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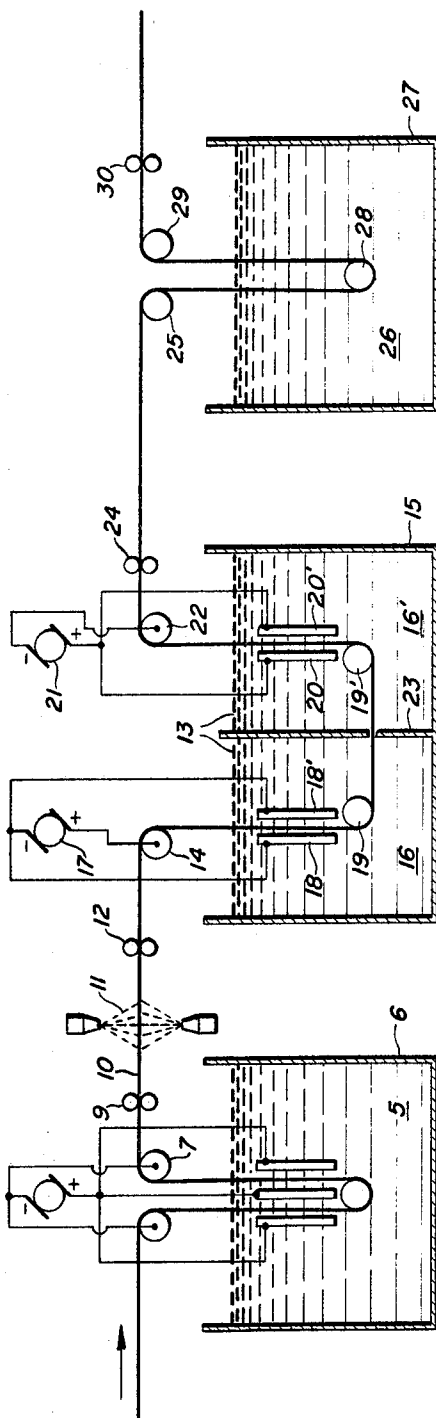
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TREATMENT FOR FERROUS SURFACES

3,479,260

Filed March 7, 1966

2 Sheets-Sheet 1

Fig. 1



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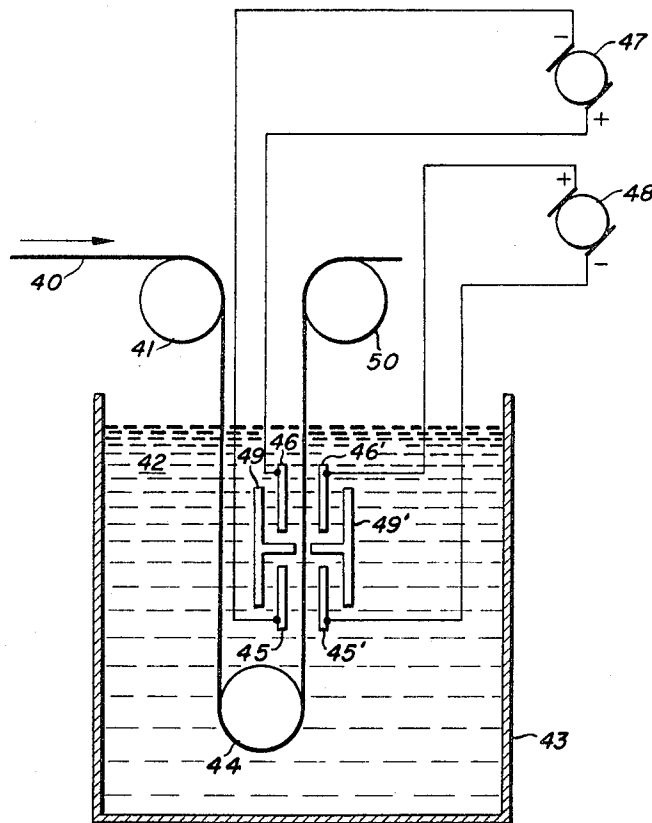
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Fig. 2



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TREATMENT FOR FERROUS SURFACES

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7 Claims

ABSTRACT OF THE DISCLOSURE

In a method of forming a protective coating on a ferrous article, the article is immersed in an aqueous electrolyte containing not less than 50 grams per liter of chromic acid, and phosphoric acid wherein the ratio of chromic acid to phosphoric acid is between 1.7:1 and 3:1. The immersed article is electrolyzed anodically for a brief interval of seconds or a fraction of a second, and then electrolyzed cathodically for a similar interval at a current density of not less than 200 amp. per sq. ft.

This invention relates to the treatment of the surface of a ferrous article, and more particularly to the passivation of steel strip.

Cold-rolled, carbon steel strip, of the type known as tinplate stock and sheet stock, is used extensively in the fabrication of finished products such as cans, container, furniture, household appliances, automobile body parts, etc.

One of the serious problems confronting the fabricator results from oxidation staining of the steel surface prior to application of a protective coating such as enamel, paint or the like. As the cold-rolled strip is often produced at points quite distant from the fabricating operation, and the time period between production of the strip and coating of the stock may extend to weeks or months, it is virtually impossible to maintain the bright, shiny appearance of the stock during the interim without some treatment of the stock.

Many attempts have been made to develop an inexpensive, light weight, compatible, rust-preventive coating for the strip, which can be applied to the strip shortly after it comes from the rolling mill. Most of these attempts have fallen short of expectations due to the varied requirements of such a treatment. Obviously, it is desirable to produce such an interim treatment inexpensively. The treatment should give complete protection from oxide stain for a period of many days, and under conditions of uncontrolled humidity, to maintain the normal appearance of the steel surface when fabricated. Other requirements for the protective coating are compatibility with a subsequently applied lacquer or enamel, and, in the case of stock used for food and beverage containers, non-toxic properties, as well as prevention of contamination of the material subsequently stored in the container.

Accordingly, it is a primary object of this invention to provide a coating for steel strip surfaces which will inhibit formation of oxides on the strip surfaces during storage.

Another object is to provide an inexpensive method of forming the coating rapidly under mill conditions.

A further object is to provide a coating which will produce the proper adherence when used as an undercoat for coatings, particularly resins, normally applied as metal container coatings.

Another object is to provide a coating which greatly reduces filiform or exfoliation corrosion under an applied resin coating, particularly at sites of damage or cut edges.

Another object is to provide a coating for a ferrous article such as steel strip, having on its surface a coating of another metal such as chromium.

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We have found that the foregoing objects can be attained by treating the steel strip electrolytically in a bath of chromic and phosphoric acids.

The method comprises, broadly, treating the strip anodically, followed by treating the strip cathodically, in an aqueous electrolyte of chromic acid and phosphoric acid, and then rinsing the strip in water.

By this method a coating is formed on the strip which protects the integrity of the surface for a matter of months in normal storage. The method is particularly adaptable to processing large coils of continuous strip of any conventional width. The coating treatment can be applied to one, or both sides of the strip as desired. The treatment is applied rapidly, being completed in a matter of seconds, and is easy to control.

In the drawings:

FIG. 1 is a schematic representation of the steps involved in applying a coating to continuous lengths of strip.

FIG. 2 is a schematic representation of an alternative means of forming a coating from the electrolytic bath.

For a more complete understanding of the invention, the invention will be described in detail in the following example.

Referring to the drawings, in FIG. 1 a steel strip 10, after being cleaned cathodically in alkaline cleaning solution 5 in cleaning tank 6, leaves the cleaning tank via roll 7 and, after passing through squeegee rolls 9, water spray rinse 11, squeegee rolls 12 and over roll 14, is introduced into treatment tank 15. The strip is conducted between lead electrodes 18 and 18' in electrolyte 16. Current, supplied from generator 17, is introduced, at roll 14, to a circuit formed by strip 10, the electrolyte 16 and electrodes 18, 18'. In this phase of the process, the strip acts as anode for a period of two seconds. The strip is then guided, by means of submerged rolls 19, 19', between lead electrodes 20 and 20' while immersed in that portion of the electrolytic solution shown at 16'. Current from generator 21 is supplied to the circuit formed by electrodes 20, 20', electrolyte 16' and strip 10, with said strip being in electrical contact with roll 22. In this step the current is reversed from that of the previous anodic treatment. In the second electrolytic treatment, the strip acts as cathode for two seconds. The current density at the anode in the anodic step, and at the cathode in the cathodic step, is about 300 amperes per square foot (a.s.f.).

The electrolyte in both portions of the treating tank, i.e., portion 16 and portion 16', is made up and maintained as an aqueous solution containing approximately 100 grams per liter (g./l.) of chromic acid as CrO_3 and 40 g./l. of orthophosphoric acid as H_3PO_4 . The operating temperature of the bath is about 180° F.

A slotted, electrically non-conductive baffle 23 extends approximately the full height of the solution in tank 15. This baffle permits strip 10 to pass from the anodic cell of electrolyte 16 to the cathodic cell of electrolyte 16', and effectively separates the two cells. As is well known in the art, other electrical insulation may be desired to reduce or eliminate stray currents.

After leaving treatment tank 15 by way of roll 22, the strip is passed through squeegee rolls 24 and is then carried around roll 25 to rinse tank 27 containing water rinse 26. The strip is carried through tank 27 by roll 28 and thence to exit roll 29 and squeegee rolls 30, after which the strip is dried, coiled and ready for subsequent fabrication steps. Normally electroplate oil may be applied prior to coiling, if desired.

The efficiency of the coating process is dependent on the surface condition of the strip prior to coating. The strip should be free of rust, dirt and oil. Generally, steel strip from a cold reducing mill will have a surface coating of oil. This oil should be removed by an alkaline

cleaning step. The cleaning method shown in the example at tank 6 proves highly effective for the purpose of dirt and oil removal. If there is any rust on the strip before coating, the strip should be cleaned additionally in an acid pickling bath, such as a dilute aqueous solution of slufuric acid, and thoroughly rinsed with water before the strip is introduced into the chromic-phosphoric acid treatment bath.

Panels, made from strip treated by the foregoing method, were subjected to a water spray fog in a humidity cabinet at 100° F. for 50 hours, without exhibiting a trace of rust formation.

It will be understood that the method just described represents only one mode by which the invention can be performed. An alternate means of electrolyzing the strip in the electrolyte is illustrated in FIG. 2, where the strip 40 enters the electrolyte 42 in tank 43 by way of roll 41, is guided around roll 44, and then passes between negative electrodes 45, 45' and then between positive electrodes 46, 46'. Current is supplied from generator 47 to anode 46, and the circuit is completed through the electrolyte, strip and cathode 45 to the generator. Current is supplied from generator 48 to anode 46', and the circuit is completed through the electrolyte, strip and cathode 45' to the generator. In this manner the strip is first treated anodically and then cathodically. Electrically non-conductive baffles 49 and 49' minimize parallel stray currents. After leaving the bath by roll 50, strip 40 is water rinsed, dried and coiled as in the detailed example given above.

In another example, using an electrolyte of the same composition as that of the example described above, and in which the strip was passed through the same series of steps as in the previous example, the current density was maintained at 450° a.s.f. for a 1½ second anodic, 1½ second cathodic treatment. Panels of the resultant coated strip exhibited no rust after 50 hours exposure at 100° F in the water spray fog cabinet.

While it is preferred to maintain the acid concentrations in the treating bath at approximately 100 g./l. chromic acid and 40 g./l. phosphoric acid, when operating at the rate of speed shown in the example, it has been found that much lower concentrations, down to 50 g./l. chromic acid and 17 g./l. phosphoric acid produce a coating in a matter of several seconds (total time of treatment) which is serviceable for many months under normal storage conditions. Although the bath is operable at much higher concentrations, such as 300 g./l. chromic acid and 150 g./l. phosphoric acid, such concentration are not preferred for economic reasons. Upper practical limits for chromic acid and phosphoric acid are about 150 g./l. and 75 g./l. respectively. It is preferred to use a ratio of about 2.5 parts of chromic acid to 1 part of phosphoric acid, although the operable range may be as low as 1.7 and as high as 3 parts of chromic to 1 part phosphoric.

The pH of the operating electrolyte will normally be about 0.3 or less.

Any electrode which is insoluble in the electrolyte of this invention, and which has sufficient current-carrying capacity, may be used. Examples of electrodes which may be used are those made from lead, lead alloys or platinum.

The coating produced by the method described in the examples will have a coating weight of approximately 18 milligrams per square foot. Lighter coatings, even those with coating weights in the neighborhood of from 4 to 8 milligrams per square foot of surface, are entirely adequate in certain applications.

The coating weight increases with increased bath temperature, current density and treatment time.

Practical lower and upper limits for bath temperature are 120° and 200° F., with about 180° F. being preferred.

The current density should not be less than 200 a.s.f. As presently known the practical upper limit is about 1000-1200 a.s.f.

The times given in the examples are such that, at the

current density given, a coating will be produced which is adequate for most conditions of shipping, storage, subsequent fabrications and coating application. The time of treatment, however, is quite flexible. It is not necessary that both the anodic and the cathodic steps be of the same duration, nor of the same current density. Obviously, a longer treatment time will produce a heavier coating, and, although the treatment may be continued indefinitely, a treatment time of 10 seconds anodic-10 seconds cathodic, would be more than ample to produce any conceivably desired thickness of coating. Ordinarily it will be unnecessary to subject the article to the anodic-cathodic treatment for a total time exceeding eight seconds. By increasing the current density to about 450 a.s.f., the time may be lowered to as little as 0.25 second anodic-0.25 second cathodic. At 600-800 a.s.f., a 0.15 second anodic-0.15 second cathodic treatment produces a coating which will meet commercially useful requirements. The preferred operating range for treatment of container stock of tin mill gauge is between 0.15 and 2 seconds anodic, followed by between 0.15 and 2 second cathodic at a current density of 300 to 800 a.s.f.

As an example of the use of shorter operating times, coated strip has been made by the method of this invention, in a series of four tests, using times ranging from 0.25 second anodic-0.25 second cathodic to 0.5 second anodic-0.5 second cathodic. The electrolyte contained 70 g./l. chromic acid and 35 g./l. phosphoric acid. The current density was 700 a.s.f. Samples from these tests exhibited no rusting in any case in less than 8 hours when exposed in a water spray fog cabinet at 100° F.

Further tests, four in all, in approximately the same time cycle range as those just described, were made using an electrolyte containing 100 g./l. chromic acid and 50 g./l. phosphoric acid, at a current density of 600 a.s.f. These tests produced a coating which compared favorably with those produced from the bath of lower concentration at 700 a.s.f.

In another series of four tests, conducted in the same time cycle range and again using a 100 g./l. chromic acid-50 g./l. phosphoric acid solution as electrolyte, coatings were formed on strip at a current density of 800 a.s.f. The coatings produced in this series were somewhat heavier than those produced under similar conditions, but at 700 a.s.f.

In still another series of tests, a steel strip, having an electroplated chromium coating, was treated according to the method of this invention. The thus treated strip exhibited excellent corrosion resistance and can enamel adhesion.

It has been observed that the effectiveness of the chromic-phosphoric acid electrolyte improves after a working-in period. This is probably due to a build-up of reduced, or trivalent, chromium in the electrolytic bath. Usually, after several hours of operation, bath effectiveness reaches a level which is maintained over a period of many days, provided the normal additions of bath components are made to compensate for depletion due to formation of the passivating coating and dragout.

Tests indicate that the coating comprises mainly three components. These are hydrated chromic oxides in a major amount, with lesser amounts of chromium phosphate and elemental chromium.

To obtain good adherence of subsequently applied organic coatings, it is important that the strip is thoroughly rinsed with water to remove residual hexavalent chromium, which may be carried out of the treatment bath on the surface of the coated strip.

The resultant coating of this invention, in addition to providing a rust-proof surface during long periods of shipment or storage, presents a clear coating for the steel. The coating is compatible with the resinous coatings commonly applied to the interior surfaces of cans. Excellent adherence is obtained between resinous coatings and the coated base metal.

We claim:

1. The method of applying a corrosion resistant coating to a ferrous article which comprises immersing the article in an aqueous electrolyte containing not less than 50 g./l. chromic acid (CrO_3) and containing phosphoric acid (H_3PO_4), the ratio of chromic acid to phosphoric acid being about 1.7:1 to 3:1, electrolyzing the article anodically for not less than 0.15 second, then electrolyzing the article cathodically for not less than 0.15 second, the current density during electrolysis being not less than 200 a.s.f., and rinsing said article.

2. The method according to claim 1 in which the electrolyte contains between 50 and 300 g./l. chromic acid, and the article is electrolyzed anodically for from 0.15 to 10 seconds and is electrolyzed cathodically for from 0.15 to 10 seconds at a current density during electrolysis of from 200 to 1200 a.s.f.

3. The method according to claim 2 in which the amount of phosphoric acid in the electrolyte is from 17 to 150 g./l.

4. The method according to claim 1 in which the electrolyte contains between 50 and 300 g./l. chromic acid, and the article is electrolyzed anodically for from 0.15 to 2 seconds and is electrolyzed cathodically for from 0.15

to 2 seconds at a current density during electrolysis of from 300 to 800 a.s.f.

5. The method according to claim 4 in which the amount of phosphoric acid in the electrolyte is from 17 to 150 g./l.

6. The method according to claim 5 in which chromic acid and phosphoric acid are present in amounts of from 50 to 150 g./l. and from 17 to 75 g./l. respectively.

7. The method according to claim 1 in which the article is steel strip.

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