

146

Patented Apr. 6, 1943

2,315,568

UNITED STATES PATENT OFFICE

2,315,568

CLEANING STEEL SURFACES

Christian J. Wernlund, Niagara Falls, N. Y., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application September 28, 1939.
Serial No. 296,973.

7 Claims. (Cl. 204-145)

This invention relates to the cleaning of iron and steel surfaces, especially to prepare such surfaces for subsequent electroplating.

The removal of oxides, such as scale or rust from iron or steel surfaces prior to electroplating is commonly done by pickling operations, for example with sulfuric acid. Various other cleaning solutions also are used, such as cyanide solutions, caustic solutions, soaps, and the like to remove various foreign matter in addition to oxide scale from the surface of the steel. In some processes several different cleaning operations are combined in order to obtain complete removal of different kinds of foreign matter.

I have devised an improved method for cleaning steel and iron surfaces, an object of which is to clean iron and steel having oxide or other foreign matter thereon so as to produce clean bright surfaces suitable for subsequent electroplating. A further object of my invention is to clean the surface of iron or steel wire which has on its surface lime or other drawing compound in addition to oxide scale or rust. Other objects of my invention will be apparent from the following description.

In accordance with the present invention iron or steel surfaces to be cleaned are first given an anodic treatment in an aqueous solution of sulfocyanide and are then treated in an acid solution which is capable of dissolving iron oxide. Preferably the acid treatment is electrolytic, the surface to be cleaned being the anode. However, a nonelectrolytic treatment in the acid solution or a cathodic electrolytic treatment also may be used.

The anodic treatment with acid is preferred since it acts more rapidly and produces a brighter surface than the nonelectrolytic or cathodic methods.

In practicing my invention the anodic treatment in the sulfocyanide solution effects complete separation of all oxide scale and other foreign material from the surface of the steel but usually leaves a dark deposit on the surface. The acid treatment completes the cleaning operation, removing the dark deposit left by the sulfocyanide solution and producing a clean, bright surface, excellently adapted for subsequent electroplating. The time of treatment required in both steps will vary depending upon the specific sulfocyanide and acid used, and on other factors, such as temperature, current density, and concentrations of the ingredients, as more fully explained below. In general, the time of treatment in each step will be in the order of 1 to 5 minutes.

In the first step of my process, that is, treatment in the sulfocyanide solution, that is, a solu-

tion containing sulfocyanide ions, any soluble sulfocyanide may be used, for example, ammonium sulfocyanide (NH_4CNS) or the sulfocyanide of sodium, potassium, calcium, barium, or strontium.

I prefer, however, to use an alkali metal sulfocyanide by which term I mean to include ammonium sulfocyanide. In this step the article to be treated is made the anode and a suitable direct electric current is applied. The current density employed is not critical but may be varied as desired. It is preferable not to use a current density which is too low, as this will increase the length of time required for complete separation of foreign matter from the base metal. Generally, a current density of from 40 to 100 amperes per square foot is suitable but higher current densities may be used if desired. The temperature of the sulfocyanide solution may be varied from room temperature to the boiling point of the solution; generally, a temperature of about 60 to 80° C. is preferable. The preferred concentration of the sulfocyanide will vary chiefly with the desired time of treatment and with the solubility of the sulfocyanide used. When using ammonium sulfocyanide or sodium sulfocyanide, I prefer to maintain the sulfocyanide concentration of from 2 to 16 ozs. per gallon.

In the second step of my process I use an acid solution which is capable of dissolving iron oxides. A variety of acids may be used for this purpose either alone or in mixtures thereof, for example sulfuric acid, hydrochloric acid, nitric acid, citric acid and acetic acid. The action of the various known acids on iron oxides is well known and the proper selection of acid and its concentration in the solution will be apparent to the skilled chemist. I generally prefer to use a sulfuric acid solution, the concentration of which may vary from about 5 to 75% by weight of H_2SO_4 . I have obtained the best results, in cleaning steel surfaces, with a sulfuric acid solution of 40 to 50% concentration. While the acid solution may be used nonelectrolytically or as a cathodic electrolytic cleaner, I prefer to use the acid solution as an anodic electrolytic cleaner at a relatively high current density, for example 100 to 250 amperes per square foot or higher. While lower current densities may be used, the results at lower current densities are similar to those obtained without the use of the electric current, namely, a considerably longer time is required to effect complete cleaning. Also I have found that generally a brighter surface is obtained by the use of the higher current densities, the work being the anode. The current density also will vary

when other acids are used. For example, it is impossible to use a high current density with the weaker acids, such as acetic acid or citric acid. The acid treatment is satisfactory when carried out at ordinary room temperatures, although higher temperatures, up to the boiling point of the acid solution may be used satisfactorily if desired. I have found that generally the best results are obtained with a warm acid solution, e. g. at 40 to 60° C.

Generally, I prefer to add an acid inhibitor to the acid solution to prevent undue attack of the base metal by the acid. Acid inhibitors are a well-known class of chemicals which are commonly added to acid pickling solutions for pickling iron or steel. The following typical acid inhibitors are examples of inhibitors which are suitable for use in my process: aldehydes, such as furfural; aldehyde derivatives, such as the condensation products of aldol with alpha naphthylamine; organic sulfides of the type



such as thiuram sulfide; saturated heterocyclic compounds containing at least three different atoms in the ring, two of the atoms preferably being nitrogen and carbon, such as N-(parahydroxy-phenyl) morpholine, thiocyanates, such as lauryl pyridinium thiocyanate; mustard oils, such as allyl isothiocyanate; cinchona bark alkaloids and their derivatives, such as sulfurized quinoline; thioureas, such as di-orthotolyl thiourea; sulfonated oils, such as ichthyol; thiazoles, such as anilinobenzthiazole; thioglycollic acid and its derivatives, such as ethyl thioglycollic acid and diphenyl thiohydrantoin; petroleum oil residues and waste acids; extracts from destructive distillation of carbonaceous matter; oil refinery waste; and pyridine bases.

In one preferred method for practicing my invention, a steel surface to be cleaned is first treated anodically in a sulfocyanide solution containing about 8 ozs. per gallon of either sodium sulfocyanide or ammonium sulfocyanide at a temperature of about 80° C., utilizing an anode current density of 60 to 70 amperes per square foot. This anodic treatment is continued for a period of one to two minutes. The steel article then is made the anode in a 45% sulfuric acid solution which contains sulfurized quinoline or other acid inhibitor. The acid solution is warmed to about 40 to 60° C. and the anode current density is 100 to 250 amperes per square foot. The treatment in the acid solution is continued for about one minute. The cleaned article then is water rinsed to remove adhering acid. If desired, the water rinse may be dispensed with, if the adhering acid is not incompatible with the subsequent electroplating operation. After this treatment the steel article will have a bright, clean surface and is ready to be electroplated.

In the above described anodic treatments, types of cathodes commonly employed in anodic cleaning operations may be used. For example, cathodes of iron, steel, carbon or lead are suitable for practicing my process.

I am aware that heretofore it has been proposed to clean iron or steel articles anodically in alkali metal cyanide solutions. I have tested such methods and have found that they do not produce the advantageous results obtained by my herein-described process. Also, I have found that equal cleaning action cannot be obtained when anodic treatment in a cyanide solution is used in place

of the treatment in sulfocyanide solution, in practicing my process.

My hereindescribed method is especially well adapted for cleaning cold-drawn steel wire to prepare it for electroplating. Such wire usually has on its surface lime or other material used as drawing lubricant and also may have rust spots on the surface. The removal of the drawing lubricants, such as lime which usually fills small cracks and crevices on the surface of the wire, is exceedingly difficult by ordinary means and usually mechanical means, such as brushing or the like, are required to effect its complete removal. It is also difficult to remove the rust spots without undue attack of the underlying steel by the usual pickling processes, especially when such methods are sufficiently drastic to remove the drawing lubricant from the wire. When such wire is cleaned by my process, a complete removal of all foreign matter is attained in a short time and no mechanical treatment is required. The surface of the treated wire is bright and clean and in excellent condition for subsequently producing thereon electrodeposits of good adherence. My process likewise is well adapted for cleaning high-carbon steels and alloy steels.

I claim:

1. A process for cleaning the surface of a ferrous metal article, which comprises making said article the anode in an electrolyte consisting essentially of a solution containing sulfocyanide ions in concentration equivalent to at least about 2 ounces per gallon of alkali metal sulfocyanide and thereafter contacting said article with an acid solution which is capable of dissolving iron oxides.

2. The process according to claim 1 in which the said article is made the anode in the said acid solution.

3. A process for cleaning the surface of a ferrous metal article, which comprises making said article the anode in an electrolyte consisting essentially of a solution of an alkali metal sulfocyanide containing at least about 2 ounces per gallon of said sulfocyanide and thereafter making said article the anode in a sulfuric acid solution which is capable of dissolving iron oxides.

4. A process for cleaning the surface of a ferrous metal article, which comprises making said article the anode in an electrolyte consisting essentially of a solution of an alkali metal sulfocyanide containing at least about 2 ounces per gallon of said sulfocyanide and thereafter making said article the anode in a sulfuric acid solution which is capable of dissolving iron oxides, at an anodic current density in said acid solution of not less than about 100 amperes per square foot.

5. A process for cleaning the surface of a ferrous metal article, which comprises making said article the anode in an electrolyte consisting essentially of a solution of ammonium sulfocyanide containing at least about 2 ounces per gallon of said sulfocyanide and thereafter making said article the anode in a sulfuric acid solution which is capable of dissolving iron oxides, at an anodic current density in said acid solution of not less than about 100 amperes per square foot.

6. A process for cleaning the surface of a ferrous metal article, which comprises making said article the anode in an electrolyte consisting essentially of a solution of sodium sulfocyanide containing at least about 2 ounces per gallon of said sulfocyanide and thereafter making said article the anode in a sulfuric acid solution which is capable of dissolving iron oxides, at an anodic

146

2,315,568

3

current density in said acid solution of not less than about 100 amperes per square foot.

7. A process for cleaning the surface of a ferrous metal article, which comprises making said article the anode in an electrolyte consisting essentially of an electrolyte containing two to sixteen ounces per gallon of an alkali metal sul-

5 focyanide at a temperature of 60 to 80° C. and an anodic current density of 40 to 100 amperes per square foot and thereafter making said article the anode in an electrolyte containing 40 to 50% by weight of sulfuric acid at an anodic current density of 100 to 250 amperes per square foot.

CHRISTIAN J. WERNLUND.