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METHOD OF APPLYING SULFIDE COATING ON WIRES FOR DRAWING AND COMPOSITION THEREFOR

John A. Henricks, Logansport, Ind., assignor to Devex Corporation, Cleveland, Ohio, a corporation of Ohio

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This invention relates to the treament and lubrication of ferrous metal surfaces to prepare them for deforming and drawing operations.

This application is a continuation-in-part of my copending application, Serial No. 274,839, filed March 4, 1952, now abandoned, which in turn is a continuation-in-part of my application, Serial No. 193,290, filed October 31, 1950, now reissued Patent No. 24,017, and formerly U. S. Patent No. 2,588,234.

Integral coatings are generally used on surfaces of ferrous metals to be subjected to extreme pressure and surface temperature such as encountered in drawing operations. The most versatile integral coating used as a base lubricant in metal drawing is one consisting principally of iron sulfide since it is fusible and generally has more resistance to high-acidity drawing lubricants than other coatings such as iron phosphate and iron oxalate coatings. While such iron sulfide coatings may be formed on the ferrous metal surfaces while immersed in an aqueous solution, the surface must be freshly cleaned or pickled before the sulfurizing step.

One object of the present invention is to provide a method for applying an integral iron sulfide coating over scaled metal surfaces.

Another object is to provide a method of forming an iron sulfide film on a ferrous metal surface without regard to whether the surface is scaled or freshly pickled.

According to the present invention, an integral iron sulfide coating is formed on ferrous metal stock, whether its surface has been cleaned by pickling or not, by applying an alkaline sulfurizing agent to the surface of the stock and thereafter heating it in an annealing furnace, a flash baker, or the like to thermally form an iron sulfide coating on said surface.

Suitable sulfurizing agents are reducible alkaline sulfur compounds such as the thiosulfates, sulfites, and tetrathionates of sodium, potassium, calcium and ammonium. These sulfurizing agents can convert a ferrous layer of the stock to iron sulfide and alkali ferrates when heated to at least 900° F. and preferably a red heat. A versatile integral coating is obtained which allows the metal to be cold-worked without harming tools and dies.

Even heavily scaled pieces from hot rolling operation can be cold-worked without the pickling step by covering the work with a coating of the alkaline sulfurizing agent of the present invention which is preferably sodium thiosulfate, sodium sulfite, and sodium tetrathionate.

The above mentioned sulfurizing agents may be used alone in a water solution in amounts preferably of about 3% to 8% by weight although when freshly pickled stock is used, even as low a percentage as ½ or 1 may be used to obtain benefits of the present invention. Generally, higher percentages of sulfurizing agents may be used such as 15% to 20% although over 40% or 50% by weight of the sulfurizing agent decreases the valuable lubricant base properties of the integral coating, and

the use of such larger amounts of the sulfurizing agent is expensive.

Other compounds may be used with the sulfurizing agent when processing carbon steel compounds to provide additional lubrication during the forming operation, suitable compounds being alkali metal salts generally melting at from about 500 to 900° C. These alkali metal salts or pigments may be added to the alkaline sulfurizing agents along with other materials such as starch which may be used as a peptizing agent. When other materials are used, sulfurizing agents should preferably comprise about 5% to 50% by weight of the total dry mixture of the composition, and the total weight of the sulfurizing agents by weight should not be over 40% or 50% by weight of the aqueous bath solution as previously described.

Any of the conventional drawing lubricants, such as a soap type comprising calcium or aluminum stearate, may be used over the iron sulfide coating provided by the present invention. As is well known, the usual box soap powders for wire drawing are mixtures of about 30% to 50% calcium or aluminum stearate and the balance lime, although high titre sodium soap powders are used for some applications.

The following examples illustrate my invention:

Example I

Scaled stainless steel rods were immersed in an aqueous bath containing 8% by weight of sodium thiosulfate. The coating of sodium thiosulfate was dried at about 200° F. and thereafter the rods and coatings were heated in an annealing furnace at a temperature of 1500° F. for 2 minutes to form an integral iron sulfide coating on the surface. The rods were then drawn through a series of dies with the aid of a soap type drawing lubricant to greatly reduce the original cross-sectional area. The drawn rods had a bright and scratch-free surface.

Example II

Stainless steel rods were pickled for 5 minutes in a 15% sulfuric acid bath containing 15 pounds sodium chloride per 100 gallons of solution at a temperature of 195° F. These pickled rods were processed in a similar manner to the scaled rods of Example I except that the sodium thiosulfate bath was substituted for by an aqueous bath containing 3% by weight of sodium sulfite. Similar results were obtained from the drawing operation, the drawn rods having bright and scratch-free surfaces.

After steel has been hot rolled and initially shaped, the pieces have to be annealed to restore the ductility for further cold work. In the vast majority of cases, the anneal is performed in an uncontrolled furnace at atmospheric pressure so that the work becomes heavily scaled and must be pickled before further cold work or drawing can be performed. When the work is covered with an alkaline film of a sulfurizing agent and heated, however, the heavy scaled layer on the hot rolled steel is converted to ferrous sulfide and the work made ready for cold drawing and shaping. In this way, I eliminate the pickling step and utilize the annealing step to deposit a layer of ferrous sulfide on the metal.

The alkaline sulfurizing agent consists of a fusible alkali metal salt and a reducible sulfur compound that will convert the ferrous layer to iron sulfide and alkali ferrates when heated to a red heat and thus give an integral coating which can be cold worked without harming the working tools and dies. The magnetic iron oxide usually formed during hot rolling and annealing is highly abrasive to tools and dies. In addition to the fusible alkali salts and sulfurizing agents, fusible pigments can be incorporated or dispersed into the alkaline layer. A

combination of pigments with an alkali coating is preferred for carbon steel while an unpigmented film can be used for stainless steel.

A suitable alkaline type coating is given below. The mole fraction of each chemical is given so that chemically equivalent compounds can be readily substituted by anyone skilled in the art.

Example III

Ingredients	Molarity	Typical Mix, Parts Dry Wt.
Sodium hydroxide	0.2	8
Sodium carbonate	0.1	11
Sodium thiosulfate	0.1	25
Sodium metasilicate or Trisodium phosphate	0.1	38
Sulfur	0.3	10
Starch		8

This is made up into a 15% to 33% aqueous solution and applied to the work by dipping in the hot solution prior to annealing. Tenth molar sodium borate or sodium silicate can be used as a fusible alkali salt component in place of the 0.1 mole trisodium phosphate shown. Likewise, the chemical equivalent sodium sulfide, sodium sulfite, polysulfide, or polythionate can be substituted for sodium thiosulfate. The free sulfur in the above formula will be taken up in any case to form sulfides and polythionates. This film has additional complex chemical reactions when the work is heated. Iron sulfide and alkali ferrates are formed and when phosphates are used as the fusible salt, certain ultramarine type silicates are formed.

The work is dipped in the solution which is heated up to 180°–200° F. and the hot solution allowed to dry on the work before being placed in an annealing furnace or passed through a continuous open flame gas annealer.

In order to further augment the sulfurizing action brought about by the thermal decomposition of the alkaline sulfurizing agent, the hot metal may be transferred from the annealing furnace or flash baker and quenched in an alkaline aqueous solution of a reducing sulfur compound such as sodium thiosulfate, sodium sulfite and sodium sulfide. This sulfurizing action obtained in the quenching bath complements the predominant sulfurizing action caused by thermal decomposition of a sulfur compound.

It is to be understood that in accordance with the provisions of the patent statutes, the particular form of product shown and described and the particular procedure set forth are presented for purposes of explanation and illustration and that various modifications of said product and procedure can be made without departing from my invention.

Having thus described my invention, I claim:

1. The method of reducing the abrasive nature of the mill scale formed on steel at elevated temperatures, comprising the steps of precoating the ferrous surface with a fusible alkaline film containing sulfur that will thermally react with iron to form a fusible ferrous film and thereafter annealing the steel.

2. The method of claim 1 wherein the precoat action is further augmented by quenching the precoated and heated ferrous metal in an alkaline aqueous solution of a reducing sulfur compound to complement the action of the original alkaline sulfur precoat.

3. A method of preparing surfaces of ferrous metal stock for drawing comprising the steps of pickling said stock, immersing said stock in an aqueous bath containing an alkaline sulfurizing agent to form a coating on said stock and thereafter heating the coating to at least about 900° F. so that an integral coating comprising principally iron sulfide is formed on the surfaces.

4. A method of preparing surfaces of ferrous metal stock for drawing comprising the steps of hot rolling and initially shaping said stock, immersing said stock having iron oxide scale on its surface in an aqueous bath containing an alkaline sulfurizing agent to form a coating on said stock and thereafter heating the stock to at least about 900° F. so that an integral coating comprising principally iron sulfide is formed on the surface.

5. A method of preparing ferrous metal stock having scaled surfaces for cold drawing or the like comprising the steps of applying an aqueous solution of an alkaline sulfurizing agent over said surfaces, and annealing said stock to form an integral coating comprising principally iron sulfide on the surface.

6. A method of drawing ferrous metal stock comprising the steps of applying an aqueous solution of an alkaline sulfurizing agent on the surface of said stock, annealing said stock to form an integral iron sulfide coating on the surface, and thereafter drawing the stock.

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