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Fisher et al.

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[54] **PROCESS FOR IMPROVING BATCH ANNEALED STRIP SURFACE QUALITY**

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[58] **Field of Search** 148/12.1, 16, 16.7

[56] **References Cited**

UNITED STATES PATENTS

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3,725,141	4/1973	Hill	148/16.7

FOREIGN PATENTS OR APPLICATIONS

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[57] **ABSTRACT**

A process is described for eliminating surface discoloration of batch annealed steel products, where said discoloration has been described as graphite staining. Said process is characterized by an annealing step which includes the introduction of a small quantity of CO_2 to the annealing atmosphere comprising hydrogen and nitrogen.

3 Claims, No Drawings

PROCESS FOR IMPROVING BATCH ANNEALED STRIP SURFACE QUALITY

CROSS-REFERENCE TO RELATED APPLICATION

This application is a companion case to Ser. No. 417,851 filed concurrently with this application and assigned to the assignee herein, entitled "Black Plate Steel and Method."

BACKGROUND OF THE INVENTION

This invention is directed to a process for improving batch annealed strip surface quality, more particularly to the annealing process wherein a washed steel strip in coil form is subjected to an atmosphere comprising nitrogen, hydrogen and a small quantity of carbon dioxide.

While this invention has particular utility in the production of tin plate, it is not intended to be so restricted as it is applicable to other steel products where surface quality is critical. However, for convenience, the discussion to follow will be directed primarily to the processing of steel for use as tin plate, more specifically, the procedures leading to final electrolytically tinning.

Generally, the processing of the steel follows a conventional practice resulting in a hot-mill coil as thin as about 0.065 inch or as thick as about 0.125 inch. From the hot-mill, the coil is subjected to a pickling treatment to remove the hot-mill scale and oxide. To facilitate the severe cold reduction of the strip, which may run as high as 90%, a lubricant or oil is applied to the surfaces thereof. The cold-reduced steel strip, which is generally quite hard, must be softened by annealing, i.e., batch or continuous. Following the anneal, the steel strip may be temper rolled to insure the proper degree of flatness and improve surface quality for the subsequent tinning operation; or the strip may be further reduced, prior to tinning, to impart certain certain desirable metallurgical and physical properties.

Heretofore, certain types of surface quality problems were noted with batch annealed steel and much of the effort by the prior art was directed at the solving thereof. One of said problems was the appearance of a carbon edge or snakey-edge. A second problem, the solution of which is the discovery herein, was the appearance of a relatively continuous or patchy staining of the sheet or strip surface. Through the discoveries herein, the latter problem has been defined, for convenience, as graphite staining. With one or both of said problems, any attempt to apply a tin coating resulted in relatively poor adherence or substandard corrosion protection and non-uniform appearance.

The first of said problems has long been recognized by the steel industry, and the approaches and/or theories postulated to solve it have followed various paths leading to different conclusions with sometimes indeterminate results. For instance, the different approaches were in part a result of variations in the processing sequence described above. Very often the cold-rolled steel strip was box annealed with the oil or lubricant still on the surfaces thereof. To such practitioners, the appearance of carbon edge was attributed to the breakdown or cracking of the lubricants used for rolling which, as indicated above, are present on the surfaces thereof during anneal.

Others postulated that the problem arises during annealing from the catalytic breakdown of carbon containing gases, and that the primary catalysts for this

breakdown are the presence on the steel surface of minute iron particles dislodged during rolling. U.S. Pat. No. 3,725,141 to Hill presents additional background as to the problems and the attempts by the prior art to solve them. A common factor of each approach was the assumption that carbon deposition caused carbon edge or snakey-edge, and that their attempts were directed at means to eliminate said deposition.

The present invention evolved as a result of the recognition that the two problems are totally different and that the mechanism involved therein are different. It is now believed that graphite staining is at least in part the result of carbon diffusing from within the steel to the strip surface. As will be explained hereinafter, the present invention deals with the annealing of a washed steel strip which has had substantially all of the oil and lubricants removed therefrom. Obviously then there can be no breakdown or cracking of the lubricants during the anneal. In any case the theoretical approach and solutions herein are not found in the prior art.

SUMMARY OF THE INVENTION

This invention relates to a method for eliminating graphite staining of cold rolled and washed steel subjected to a process anneal. The improved surface quality thereof is achieved by a procedure which includes batch annealing said steel at temperatures between about 1100° F. to 1300° F. in a non-oxidizing atmosphere comprising hydrogen, nitrogen and about 3 to about 9%, by volume, carbon dioxide, preferably between about 4 to about 8% carbon dioxide.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

In the preferred practice of this invention, a tightly wound coil of steel strip or a plurality of stacked coils are placed on a generally raised base of a conventional furnace with the coil axes vertical. An inner cover is placed over the coils and sealed about said base such as by sand or other means well known in the art. An annealing furnace hood is then placed over said inner cover in preparation for the annealing cycle. Heating means, which may be radiant heating tubes or other conventional heating mechanism, also form part of the annealing furnace along with suitable conduits connected thereto through the raised base. By means of the latter the air is purged from the inner cover permitting the introduction of a protective atmosphere, the criticality and nature of which will become apparent hereinafter.

Before discussing the annealing cycle, it will be appreciated from the initial discussion that various practices are followed in the processing cycle. No attempt will be made to explain why certain practices are followed except to say that the particular problems noted herein are not significant or even apparent in some of said practices. For example, where a continuous-annealing practice is followed, i.e., rapid heating with complete bathing of surfaces in annealing atmosphere, the said surface problems are not apparent.

For the batch annealed products, both tight and open coils may be annealed. With the latter, spacers are provided between adjacent convolutions of the coil thus permitting the annealing atmosphere to reach the inner portions of the said coil. Where such a practice is followed, graphite staining is not a significant problem. Hence, it is only where tight coils are batch annealed

that such problems become serious concerns to the operators. For these reasons, the present invention is directed to a batch or process anneal of tight coils.

The evidence or existence of the problems noted herein are not such as can be measured quantitatively or against a standard. Graphite staining, as well as carbon edge, are evident from visual inspection. The latter is characterized by a wavy band, varying in degrees of darkness, along the outside of the strip. Experience has shown that such a condition affects the coatability of the steel, whether it be metallic coated, such as electrolytic tinning, or coated with a non-metallic, i.e., bonderized, painted, or thermally cured resinous coating. In any event, graphite staining appears as dull gray patches or may be relatively continuous throughout the entire strip width of the strip surface. With graphite staining, there is not only a problem with coating appearance, but difficulties arise if a subsequent temper rolling or cold reduction is desired.

With this explanation, consideration may now be given to the details of the annealing cycle. Heretofore, the conventional annealing cycle employed an atomosphere comprising a mixture of hydrogen and nitrogen containing between about 4% to 25% hydrogen and the remainder nitrogen.

The present invention represents an improvement thereover in that the atmosphere is further limited such that to the standard HN gas there is introduced a quantity of carbon dioxide between about 3% to 9%. Specifically, the annealing atmosphere of this invention comprises a non-oxidizing mixture of gases consisting essentially of, by volume:

Gas	Broad Range	Preferred Range
H_2	4 to 25%	4 to 25%
CO_2	3 to 9%	4 to 8%
N_2	balance	balance

To demonstrate the effectiveness of the above described atmosphere in eliminating serious graphite staining, stacked sheet samples were subjected to various annealing atmospheres. The steel's chemistry is reported in TABLE I, followed by the observed results in TABLE II. Procedurally, cold rolled full hard steel sheets, having the chemistry listed in TABLE I and with the tandem mill oil still on the surfaces thereof, were cut into 4 inch x 8 inch panels. To remove substantially all of said oil, the panels were washed by dip cleaning and scrubbing in a 190° F. alkaline cleaning solution (PENNWALT 30 ORTHOSIL, a trademark of Pennwalt Corporation). After cleaning, the panels were rinsed and blown dry with compressed air. To simulate a tight coil, a number of packs of about 30 panels were assembled by stacking the panels on top of one another. The stacks were held tight by compressing each between oversized stainless steel plates. Each stack or pack was drawn tightly together by stainless bolts passing through the outer edges of the stainless plates and alongside the stacked steel panels within.

The pack assembly was then placed in a stainless steel tank or cover and welded shut. The desired annealing atmosphere was fed into the tank through an inlet nozzle, circulated thereabout, and permitted to exit via an outlet nozzle. Additionally, a thermocouple was inserted through the outlet nozzle to monitor the temperature inside the tank. The tank, with gas lines and thermocouple attached, was placed in a furnace and the annealing cycle begun. The temperature of the furnace and tank was raised to about 1200° F. and the panels soaked for about 10 hours. At the end of the soak, the tank was removed from the furnace and allowed to cool with the gas lines still connected feeding the desired atmosphere. When the tank was completely cooled down, it was opened and the panels removed and examined.

TABLE I

	CHEMISTRY					
Steel	C	Mn	P	S	Cu	Sn
A	.08	.27	.004	.004	.014	—
B	.08	.32	.005	.013	.012	<.002
C	.09	.46	.005	.030	.014	.004

TABLE II

	RESULTS				
Test	Atmosphere, Vol. %			Graphite	Carbon
Series	H_2	N_2	CO_2	Staining	Edge
A1	4	96	—	Heavy	No
B1	4	96	—	Heavy	No
C1	4	96	—	Very Light	No
A2	4	92.6	3.4	Variable Degrees	No
B2	4	92.6	3.4	Very Light	No
C2	4	92.6	3.4	No	No
A3	3.6	89.6	6.8	No	No
B3	3.6	89.6	6.8	No	No
C3	3.6	89.6	6.8	No	No
A4	3.7	86.8	9.5	No	Yes
B4	3.7	86.8	9.5	No	Yes
C4	3.7	86.8	9.5	No	Yes
A5	17	76	7	No	No
B5	17	76	7	No	No
C5	17	76	7	No	No

It is clear from the results above that the steel panels, irrespective of chemistry, were successfully treated in the preferred atmosphere of this invention. As the annealing atmosphere approached the leaner portion of the range (series 2) some graphite staining was observed in the low maganese steels. For a more detailed discussion on the effects of composition in controlling graphite staining, reference is made to said copending application. Finally, when the atmosphere was too high in CO_2, a carbon edge began to appear. It would thus appear that carbon edge can readily be controlled by minimizing the quantity of carbon dioxide in the annealing atmosphere. However, experience has shown that when stacked coils are annealed in a commercial DX gas, nominally containing about 10% CO, 5% CO_2, 15% H_2, balance N_2, some carbon edge and graphite staining will appear. Thus, while small amounts of CO might be tolerated in the annealing atmosphere, it is obvious that significant amounts of CO are detrimental to the attainment of the results desired herein.

In any case, by the procedure described herein, an effective means is taught for eliminating the problem of graphite staining.

We claim:

1. A process of annealing a coil of steel strip, where adjacent convolutions thereof are in contact with one another, comprising the steps of placing said coil in an

enclosure, introducing into said enclosure a non-oxidizing gas consisting of, by volume, hydrogen in an amount between about 4% to about 25%, about 3% to about 9% carbon dioxide, balance nitrogen, and heating said coil in said non-oxidizing gas to a temperature between about 1100° F. to about 1300° F.

2. The process according to claim 1 wherein said carbon dioxide is present in an amount between about 4% to about 8%.

3. The process according to claim 1 wherein said coil is soaked at the temperature between about 1100° F. to about 1300° F., and said non-oxidizing gas is maintained for at least the time during the soaking period.

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