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Atkiss et al.

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[54] **PREANNEAL RINSE PROCESS FOR INHIBITING PIN POINT RUST**

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[52] **U.S. Cl.** **148/18;** 148/6.14; 148/6.15; 148/6.16; 148/6.2; 148/12.1; 148/13.1; 148/26

[51] **Int. Cl.**[2] **C21D 1/48;** B23K 35/34

[58] **Field of Search** 148/18, 6.14, 26, 27, 28, 148/12.1, 13.1, 20.6, 6.15, 6.2, 6.16

[56] **References Cited**

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[57] **ABSTRACT**

This invention relates to a process for inhibiting the formation of pin rust on steel sheets or strip which occurs during storage or in transit after annealing. According to our process, cold rolled steel is treated prior to annealing with a dilute aqueous rinse solution containing one or more particular water soluble chemical compounds. The rinse solution is dried on the steel prior to annealing to leave a residue of the chemical compound which inhibits rusting of the steel strip after annealing.

3 Claims, No Drawings

PREANNEAL RINSE PROCESS FOR INHIBITING PIN POINT RUST

BACKGROUND OF THE INVENTION

In the steel making process, the metal must be annealed to relieve the stresses which develop during the cold reduction process. Annealing involves heating the metal to around 1200°F. for about 10 hours. This high temperature treatment leaves the metal susceptible to corrosion in the form of pin point rust. If the annealed metal is stored or shipped during periods of high relative humidity, considerable rust develops. The rust formation reduces the value of the strip for further processing and is often severe enough so that the strip must be scrapped.

When rust inhibitors are applied to steel strip after annealing, the strip must be uncoiled for application of the inhibitor and then recoiled — an expensive operation. Certain mineral oils have been used on the strip after annealing with varied success. When oil is used as the rust inhibitor, it must be removed before the strip can be subjected to certain finishing operations such as painting.

Shoemaker, in U.S. Pat. No. 3,668,021, offered one solution to the rust problem by disclosing the application of an aqueous suspension (dispersion) of calcium hydroxide to the strip prior to annealing. The disadvantages of this method stem from the water-insolubility of calcium hydroxide. For example, it is necessary to continuously agitate the slurry to provide a uniform dispersion of the suspended solids. In addition, the application of insoluble solids tends to give non-uniform coatings of the rust inhibiting substance which result in localized pin point rusting. Another difficulty is that the residue left from treatment with an insoluble compound can be deposited on the temper rolls in the subsequent processing of the strip.

DETAILED DESCRIPTION OF THE INVENTION

We have now discovered that certain chemical compounds are effective inhibitors of rust on annealed steel. The rust inhibiting compounds are applied in aqueous solution to the cold rolled steel, either in the form of strip or flat sheets, after which the water is evaporated to dryness leaving a film or coating of the chemical compound on the steel. A particular advantage in the use of a solution of rust inhibiting compound is the ease in obtaining a thin film or coating of uniform thickness on the metal as compared to the difficulties in maintaining and supplying an aqueous slurry to the steel coils and sheets.

The chemical compounds are applied to the steel before annealing and are ready to function as rust inhibitors in the post anneal period.

Prior to the application of the rust inhibiting compound, the metal sheets or coils may be cleaned in a conventional cleaning solution which is usually a hot aqueous alkaline solution. A particularly effective cleaning treatment is to electro-clean with hot aqueous silicate solution, followed by rinsing with water and scrubbing, if necessary, to remove soil.

The chemical compounds which we have found useful as rust inhibitors for annealed steel are one or more of the following compounds:

sodium tetraborate
ammonium fluosilicate
chromic acetate
ammonium fluoborate
monobasic aluminum formate
potassium acid pyro antimonate
ammonium molybdate
antimony oxide
antimony trifluoride
ammonium metatungstate
antimony oxalate
ammonium titanium fluoride
ammonium silico
tungstate
zinc fluoborate
tin fluoborate
tri phenyl antimony

The post anneal rust inhibiting compounds are effective in aqueous solution at a concentration ranging from 5 grams/liter to saturated solutions. The rust inhibiting solutions are applied to the steel coils or sheets by immersion, spraying, roller coating or by any other convenient method known in the art to contact the metal with a solution and leave a film of the solution on the metal. The temperature of application of the solution to the steel is not important and may range from room temperature to about 200°F. Because of limited solubility of antimony oxide in water, temperatures at the higher end of the range are required for the compound.

Following application of the solution of the rust inhibiting compound to the metal, the water is evaporated in any convenient manner such as by air drying at ambient temperature or by the application of radiant heat or gas flame to leave a coating or film of the chemical compound of the steel. The temperature of the steel is not important during this drying process and may range from ambient temperature to about 300°F. Following the drying step, the steel is annealed by any standard annealing process, for example by bringing its temperature to about 1100° to about 1300°F. for about 10 hours in a conventional protective gas atmosphere, usually 5% hydrogen and 95% nitrogen.

The rust inhibiting compounds of my invention may be combined in aqueous mixture with other additives which are useful in either the annealing process or in the post annealing treatment of the steel. For example, the compounds used to prepare steel surfaces for tin plating as discussed in U.S. Pat. No. 3,632,487 to prevent staining, dewetting and dullness may be combined with the rust inhibitor additives.

After the rust inhibiting compounds of my invention are applied to the cold rolled steel, it is dried and then annealed using either conventional continuous annealing or batch annealing techniques. If the steel is in strip form, it is recoiled before batch annealing. Following annealing, the strip is usually given a temper roll or skin pass, resulting in a hardened bright surface. After temper rolling, the coil or strip is placed in the mill storage area where it is subject to the humidity variations of the climate.

The best mode of carrying out my invention will be evident from a consideration of the following examples.

EXAMPLE 1

Three by 6 inch panels of full hard steel from a typical 5 stand mill were electro-cleaned in a 30 gram per liter sodium orthosilicate solution at 40 amperes per square foot for 8 seconds, followed by scrubbing, rins-

ing with water, a second electro-cleaning for 4 seconds, a water rinse and then given a final rinse at room temperature with the rust inhibiting compounds. Separate panels were rinsed with 0.025 molar solutions (approximately 5 grams/liter) of either antimony trifluoride, ammonium fluosilicate or ammonium titanium fluoride. The panels were then dried in hot air until all water was evaporated. Additional panels for control purposes were processed in the same manner omitting the final rinse.

The panels were stacked, placed in an annealing chamber, and squeezed together by placing a ½ inch steel plate on top of the stack to simulate a tightly wound coil of strip steel as formed in a commercial plant. The annealing chamber containing the panel bundle was charged to an annealing furnace and subjected to the T-1 batch annealing cycle (essentially 10 hours at 1185° to 1230°F., requiring about 3 hours to reach said temperatures, and followed by about a 12 hour cooling cycle) under a protective gas atmosphere consisting of 5% hydrogen and 95% nitrogen.

The metal was removed when the temperature had dropped to 260°F., and the panels were placed in constant humidity chamber held at 65 percent relative humidity at 75°F.

After 9 days, the panels were removed and examined for pin point rust. It was observed that the panels treated with antimony trifluoride were free of pin point rust; the panels treated with ammonium fluosilicate had only a trace of rust. The panels treated with ammonium titanium fluoride had more rust than the panels treated with antimony trifluoride and ammonium fluosilicate but considerably less rust than the control panels which showed severe pin point rust.

EXAMPLE 2

Following the procedure of Example 1 panels were prepared using an orthosilicate electro-cleaner at 8 ounces per gallon at 190°F. with four cleaning cycles of 2 seconds each, followed by a scrubbing and a final electro-cleaning and water rinse. Current density was 90 amperes per square foot. Following the last rinse the cleaned panels were immersed in the respective rust inhibiting solutions which were at 0.025 molar concentration at 170°F. for 5 seconds. Following the rust inhibiting rinse, the panels were passed through rubber wringers and then dried in hot air.

The panels were then subjected to annealing and constant humidity conditions for 9 days as explained in Example 1. Examination of the panels for pin point rust showed the following conditions of rust inhibition:

RINSE ADDITIVE	PIN POINT RUST INHIBITION
sodium tetraborate	fair
sodium fluoride	poor
ammonium fluosilicate	good
barium nitrate	poor
solution of nickel nitrate, ammonium fluosilicate and chromic acetate	good
cobalt nitrate	poor
ammonium fluoborate	excellent
nickel nitrate	poor
potassium acid pyro antimonate	fair
solution of nickel nitrate and calcium nitrate	poor
monohydrazine sulfate	poor
ammonium molybdate	fair
sodium nitride	poor
solution of aluminum formate and phosphoric acid	good

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RINSE ADDITIVE	PIN POINT RUST INHIBITION
ammonium fluoride	poor
aluminum formate	fair
triphenyl antimony	good
zinc chloride	poor
antimony trifluoride	excellent
ammonium oxalate	poor
ammonium molybdate	fair
solution of antimony trifluoride and calcium nitrate	excellent
ammonium fluozirconate	poor
solution of antimony trifluoride and ammonium fluoborate	good
ammonium nitrate	poor
solution of antimony trifluoride, aluminum formate and phosphoric acid	good
magnesium chloride	poor
solution of antimony trifluoride and ammonium hydroxide	excellent
ammonium tungstate	fair
ammonium chloride	poor
antimony oxalate	excellent
ammonium fluotitanate	good
ammonium sulfate	poor
antimony trioxide	good
ammonium silico tungstate	good
ammonium acid phosphate	poor
zinc fluoborate	excellent
ferric chloride	poor
tin fluoborate	excellent

We claim:

1. The process for inhibiting pin point rusting of cold rolled annealed steel comprising contacting the steel prior to annealing with an aqueous rinse solution consisting essentially of one or more rust inhibiting compounds at a concentration ranging from about 5 grams/liter to saturated solution and selected from the group consisting of:

sodium tetraborate, ammonium fluosilicate, ammonium fluotitanate, chromic acetate, ammonium fluoborate, ammonium silico tungstate, potassium acid pyro antimonate, ammonium molybdate, monobasic aluminum formate, antimony trifluoride, ammonium metatungstate, antimony oxalate, ammonium titanium fluoride, silicon metatungstate, zinc fluoborate, tin fluoborate, and triphenyl antimony

to wet the steel with rinse solution, drying the wetted steel to leave a residue of rust inhibiting compound on the steel, and finally annealing the steel in a protective gas atmosphere at a temperature of about 1100° to about 1300°F.

2. The process of claim **1** in which the steel is cleaned prior to contacting it with the aqueous solution of the rust inhibiting compound.

3. The process for inhibiting pin point rusting of cold rolled annealed steel comprising contacting the steel prior to annealing with an aqueous rinse solution consisting essentially of one or more rust inhibiting compounds at a concentration ranging from about 5 grams/liter to saturated solution and selected from the group of antimony compounds consisting of:

antimony acetate, potassium acid pyro-antimonate, triphenyl antimony, antimony trifluoride, and antimony oxalate

to wet the steel with rinse solution, drying the wetted steel to leave a residue of rust inhibiting antimony compound on the steel and finally annealing the steel in a protective gas atmosphere at a temperature of about 1100° to about 1300°F.

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