**, for a period of time of the order of one-half minute, to produce an extremely uniform and fine phosphate coating.

The metal forms large quantities of gaseous bubbles when the solution is first applied to the activated surfaces. It is believed that the bubbles consist mainly of hydrogen gas. After a fraction of a minute, the bubbling ceases and the reaction is substantially complete. It is generally desirable to prolong the application of the solution to the metal surface for a short period of time beyond the point at which the gaseous bubbles cease to be given off.

The extremely rapid formation of a protective phosphate coating at this stage of the process constitutes one of the unexpected results of the invention. In particular, zinc surfaces acquire an almost velvety and clean-appearing surface of very fine crystalline nature.

In treating ferrous metals, for example, stampings of all types, a solution for use in receptacle **14** more suitable than the one given above for zinc is suggested:

Manganese phosphate	pounds	1¾
Phosphoric acid 84%	do	5
Sodium nitrate	do	½
Cupric nitrate	ounce	¼

Water to make one gallon.

The gallon of solution is diluted with water to make a 3% solution.

The main purpose of the sodium nitrate in the above formula is to provide an oxidizing agent to react with small amounts of nascent hydrogen which are produced when the solution reacts with

the metal surface. Unless the hydrogen is oxidized or removed as large bubbles of hydrogen gas, the adherent nascent hydrogen adheres to the metal surface and blankets the action of the solution. Therefore, a non-uniform coating may result. The oxidizing agent will immediately react with the bubbles of nascent hydrogen and remove them from the surface of the metal. Other oxidizing agents, such as sodium or potassium nitrite, are suitable for this purpose.

Zinc phosphate may be introduced to replace a part of the manganese phosphate in the solution for treating ferrous metals. Generally, the presence of one or more of the group consisting of zinc, copper and manganese greatly expedites the reaction of the ferrous metal with the phosphate solution.

Numerous other solutions capable of producing phosphate coatings upon metal are known to the art and their reaction with activated metal surfaces is equally feasible to produce a protective coating.

After an adequate crystalline phosphate coating has been produced upon the metal surface, the metal surfaces are rinsed with water 18 contained in receptacle 20. For best results, the surfaces are subjected to a sealing treatment at 22 with chromic acid solution 24. The chromic acid 24 consists of an aqueous solution of 7½ ounces of chromic acid per 100 gallons of water. The water rinse 20 is not necessary with the sealing treatment of chromic acid. Only a few seconds application of the chromic acid solution is necessary to secure a sealing of the phosphate coating to improve the corrosion resistance.

The metal, after a sealing treatment at 22, may be passed through a drying oven 26 to completely dry the surface for subsequent operations, such as applying of an organic finish.

Alternatively, it has been discovered that the water rinse and drying oven steps in the process may be dispensed with if the chromic acid solution 24 is heated to a temperature of about 190° F., or even higher, sufficient heat being imparted by the hot chromic acid solution to the metal so that after removal from the solution, the metal dries automatically in air.

Microscopic examination of the coated metal surface reveals a structure somewhat as shown in Fig. 2. The base metal 30 has a distinct and separate layer 32 which is of substantially uniform thickness, and appears to be keyed to the metal 30. The coating 32 is extremely durable and will withstand both chemical and mechanical abuse. Abrasion or scratching is necessary to remove the coating 32. Such coating is uniformly deposited over all the recesses and other irregularities in the surface of metal body 30.

Referring to Figs. 3 to 6, there are shown photomicrographs at a magnification of 300X of samples of material treated with prior art solutions and as disclosed herein.

Fig. 3 shows a coarse, crystalline surface deposit of phosphates on zinc plated steel. The deposit is nonuniform with large spaces between crystals. Such a surface deposit produces an unsatisfactory protective coating.

The coarse nature of the phosphate deposit in Fig. 3 requires the application of two or more coatings of organic finish to produce a smooth surface. The organic finish does not adhere any too well to the large crystals and its life is relatively short.

For comparison, Fig. 4 shows a similar zinc plated steel member as in Fig. 3, with a phosphate coating produced by a predip of disodium phosphate-titanium solution followed by the same phosphate coating solution as employed alone for the Fig. 3 coating. The uniform and fine grained phosphate deposit in Fig. 4 is an outstanding feature. There are no open spaces in Fig. 4 as exist in Fig. 3.

The fine grained phosphate coating in Fig. 4 has been satisfactorily coated with a single coating of organic finish to produce a smooth, commercial outer surface. Due to its better corrosion-proofing organic finishes last longer when applied to the Fig. 4 surface. The bonding of the finish to the metal is enhanced by the fine grained phosphate deposit.

Fig. 5 is a photomicrograph at a magnification of 300X of an ordinary steel member with the usual type of phosphate coating produced thereon. Not only is the protective phosphate coating coarse grained, but its protection is limited. It is customary to require that organic finishes be applied to ferrous metals within a few hours after the phosphate treatment. Otherwise, in a few days, rusting will be visible.

Fig. 6 is a photomicrograph at a magnification of 300X of a steel member treated similarly to Fig. 5 with a disodium phosphate-titanium predip prior to application of a phosphate solution. The effectiveness of the predip in producing a fine grained, highly protective phosphate is evident. The Fig. 6 phosphate coating shows the same superiority over the prior art coatings as does the zinc plated member subjected to the predip.

While occasionally in prior art practice protective coatings have been secured whose appearance to the naked eye appears to correspond to that produced by the present process involving an activating pretreatment, corrosion tests have revealed a decided difference in the quality of the coatings with better corrosion resistance produced by the invention in this case. Ordinary zinc plating on a steel base will turn completely white after 12 hours in a steam chest at 140° F., due to the corrosion of the zinc. The same type of zinc plated member subjected to a standard phosphate composition treatment, without an activating pretreatment, exhibits an improved resistance to corrosion in the steam chest: After 12 hours a few white spots will be apparent on the surface of such metal. When zinc plated members similar to those tested above were given an activating pretreatment, followed by a phosphate surface treatment as detailed in Fig. 1, at least 14 days elapsed before any sample showed a sign of corrosion in the steam chest operating at 140° F. Generally the members are capable of withstanding a month in the steam chest before any extensive degree of corrosion is evidenced in activated material.

When the three types of material were additionally coated with an organic finish, an almost equivalent proportionality in the resistance to corrosion was obtained. Samples in which an activating pretreatment was applied to zinc prior to a phosphate treatment lasted over 25 times as long at 140° F. in a steam chest before failure of the organic finish was observed, as compared to the other types of material.

It will be seen by this process that not only has the processing time been cut down to a minimum, as compared to the time required in the prior art to produce a phosphate coating, but

also coatings of a superior corrosion resistance are deposited or formed on the metal. Furthermore, certain metals which have been treated with the greatest of difficulty heretofore are expeditiously and economically treated to produce an exceedingly durable phosphate coating. The phosphate coating is so uniform that a single coating or organic finish is frequently sufficient to produce the final product, as compared to the prior art in which two or more applications of organic finish have previously been necessary.

Since certain changes may be made in the above invention and different embodiments of the invention may be made without departing from the scope thereof, it is intended that all matter contained in the above-described disclosure or taken in connection with the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

I claim as my invention:

1. A composition which when in aqueous solution is capable of activating ferrous and zinc metal surfaces to provide for the application of protective phosphate coatings which comprises sodium pyrophosphate and more than 0.005% by weight of titanium, the titanium being present as a compound.

2. A composition which when in aqueous solution is capable of activating ferrous and zinc metal surfaces to provide for the application of protective phosphate coatings which comprises 80% and over of sodium pyrophosphate and from 0.02% to 20% by weight of titanium, the titanium being present as a compound.

3. An aqueous solution for use in activating ferrous and zinc metal surfaces comprising from 0.1% to 2.0% of sodium pyrophosphate and 0.005% to 0.05% of titanium, the titanium being present as a compound.

4. An aqueous solution for activating ferrous and zinc metal surfaces to accelerate the formation of corrosion resisting coatings thereon comprising sodium pyrophosphate and at least one titanium compound.

5. In the process of treating ferrous and zinc metal surfaces prior to producing thereon corrosion resisting phosphate coatings, the step comprising applying to the metal surface an aqueous solution of sodium pyrophosphate and at least one titanium compound to activate the metal surface.

6. The process of treating ferrous and zinc metal surfaces to provide corrosion resisting coatings thereon which comprises, in combination, applying an aqueous solution having from 0.1% to 2.0% sodium pyrophosphate and 0.005% to 0.05% titanium, the titanium being present as a compound, to activate the metal surface and applying a solution of phosphoric acid, phosphates, and an oxidizing agent to the activated metal surface to produce a protective phosphate coating thereon.

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