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[54] **METHOD AND COMPOSITIONS FOR THE PREVENTION OR REDUCTION OF SPECK RUSTING OF COLD ROLLED, ANNEALED STEEL PRIOR TO TEMPER ROLLING**

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[58] **Field of Search** 148/12.1, 29; 72/41, 42, 72/43; 252/49.5

[56] **References Cited**

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[57] **ABSTRACT**

A method and composition for the prevention or reduction of speck rusting of cold rolled, annealed steel prior to temper rolling wherein phosphoric acid or the ammonium hydroxide neutralization products of phosphoric acid are added to the rolling emulsions used during the cold rolling step. The invention contemplates the use of conventional oil-water cold rolling emulsions to which the above noted additions are made in an amount of from about 200 to about 500 ppm as PO_4.

10 Claims, No Drawings

METHOD AND COMPOSITIONS FOR THE PREVENTION OR REDUCTION OF SPECK RUSTING OF COLD ROLLED, ANNEALED STEEL PRIOR TO TEMPER ROLLING

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a rust preventative method and compositions therefor, and more particularly to a method and compositions for the prevention or reduction of speck rusting of cold rolled, annealed steel during storage prior to temper rolling.

2. Description of the Prior Art

As used herein and in the claims the term "cold rolled, annealed steel" refers to flat rolled sheet steel products other than stainless steels.

In the typical processing of cold rolled steel, hot rolled and pickled coils are cold rolled, annealed in a reducing atmosphere and then temper rolled. During the cold rolling, oil-water emulsions are used for cooling and lubrication.

In the usual practice, following the annealing step the coils are generally stored for a period of time awaiting temper rolling. During this storage period no protection against atmospheric corrosion is provided and substantial speck rusting can occur, especially in the humid summer months.

The type of rusting which occurs during this storage period is well known in the art and has been variously termed "speck rusting," "speckled rusting" and "pinpoint rusting." This terminology applies to the fact that the rusting occurs in the form of small pinpoint patterns. This type of rusting normally does not penetrate the steel but forms as a film which can be peeled off revealing an unetched surface thereunder. However, under severe conditions etching of the steel can occur.

Prior art workers have expended much time and effort in an attempt to identify the nature of speck rust, its causes and means for preventing it. Best efforts seem to show that speck rust occurs by virtue of surface contamination of the steel before, during and after cold rolling. The speck rust, itself, develops under storage conditions. Analysis shows that the contaminants comprise hygroscopic crystals containing chlorides and sulfates. These crystals absorb moisture from the air and act as rust nucleants from which the speck rust films grow. The salts which remain on the surface of the steel after cold rolling are numerous and complex. These salts may include any number of combinations of ions such as K^+, Na^+, Ca^{++}, Mg^{++}, Fe^{+++}, Fe^{++}, Cl^-, SO_4^-, CO_3^-, NCO_3^-, and possibly others. During the annealing step, following cold rolling, change or exchange of these compounds in addition to the reducing of some can occur. Since such a large number of reactions may occur, the products after annealing are not obvious. It is known, however, that chlorides and sulfates of magnesium, calcium and sodium will cause speck rusting during a storage period in a humid environment.

Prior art workers have approached this problem by attempting to eliminate the sources of contamination and to minimize the conditions promoting the formation of speck rust. For example, virgin rather than recirculated water (which might have accumulated contaminants from previous processing steps) was used in the final spray rinse following the pickling step prior to cold rolling. Improved blowoff means in association with the cold rolling mill were provided to assure better and more efficient wiping of the coil. Steps were also taken to prevent the formation of contaminant-containing condensation on the equipment which might drip on the cold rolled steel. Finally, measures were taken to reduce the storage time between the annealing step and the temper rolling step. An excellent discussion of prior art work in this field is found in the article entitled "Causes and Elimination of Speckled Rust on Cold Rolled Sheets", by L. C. Pasztor and W. J. Stazyk: Blast Furnace and Steel Plant, December, 1967, pp. 1,103–1,107.

These prior art steps have made important contributions toward the solution of the speck rust problem and reductions in the tremendous cost of rejected material. Nevertheless, since the hygroscopic contaminants may originate from so many sources, including the pickle-rinse operation, the cold rolling emulsions, the annealing gases, the compressed air blowoff means and the atmosphere surrounding the cold rolling mill, prior art efforts have not brought about a complete solution to the problem.

The present invention is based upon the discovery that the addition of phosphoric acid or ammonium hydroxide neutralization products of phosphoric acid to the cold rolling emulsions will provide temporary atmospheric corrosion protection to the steel during storage after annealing and will successfully eliminate speck rust. It has further been found that such additions will also improve lubricity and thus rolling, particularly on the light gauge material, and will reduce the iron level in the rolling emulsions. It will be understood by one skilled in the art that the presence of iron in the rolling emulsions as iron fines or iron soaps causes the steel surface after annealing to be dirty. Reduction of iron in the rolling emulsions results in a more desirable, clearer surface on the steel after annealing.

It is standard practice in the industry to utilize phosphoric acid additions to the cold rolling emulsions to adjust the pH of the emulsions. The makeup water for the emulsions is often passed through a lime softening process prior to use. After such a lime softening process, the pH of the makeup water may be as high as 10.1. This water is then neutralized to the desired pH of about 5.5 to 8.0 for compatibility with the emulsion. The neutralization of the water requires on the order of 10 ppm PO_4 which is not sufficient to inhibit speck rusting. Furthermore, organic phosphates are sometimes added to the rolling emulsions as extreme pressure lubricants. These organic phosphates may break down to form orthophosphates during the ordinary rolling mill operation. The concentration of orthophosphate produced in this manner, however, is again much less than the amount required to inhibit speck rusting. As far as applicant is aware, no additive to the rolling emulsions has been used specifically to combat speck rusting.

SUMMARY OF THE INVENTION

In the conventional process for the manufacture of cold rolled steels, including the steps of hot rolling, pickling, cold rolling, annealing, storing and temper rolling, phosphoric acid or ammonium hydroxide neutralization products of phosphoric acid are added to the conventional cold rolling oil-water emulsions to provide temporary atmospheric corrosion protection of the steel against speck rusting during the storage step after annealing. Steps are taken, as will be described

hereinafter, to maintain the pH level of the cold rolling emulsions within the range of from about 5.5 to about 8.0.

The invention contemplates the use of conventional oil-water emulsions. Phosphoric acid or the ammonium hydroxide neutralization products of phosphoric acid are added to the emulsions in an amount of from about 200 to about 500 ppm as PO_4. The neutralization products contemplated comprise $NH_4H_2PO_4$, $(NH_4)_2HPO_4$ and possibly $(NH_4)_3PO_4$ or mixtures of H_3PO_4 and NH_4OH.

During the conventional annealing step in a reducing atmosphere, the additives react with the contaminating salts on the surface of the steel to remove sulfur and chlorine as volatile components, the remaining salt residues on the steel surface being non-aggressive (i.e. non-rust promoting).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the usual process for making cold rolled steel, the steel is hot rolled to hot band, pickled-rinsed, cold rolled to final gauge, annealed and subjected to temper rolling. Conventional oil-water emulsions are used during the cold rolling for lubrication and cooling. As used hereinafter and in the claims, the term "conventional oil-water emulsions" is intended to refer to mixtures of oil and water in a ratio between 1/200 and 1/8. The oil consists of a mixture of some or all of the following components in various quantities: triglycerides, fatty acids, hydrocarbons, emulsifiers, phosphate esters and bactericides. PENNWALT KS-631 by the Pennwalt corporation of Philadelphia, Pennsylvania, and Nalco 7-0 by Nalco Chemical Company of Chicago, Illinois, are typical examples of such oil-water emulsions. The annealing step is generally conducted in a reducing atmosphere. There atmospheres are well known in the art. Dry 85% nitrogen, 15% hydrogen gas is exemplary of such a reducing atmosphere.

After the annealing step, it is general practice to store the coils for a period of time awaiting temper rolling. During this storage period, no protection against atmospheric corrosion is provided and speck rust can form on the steel. Such speck rust is brought about by surface contamination of the steel by hygroscopic crystals containing chlorides and sulfates of potassium, sodium, clacium and magnesium. These contaminants may originate in the pickle-rinse step, the cold rolling emulsions, the annealing gases, the blowoff means of the rolling mill and in the atmosphere surrounding the rolling mill. Warm, humid conditions during the storage of the steel prior to temper rolling tend to promote the formation of speck rust.

Since it is not possible to completely eliminate these contaminants from the steel making process, the present invention is based upon a discovery that these contaminants may be rendered in a non-aggressive form so that they will not result in speck rust formation during the storing of the cold rolled steel. To this end, phosphoric acid or neutralization products of phosphoric acid and ammonium hydroxide are added directly to the conventional oil-water cold rolling emulsions. These neutralization products include $NH_4H_2PO_4$, $(NH_4)_2HPO_4$and possibly $(NH_4)_3PO_4$ or mixtures of H_3PO_4 and NH_4OH.

With such addition to the cold rolling emulsions, the steel is otherwise processed in the standard manner. This, in turn, results in a carryover on the steel surface of both the contaminants and the addition to the annealing step. The addition of one or more of the above noted additives has been found to alter the usual reactions at the surface of the steel during the annealing step in the reducing atmosphere. The additive reacts with the K, Na, Ca, Mg, SO_4 and the Cl salts on the surface of the steel. Sulfur and chlorine are removed during the anneal as volatile components. After the anneal, there will remain on the surface of the steel non-aggressive annealed residues. For example, sodium which would ordinarily come through such an anneal as Na_2S or NaCl (both aggressive salts) may now be in the innocuous form sodium calcium phosphate.

In the practice of the present invention additions to the rolling emulsions can be made as any of the above listed additives. As is well known in the art, the stability of oil-water emulsions in use today is strongly dependent upon the pH of the emulsions. The pH range for best emulsion operation is from about 4.5 and preferably from about 5.5 to about 8.0. For this reason, the preferred additions would be $(NH_4)H_2PO_4$ or $(NH_4)_2HPO_4$ or mixtures thereof. If pH variations are encountered, the pH may be further adjusted by H_3PO_4 or NH_4OH additions.

The pH of the oil-water emulsions should be above about 4.5 to avoid corrosion of the steel before the annealing step can be performed. The upper limit of about 8.0 is suggested because at higher pH levels, emulsions do not perform well in providing lubrication or the emulsions may become unstable. There is no known upper limit on pH from the standpoint of speck rust prevention. Thus if emulsions are developed which will perform well at higher pH values, they would be compatible from the standpoint of the above listed additives.

There are many factors which determine the pH at which a given rolling emulsion will perform well. Many of these factors are not fully understood. In the practice of this invention the additive or mixture of additives should be chosen to achieve the desired pH value for the rolling emulsion used. Despite this, the pH will vary with time over a period of days. As indicated above, these pH variations can be compensated for by H_3PO_4 or NH_4OH additions to maintain the pH at the level specified by the emulsion requirements.

It has been determined that in order to achieve protection against speck rust the additives should be added to the conventional oil-water emulsions in an amount of from about 200 ppm to about 500 ppm at PO_4. It has further been determined that these additions improve lubricity and thus rolling, particularly in the case of light gauges. When additions are made of at least 200 ppm as PO_4, the iron level in the rolling emulsion is reduced. When the concentration of the additive or additives rises above about 500 ppm as PO_4, however, the pH of the emulsion drops and the iron level of the emulsion increases, both constituting undesirable results. Based upon compatibility with the conventional oil-water emulsions, lubricity, iron level and pH control of the emulsions, it is preferred to add the additive or additives in a range of from about 250 to 450 ppm as PO_4. The amount of additions made, within the ranges stated above, will depend upon such factors as the contaminant level of the water used in the emulsions, the oils used, the amount of contaminants in the atmo-

sphere about the rolling mill and the like. These factors may be readily determined and evaluated by one skilled in the art.

To illustrate the present invention reference is made to the following experiments or examples.

EXAMPLE I

Water having an initial composition given in Table I below was evaporated to dryness.

TABLE I

INITIAL WATER COMPOSITION IN mg per liter						
pH	Total Alkalinity as $CaCO_3$	Ca as $CaCO_3$	Mg As $CaCO_3$	Cl	SO_4	Na
7.9	280	224	116	40	45	17

A first sample of 400 mg of the residue was tested for sulfur and chlorine content before and after being annealed in an atmosphere of 15% H_2 and 85% N_2 for 4 hours at 1,300°F. A second sample of 400 mg of the residue was mixed with 600 mg of $(NH_4)_2$ HPO_4 and subjected to the same type of anneal. Thereafter the second sample was tested for sulfur and chlorine content. The results are given in Table II below.

TABLE II

	S in mg	Cl in mg
First Sample before Anneal	.012	.030
First Sample After Anneal	.010	.033
Second Sample After Anneal	<.022	<.001

The results shown in Table II demonstrate the removal of both sulfur and chlorine from the residue by the addition of $(NH_4)_2$ HPO_4.

EXAMPLE II

Water-salt residues were prepared in the following manner. Tap water having the following composition was used.

TABLE III

INITIAL TAP WATER COMPOSITION IN mg per liter				
Ca as $CaCO_3$	Mg as $CaCO_3$	Cl	Fe	pH
148	68	40	.02	8.6

Samples of the tap water alone and samples of the tap water with 400 ppm $NH_4H_2PO_4$ were evaporated to dryness. A commercial rolling oil emulsion concentrate (Nalco 7-0) corresponding to an amount equal to 1% of oil by volume in the water evaporated was added to the residues from both types of samples. These residues were thereafter annealed in an atmosphere of 15% H_2 and 85% N_2 at 1,300°F for 4 hours in decarburizing enameling iron containers. A fraction of the residues were tested qualitatively for sulfur by adding an excess of $Cu(NO_3)_2$. The solutions were filtered and then tested qualitatively for chlorine by the addition of $AgNO_3$. The containers with the annealed residues were exposed in a humidity cabinet for 1 day to an atmosphere at 90°F and 63% relative humidity. The results are shown in Table IV below.

TABLE IV

	Cl^- after evaporation	Cl^- after anneal	S^{--} after anneal	Rust after exposure
Water and oil samples	yes	yes	yes	yes
Water, Oil and $NH_4H_2PO_4$ samples, annealed	yes	no	no	no

As can be seen from Table IV, the $NH_4H_2PO_4$ addition resulted in removal of S^{--} and Cl^- from the residues which were no longer corrosive to steel.

Modifications may be made in the invention without departing from the spirit of it.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for making cold rolled steel comprising the steps of hot rolling to hot band, pickling, rinsing, cold rolling to final gauge, annealing, and temper rolling, the improvement comprising the steps of providing a conventional oil-water rolling emulsion for said steel during said colo rolling step, adding to said emulsion at least one material chosen from the class consisting of $NH_4H_2PO_4$, $(NH_4)_2$ H PO_4, $(NH_4)_3$ PO_4 and mixtures of H_3PO_4 and NH_4OH to said emulsion in an amount of from about 200 to about 500 ppm as PO_4 and maintaining the pH of said emulsion containing said addition above about 4.5 whereby to prevent the formation of speck rust on said steel prior to said temper rolling step.

2. The process claimed in claim **1** wherein said pH of said emulsion containing said addition is maintained within the range of from about 5.5 to about 8.0.

3. The process claimed in claim **1** wherein said material added to said emulsion is added in an amount of from about 250 to about 450 ppm as PO_4.

4. The process claimed in claim **1** wherein said material added to said emulsion is chosen from the class consisting of $NH_4H_2PO_4$, $(NH_4)_2HPO_4$ and mixtures thereof.

5. The process claimed in claim **4** wherein said material added to said emulsion is added in an amount of from about 250 to about 450 ppm as PO_4.

6. A cold rolling emulsion for use in cold rolling steel comprising a conventional oil-water emulsion and from about 200 to about 500 ppm of at least one material chosen from the class consisting of $NH_4H_2PO_4$, $(NH_4)_2$ HPO_4, $(NH_4)_3PO_4$ and mixtures of H_3PO_4 and NH_4OH said cold rolling emulsion having a pH above about 4.5.

7. The cold rolling emulsion of claim **6** having a pH within the range of from about 5.5 to about 8.0.

8. The cold rolling emulsion of claim **6** wherein said material is present in an amount of from about 250 to about 450 ppm.

9. The cold rolling emulsion of claim **6** wherein said material is chosen from the class consisting of $NH_4H_2PO_4$, $(NH_4)_2HPO_4$ and mixtures thereof.

10. The cold rolling emulsion of claim **9** wherein said material is present in an amount of from about 250 to about 450 ppm.

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