METHOD OF PREVENTING THE SURFACE STAINING OF COLD ROLLED STEEL

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This invention relates to the production of cold rolled steel. It is more specifically concerned with mitigating the surface staining of box-annealed, cold rolled steel.

The conventional production of cold rolled steel involves a sequence of operations including the hot rolling of a suitable steel ingot to form a slab which is further reduced in thickness by additional hot rolling to produce the sheet in sheet form. After the hot rolled sheet strip is formed, it is introduced into a pickling bath containing sulphuric acid or other suitable material for effecting the removal of the scale formed during the hot rolling operation. Thereafter the hot rolled sheet steel is again reduced in thickness by a cold rolling operation. The cold reduced sheet is annealed in a furnace at an elevated temperature to provide the desired ductility characteristics and finally tempered rolled. Generally the strips are coiled after each operation to facilitate handling. Collateral steps employed in the strip production include a pickling operation subsequent to the pickling step in which the pickling acids and other deleterious materials such as iron sulfate formed during the pickling step are removed. In addition, to facilitate the cold rolling of the steel an oleaginous rolling solution applied to the sheet strip surface is employed as a lubricant. During the cold reduction a water coolant as well as a roll cleaning solution in the form of an oil and water emulsion are streamed on the rolls of the mill employed.

In the production of hot rolled, pickled, cold-reduced and box-annealed, low-carbon steel, dark brown stains, smudge and characteristic black edges ("snakes") appear on the sheet steel strip after the annealing operation. It has been reported that the appearance and frequency of these conditions vary as widely as the many explanations are given for their occurrence. According to this invention, it has been found that surface stains especially the "black edge" or "snacky edge" found on the strip after annealing can be prevented or mitigated by employing water in the rinsing operation in which is incorporated a water-soluble sequestering agent which will combine with the "hardness constituents," e.g. calcium and magnesium ions present in the industrial water used, to form stable, water-soluble chelates of these hardness constituents. An additional feature of this invention resides in the use of sequestering agent-containing industrial water as a substitute for the conventional oil-emulsion type roll cleaning medium used during the cold reduction step of the steel producing process.

FIGURE I is a block schematic diagram illustrating the various steps which are employed in the production of cold rolled steel by hot rolling, acid pickling, cold reducing and annealing.

Referring to the drawing, it will be seen that the essential steps involved in the production of cold rolled steel include hot rolling a suitable steel ingot which has been heat treated to an elevated temperature determined by the steel being rolled to produce a 4"-6" slab, and thereafter a sheet like strip having a thickness of .075"-1.25".

The strip thus produced is then introduced into a pickling bath, which is at a temperature of about 190°-200° F., containing sulphuric acid or other suitable material for removing the scale formed during the rolling operation. To remove the acid used in the pickling step, as well as other undesirable materials which form during the pickling operation, from the strip surface, the strip is passed through a water rinse. The water employed in this rinsing step generally is conventional, industrial hard water which is untreated and has varying "hardness" as determined chiefly by the presence of mineral matter such as calcium, magnesium carbonates and calcium sulfate, and others. After the water rinse step, a mineral lubricating oil generally containing extreme pressure agents, antioxidants and corrosion-inhibitors is applied to the strip surface which functions as a lubricating roll, and the hot-rolled strip is cold rolled in a suitable continuous mill, i.e., a four high five stand rolling mill. In the cold rolling step, a water coolant is applied to the mill rolls, as well as an oleaginous emulsion which functions as a roll cleaner to facilitate the removal of any foreign substances which may adhere to the surfaces of the roll. In the finishing steps of the operation, the cold reduced sheet is annealed in order to restore the ductility to the cold reduced sheet material and thereafter tempered rolled to provide the desired stiffness.

The annealing employed is either so called "box annealing" or continuous annealing. In the former the rolled reduced steel strip is coiled and the coils inserted in an enclosed furnace and heated to a selected elevated temperature for the desired length of time. It is with this type of annealing that the instant invention is concerned. In using the annealing furnace the sheet steel strip is treated in coil-form. In carrying out the instant invention a sequestering agent which will combine with objectionable metal ions which impart "hardness" to the industrial water used in the various operations to form stable, water-soluble chelates of these metals, is introduced into the hard water employed in the rinsing operation subsequent to the pickling operation. In addition an aqueous solution of these sequestering agents is used as a roll cleaner. By employing sequestering agents which will combine with the undesirable metal ions in the industrial, hard water, the surface of the steel strip will be substantially free from any insoluble precipitates which may have been incorporated therein during the rinsing operation and resulting from the retention of water containing these insoluble precipitates on the strip surface. By employing the sequestering agent solution in the aforementioned services a substantial reduction in the surface staining box-annealed, cold reduced strip steel results.

Sequestering agents which can be employed in carrying out the instant invention, include any organic or inorganic sequestering agent which will combine with objectionable metal ions which impart "hardness" to conventional, industrial, hard water to form stable, water-soluble chelates of these metals. The most widely used of the sequestering agents of this type are the various condensed phosphates. Examples of such phosphates include sodium pyrophosphate, sodium tripolyphosphate, sodium trimetaphosphate, sodium tetrametaphosphate, sodium polyphosphate, and others. Suitable condensed phosphates include sodium phosphate having a ratio of Na₂O:PO₄ of 1.34-1.1.
The following is a table of some condensed phosphates:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Name(s)</th>
<th>Structure</th>
</tr>
</thead>
</table>
| Crystalline       | Sodium pyrophosphate                         | \[
\begin{array}{c}
\text{Na}_2\text{O} - 5\text{P}_2\text{O}_5 \\
\end{array} \] |
| \(\text{Na}_2\text{P}_2\text{O}_7\) (and hexahydrate) | Sodium trimetaphosphate                     | \[
\begin{array}{c}
\text{Na}_2\text{O} - 3\text{P}_2\text{O}_5 \\
\end{array} \] |
| \(\text{Na}_2\text{P}_3\text{O}_7\)          | Sodium trimetaphosphate                     | \[
\begin{array}{c}
\text{Na}_2\text{O} - 2\text{P}_2\text{O}_5 \\
\end{array} \] |
| \(\text{Na}_2\text{P}_4\text{O}_{12}\)       | Sodium tetrametaphosphate                   | \[
\begin{array}{c}
\text{Na}_2\text{O} - \text{P}_2\text{O}_5 \\
\end{array} \] |
| Glasses           | A mixture of compounds in the composition range: \[1 \text{ Na}_2\text{O} : 1 \text{ P}_2\text{O}_5 - 1.34 \text{ Na}_2\text{O} : 1 \text{ P}_2\text{O}_5\] | \[
\begin{array}{c}
\text{Na}_2\text{O} - \text{P}_2\text{O}_5 \text{O}_n \\
\end{array} (n > 1) \] |

In selecting the sequestering agent one which is effective over a wide range of pH should be used. However, if desired, the pH of the several environments can be controlled by conventional means in order to permit the use of a selected sequestering agent.

Although the inorganic compounds set forth above, are the preferred reagents for use as sequestering agents in carrying out the instant invention, there are available other inorganic and organic water soluble chelating agents which can also be employed in this invention. For a more complete discussion of other water soluble metal chelating compounds which will combine with the undesirable ions of the industrial hard water used in carrying out the instant invention in conjunction with the production of box-annulled, cold-rolled steel, reference is made to “Chemistry of the Metal Chelate Compounds,” Martell et al., Prentice Hall, 1952.

As hereinbefore mentioned an additional feature of this invention is the use of sequestering agent-containing hard water as a substitute for the oleaginous roll cleaners employed in the prior art processes for cleaning the rolls of mills employed in the cold reduction of strip material. The roll cleaners employed in the prior art processes generally contain sodium soaps, free fatty acids or saponifiable esters used in producing the oil-water emulsion. These constituents will interact with the calcium, magnesium or other precipitate-forming metals in the water which is employed as a cooling medium. In this instance, the substitution of the sequestering agent containing aqueous solution for the oleaginous emulsion conventionally employed as the roll cleaner obviates the formation of undesirable precipitates caused by the hard water.

Subsequent to the cold reduction step the cold rolled sheet is box-annulled at an elevated temperature within the range of about 1200°-1500° F. preferably 1200°-1300° F. depending upon the steel composition. The resultant cold-rolled, box-annulled strip steel has excellent lacquer adherence, no annealing strains and good plating properties.

The amount of sequestering agent which is employed in the rinse water utilized to remove the acids and reaction products resulting from the acid pickling of the hot rolled steel as well as the roll cleaner which is employed as an aid in the cold reduction of the hot rolled strip, will depend upon the sequestering agent which is employed as well as the amount of calcium and magnesium salts which are present in the industrial hard waters which are to be used. In general, sufficient amounts of sequestering agent to form stable, water soluble chelates of the objectionable metal ions which impart hardness to the industrial hard water are used. Industial hard waters will contain 75 to 500 p.p.m. of hardness constituents. Accordingly, to effect the combining of these undesirable ions with the sequestering agent which is employed, about 0.5-10% by weight of sequestering agent is utilized. For example, in conditioning an industrial water obtained from Lake Michigan, having a total hardness of 140-150 p.p.m., a 2% by weight aqueous solution of tetra sodium pyrophosphate is used to provide satisfactory results.

Steels which can be treated in accordance with the instant invention to avoid box-annulling stains include the low carbon steels, as well as other steel alloys which are produced in sheet form by cold rolling and box annealing.

To illustrate the instant invention, a low carbon SAE 1020 steel ingot 26 inches by 54 inches, after having been stripped from its mold, is reheated in a soaking pit to about 2300-2400° F. The ingot is hot rolled into a 3" slab and thereafter hot rolled to produce a sheet material having a thickness of approximately 0.10". The reduction by hot rolling is carried out in a 4-high 5 stand continuous mill. The sheet material is passed through a pickling operation where the scale was removed by immersion of the sheet in an aqueous pickling solution containing about 15% sulphuric acid. In order to remove the acid from the surfaces of the strip material as well as the other reaction products which were formed on the surfaces of the strip during the pickling operation, the strip was immersed in a countercurrent aqueous bath containing 2% by weight solution of sodium pyrophosphate. Thereafter the rinsed strip material is cold reduced in a 4-high 6 stand cold strip mill to a thickness of approximately 0.05 inch. In the course of the cold reduction step a roll cleaner consisting essentially of a 2% by weight solution of sodium pyrophosphate is continuously streamed upon the rolls of the mill. Because of the large amount of cooling water necessary in carrying out this operation, the water is not pre-conditioned with
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a sequestering agent. The cold reduced strip in coil form is then annealed in a box-annealing furnace at a temperature of 1200°-1300° F, and subsequently temper rolled. The annealed strip was free from surface staining or other annealing strains.

The foregoing example is only illustrative of the instant invention and can be varied by one skilled in the art without departing from the scope of the invention as defined by the appended claims.

What is claimed is:

1. In the production of hot-rolled, pickled, cold-reduced and box-annealed low-carbon, steel strip, the step which comprises immersing a hot-rolled steel strip in a pickling solution and thereafter rinsing the steel strip with an aqueous solution of a hard water containing sufficient amounts of a water-soluble, inorganic condensed phosphate to combine with objectionable, precipitate-forming metal ions in said hard water to form stable, water-soluble, chelates of said ions whereby residual pickling solution and reaction products formed during said pickling are substantially removed from the steel strip surfaces, and cold reducing and box annealing said strip.

2. In the production of steel strip in accordance with claim 1 in which the condensed phosphate is sodium pyrophosphate.

3. In the production of steel strip in accordance with claim 2 in which the aqueous solution of hard water contains 1/2–10% by weight of sodium pyrophosphate.

4. In the production of hot-rolled, pickled, cold-reduced and box-annealed low-carbon, steel strip, the step which comprises cleaning mill rolls employed in cold reducing a hot-rolled, pickled steel strip by streaming on said rolls during the cold reduction of said steel strip a roll cleaner consisting essentially of an aqueous solution of a hard water containing sufficient amounts of a water soluble inorganic condensed phosphate to combine with the objectionable, precipitate-forming, metal ions in said hard water, to form stable water soluble chelates of said metals.

5. In the production of steel strip in accordance with claim 4 in which the condensed phosphate is sodium pyrophosphate.

6. In the production of steel strip in accordance with claim 5 in which the aqueous solution of hard water contains 1/2–10% by weight of sodium pyrophosphate.

7. In the method of producing low-carbon steel strip which comprises hot rolling a low-carbon steel to produce a steel strip, pickling said steel strip with a pickling solution, rinsing said steel strip, cold rolling said steel strip, and thereafter box annealing the cold rolled steel strip, the improvement which comprises rinsing said steel strip with an aqueous solution of a hard water containing sufficient amounts of a water-soluble, sequestering agent to combine with objectionable, precipitate-forming metal ions in said hard water to form stable, water-soluble, chelates of said metal whereby residual acid pickling solution and reaction products formed during said pickling are removed from the steel strip surfaces, applying an oleaginous rolling solution to the strip, cold reducing the thickness of the steel strip and thereafter box annealing the cold-reduced strip, said cold reducing being carried out in a rolling mill wherein a roll cleaner solution consisting essentially of an aqueous solution of a hard water containing sufficient amounts of a water-soluble inorganic condensed phosphate to combine with an objectionable precipitate forming metal ions in said hard water to form stable, water-soluble chelates of said metals is streamed over the rolls of said mill.

8. In the production of steel strip in accordance with claim 7 in which the condensed phosphate is sodium pyrophosphate having a ratio of Na2O:P2O5 of 1.34–1:1.

9. In the production of steel strip in accordance with claim 8 in which the aqueous solution of hard water contains 1/2–10% by weight of sodium pyrophosphate.

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