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TREATED STEEL SHEET AND PROCESS

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This invention relates to a corrosion-resistant ferrous sheet and the method of producing same. It relates particularly to a ferrous sheet having thereon a coating which is corrosion-resistant and has paint-bonding characteristics and can withstand temper-rolling and the usual bending, drawing, stamping, and spot-welding operations incident to fabricating articles therefrom without losing its bare corrosion-resistance or paint-holding characteristics.

The object of this invention is a ferrous sheet which will have satisfactory resistance to corrosion during transportation and manufacture without the aid of further treatment, which can be bent, drawn, spot-welded and otherwise treated in the usual manufacturing processes without difficulty and which will present a surface to which paint, varnish, or other finishing coats will firmly adhere.

In the manufacture of sheet metal products, the sheets of metal customarily are produced at one place and the manufacture of the sheets into articles occurs at another place and time. During the transportation and storing of sheets of iron or steel, corrosion will take place unless some means is provided to prevent such corrosion. Also, paint, varnish, and other siccative coats which are applied and dried upon the surface, and which are customarily employed in finishing sheet metal articles, both for purposes of appearance and as protection against corrosion, do not adhere well to bare metal. In many lines of manufacture, it has become usual to treat the surface of the metal of the manufactured article so as to produce a phosphate or similar coating thereon to which the paint, varnish, or enamel will adhere better than to the bare metal.

The ordinary processes by which phosphate coatings are produced upon manufactured articles in order to bond paint thereto are not entirely satisfactory for application to the sheet before its manufacture into articles. Amongst other reasons for this is the fact that the phosphate coating is an electric insulation and interferes with spot-welding, frequently employed in manufacturing the sheets into the finished articles.

Many other methods of coating sheets of iron and steel for protection against rust or to form a better surface for receiving a siccative coat, or both, have been proposed and used to some extent. However, substantially all of the paint-bonding coatings resulting from these different methods have defects which interfere with their successful employment upon sheets prior to man-

ufacturing. Coatings which are effectively corrosion-resistant during storage and/or shipment before manufacture are apt to interfere with the manufacturing processes or lose their value because of the manufacturing processes.

I have discovered that if ferrous sheets, before fabrication, are plated with thin layers of certain metals and thereafter coated with certain solutions containing hexavalent chromium, as chromic acid on a dichromate, and the PO_4 radical, a highly superior product is obtained which provides excellent corrosion-resistance both before and after fabrication, as well as providing a suitable paint base on the fabricated articles.

The metals which can be successfully employed in the plating step are: cadmium, nickel, lead, copper and mixtures and alloys thereof. Of the metals, cadmium and nickel are especially effective, and brass is a very good alloy.

The solution containing the hexavalent chromium, which is applied to the plated metal, may vary in composition. If dichromates are included, preferably they are of metals other than the alkali metals.

This treatment is especially effective where the solution is applied to a metal with which the chromium compound will react to some extent, at least when the metal, the solution, or both are heated.

But it is preferable that there shall be comparatively little reaction with the metal at room temperature, and in many instances there is no perceptible reaction at room temperature.

It will be seen that the resulting coatings which are on the metal, depending on the type of treatment, may comprise one of the plated metals mentioned and a hexavalent chromium compound, usually with some trivalent chromium either from the solution used, or from reduction of some hexavalent chromium, with oxygen compounds of phosphorus. Usually, there will be some of the plated metal in chemical combination due to action of the solution.

It is to be understood that, when maximum benefits are to be derived, the solutions should be dried onto the plated metal until substantially insoluble in water so as to form a permanent part of the article.

It is a general characteristic of these coatings where reaction with the plated metal is relatively slight to assume a somewhat glassy and non-crystalline appearance.

There is a tendency for the coatings to fracture when distorted by bending, drawing, or other operations where a stress is set up. However, the

adhesion of the film to the metal is sufficiently great so that considerable fracturing can occur without undue loss of the coating from the metal surface.

Because of the nature of chromic acid-containing solutions, they are prone to creep from edges of the metal, especially where there is heat applied during the drying operation.

Reaction between the hexavalent chromium solution and the metal lessens the tendency to creep. Electrolytically deposited plates are in many cases more reactive with the solution than is a plate of the same metal produced by applying molten metal or where a thin layer of the metal is applied to a ferrous base by means of heat and pressure. However, any method of obtaining a thin plate on a ferrous sheet is within the scope of this invention. Care must be taken to obtain layers sufficiently thin to permit drawing and forming operations without undue loss of the plated metal.

An outstanding advantage of the metal plate is its ability to be drawn during manufacturing operations while remaining a continuous covering plate. Electrolytically plated metal is in many cases better in this respect than plates applied by other means and for this reason electrolytic plating is preferred.

Unless there is sufficient reaction between the hexavalent chromium solution and the plated metal, it is desirable to treat the metal in some way in order to deposit by chemical action a slight coating on the metal which is more reactive with the hexavalent chromium solution than is the plated metal. The formation of this coating may be accomplished by means of solutions of sufficient oxidizing ability to produce a coating containing an oxide of the metal treated, or insoluble salts of the acid used resulting from reaction with metal treated may form the coating. Care, however, must be taken in this case to produce a sufficiently thin coating so it will not interfere with subsequent welding operations.

If preferred, the preliminary coating may be formed by heating the metal in an oxidizing atmosphere. Care must be taken, whichever method of forming the coating is selected, to avoid the production of such a heavy coating that, during the drying on of the chromium-containing solution, the hexavalent chromium is entirely reduced, or, that manufacturing operations will be interfered with or will destroy the effectiveness of the coat.

Where solutions are employed to produce the coating to which the hexavalent chromium solution is applied, soluble compounds of metals below the metal being coated may be used where it is advantageous to decrease the coating time.

In some cases, the solution employed in the first step is washed off before the second solution is applied, but in some cases this is not necessary. Where the first solution contains ingredients which may interfere with the action of the second solution, and especially if the second solution is applied by immersion or by a washing action that involves recirculating the solution, a rinse is indicated between the first and second treatment, and such an intermediate rinse can be used without detriment except where the first step leaves but a very small amount of the products of its reaction on the surface of the metal, or where a water rinse would remove the products of the first reaction too completely, or where it is helpful to have some of the first solution

as well as its products on the surface of the work for reaction with the second solution.

Under usual conditions it is preferred that the second solution should be applied before the first coating is more than superficial, and before there is over one gram on a square yard of surface; since for best results the coating obtained by drying on the hexavalent chromium solution should comprise the major part of the final coating.

A simple etching, as by sulphuric, hydrochloric, acetic, or any etching acid, if not rinsed excessively, leaves some salt of the metal at the surface of the work, and where the second step follows promptly and the tendency of the second solution to creep is not too great, this remnant of salt, although invisible, is sufficient to overcome the tendency to creep and to result in a better bond between the metal and the dried film of the second solution. Such treatment may be employed where the metal of the plate and the hexavalent chromium compound are of kinds that will avoid excessive creeping when the solution is applied promptly over the electrolytically deposited metal, but where an interval has occurred between plating and applying the solution or the plating has been applied by molten metal rather than electrolytically, a more substantial treatment is recommended.

In some instances, this treatment may comprise applying a film of phosphoric acid and drying it completely or partially, then applying a solution of chromic acid or dichromate. This procedure eliminates the necessity of other treatment of the metal to obtain good wetting.

It is highly advantageous with any of the treatments mentioned for obtaining uniform films of the chromium-containing solution, to have the surface wet at the time it is applied.

The coating from the hexavalent chromium containing solution is somewhat improved by the presence of trivalent chromium. It may be added as such, or may be provided as hexavalent chromium and reduced. A convenient way of reducing the hexavalent chromium is by hydrogen peroxide or a substance having an equivalent reducing effect, which will not by its oxidizing action leave deleterious by-products in the solution. If the hexavalent chromium is partially reduced to provide the trivalent chromium, this should be taken into consideration in the amount of chromic acid added. The amount of trivalent chromium may be varied, but good results have been obtained with about one-fifth as much trivalent chromium as there is of hexavalent chromium.

The following specific illustrations are given to point out the advantages of the invention, it being understood that they are given only by way of example, however, since many variations may be made within its teaching.

In the examples given below, steel panels were first cleaned by heating them at 700° F. for four minutes to produce a thin oxide layer which was removed by immersion in dilute hydrochloric acid at room temperature for one minute after which the panels were rinsed with water, they then received an electroplate of cadmium .00005 inch in thickness.

All of the panels were kept wet with water until the various hexavalent chromium-containing solutions were applied.

Example 1.—An aqueous solution containing 6% zinc dichromate and 3% phosphoric acid was applied by dipping after which the panels were dried for 15 minutes at 600° F.

Example 2.—Same as Example 1 but the solution contained 6% zinc dichromate and 6% phosphoric acid.

Example 3.—Same as Example 1 except that 6% cadmium dichromate was substituted for zinc dichromate.

Panels prepared according to each of the examples were distorted in certain areas by an Olsen testing machine in order to stretch the metal and the coating applied to it after which the panels were finished with a baked synthetic enamel. The paint was scratched through to the metal so it was exposed both on the distorted and smooth areas. All of the panels were then placed in a standard salt spray and tested for a total of 478 hours. At the end of this time inspection of the pieces showed the paint to be in excellent condition on both the level and distorted areas, no creepage at all being present on the great majority of the level areas and very little if any on the distorted areas. To illustrate, on duplicate panels prepared according to Example 1, one panel showed no creepage whatever on any area while on the other, the level areas were perfect and with a creepage of the paint on the distorted areas amounting at the most to only $\frac{1}{2}$ of an inch from the scratch.

The advantage of the treatment using the plated metal covered with the hexavalent chromium solution becomes apparent when compared to the two treatments employed separately, for example, panels which had been cadmium plated the same as in the examples and painted and tested without the chromium-containing solution being applied, rated a failure in 478 hours, both on the level and the distorted areas. A rating of failure is equivalent to a creepage of the paint $\frac{1}{2}$ inch from the scratch.

On the other hand unplated steel panels which were given a light oxide coating to obtain wetting and then coated with a solution containing 6% phosphoric acid, 3% chromic acid and .5% trivalent chromium and baked 15 minutes at 550° F., then painted and tested the same as the examples above, although perfect on the level areas showed a very decided creepage on the distorted portions.

As indicated before it is important that any rust-proofing paint-holding coating applied to steel before fabrication should have good bare corrosion resistance. The following examples show conclusively the advantage in this respect of the two-step process of the invention.

Panels were prepared and plated exactly the same as in the previous examples and various aqueous chromium-containing solutions applied and baked as before, however, instead of being painted the panels were subjected to Detroit outdoor industrial atmosphere for a period of 700 hours. These pieces were distorted in certain areas the same as in the previous examples.

In no case with the following hexavalent chromium solutions applied was there any sign of corrosion on either the distorted or smooth areas.

Example 4.—6% cadmium dichromate plus 6% phosphoric acid.

Example 5.—3% chromic acid plus 6% phosphoric acid.

Example 6.—3% chromic acid plus 6% phosphoric acid plus .5% trivalent chromium.

Example 7.—1.13% chromic acid plus 9.22 of 75% phosphoric acid, .307% ferric iron, 1.83% trivalent chromium.

Cadmium plate without further treatment at the end of 700 hours was covered with a uniform layer of white corrosion products.

The formula of Example 6 was also included in the test only applied to steel in which case the steel was first given a thin oxide coating to obtain good wetting. At the end of the 700 hour test the distorted areas had failed completely and were covered with heavy rust. The smooth areas were about 80% covered with heavy rust. When compared with the results in Example 6 the value of the cadmium plate when used in combination with the hexavalent chromium-containing solution becomes very apparent.

Excellent results have also been obtained with nickel electroplate. Steel panels were prepared the same as in the previous examples but were plated with .00005 inches of nickel, that thickness being ample to afford material protection when protected as proposed by this invention, and a thickness not greater than that being preferable.

The plated articles were coated with the following solutions and in each case were baked 15 minutes at 550° F.

Example 8.—3% zinc dichromate plus 3% phosphoric acid.

Example 9.—6% zinc dichromate plus 6% phosphoric acid.

Example 10.—3% nickel dichromate plus 3% phosphoric acid.

Example 11.—6% nickel dichromate plus 6% phosphoric acid.

The panels were distorted in certain areas as in the previous tests, finished with paint and tested in the same manner in salt spray. Practically no creepage of the paint was obtained in any case by the end of the test or 479 hours. The maximum amounted to only $\frac{1}{2}$ of an inch.

Panels which were nickel plated but which received no coating with the chromium-containing solution tested in the same manner had failed in many places, that is the paint had become loose at least $\frac{1}{2}$ inch away from the scratch.

Example 12.—Sheets of steel were electroplated with .0001 inch of nickel. Some of these were then coated with a solution containing 6% phosphoric acid, 3% chromic acid, and 0.5% Cr+++ and baked for 10 minutes at 500° F. The entire lot of pieces was then drawn into a cuplike shape so that there was an overall elongation of the metal of approximately 14 per cent. The untreated pieces, along with the treated ones which had been cleaned and rinsed with a weak chromic acid solution, were finished with one coat of a synthetic enamel. Other pieces, consisting in one case of bare untreated steel, and in the other, pieces having on their surface a flash coating consisting mainly of oxides of iron together with some chemically combined arsenic, and treated with the above hexavalent chromium-phosphate solution but without the nickel plate, were drawn, cleaned, and the treated pieces rinsed in dilute chromic acid and likewise painted. The different drawn pieces were then scratched across the surface in several places to expose the metal underneath the paint and subjected to a standard salt spray test. After 359 hours, the painted, untreated steel was considered a failure; the paint having become detached over large areas. After 717 hours, the nickel plated and painted pieces were also failures. At 883 hours, which was the end of the test, the average creepage of the treated steel was $\frac{1}{2}$ inch each side of the scratches, while with the treated nickel the maximum creepage was $\frac{1}{2}$ " and in a number of places there was no loss of paint adhesion whatever.

Example 13.—Other pieces, treated the same as those just mentioned, but without the finish coat

of paint, were immersed in water at 100° F. for 21 hours. In the following, the figures are related to a standard method of rating in which 0=perfect and 5=failure. At the end of the test the untreated steel rated 3, or a 60% degree of rusting. The steel treated with the chromium-phosphate solution rated 2, or a 40% degree of rusting. The nickel plated steel rated 1.5, or a 30% degree of rusting, while the nickel plated steel treated with the chromium-phosphate solution had a rating of but .5 or a 10% degree of rusting.

Example 14.—In other tests, steel was plated with .00001 and .00005 inch of cadmium. One half of the pieces were coated with a solution containing 6% phosphoric acid, 3% chromic acid, 0.5% Cr⁺⁺⁺, then baked for 10 minutes at 500° F. These sheets were then bent through 180° and straightened. Other areas were subjected to impact in order to stretch the metal and deliberately fracture the coating. All of the sheets were then subjected to a standard salt spray test for 44 hours. At that time, all of the pieces with the .00005 inch of cadmium plate were perfect, showing no rust whatever. Those with the .00001 inch of plate, but without the chemical treatment, had failed, showing rust over the entire surface, while those with the same thickness of plate but which had also received the chemical treatment were perfect, showing no rust, including the bent and impacted areas.

The advantages of the combination of the plated metal and the chromium-PO₄ treatment can readily be appreciated when these results are compared to steel sheets that had been given the oxide-arsenic pretreatment previously referred to, then coated with the chromium-phosphate solution. At the end of 44 hours in the same test, these rated only slightly under a failure on the bent and impacted areas (4.7 on the basis previously given).

As stated before, there is some variation in the susceptibility to attack of the plated metals by the chromium-containing solutions, and in some cases it will be necessary to take this point into consideration if it is desired to have a pre-determined amount of the plated metal left after the solution has been applied and baked.

The chromium-containing solutions given may be applied in various ways. They may be applied simply by dipping the metal into the solution, draining and drying if an unusually heavy film is desired, or after immersing the metal, the sheets may be run between rolls made of a material, such as steel which is not attacked by the solutions, to remove the excess solution and leaving only a thin film. In this case, it is advisable to employ rolls having a surface similar to the effect produced by knurling to avoid removing too much of the solution.

Another method of application is by spraying, similar to the manner in which paint is applied.

In regular production of the coated sheet, it is most advantageous to have all necessary operations take place consecutively without interruption. The plating, the treatment, if necessary, to provide wetting, the application of the hexavalent chromium-containing solution and the drying, together with whatever rinsing operations are necessary, may be carried out in a single unit constructed for the purpose.

In building up the solutions, they may be prepared entirely with the acids or salts of the acids may be used; that is, dichromates may be used in place of chromic acid along with phosphates.

For best results, however, it is preferred that the solutions, when applied, contain some acid.

Both the proportions and concentration of chemicals used are subject to wide variation. If relatively strong solutions are employed, an increase in baking time and/or temperature may be advisable to render the film insoluble over that required for weaker solutions.

Care should be exercised in the selection of the composition of the chromium-containing solution as well as any pretreating steps employed to avoid the necessity of temperature high enough to cause melting of the plated metal. For example nickel and copper will withstand higher temperatures than cadmium or lead.

The amount of phosphoric acid should not be so out of proportion to the hexavalent chromium compound that an excessive attack is obtained on the plated metal since this will lessen the effect of the entire treatment. After the applied final solution is completely dry, there should still remain a substantially continuous layer of the plated metal underneath on the steel surface.

The oil and drawing compounds used in forming or drawing the treated sheet must be removed before paint is applied. Alkali cleaners are most commonly used for this purpose. It has been found that if, after the use of such cleaners, the object is given a final rinse in chromic acid, or a dichromate, preferably other than the alkali metal dichromates, decidedly superior results are derived because blistering of the applied paint is reduced to a minimum. The rinsing of the surface not only serves to neutralize any residual alkali from cleaning, but also reduces the ill effects from hardness inherent in the water. Amounts of chromic acid or dichromates as low as 2 grams per gallon are satisfactory.

Phosphoric acid may also be used for this purpose but is less desirable because especially lined tanks are necessary. However, a combination of chromic acid or dichromate and phosphoric acid may be used with complete satisfaction in steel tanks because the action of the phosphoric acid is then inhibited.

These final rinse solutions are permanently retained on the surface and are not rinsed off before painting the treated objects. All that is necessary is that they are dried sufficiently to remove the moisture.

What I claim is:

1. A ferrous sheet having thereon a plating not over .0001" thick of metal of the group consisting of cadmium, nickel, lead, and copper, and having the plating covered with a thin glassy coating formed by baking thereon a solution containing hexavalent chromium and the PO₄ radical.

2. A ferrous sheet electroplated with cadmium, and having the plating covered with a thin, corrosion-resistant, paint-holding coating of glassy appearance and substantially insoluble in water and formed by baking thereon a solution containing hexavalent chromium and the PO₄ radical.

3. A ferrous sheet electroplated with nickel, and having the plating covered with a thin, corrosion-resistant, paint-holding, weldable coating of glassy appearance and, substantially insoluble in water and formed by baking thereon a solution containing hexavalent chromium and the PO₄ radical.

4. A ferrous sheet carrying an electroplate of nickel of not over .00005 inch thick, said plate covered with a thin, corrosion-resistant, paint-holding, weldable coating of glassy appearance, substantially insoluble in water and formed by

baking thereon a solution containing as the major portion of its coating chemicals, hexavalent chromium and the PO_4 radical.

5. The method of producing corrosion-resistant, paint-holding coatings on ferrous sheets which comprises electroplating a ferrous sheet with metal of the group consisting of cadmium, nickel, lead, and copper, and baking on the plating a solution containing hexavalent chromium and the PO_4 radical and regulating the concentration of the solution and the amount of the solution baked onto the metal so that the baked coating is thin enough to retain its paint-holding characteristics after the usual bending, drawing, and stamping operations incident to fabricating sheet metal articles and continuing the baking until the coating is substantially insoluble in water.

6. The method of producing corrosion-resistant, paint-holding coatings on ferrous sheets which comprises electroplating a ferrous sheet with cadmium, and baking on the plating a solution containing hexavalent chromium and the PO_4 radical and regulating the concentration of the solution and the amount of the solution baked onto the metal so that the baked coating is thin enough to retain its paint-holding characteristics after the usual bending, drawing, and stamping operations incident to fabricating sheet metal articles and continuing the baking until the coating is substantially insoluble in water.

7. The method of producing corrosion-resistant, paint-holding coatings on ferrous sheets which comprises electroplating a ferrous sheet with nickel, and baking on the plating a solution containing hexavalent chromium and the PO_4 radical and regulating the concentration of the solution and the amount of the solution baked onto the metal so that the baked coating is thin enough to retain its paint-holding characteristics after the usual bending, drawing, and stamping operations incident to fabricating sheet metal articles and continuing the baking until the coating is substantially insoluble in water.

8. The method of producing corrosion resistant, paint-holding coatings on ferrous sheets which comprises electroplating a ferrous sheet with copper, and baking on the plating a solution containing hexavalent chromium and the PO_4 radical and regulating the concentration of the solution and the amount of the solution baked onto the metal so that the baked coating is thin enough to retain its paint-holding characteristics after the usual bending, drawing, and stamping operations incident to fabricating sheet metal articles and continuing the baking until the coating is substantially insoluble in water.

9. The method of producing corrosion-resistant, paint-holding coatings on ferrous sheets which comprises plating a ferrous sheet with metal of the group consisting of cadmium, nickel, lead, and copper, treating the plated surface to render it more reactive with a solution containing hexavalent chromium, and then applying and baking on a solution containing hexavalent chromium and the PO_4 radical in such amount that compounds of chromium and of PO_4 furnish the major portion of the baked coating, and regulat-

ing the concentration of the solution and the amount of the solution baked onto the metal so that the baked coating is thin enough to retain its paint-holding characteristics after the usual bending, drawing, and stamping operations incident to fabricating sheet metal articles.

10. The method of producing corrosion-resistant, paint-holding coatings on ferrous sheets which comprises electroplating a ferrous sheet with cadmium, treating the cadmium surface to make it more reactive chemically, and then applying and baking on a solution containing hexavalent chromium and the PO_4 radical in such amount that compounds of chromium and of PO_4 furnish the major portion of the baked coating, and regulating the concentration of the solution and the amount of the solution baked onto the metal so that the baked coating is thin enough to retain its paint-holding characteristics after the usual bending, drawing, and stamping operations incident to fabricating sheet metal articles and is substantially insoluble in water.

11. The method of producing corrosion-resistant, paint-holding coatings on ferrous sheets which comprises electroplating a ferrous sheet with nickel, treating the nickel surface to make it more reactive chemically, and then applying and baking on a solution containing hexavalent chromium and the PO_4 radical in such amount that compounds of chromium and of PO_4 furnish the major portion of the baked coating, and regulating the concentration of the solution and the amount of the solution baked onto the metal so that the baked coating is thin enough to retain its paint-holding characteristics after the usual bending, drawing and stamping operations incident to fabricating sheet metal articles and is substantially insoluble in water.

12. The method of producing corrosion-resistant, paint-holding coatings on ferrous sheets which comprises electroplating a ferrous sheet with copper, treating the copper surface to make it more reactive chemically, and then applying and baking on a solution containing hexavalent chromium and the PO_4 radical in such amount that compounds of chromium and of PO_4 furnish the major portion of the baked coating and regulating the concentration of the solution and the amount of the solution baked onto the metal so that the baked coating is thin enough to retain its paint-holding characteristics after the usual bending, drawing, and stamping operations incident to fabricating sheet metal articles and is substantially insoluble in water.

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