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HOT-DIP METAL COATING PROCESS

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ABSTRACT OF THE DISCLOSURE

Process for hot-dip metal coating of iron and steel articles wherein the articles are coated and protected from corrosion prior to the metal coating by a coating of alpha-olefin polysulfones which depolymerize and vaporize in the flux normally used in hot-dip metal coating processes.

This invention relates to a process for the hot-dip coating of iron and steel articles, i.e. ferrous articles, with molten zinc, lead, tin or alloys of these metals. The process is characterized by the improvement wherein the iron or steel articles are coated with a shop coating of a thin film of resinous alpha-olefin polysulfones after they have been descaled and cleaned so that they can be stored for a relatively long period of time indoors or outdoors and/or transported to a coating works and then given a hot-dip coating without further treatment.

It is known to treat iron or steel articles with several types of rust-preventive compositions. Examples of these types are petrolatum compositions, oil compositions, dry film compositions, bituminous compositions as illustrated by U.S. Pat. 2,492,848 to Crouch et al., oil-emulsion compositions, and water-displacing polar compositions. These known rust preventatives suffer from the disadvantage that they must be removed by solvents, scraping, sandblasting or wire brushing before the substrate metal is suitable for subsequent hot-dip metal coating.

It has now been discovered that iron and steel articles which are to be metal coated by a hot-dip process can be cleaned, coated for storage, and subsequently hot-dipped without the necessity of removing the coating or recleaning before the hot-dipping. This desirable objective is accomplished by applying a thin film of an alpha-olefin polysulfone resin to the cleaned article before storage. When this coated article is placed in the flux bath normally associated with one of the hot-dipping processes, the olefin polysulfone breaks down or depolymerizes into volatile products (predominately sulfur dioxide and the particular alpha-olefin used) which are then vaporized by the heat of the flux bath and exhausted away from the articles to be coated. The present process is unique and advantageous in that the articles are protected up to the moment of use in metal coating whereupon the resinous coating is removed by the flux bath itself and that the flux bath does not become contaminated by the coating by-products since they are compounds of a low boiling point and are present in an extremely small amount because only a thin film of the polymer is used. The previously known rust preventive compounds contain high boiling compounds which cross-link, polymerize, or carbonize in the heat of the flux bath and thus would contaminate it and cause imperfect metal coatings on the iron or steel substrate if they were not first removed by solvents, brushings, etc.

The iron and steel articles to which this invention is applied are commonly known as mill products and this term is generic to hot rolled rod, bars, sheets, strips and tubing of iron and steel. The invention is also applicable to cold rolled steel sheets, bars and strips but in this case, the only pretreatment step needed before the application

of the olefin polysulfone resin is one of degreasing to remove the oil commonly applied to cold rolled steel.

Obviously, the process of this invention can also be applied to iron and steel castings, stampings, forgings, etc., if it is desired to give them a hot-dip coating.

The resin used to coat the iron and steel articles in this invention is a copolymer of sulfur dioxide and a pure alpha-olefin, or mixtures of alpha-olefins, wherein the alpha-olefin has a carbon range of six to twenty-six. In other words, the alpha-olefins can range from 1-hexene to 1-hexacosene and can be made up solely of one alpha-olefin or a mixture of them.

Alpha-olefin polysulfonates made from monomers having less than six carbon atoms are not preferred in this invention since they have a relatively high decomposition temperature (about 419–572° F.) and thus may not completely vaporize in the heat of the flux bath. On the other hand, polysulfones made from monomers having more than twenty-six carbon atoms have a decomposition temperature of less than about 230° F. but suffer from the disadvantage that the olefin monomers are harder to vaporize and tend to carbonize in the flux bath.

The alpha-olefin polysulfones used in this invention are well known and can be prepared by known processes. The history, preparation, and uses of polysulfones is set forth in volume 13 of the book entitled "High Polymers" Part III, chapter 15, pages 225–270 (1962) by Fettes and Davis. Even numbered alpha-olefins of various carbon chain lengths useful to make the polysulfones used herein are commercially available from the catalytic polymerization of ethylene and are well known in the art. See for example U.S. Pat. 3,160,672 to Pearson et al. The odd numbered alpha-olefins of various carbon chain lengths are also commercially available from the cracking of petroleum waxes. These cracked waxes also contain diunsaturates which will cause cross-linked polymers to be produced. This is undesirable for the purposes of this invention since the polysulfone must be soluble and film-forming. Cross-linked polysulfones, on the other hand, will gel the solvents useful in this invention. If, however, the diunsaturates are removed, these cracked waxes are quite suitable for use in the preparation of the polysulfones useful for purposes of this invention. Examples of suitable olefin polysulfones are found in U.S. Pats. 2,652,368 and 2,853,373. Generally, the useful polysulfones will have a molecular weight range of 1×10^5 to 1×10^7.

The solvents which may be used in this process to coat the iron and steel articles with the polysulfone resins can be halogenated hydrocarbons and hydrocarbon solvents. Examples of the halogenated hydrocarbons are 1,1,2-trichloroethylene, perchloroethylene, methylene chloride, 1,1,1-trichloroethane, trichlorotrifluoroethane, 1,2-dichloroethylene and mixtures thereof.

Examples of the hydrocarbon solvents that can be used are benzene, toluene, hexane, petroleum ether, Stoddard solvent, etc. Other solvents which can be used to apply the polysulfone coating are for example, ketone, such as methyl ethyl ketone, methyl isobutyl ketone and ethyl phenyl ketone, esters such as butyl acetate, ethers such as diethyl ether, dibutyl ether and the like. The halogenated solvents are preferred since they are non-inflammable and can be readily recovered for reuse by conventional equipment.

The above alpha-olefin polysulfone resins are coated by means of the above mentioned solvents on the cleaned iron and steel articles to give a thin continuous coating of resin. The coating rate can be in the range of 100 to 10,000 square feet of substrate surface per pound of resin. The preferred coating rate is 600 to 1500 square feet of substrate surface per pound of resin. Since this preferred rate corresponds to a film thickness in the range of 0.344

to 0.1375 mil or 0.00034 to 0.00014 inch, this can be considered a "thin" coating compared to the prior art usage of coatings having a thickness of 5 mils or 0.005 inch.

The metal used for the hot-dip coating can be any one of the conventional hot-dip metals such as zinc, tin, lead or their alloys. Small amounts of tin (up to 1%) are usually added to a zinc galvanizing bath to give a white cast and enlarged spangles. Likewise a small amount in the order of .02–0.2% of aluminum will increase the brightness of galvanized coating. Likewise, the tin coating bath may have small amounts of alloying metals to enhance various characteristics of the final coating. When the coating bath comprises about 80% lead with the remainder mostly tin, the final coated product is known as terne plates or terne sheets.

In general, the resin coating step of this invention consists of dipping, spraying or brushing the previously cleaned ferrous articles with a dilute solution of the polysulfone resin in a solvent such as a halogenated hydrocarbon or solvent of the types enumerated above. Usually a 1–5% by weight solution of the resin is adequate. Repeated coatings by any of the above methods are used to give the desired weight pickup of the resin. However, a single dip with a higher concentration of the resin is desirable for production runs of the process.

The ferrous articles must be cleaned by conventional metal cleaning steps prior to the resin coating steps. A typical cleaning sequence for hot rolled steel products is to dip the parts in a hot (200° C.) caustic solution for about three minutes followed by a dip into a hydrochloric acid solution for about two minutes. These steps, commonly called degreasing and pickling, are followed by a rinsing step with a dilute alkaline solution such as dilute sodium hydroxide to neutralize the excess acid, by a water wash, and a drying step before the resin coating is applied.

For cold rolled ferrous products, the cleaning steps are much simpler since the surface is not oxidized or rusted. These products come from the mill with a coating of a light oil which can be removed by any of the above mentioned halogenated hydrocarbon solvents in a standard degreasing operation. Perchloroethylene is especially efficacious in this regard and is preferred over the others.

In the event that the cold rolled ferrous articles become rusted before they are coated with the polysulfone resin, it is apparent that they must be given the above standard degreasing and pickling steps.

The following examples are presented to illustrate the invention and are not to be construed as a limitation on the scope of the invention.

EXAMPLE 1

Twenty panels of cold rolled steel (3 x 6 x 0.032 inches thick) ("Q" panels) are degreased in a bath of perchloroethylene, rinsed and dried. The cleaned panels are then divided into five sets of four panels each. The first three sets of fours panels are then dipped into a solution of C_{16}–C_{20} alpha-olefin polysulfone resin (prepared by copolymerizing a mixture of C_{16}, C_{18}, and C_{20} alpha-olefins and sulfur dioxide and having a molecular weight of about 1×10^6) in perchloroethylene containing 2.44% by weight of the polysulfone. A panel to be coated is weighed, dipped into the solution, dried, and reweighed until the desired weight pickup is achieved. The fourth and fifth set of panels are not coated and serve as controls. After several repeated dippings and drying steps the coating step is halted when the first set contains a polymer surface loading of 360 square feet per pound of polymer, the second set contains 1550 square feet per pound of polymer, and the third set contains 4350 square feet per pound of polymer.

The three coated sets and one control set (fourth set) are then exposed to the mildly corrosive atmosphere in a laboratory at about 65% relative humidity and about 72° F. for one month. The second control set (fifth set) is wrapped in a bag of polyethylene and placed in a drawer to protect it from the laboratory atmosphere. At the end of this period, it is noted that the uncoated panels of the fourth set have rust spots over about fifty percent of their area. The coated panels of sets 1–3 are substantially rust-free. The fifth set is also free of rust.

All the five sets are then galvanized by the wet galvanizing process in which a molten zinc bath, at a temperature of about 830° F. and having a flux blanket of molten ammonium chloride, is used. Each of the panels is dipped into the bath for a period of three minutes, withdrawn, drained, and cooled. No adverse effect of the polysulfone coating on the flux is observed.

It is noted that the uncoated control panels, i.e., the fourth set, do not galvanize completely because of the rust spots. The unexposed, uncoated, rust-free control panels, i.e., the fifth set, galvanize completely with an adherent coating of zinc equal in all respects to the polysulfone coated sets, i.e., sets 1, 2 and 3.

EXAMPLE 2

Twenty panels of 3 x 6 x 0.032 inches thick cold rolled steel panels are degreased in the manner set forth in Example 1. The cleaned panels are then divided into five sets of four panels each. The first three sets of these cleaned panels are coated with a solution of 1-octene polysulfone resin containing 5.15% by weight of the polysulfone in the manner of Example 1 to give three sets with the same high, intermediate and low loadings respectively.

The three coated sets and the fourth uncoated set are then given a semi-tropical outdoor exposure of one month during which time the panels experience an industrial chemical atmosphere including sunlight, rain, high humidity and high temperatures. The fifth set is uncoated and preserved by enclosing it with a bag of polyethylene in a laboratory drawer. At the end of this time, it is noted that the uncoated panels are completely rusted whereas the coated panels are rust free.

All the five sets are then tin-coated in a bath of molten tin at a temperature of about 550° F. having a molten flux cover of 78% by weight of zinc chloride and 22% by weight of sodium chloride. Each of the panels are dipped into the bath for a period of four minutes, withdrawn, drained and cooled.

It is noted that the rusted panels have no tin coating and that the first three coated and protected sets tin plate as well as the uncoated, unexposed fifth set.

EXAMPLE 3

In a manner similar to the foregoing examples, five sets of four panels are prepared and three sets of these panels are coated with a solution of 1-hexacosene polysulfone resin containing 1.9% by weight of the polysulfone to give loadings of 360, 1550 and 4350 square feet per pound of resin.

Four sets of these panels, three coated and one uncoated, are exposed to the same conditions as Example 1. The fifth set is uncoated and unexposed as in Example 1.

All five sets are then lead alloy-coated in a molten bath of 80% by weight of lead and 20% by weight of tin at a temperature of 750° F. having a flux cover of 73% by weight of zinc chloride, 18% by weight of sodium chloride and 9% by weight of ammonium chloride. Following an immersion time of three minutes, each panel is withdrawn, drained and cooled.

Substantially the same results are obtained as above with the protected or coated sets being equal to the uncoated unexposed fifth set in their ability to take and retain the lead alloy coating. The fourth set rusted and did not take the lead alloy coating.

Following the procedures set forth in the above examples alpha-olefin polysulfones prepared from commercial available cracked wax fractions having odd and even numbers of carbon atoms can be used to coat the steel

panels to achieve substantially the same efficacious results provided the diunsaturated fractions are removed as aforesaid. Examples of these cracked wax polysulfones are those made from alpha-olefin mixtures having C_6–C_7 carbons, C_{11}–C_{12}–C_{13}–C_{14} carbons, and C_{15}–C_{16}–C_{17}–C_{18}–C_{19}–C_{20} carbons.

I claim:

1. A process for the hot-dip coating of iron and steel articles with a metal of the group consisting of zinc, lead, tin and alloys of these metals which essentially comprises the steps of

(a) degreasing the articles,

(b) pickling the articles with an acid bath,

(c) coating the articles with a resinous copolymer of sulfur dioxide and a member of the group consisting of an alpha-olefin of 6–26 carbon atoms and mixtures thereof whereby the cleaned and coated articles are rendered resistant to corrosion for a substantial period of time during storage and can be immediately used without further treatment thereafter in a hot-dip coating bath of a metal of the foregoing group,

(d) dipping said coated articles into a molten bath of a metal of the foregoing group for a period of time to achieve a substantial coating, said bath having a flux blanket on the surface thereof, whereby the copolymer coating is deploymerized by the heat of the flux blanket and the coating by-products are vaporized, and

(e) recovering the resulting metal coated articles.

2. A process as set forth in claim 1 wherein the hot-dip coating consists essentially of zinc.

3. A process as set forth in claim 1 wherein the hot-dip coating consists essentially of tin.

4. A process as set forth in claim 1 wherein the hot-dip coating consists essentially of lead.

5. A process for the hot-dip coating of cold rolled steel articles with a metal of the group consisting of zinc, lead, tin and alloys of these metals which comprises essentially the steps of

(a) degreasing the articles,

(b) coating the articles with a resinous copolymer of sulfur dioxide and a member of the group consisting of an alpha-olefin of 6–26 carbon atoms and mixtures thereof whereby the cleaned and coated articles are rendered resistant to corrosion for a substantial period of time during storage and can be immediately used without further treatment thereafter in a hot-dip coating bath of a metal of the foregoing group,

(c) dipping said coated articles into a molten bath of a metal of the foregoing group, said bath having a flux blanket on the surface thereof,

(d) recovering the resulting coated articles.

6. A process as set forth in claim 5 wherein the hot-dip coating consists essentially of zinc.

7. A process as set forth in claim 5 wherein the hot-dip coating consists essentially of tin.

8. A process as set forth in claim 5 wherein the hot-dip coating consists essentially of a lead-tin alloy.

9. A process as set forth in claim 5 wherein the alpha-olefin consists of mixed alpha-olefins of 16, 18 and 20 carbon atoms.

10. A process as set forth in claim 5 wherein the alpha-olefin consists of 1-hexene.

11. A process as set forth in claim 5 wherein the alpha-olefin consists of 1-hexacosene.

12. In a process for the hot-dip coating of iron and steel articles with a metal of the group consisting of zinc, lead, tin and alloys of these metals wherein the articles are cleaned and metal coated a substantial period of time after the cleaning step, the improvement which comprises coating the articles with a resinous copolymer of sulfur dioxide and a member of the group consisting of an alpha-olefin of 6–26 carbon atoms and mixtures thereof after the cleaning step to render the articles resistant to corrosion until they are metal coated without removal of the resinous copolymer.

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