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PROCESS FOR REDUCING CORROSION

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This invention relates to improvement in the cathodic process of protecting ferrous objects from corrosion and to the preparation of the articles so protected.

The term ferrous surfaces is used in this specification to mean articles made of iron, iron alloys and various types of steel.

The protection of ferrous articles from corrosion by cathodic methods is frequently accomplished by using the so-called sacrificial anodes which are so made of metals more active than iron. In this process the sacrificial anode forms an electrolytic cell with the ferrous article, and the sacrificial anode is eroded away in preference to the ferrous surface, thus protecting the ferrous surface from corrosion. Cathodic protection can also be provided by impressing an external current on the ferrous article rendering it electronegative with respect to its surroundings. The current density required to protect a coated article is dependent on the ohmic drop through the coating and the current required to polarize surface areas of metal exposed by pinholes, flaws or breaks in the coating.

In coated ferrous articles which are cathodically protected the rate of creeping of electrolyte under the coating at a damaged area is much greater than the rate of creeping of electrolyte under the coating at a damaged area in articles not cathodically protected. The infusion of electrolyte causes a loss of adhesion with concomitant disbonding of the coating and an accumulation of water and electrolyte forms under the loosened coating. In these areas metal corrosion can take place and cathodic protection is not sufficient to prevent it.

According to this invention ferrous articles first treated to provide a phosphate coating on the surface of such articles and then coated with a fused resin coating have a reduced rate of disbonding of the coating when the article is exposed to electrolyte solutions under cathodic protective conditions.

The practice of the invention is illustrated in the following examples:

EXAMPLE 1

A fusion blend of 70 parts by weight of a 70/30 ethylene terephthalate-neopentyl terephthalate copolyester resin which had a glass temperature of 72° C. and an intrinsic viscosity of 0.650, 30 parts by weight of a copolyester of ethylene glycol, neopentyl glycol, terephthalic acid and sebacic acid in which the ethylene glycol units and neopentyl glycol units were present in the ratio of 80:20 and the terephthalic acid units and sebacic acid units were present in the ratio of 80:20 which had a glass temperature of 23° C. and an intrinsic viscosity of 0.775 and 5 parts of titanium dioxide powder was prepared by mixing in a Banbury type mixing apparatus at a temperature in the range of from room temperature to 135° C. for 10 minutes. It was then discharged from the mixer and ground to a powder having a particle size of less than 40 mesh, U.S. Standard. The powdered resin compound was placed in an Armstrong Model C Vibro-Fluidizer apparatus and the particles were suspended or fluidized by passing dry air at a rate of 40 cubic feet per hour through the layer of particles.

A piece of 1½" diameter iron pipe 8 inches long was grit blasted to bright metal and vapor degreased by treatment with trichloroethylene. It was then heated in a forced

draft oven to 300° C. The hot pipe was removed from the oven and immersed in the fluidized powder compound in the Fluidizer apparatus for 3 seconds, removed from the Fluidizer and allowed to fuse in air for 20 seconds and then quenched in cold water for about 2 minutes.

The coated pipe was then tested in an accelerated aging test known as the "Salt Crock Test" as follows:

A ⅜" diameter "damage" hole was drilled through the coating 2⅝" from one end of this pipe. The end was stoppered, bound with two or three turns of vinyl electrical tape, dipped in a vinyl patching compound and air dried for 16 hours. The coating was ground off the other or free end of the pipe sample and an alligator battery clip was attached making a sound electrical connection. The closed end of the pipe sample was then immersed in an electrolyte bath along with a one inch diameter graphite rod with a ¾ inch space separation between them.

The electrolyte solution contained 0.317 gram of each of the following salts: sodium chloride; sodium sulfate; and sodium carbonate (all calculated on anhydrous basis) per liter of distilled water. The drilled "damage" hole was positioned so that it faced the graphite rod. The pipe sample was connected to the negative pole of a 6-volt DC power source. The graphite rod was connected to the positive pole of the power source. The power was applied to the pipe and the graphite rod by the power source over a period of 30 days. The solution level in the bath was maintained by the periodic addition of distilled water.

The coating was examined for disbonding around the "damage" hole by making parallel cuts through the coating about ⅛ inch apart and peeling a strip of coating back from the edge of the drilled hole in four directions. The distance from the edge of the hole which the coating can be peeled is measured in each direction and an average value calculated.

After the 30 day Salt Crock exposure the coating exhibited a disbonding of 1¼ inches.

EXAMPLE 2

An 8 inch piece of iron pipe of the type used in Example 1 was cleaned in an alkali bath and pickled in a 10 per cent phosphoric acid bath.

The thus treated pipe was then dipped in a phosphating solution made of 5 parts of Meta Bond 14 in 95 parts of water maintained at a temperature of 90° C. for 5 minutes and rinsed with a dilute chromic acid solution. "Meta Bond 14" is a trade-name for a commercial product of the International Rustproof Corporation whose composition is approximately as follows:

Radical		Percent by weight
Zn		9.92
Fe	Less than	1.0
Al	Less than	1.0
Ca		5.35
NH_4		1.35
NO_3		16.20
Cl		5.19
Total PO_4		18.91
Water		Balance
Free H_3PO_4		9.90

The thus treated pipe was then coated with the polyester resin compound in the same manner described in Example 1. The coated pipe was tested according to the procedure used in Example 1. After the 30 day Salt Crock Test the coating exhibited an average disbonding of 3/16 inch.

EXAMPLE 3

An 8 inch piece of iron pipe of the type used in Example 1 was grit blasted to bright metal, cleaned in an alkali solution and then dipped in a phosphating solution maintained at a temperature of 90° C. for 5 minutes as in

Example 2 and rinsed with dilute chromic acid. The thus treated pipe was coated with polyester resin compound by the same procedure used in Example 1. The coated pipe was then tested according to the procedure used in Example 1. After the 30 day Salt Crock Test the coating exhibited an average disbonding of 3/16 inch.

After the metal article has been treated with phosphate, rinsed with chromic acid, and dried it can be stored prior to coating with resin or it can be coated immediately after it has been treated and dried, if desired. The improved reduced rate of disbonding is still obtained whether the coating is applied immediately or after storage.

Generally, prior to treating with phosphate the metal is cleaned by grit blasting, by vapor degreasing, by alkali-cleaning, by pickling, or by a combination of these methods When oil or grease are on the surface of the metal, degreasing is generally performed.

The invention has been illustrated particularly with respect to the use of a polyester resin blend. Other blends or other polyester resins can be used. Representative examples of such resins are the polyesters of terephthalic acid, bibenzoic acid, the naphthalene dicarboxylic acids with glycols such as the polymethylene glycols and copolyesters of these acids with modifying amounts of other acids and other glycols. Especially suitable polyester resins are the blends disclosed in co-pending application Ser. No. 301,598, filed Aug. 8, 1963. Other resins such as the polyethylenes, polyamides, polystyrene, vinyl resins and epoxy resins can also be used. The resins may contain plasticizers, pigments, coloring agents and other compounding ingredients. If desired, a primer coat can be applied to the article after the phosphate treatment and before it is coated with resin. Thus, primer coats of rubber, plastics, epoxy resin or other types of primers can be applied.

The invention has been particularly described with respect to treating the metal to produce a microcrystalline zinc phosphate coating. Other phosphate treatments can be used. The preferred treatments coat the ferrous article with amorphous or microcrystalline phosphate coatings such as amorphous zinc phosphate and microcrystalline zinc phosphate. The size of the phosphate crystals can be adjusted by the addition of modifiers to the phosphate solutions.

The articles coated may be of any desired shape. The articles may be sheets, castings, pipe, rods and the like. Any of the several powder coating methods can be used to apply the coating of fused resin. Thus the articles can be coated by the fluidized bed process, the electrostatic powder coating process, the cyclone process or the flame spray process, and the advantages of the invention obtained.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

What we claim is:

1. In the cathodic process of protecting ferrous articles from corrosion the improvement which comprises subjecting a ferrous article to a treatment that forms a phosphate coating on the surface of the article, then coating it with a fused resin, and then cathodically protecting said article.

2. The process of claim 1 in which the phosphate coating formed is an amorphous coating of zinc phosphate.

3. The process of claim 1 in which the resin coating formed on the article is a polyester resin coating.

4. The process which comprises treating a ferrous article with a solution that forms zinc phosphate coating on the surface of the article, drying the treated article, heating the article and immersing it in the dense phase of a fluidized bed of polyester resin particles while the article is heated to a temperature at least as high as the fusion temperature of the resin particles but below the decomposition temperature of the particles until a layer of resin of desired thickness is formed on the article, allowing the resin particles to fuse into a continuous coating, cooling the coated article, and then cathodically protecting said article.

5. The process of claim 4 in which the zinc phosphate coating formed is amorphous.

6. The process of claim 4 in which the zinc phosphate coating formed is microcrystalline.

7. In the cathodic process of protecting ferrous articles from corrosion the improvement which comprises forming a phosphate coating on the surface of said article, then coating it with a fused resin coating and then forming an electrolytic cell in which the thus coated article is the cathode.

8. In the cathodic process of protecting ferrous articles from corrosion in which a current is impressed on said article to make it electronegative with respect to its surrounding environment the improvement which comprises forming a phosphate coating on the surface of said article, coating it with a fused resin coating and then impressing the current on the article to make it electronegative.

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