ABSTRACT: Oxalate conversion coating method for stainless steel suitable for cold-working thereof which is characterized in that stannous salt is added into the treating solution consisting of principal agent of oxalic acid and/or oxalates, activating agents and oxidizing agents.
OXALATE CONVERSION COATING METHOD FOR STAINLESS STEEL

This invention relates to an improved oxalate conversion coating method for stainless steel.

The object of the present invention is to provide a method for preparing oxalate conversion coating on the surface of stainless steel, which is adhered tightly and firmly to said surface and having proper thickness.

Furthermore, the object of the present invention is to provide an improved method for preparing conversion coating which is suitable for lubricating for cold-working of stainless steel, especially for high speed and deep cold-drawing of stainless steel wires or pipes.

Stainless steel, for example 18-8 stainless steel, is insoluble in oxalic acid solution as the surface of the steel is covered by chromium-nickel oxide, accordingly, in order to form oxalate coating on the surface, it is necessary to add activating agents (etching agents) and oxidation accelerators to said oxalic acid solution.

Various agents are known in the prior art as disclosed in the specifications of German Pat. Nos. 1,076,463 and 1,179,437, U.S. Pat. Nos. 3,121,033 and 3,130,087, Swiss Pat. No. 375,965, etc., which may be listed as follows:

a. Principal agents:
   Oxalic acid and/or oxalates
   b. Activating agents:
      Hydrochloric acid, hydrofluoric acid, thiocyanic acid and their salts.
   c. Oxidizing agents:
      Thiosulfates, sulfites, bisulfites, nitrates, nitrites, chlorates and organic oxidizing agents.
   d. Others:
      Phosphoric acid, sulfuric acid, boric acid, and their metal salts such as magnesium, calcium and zinc salts.

Oxalate coating is by nature porous crystalline coating and adsorbs lubricants, so that the coating is suitable for cold-working of metals as lubricating coating, especially for the drawing of iron or steel wires and pipes. However, stainless steel is different from the ordinary steels in poor adhesion with the coating layer, and there has never been known any coating which meets the requirements for the recent high-speed stainless steel drawing processes.

In the ordinary process of drawing for stainless steel wires or pipes, the limits of drawing speed and contraction percentage (reduction of section) are 10 m/min. and 20 percent, respectively, and much more severe requirements such as 20 m/min. in drawing speed and 30 percent in contraction percentage could not be carried out without difficulties such as peeling of coating and of metal, and the coating formed by the prior process has not sufficient thickness (at least 10μ, or 10 g/m² in the coating weight) as to prevent the direct contact of metals and tools to be drawn and as to keep the lubricants and adhesiveness as to prevent the peeling of coating.

As the results of many and diverse investigations, the inventors of the present invention have achieved an improved process to solve the above problems. That is, an improved oxalate conversion coating can be formed on the surface of stainless steel by adding 0.01-2 g/l. (calculated as Sn) of stannous salts into the solution consisting of principal agent (oxalic acid and/or oxalates), activating agent and oxidizing agent.

In accordance with the process of the present invention, oxalate coating suitable for cold-drawing which is 18-30μ in the thickness and is adhered tightly onto the surface of stainless steel can be obtained. And it has been confirmed that the coating formed in accordance with the process of the present invention on stainless steel such as stainless steel pipe does not cause any of the above-mentioned troubles in the process of drawing of 20 m/min. in drawing speed and 30 percent or more in contraction percentage.

The reason for the aforesaid effects and the mechanism as to the function therefore by the addition of stannous salts in accordance with the present invention have not been made clear; however, the following facts are considered to be brought about, that is:

a. the stannous salts added activate the surface of the steel by accelerating the etching of the surface as the initial reaction, and
b. the salts promote the growth of the coating serving as crystal nuclei for depositing ferrous oxalate, which is the principal constituent of the coating. That is to say, the addition of the salts will bring about an improvement in coating adhesion, an increase of coating weight (coating thickness) and making the crystal grains fine and dense.

In the following, the composition of the treating solution of the present invention will be shown.

The characteristic feature of the present invention is the addition of stannous salts into oxalic acid and/or oxalates solution. For the stannous salts, stannous oxide (SnO), stannous fluoride (SnF₂), stannous sulfate (SnSO₄), stannous chloride (SnCl₂), etc. can effectively be employed, in which 0.01-2 g/l. of at least one of them is added. The effect of etching or activating in the initial reaction cannot be expected in the concentration less than 0.01 g/l. of stannous salts, and the addition more than 2 g/l. of the salts does not cause any additional effects in the improvement of adhesiveness and increase of the thickness of the coating.

The compositions of the agents other than stannous salts are not restricted to certain ranges in theplane with the ends of stainless steel to be coated and the conditions of drawing, following the ranges of the compositions, however, will be suitable to expect a most desirable result. The concentration of the principal agents, i.e., oxalic acid and/or oxalates, shall be within the range of 5-100 g/l. The solution in the concentration less than 5 g/l. will produce coating of less than 10μ in the thickness (less than 10 g/m² in the weight of coating) which is not desirable for drawing, and the additional advantage cannot be expected by using a solution more than 100 g/l. of the acid. As being understood from the aforesaid patent specifications, any equivalent mols of oxalate or a mixture of oxalic acid and oxalate can be used in place of oxalic acid alone.

As for the activating agents, 0.1-20 g/l. (calculated as Cl or F, or Cl plus F) of at least a compound selected from the group consisting of hydrochloric acid, hydrofluoric acid, their alkali salts, hydroxycarboxylic acid, hydrobromic acid, and their alkali salts shall be added. The addition of the activating agent in the concentration of less than 0.1 g/l. is insufficient for the coating formation as the etching effect to the metal surface is poor, and the addition of the agent more than 20 g/l. causes excessive etching of the metal and the surface of the metal will also be dissolved excessively, therefore desirable coating cannot be obtained.

As for the oxidizing agents, 0.1-20 g/l. of at least one selected from the group consisting of thiosulfuric acid, sulfuric acid, their alkali salts which release sulfur or oxygen, nitric acid, nitrous acid, their alkali salts, and sodium nitrobenezensulfonate shall preferably be added. The addition of the oxidizing agent in the concentration of less than 0.1 g/l. is not sufficient to expect the oxidizing effect, and in the concentration of more than 20 g/l., the coating formation is inhibited resulting in several microns of thin coating, and the obtained coating is not preferable for drawing.

In addition to the above-mentioned composition, it has been observed that the adhesion of the coating can be further improved by adding 0.5-15 g/l. of alkali phosphates (calculated as PO₄). The oxalate conversion coating can be applied on the surface of stainless steel which has been treated with degreasing and pickling in advance by immersing the steel into the above-mentioned solution at a temperature of 40°-98° C. for 2-40 minutes in the ordinary manner. The coating thus formed is oxalate coating which is firmly adhered onto the surface of the metal in the form of porous crystalline lubricating layer. The main constituent of the coating is ferrous oxalate and the thickness thereof is about 15-25μ (15-25 g/m² in weight).
Subsequently, the thus-coated metal is applied with oil lubricant and is subjected to drawing. In the aforementioned high-speed drawing, any of peeling of the coating and seizure is not caused and products with fine and smooth surfaces are obtained, because the oxide coating is firmly adhered to the stainless steel and the thickness of the coating is proper.

The nature, principle and details of the invention will be more apparent to those skilled in the art from the following detailed description with respect to preferred embodiments of the invention.

**EXAMPLE 1**

Experiment was carried out in accordance with the following conditions:

**Test Pieces:**
Stainless steel sheets (SUS 27, which corresponds to U.S. standard AISI 304, and 50x100x0.5 mm. in the size thereof). Composition of the treating solution:

| Oxalic acid, (COOH)₂2H₂O | 35 g/l. |
| Sodium biphosphate, Na₂HPO₄ | 1.0 g/l. |
| Sodium thiosulfate, Na₂S₂O₃ | 0.5 g/l. |
| Stannous oxide, SnO | 1.0 g/l. |
| Water | remainder |

Treatning conditions:

| Temperature | 88°-93°C. |
| Dipping time | 10 minutes |

The thickness of the oxide coating obtained by the above-mentioned step was 18μ (weight of coating 18 g/m²).

The test piece thus coated was then applied with a piece of self-adhesive tape, and the tape was peeled off rapidly to test the adhesiveness of the coating. Another test piece thus coated was immersed in chromic acid solution to remove the coating, and the weight of the coating was calculated by the difference between the weight before said removal and that of after the removal.

Other test pieces were treated by the above-mentioned step except that the stannous oxide was excluded, for comparison. The tests of adhesion and weight of the coating was also carried out in the same manners. The results are shown in the following table 1. The results of the former of the invention show an improvement in adhesion of coating and an increase of weight of coating as compared with the latter results.

**TABLE 1**

| Treating Solution | Added 1 g/l. of SnO (Soln. of the present invention) | Not added SnO |
| Adhesion Test | Coating was not peeled at all. | Coating was peeled off. (metal surface was exposed.) |
| Weight of Coating | 18.0 g/m² | 14.3 g/m² |

**EXAMPLE 2**

The coating of the present invention was formed in accordance with the following conditions:

**Test pieces:**
The same as those in Example 1. Composition of the treating solution:

| Oxalic acid, (COOH)₂2H₂O | 50 g/l. |
| Sodium fluoride, NaF | 4.5 g/l. |
| Boric acid, H₃BO₃ | 0.2 g/l. |
| Sodium m-nitrobenzenesulfonate | 3.0 g/l. |
| Sodium thiosulfate, Na₂S₂O₃ | 1.0 g/l. |
| Stannous fluoride, SnF | 1.5 g/l. |
| Water | Remainder |
| pH | 1.1 |

Treatning conditions:

**EXAMPLE 3**

The oxide coating of the invention was formed in accordance with the following conditions:

**Test pieces:**
The same as those example 1. Composition of the treating solution:

| Oxalic acid, (COOH)₂2H₂O | 45 g/l. |
| Sodium chloride, NaCl | 15 g/l. |
| Sodium fluoride, NaF | 6.3 g/l. |
| Sodium thiosulfate, Na₂S₂O₃ | 2.3 g/l. |
| Stannous oxide, SnO | 1.3 g/l. |
| Water | remainder |
| pH | 0.9 |

Treatning conditions:

| Temperature | 70°-75°C. |
| Dipping time | 20 minutes |

The thickness of the coating formed on the test piece was about 20μ (weight of coating about 20 g/m²), and the coating was adhered firmly to the metal.

The comparison tests as disclosed in example 1 were carried out and similar results were obtained.

**EXAMPLE 4**

A stainless steel pipe (made of SUS27, outside diameter 40 mm and thickness 1.2 mm.) was treated with the same solution and conditions as disclosed in example 1 to obtain oxide coating, and was drawn in the conditions of 20 m/min in drawing speed and 30 percent in contraction percentage. The outside and inside surfaces of the drawn pipe were smooth and any trouble and defect were not observed.

Another stainless steel pipe was treated in the same manner and was drawn in the conditions of 20 m/min in drawing speed and 40.8 percent in contraction percentage. Nevertheless, peeling of the coating and seizure did not occur, which is a wonder in the field of cold-drawing technology.

Furthermore, another stainless steel pipe was treated by the same condition as in example 1 except that the stannous oxide was excluded, and was drawn in the condition of 20 m/min. speed and 30 percent contraction. As a result, peeling on several portions occurred and excessive contractions were caused at the peeled portions of the pipe, and in addition to that, deformations of the tools therefor were observed.

Accordingly, it will be understood that the process of the present invention is by far superior to the ordinary ones.

What is claimed is:

1. An aqueous oxalate conversion coating composition suitable for coating stainless steel comprising incorporating into the composition an oxidizing agent and a water-soluble stannous salt of from about 0.01 to 2 grams/liter, calculated as Sn.  
2. The composition of claim 1 wherein the stannous salt is selected from the group consisting of stannous oxide, stannous fluoride, stannous sulfate and stannous chloride.  
3. The composition of claim 1 having further incorporated therein an activating agent selected from the group consisting
of chloride and fluoride ions in an amount from 0.1 to 20 grams/liter, calculated as fluoride or chloride.

4. A method for coating stainless steel comprising applying the composition of claim 1 to stainless steel for a period of time sufficient to coat the metal surface.

5. A method for coating stainless steel comprising applying the composition of claim 2 to stainless steel for a period of time sufficient to coat the metal surface.

6. A method for coating stainless steel comprising applying the composition of claim 3 to stainless steel for a period of time sufficient to coat the metal surface.