Cold rolled steel strip is treated, prior to annealing, with a dilute aqueous rinse solution containing soluble calcium salt or a soluble ferricyanide or ferrocyanide salt or a mixture of soluble calcium salt with sodium nitrite or soluble ferricyanide or soluble ferrocyanide. The residues of said rinses inhibit rust formation on the annealed strip during storage and transit.

5 Claims, No Drawings
PREANNEAL RINSE PROCESS FOR INHIBITING RUST ON STEEL STRIP

This invention relates to a method of increasing the oxidation (i.e., rust) resistance of ferrous strip, and more particularly concerns the rinse treatment of cold-rolled steel strip, prior to annealing thereof, with a soluble calcium salt or a soluble ferricyanide or ferrocyanide salt or a mixture of the calcium salt with sodium nitrite or the soluble ferricyanide or ferrocyanide, in dilute aqueous solution, to leave a thin layer of the residue from such rinse solution on the strip during annealing and subsequent storage and transit. The rust formation problem with steel strip dealt with by this invention is to be distinguished from the problem of preventing defects in electrolytically coated tinplate (i.e., preventing staining or dewetting of tin-coated surface) in which the steel strip is treated with a dilute aqueous rinse of a material that remains on the strip during batch annealing and is capable of reacting with carbonaceous material thereon during the batch annealing cycle. (Brown et al., U.S. Pat. No. 3,632,487, and a similar treatment for chromium and chromium oxide coated strip, Brown et al. application Ser. No. 231,747, filed Mar. 3, 1972, now U.S. Pat. No. 3,756,926.

Cold-rolled, annealed, steel strip is subject to rusting caused by oxidation of the ferrous metal, particularly where processing water used in the mill has a high content of dissolved chlorides and/or sulfates. The rust formation, which is more pronounced when the coiled strip is in humid environment, reduces the value of the strip for further processing and is often severe enough so that the strip must be scrapped. 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 could result in localized pinpoint 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.

In accordance with the present invention, the cold-rolled steel strip is treated with an aqueous dilute rinse solution containing an effective rust-inhibiting amount of calcium ion or ferricyanide ion or ferrocyanide ion, or mixture of calcium ion with sodium nitrite or ferricyanide or ferrocyanide ion. (Sodium nitrite has previously been used as a rust inhibitor for ferrous metals, but not for the purpose or in the specific utility embodied herein, and not in combination with a soluble calcium salt component.) The components of the rinse solution of this invention are water-soluble materials, which property provides uniform coatings, simplifies the handling techniques and equipment requirements, and reduces the opportunities for residues to interfere with the temper rolling operation. The soluble calcium salt operable herein has a solubility in water of at least 1.88 g/liter of Ca²⁺ ion, and preferably at least about 3.76 g/liter of Ca²⁺ ion (at 70°F.). Representative of such salts are, for example,
calcium benzoate
calcium butyrate
calcium chromate
calcium ferrocyanide
calcium ferricyanide
calcium formate
calcium fumarate
calcium d-gluconate
calcium glycerophosphate
calcium isobutyrate
calcium iodide
calcium lactate
calcium α-methylbutyrate
calcium nitrate
calcium nitrite
calcium propionate
calcium salicylate
calcium dithionate
calcium maleate
calcium valerate

Various salts of calcium whose anions are promoters of corrosion, e.g., calcium sulfate and calcium chloride, are to be avoided, as well as those likely to stain steel during annealing, such as calcium permanganate. Calcium chromate, mentioned above, can be used except where the steel strip is ultimately to be coated with tin because chromate interferes with the tin-plating process.

The soluble ferrocyanide or ferricyanide salts operable herein have a solubility in water of at least 0.94 g/liter of Fe(CN)₆ moity and preferably about 1.88 g/liter of ferricyanide or ferrocyanide. Representative of such salts are, for example,
ammonium ferricyanide
ammonium ferrocyanide
calcium ferricyanide
calcium ferrocyanide
ammonium ferricyanide
potassium ferricyanide
sodium ferricyanide
strontium ferricyanide

Before carrying out the process of this invention, it is expedient to subject the cold rolled steel strip to a conventional electrocleaning and rinsing operation, accomplished with a hot aqueous alkaline silicate solution, followed by rinsing and scrubbing. It has been observed that the process of this invention appears to provide a synergistic improvement in subsequent corrosion resistance when used in conjunction with prior electrolytic cleaning with silicates in caustic aqueous solution. The use of alkali silicate solutions for cleaning steel strip (e.g., sodium orthosilicate or sodium metasilicate) is well known and is described, for example, in the articles by L. J. Brown and J. E. Lippy, Jr. in Plating, February, 1966, "Silicates as Cleaners in the Production of Tinplate" and II. "Influence of Batch Anneal", October, 1971; and the text by W. E. Hoare et al., The Technology of Tinplate, St. Martin's Press, 1965.

Following the foregoing cleaning operation, the strip is contacted with the rust-inhibiting rinse solution embodied herein, either by immersion or by spray application, conveniently at ambient temperature, although rinse temperatures ranging from about 50° to about 200°F. may be employed, temperature of the rinse not being a critical factor. Said dilute aqueous rinse solution, containing in admixture the dissolved calcium salt
3,919,000

or ferricyanide or ferrocyanide, or mixture of calcium ion with the nitrite, ferricyanide or ferrocyanide, above mentioned, will usually have said components present in amounts providing from about 0.25 to 3 ounces of calcium ion per gallon of solution, and from about 0.13 to 3 ounces per gallon of sodium nitrite, or ferricyanide or ferrocyanide ion, when present. Preferred concentrations range from 0.5 to 1.5 oz./gallon of calcium ion and from 0.26 to 1.5 oz./gallon of the additional nitrite or ferrocyanide or ferricyanide ion.

After the brief immersion in or spraying with said rinse solution, the steel strip is permitted to air-dry, either at ambient temperatures or at elevated temperatures, e.g., up to about 300°F, thus depositing a thin uniform film of the rinse solution residues thereon. The treated steel strip is subsequently annealed, using either conventional continuous annealing or batch annealing techniques. In continuous annealing the treated strip is passed through an annealing oven at such a rate to provide an annealing period of approximately 20 seconds at a temperature of about 1200°F to 1220°F, followed by a controlled cooling cycle, in a protective gas atmosphere, e.g., consisting of 5 percent hydrogen and 95 percent nitrogen, i.e., a reducing gas atmosphere. In batch annealing the strip is wound into a tight coil and subjected to the "box annealing" cycle, i.e., about ten hours at 1220°F, followed by a cooling cycle, all taking place under a protective gas atmosphere.

Following the annealing operation, the steel strip is usually stored to await further processing. It is during this storage period that rust formation is observed on steel strip that has not been treated with an inhibiting composition.

The good results of this invention are verified by a laboratory simulation of commercial steel strip manufacture and annealing. In these tests 3 inch × 6 inch panels (about 0.009 inch thick) of cold-rolled steel strip are electrocleaned in conventional alkaline sili cate (sodium orthosilicate) cleaning solution. Half of the panels (the controls) are waterrinsed, and dried. The other half are dipped in an aqueous solution of one or more rust-preventing agents at various concentrations, and then dried. The various rinse compositions are summarized as follows:

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Rinse Solution</th>
<th>Calcium Acetate</th>
<th>Calcium Nitrate</th>
<th>Sodium Potassium</th>
<th>Potassium Ferrocyanide</th>
<th>Corrosion Resistance</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>

I claim:

1. A process for inhibiting rust formation on cold-rolled steel strip which comprises contacting the strip, prior to annealing with an aqueous dilute rinse solution containing an effective rust-inhibiting amount of a mixture of calcium ion and sodium nitrite, the calcium ion being supplied by a soluble calcium salt having a solubility in water of at least 1.88 g/liter of Ca²⁺ ion and being free of corrosion-promoting anions selected from the group consisting of sulfate and chloride, wherein the concentration of calcium ion in the solution is from about 0.25 to 3 oz. per gallon and the concentration of sodium nitrite is from about 0.13 to 3 oz. per gallon, drying the steel strip and annealing the strip in a reducing gas atmosphere.

2. A process for inhibiting rust formation on cold-rolled steel strip which comprises contacting the strip, prior to annealing, with an aqueous dilute rinse solution containing an effective rust-inhibiting amount of a mixture of calcium ion and ferricyanide or ferrocyanide ion, the calcium ion being supplied by a soluble calcium salt having a solubility in water of at least 1.88 g/liter of Ca²⁺ ion and being free of corrosion-promoting anions selected from the group consisting of sulfate and chloride, wherein the concentration of calcium ion in the solution is from about 0.25 to 3 oz. per gallon and the concentration of ferricyanide ion is from about 0.13 to 3 oz. per gallon, drying the steel strip and annealing the strip in a reducing gas atmosphere.

3. The process according to claim 1 wherein the calcium salt is selected from the group consisting of calcium acetate, calcium benzoate, calcium butyrate, calcium chromate, calcium ferrocyanide, calcium ferricyanide, calcium formate, calcium fumarate, calcium gluconate, calcium glycophosphate, calcium isobutyrate, calcium iodide, calcium lactate, calcium o-methylbutyrate, calcium nitrate, calcium acetate, calcium salicylate, calcium dihydrogen, calcium maleate and calcium valerate.

4. The process according to claim 2 wherein the calcium salt is selected from the group consisting of calcium acetate, calcium benzoate, calcium butyrate, calcium chromate, calcium ferrocyanide, calcium ferricyanide, calcium ferricyanide, calcium ferricyanide, calcium ferricyanide, calcium ferricyanide, calcium ferricyanide, calcium ferricyanide, calcium ferricyanide, calcium ferricyanide, calcium ferricyanide, calcium ferricyanide, calcium ferricyanide.

5. The process according to claim 4 wherein the ferri cyanide or ferrocyanide ion is supplied by a salt selected from the group consisting of ammonium ferricyanide, ammonium ferrocyanide, calcium ferricyanide, calcium ferrocyanide, magnesium ferrocyanide, potassium ferricyanide, potassium ferrocyanide, sodium ferricyanide, sodium ferrocyanide and strontium ferrocyanide.

6