

[54] **COATING COMPOSITIONS FOR STAINLESS STEELS**

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[58] **Field of Search**..... **148/6.14 A, 6.24**

[56] **References Cited**

**UNITED STATES PATENTS**

2,550,660	5/1951	Amundsen .....	148/6.24
2,813,816	11/1957	Otto .....	148/6.24
3,218,201	11/1965	Otto .....	148/6.24
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[57] **ABSTRACT**

Coatings that facilitate the cold mechanical deformation of stainless steels and particularly of low-iron noble alloys are applied by contacting the metals with an acidic aqueous oxalate coating solution comprised of a solution of oxalic acid, manganese, fluoride, and sulphur- and oxygen-containing compounds. This coating solution not only increases the rate with which a coating may be deposited on more conventional stainless steels, but also makes it possible, for the first time, to obtain useful oxalate coatings on certain low-iron noble alloys utilizing practical levels of chemical activity of the bath.

**12 Claims, No Drawings**

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## COATING COMPOSITIONS FOR STAINLESS STEELS

### FIELD OF THE INVENTION

This invention generally relates to the application of lubricant receptive oxalate-type coatings to stainless steel surfaces in order to facilitate cold mechanical deformation of the metal, and this invention especially relates to the application of this type of coating to low-iron noble alloys upon which surfaces it has, in the past, proven particularly difficult to deposit a useful coating.

To facilitate the cold mechanical deformation of metals in such operations as wire drawing, drawing, rolling, stamping, extrusion and the like, it is conventional to lubricate the surface of the metal. This lubrication, in addition to permitting faster operation and deeper draws, is also advantageous in that it extends the life of the working dies and related equipment. By one well known method, the metal surfaces are first prepared by applying a lubricant absorptive coating to them, such as an oxalate-type conversion coating. This coating acts as a receptive base for common lubricants such as soaps and the like that are effective to reduce the friction in cold mechanical deformation processes.

### REPORTED DEVELOPMENTS

Oxalate coatings of the general type here referred to are discussed in the prior patent literature and may briefly be summarized as follows. British patent 683,954 discloses methods for obtaining these coatings by utilization of a solution comprised of oxalic acid, chloride ions and certain accelerators selected from the class consisting of sulphides, sulphites and thiosulphates. French Pat. No. 1,065,191 discloses the use of solutions comprised essentially of oxalic acid, phosphoric acid, and hydrogen sulphide as an accelerator. Additionally, this patent discloses that manganese or ferric ions can be introduced into the solution to facilitate coating.

In the U.S. patent literature, U.S. Pat. No. 2,550,660 discloses the use of oxalic acid in conjunction with oxygen-containing sulphur accelerators and soluble halides, particularly fluorides. More recently, U.S. Pat. No. 2,813,816 discusses oxalate-type conversion coating solutions that include oxalic acid, a mineral acid, manganese ions, and oxygen-containing sulphur accelerators. By and large, these prior art coating solutions have proved effective in applying adherent oxalate-type coatings to ferrous metals including the more common low alloy stainless steels. However, they do not produce satisfactory coatings on some of the more unreactive low-iron noble alloys.

In the context of the present invention, the expression "low-iron noble alloys" refers to those alloys in which the alloying nonferrous metals comprise the major constituents by weight and, in some instances, in which no iron is present at all. Representative formulations of some of these low-iron noble alloys are detailed in the attached examples, but generally it may be said that they include such constituents as aluminum, copper, chromium, manganese, silicon, nickel, molybdenum, cobalt, zirconium, titanium, columbium and tantalum.

Low-iron noble alloys of the foregoing type frequently display a relatively low rate of chemical reactivity and thus are not responsive to treatment in con-

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ventional oxalate coating solutions. While the chemical activity of the coating solution may be increased, as by raising the temperature and increasing the strength of the solution, particularly with respect to fluoride and the sulphur- and oxygen-containing accelerator, a point is ultimately reached at which a coating is not deposited and the solution merely functions as a pickling bath. When this point is reached before the coating solution becomes effective to produce a useful conversion coating on the metal surface, conventional oxalate coating solutions prove to be of little utility.

Accordingly, it is an object of this invention to provide a novel coating solution and process whereby an adherent coating suitable for use as an aid in cold mechanical deformation processes can be applied to the surface of low-iron noble alloys.

Another object of this invention is to provide oxalate-type coating solutions that are effective to coat low-iron noble alloys at practical levels of chemical activity of the coating solution.

Another object of this invention is to provide an oxalate-type coating solution that can be adapted and is effective to coat the surfaces of common low alloy stainless steels as well as low-iron noble alloys.

Another object of this invention is to provide a coating process and coating solution which provide considerable flexibility in the application of coatings to common stainless steels as well as to low-iron noble alloys and which process permits the coating solution to be monitored and adjusted as is required to replenish the solution and to accommodate the alloy being treated under desired variable process conditions such as the rate of coating deposition, the thickness of deposition, and the temperature of the coating solutions.

### SUMMARY OF THE INVENTION

Briefly, these and other objects of the invention are made possible by the conjoint use of soluble manganese and fluoride compounds in oxalate coating solutions, by which means an increased rate of deposition upon the surface of the alloy is obtained. In addition to providing the desired coatings, these oxalate solutions containing manganese and fluoride are also advantageous in that they permit flexibility in processing conditions such as the rate of deposition of the coating on the alloy, the thickness of the deposition and the temperature at which the coating solutions must be maintained and, with relatively minor adjustments, may be used to treat a wide range of common stainless steels and low-iron noble alloys.

#### Fluoride Activity and its Measurement

As used in this specification and the appended claims, the term "fluoride activity" does not necessarily refer to the total amount of fluoride in the coating solution, but rather refers to the ability of the solution to cause the desired chemical effect. Fluoride activity is defined and measured by observing the rate at which the fluoride-containing solution will etch a piece of lime soda glass. This definition is made necessary since certain complexes containing fluoride and certain unionized fluoride salts, such as sodium borofluoride and aluminum fluoride, do not appear to contribute materially to the activity of the acidic fluoride solution.

The control of processing conditions in the instant invention is considerably facilitated if the fluoride activity is monitored as may from time to time be re-

quired to permit adjustment of the coating solution for depletion of its fluoride content. While the fluoride activity of the coating solution can be determined by measuring the rate at which the solution will etch glass, this does not present a practical method of obtaining timely analyses. Therefore, the preferred practice of this invention, a special metering device is utilized that is capable of indicating on an immediate basis the fluoride activity of the solution. Devices of this sort are known in the art and are fully described in, for example, U.S. Pat. Nos. 3,129,148; 3,329,587; and 3,350,284. Basically, these devices include electrolytic cells adapted to receive a sample of the solution. Two electrodes are provided in the cell; and the anode is comprised of p-type silicone and the cathode is comprised of a relatively inert material such as platinum. Alternatively, an n-type silicone electrode can be used if the cell is exposed to a light of certain minimum intensity and spectral distribution. A voltage is imposed upon the electrodes of the cell and the measured current that passes through the cell bears an empirically derivable relationship to the fluoride activity of the solution being monitored.

#### Composition of the Coating Solution

The composition of the coating solution will necessarily vary from time to time depending upon the exact composition of the alloy being treated and the processing conditions that are desired to be established. As has been long recognized, no exact rules for preparing these types of conversion coating solutions can be set forth and optimum conditions can only be determined on a trial and error basis. Generally, though, the following guidelines are illustrative of the preferred materials used in preparing the coating solutions of this invention and the more usual ranges in which these materials are used.

Oxalate. The most convenient manner of adding oxalate to the solution is in the form of oxalic acid dihydrate as this will avoid the introduction of extraneous cations into the solution. Effective coating solutions can be made with the oxalate ion being present in an amount from between about 30 to 90 grams per liter and preferably in a range of from 40 to 60 grams per liter.

Accelerator. The accelerator is preferably selected from materials that contain both oxygen and sulphur and which are converted in the bath into sulphur dioxide and colloidal sulphur. Examples of such materials are thiosulphates, hydrosulphites, tetrathionates, and sulphites. Ammonium thiosulphate is a particularly convenient example of such materials. The proper amount of the accelerator is determined by titrating a 10 ml. sample of the coating solution with a 0.05N iodine solution. When the proper level of accelerator is established, the end point will be indicated when from 1 to 10 ml. of iodine have been titrated and more preferably when 2 to 6 ml. are required.

Manganese. Any manganese compound that will yield manganese ion in the solution can be used. As a lower limit, at least about 1 gram per liter of the manganese ion should be present. Amounts of manganese up to its solubility can be used.

The maximum solubility of the manganese in this solution appears to be about 6 grams per liter and the addition of further quantities of the manganese salt serves no particular purpose and only contributes to the accu-

mulation of sludge deposits in the bath. Examples of suitable manganese salts are manganese carbonate, manganese nitrate, and manganese acetate.

Fluoride. Fluorides in the form of bifluorides are generally most effective in establishing a desired level of fluoride activity in the coating solution. Hydrofluoric acid can be used also. Ammonium bifluoride is preferred due to its solubility and availability. To determine the proper fluoride activity, a fluoride activity meter is calibrated using various amounts of ammonium bifluoride and the fluoride activity of the coating solution is adjusted to obtain meter readings equivalent to those obtained with from about 4 to 50 grams per liter of ammonium bifluoride. It is not possible to narrow this broad range as the most desirable fluoride activity will depend upon the composition of the alloy to be coated. This stated range will be effective to coat essentially all common stainless steels and low-iron noble alloys.

The coating is preferably applied to the alloy by immersion in the coating solution and the coating rate can be adjusted not only by controlling the chemical makeup of the bath, but also by adjusting the temperature of the bath. For process convenience and to avoid breakdown of the coating solution and excessive gas (sulphur dioxide) evolution from the bath, lower temperatures in the range of from 120°F to 130°F are preferred although with particularly inert alloys, temperatures as high as 190°F must sometimes be used.

The detention time of the alloys in the coating solution may be varied considerably to adjust to the other operations performed on the alloys. However, it is generally preferred to have the ability to apply useful coatings in weights that are in excess of about 1,000 milligrams per square foot in times of from about a few minutes to two hours. The less reactive metals require the longer contact times. Coatings can be formed on the more reactive metals, such as stainless steel, in shorter periods of time, for example, about ten minutes.

#### EXAMPLES

In the following Examples, oxalic acid dihydrate was dissolved in water and the oxalate content of the bath was measured in terms of total acidity by titration of a 2-milliliter sample of the solution with 0.5 normal sodium hydroxide. The total acidity is given in terms of milliliters of 0.5 sodium hydroxide required to achieve a neutral end point.

The fluoride content of the bath was measured by means of a fluoride activity meter, as discussed above, with the reading in milliamps being converted to fluoride activity expressed in terms of grams per liter of ammonium bifluoride needed to achieve an equivalent reading on the fluoride activity meter. In these Examples, the fluoride was added in the form of ammonium bifluoride.

The amount of sulphur-containing salt (in all cases ammonium thiosulfate) is expressed in terms of milliliters of a 0.05 normal iodine solution required to achieve an end point in titrating against 10 milliliters of solution.

In all of the Examples herein given, low-iron noble alloys were first given a surface treatment to remove all free oil, oxide and scale, and to activate the surface and make it chemically reactive. This is best accomplished by first immersing the work piece in a molten salt bath and thereafter quenching it in cold water and pickling

and activating it in one of the following representative solutions:

- A. Sulphuric acid (66°Be) 6 to 10 gallons  
Rock salt 25 pounds  
(Temperature: 160-180°F)
- B. Sulphuric acid (66°Be) 6 to 10 gallons  
(Temperature: 140-160°F)
- C. Hydrochloric acid (20°Be) 20 gallons  
(Temperature: Room-120°F)
- D. Nitric acid (42°Be) 8 to 10 gallons  
Hydrofluoric acid (70%) 1 to 3 gallons  
(Temperature: Room-130°F)

Various alloy surfaces on which it has proved particularly difficult to form oxalate coatings were treated in coating solutions having the composition indicated in the table. These alloys had the following approximate compositions:

V — Al 2.75; Cu 2.0; Cr 20.0; Mn 0.70; Si 1.0; Ni balance

T — Cr 29.5; Si 1.4; Fe 0.25; Al 0.20; Ni balance

M — Cr 29.5; Mo 5.0; Si 1.4; Fe 0.25; Al 0.2; Ni balance

L — Co 40.0; Cr 20.0; Fe 14.5; Mn 2.0; Mo 7.2; Ni 15.0; Si 0.5; Zr 0.05; C 0.045

- C. at least about 1 g/l of manganese; and
- D. fluoride in an amount such that the fluoride activity is equivalent to that obtained from the use of about 4 to about 50 g/l of ammonium bifluoride.
- 2. A coating solution according to claim 1 wherein:
  - A. the amount of said oxalate ion is about 40 to about 60 g/l;
  - B. the amount of said accelerator is such that about 2 to about 6 ml of said 0.05 N iodine solution are acquired to obtain said end point; and
  - C. the amount of said manganese does not exceed about 6 g/l.
- 3. A coating solution according to claim 1 wherein the amount of said manganese does not exceed about 6 g/l.
- 4. A coating solution according to claim 1 wherein said accelerator is selected from the group consisting of thiosulphates, hydrosulfites, tetrathionates and sulfites.
- 5. A coating solution according to claim 2 wherein said accelerator is selected from the group consisting of thiosulphates, hydrosulfites, tetrathionates and sulfites.
- 6. A coating solution according to claim 1 wherein the source of said fluoride is ammonium bifluoride.

COATING WEIGHTS<sup>5</sup>

Example	Mn <sup>1</sup>	TA <sup>2</sup>	F <sup>3</sup>	TO <sup>4</sup>	Immersion Time (hrs.)	Solution Temp.(°F)	COATING WEIGHTS <sup>5</sup>			
							T	M	L	V
1	No	6.8	29	6.7	0.5	185	730	450	590	2360
1A	Yes	6.7	29	4.1	0.5	185	1110	1315	1790	1820
2	No	4.2	11	6.0	0.5	160	67	110	2700	2275
2A	Yes	4.2	11	4.7	0.5	160	2670	420	1440	2760
3	No	4.8	11	6.1	0.5	160	720	150	1740	480
3A	Yes	4.4	11	6.8	0.5	160	2850	540	1830	2580
4	No	5.1	12	5.3	0.5	160	90	150	1100	1050
4A	Yes	9.7	23	6.9	0.5	160	1520	480	870	3230
5	Yes	5.0	18	4.7	1.0	175	2340	1170	2300	1860

NOTES:

<sup>1</sup>Added as manganese salt in an amount sufficient to saturate solution.

<sup>2</sup>ml 0.5N NaOH to neutralize 2 ml of solution

<sup>3</sup>Equivalent g/l of ammonium bifluoride needed to obtain the fluoride activity of the solution as measured by a fluoride activity meter

<sup>4</sup>ml 0.05N I to reduce 10 ml of solution

After the coating operation had been completed, the work pieces were rinsed and neutralized. After this treatment, it was found that an adherent coating had been obtained suitable for receiving a lubricant adapted for use in metal drawing operations.

The above tabularized Examples give an indication of the effectiveness of the addition of the manganese ion to the oxalate/fluoride/thiosulphate bath. Note that with each of the alloys tested, useful oxalate coatings — that is, in excess of about 1,000 mg./sq.ft. — could be obtained by the inclusion of the manganese ion. There are some deviations between various examples, but this results from experimental error and small differences in the surface characteristics of the work pieces used.

I claim:

1. An aqueous acidic coating solution for applying conversion coatings to stainless steels and low-iron noble alloys consisting essentially of:

A. about 30 to about 90 g/l of oxalate ion;

B. a sulphur- and oxygen-containing accelerator in an amount such that about 1 to about 10 ml of a 0.05 N iodine solution is required to obtain an oxidation end point with a 10 ml sample of said coating solution;

7. A method for applying an adherent coating to stainless steels and low-iron noble alloys comprising contacting the surface thereof with the coating solution of claim 1.

8. A method for applying an adherent coating to stainless steels and low-iron noble alloys comprising contacting the surface thereof with the coating solution of claim 2.

9. A method for applying an adherent coating to stainless steels and low-iron noble alloys comprising contacting the surface thereof with the coating solution of claim 3.

10. A method for applying an adherent coating to stainless steels and low-iron noble alloys comprising contacting the surface thereof with the coating solution of claim 4.

11. A method for applying an adherent coating to stainless steels and low-iron noble alloys comprising contacting the surface thereof with the coating solution of claim 5.

12. A method for applying an adherent coating to stainless steels and low-iron noble alloys comprising contacting the surface thereof with the coating solution of claim 6.

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