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[54] **METHOD OF PREPARING TINPLATE**
4 Claims, No Drawings

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ABSTRACT: Electrolytically coated tinplate having defect-free surfaces is prepared by subjecting steel to hot-rolling pickling, cold-rolling to form strip, cleaning, rinsing in an aqueous medium containing a substance in minor concentration that remains on the steel strip and is capable of reacting with carbonaceous material during the batch annealing cycle, winding the strip into a tight coil, batch annealing, temper rolling, cleaning, pickling, and coating with tin by electrolytic means.

METHOD OF PREPARING TINPLATE

This invention concerns improved tinplate and more particularly relates to a method of providing electrolytically tin-coated steel strip free of certain unacceptable surface defects and blemishes in the tin coating.

Steel that has been hot-rolled, pickled, cold-rolled, cleaned, batch-annealed, temper-rolled or further cold reduced, cleaned, pickled and electrolytically tin-coated frequently is rejected as unuseable after undergoing these expensive treatments because of defects in the tin coating that cause the tinplate surface to appear stained or "dewetted." These surface defects are believed to be caused by a trace amount of carbonaceous material that clings to or is associated with the surface of the strip, resists all efforts to remove it by cleaning and pickling procedures used in the mills, and is converted to graphitic material during the batch annealing process.

We have discovered that a defect-free surface on tinplate, which has been tin-coated by electrolytic means, is ensured by treating the steel strip, prior to the batch annealing operation, with a minor amount of a substance that is capable of reacting with carbonaceous material on the strip during the batch annealing cycle to convert the carbonaceous material to volatile byproducts, believed to be carbon disulfide and/or carbon monoxide.

According to the process of this invention steel is subjected to the following steps to produce high quality tinplate:

1. hot-rolling a steel slab to a thickness of the order of about 0.08 inch;

2. pickling the hot-rolled steel in dilute sulfuric acid or hydrochloric acid and water-rinsing;

3. cold-rolling the steel to a strip thickness of the order of about 0.009 inch;

4. cleaning the strip in hot aqueous alkaline solution, rinsing and scrubbing;

5. rinsing the strip in an aqueous medium containing a substance in minor concentration which remains on the steel after withdrawal thereof from the aqueous medium and which can react with minor amounts of carbonaceous material on the steel at the temperatures encountered in batch annealing to form a volatile product (i.e., a product that volatilizes at temperatures of the annealing cycle);

6. winding the strip into a tight coil and batch annealing said coil at about 1,150° F. to about 1,250° F. for from about 7 to about 10 hours in a conventional protective gas atmosphere;

7. temper-rolling or further cold-reducing the strip to about 0.006 inch followed by cleaning essentially as in step No. 4, pickling, usually in dilute sulfuric acid, water-rinsing; and

8. depositing a coating of tin on the steep strip of about 0.015 to about 0.06 mil thickness by conventional electrolytic techniques.

THe active substances present in the aqueous dilute preanneal rinse employed in step No. 5 above are generally used in concentrations of from about 100 to about 2,500 p.p.m. of the aqueous medium, preferably about 500 to about 1,000 p.p.m. The operable substances are of two groups both, however, within the general class of those compounds which may react with carbonaceous material on the strip steel under batch annealing conditions to form volatile products. The first group embodies sulfur-containing compounds which may react with the carbonaceous material to yield carbon disulfide Representative of such compounds are sulfur and the alkali metal and alkaline earth metal sulfates, bisulfates, sulfites, bisulfites, thiocyanates, dithionates, thiosulfates, sulfides and polysulfides, organic sulfides, disulfides, thioethers, sulfoxides, sulfones, sulfate esters and sulfonates. Preferred materials from these classes are colloidal sulfur, ammonium sulfide, ammonium sulfate, sodium sulfate, sodium thiosulfate, ammonium xylene sulfonate, sodium sulfide, thiourea, diethylthiourea, potassium sulfate and potassium thiosulfate. The second group embodies compounds which may react with the carbonaceous material to yield carbon monoxide during the annealing Representative of such compounds are the alkali metal and alkaline earth metal oxides and hydroxides and salts that decompose at the temperatures of the batch annealing to form said alkali metal and alkaline earth metal oxides. Preferred materials from these classes are calcium hydroxide, sodium hydroxide, barium hydroxide, potassium titanium oxalate, potassium permanganate, sodium nitrite, sodium borate and sodium bicarbonate.

We have found that treatment of the strip steel with an aqueous rinse containing a material as described above, followed by conventional batch annealing and electrolytic tin-coating, eliminates stain patterns, dewetting of tin, and other surface defects generally associated with tinplate produced from defective steel as herein described.

The results and advantages of this invention were verified by a laboratory simulation of commercial tinplate manufacture. In each test six 3 inch × 6 inch panels (about 0.009 inch thick) of cold-rolled steel strip known to produce typically defective tinplate as herein described were cleaned in a conventional alkaline cleaning solution. Half of the panels (the controls) were given a water rinse and dried. The other half were dipped in aqueous media containing one of the foregoing additives of the invention, and dried. 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 "TI" batch-annealing cycle (essentially 10 hours at 1,185° to 1,230° F., requiring about three hours to reach said temperatures, and followed by about a 12-hour cooling cycle) under a protective gas atmosphere consisting of 5 percent hydrogen and 95 percent nitrogen. After cleaning, rinsing, pickling, and rinsing, the panels were tin-coated (0.015 mil coat) by electroplating in a representative phenolsulfonic acid tin solution; the matte tinplate was finally passed through an induction coil for brightening, followed by a water quench.

In all instances the tincoated "control panels" were defective because of staining, dewetting, dullness, and other surface defects. However, tin coated panels treated according to the invention with special preanneal rinse materials, as set forth in the following table, were bright and uniform. Tin-coated panels similarly treated prior to annealing with aqueous media containing dilute concentrations (500 to 1,000 p.p.m.) of inoperable substances, such s sodium chloride and ammonium chloride, showed numerous surface defects.

Preanneal rinse additive	Concentration in aqueous medium in p.p.m.
$(NH_4)_2SO_4$	250
$(NH_4)_2SO_4$	500
Na_2SO_4	500
Na_2S	500
NH_4SCN	500
Colloidal sulfur	500
$Na_2S_2O_6 \cdot 2H_2O$	500
Diethylthiourea	1,000
$(NH_4)_2SO_4$ and $NaNO_2$	400 and 100
Diethylthiourea and $NaNO_2$	800 and 200
Tetrahydroxy naphthalene sulfonate	1,000
Sodium xylene sulfonate	1,000
Thiourea	500
Thiourea	1,000
$KMnO_4$	500
NaOH	500
NaOH	1,000
$Ca(OH)_2$	500
$Ca(OH)_2$	1,000
$NaNO_2$	500
$Na_2B_4O_7 \cdot 10H_2O$	1,000
$Na_2C_2O_4$	1,000
$Na_2Ti_3O_7$	1,000

We claim:

1. A process for preparing tinplate free of surface defects which comprises treating steel according to the following sequence of steps;

a. hot-rolling a steel slab;

b. pickling the hot-rolled steel and water-rinsing;

c. cold-rolling to form steel strip;

d. cleaning the strip in aqueous alkaline solution, rinsing and scrubbing;

e. rinsing the steel strip in an aqueous medium containing in admixture from about 100 to about 2,500 p.p.m. of substance that remains on the steel after withdrawal thereof from the aqueous medium and which is capable of reacting with carbonaceous material on the steel at temperatures encountered in batch annealing to form a product that volatilizes at temperatures of the annealing cycle;

f. winding the steel strip into a tight coil and batch-annealing;

g. temper-rolling or further cold reducing the steel strip, cleaning as in step d, pickling, water-rinsing; and

h. depositing a coating of tin on the steel strip by electrolytic means.

2. A process for preparing tinplate free of surface defects which comprises treating steel according to the following sequence of steps;

a. hot-rolling a steel slab;

b. pickling the hot-rolled steel and water-rinsing;

c. cold-rolling to form a steel strip;

d. cleaning the strip in aqueous alkaline solution, rinsing and scrubbing;

e. rinsing the steel strip in an aqueous medium containing in admixture from about 100 to about 2,500 p.p.m. of material selected from the group consisting of sulfur, alkali metal and alkaline earth metal sulfates, bisulfates, sulfites, bisulfites, thiocyanates, dithionates, thiosulfates sulfides, polysulfides, organic sulfides, disulfides, thioethers, sulfoxides, sulfones, sulfate esters, sulfonates, the alkali metal and alkaline earth metal oxides and hydroxides and salts that decompose at batch-annealing temperatures to form said alkali metal and alkaline earth metal oxides;

f. winding the steel strip into a tight coil and batch-annealing;

g. temper-rolling of further cold-reducing the steel strip, cleaning as in step d., pickling, water-rinsing; and

h. depositing a coating of tin on the steel strip by electrolytic means.

3. The process according to claim 1 wherein the concentration of the substance in the aqueous medium of step (e) is from about 500 to about 1,000 p.p.m.

4. The process according to claim 2 wherein the concentration of the material in the aqueous medium of step (e) is from about 500 to about 1,000 p.p.m.

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