United States Patent Office 2,706,171 Patented Apr. 12, 1955

2,706,171

STRIPPING CHROMIUM PLATING FROM ZINC ELECTROLYTICALLY

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No Drawing. Application March 9, 1953, Serial No. 341,372

5 Claims. (Cl. 204—56)

This invention relates to the removal of platings from articles made from alloys consisting principally of zinc. For example, by the present invention chromium, nickel and copper can be removed electrolytically in such a manner as to avoid any significant corrosion, pitting, or dissolving of the zinc base metal.

For many decades it has been the practice to electroplate articles made of zinc alloys. For example, cigarette lighter parts have been mass-produced by methods such as die casting. In any electroplating operation operated on an industrial basis, it is inevitable that a small percentage of the articles will be imperfectly electroplated and will constitute rejects. Heretofore there has been no entirely satisfactory method for salvaging such rejects or imperfectly plated articles. Conventional stripping procedures removing the plating also dissolved significant amounts of zinc, pitting the articles, and altering their dimensions. Most chromium-plated zinc articles have been so irregularly shaped that the platings have been stripped from different zones of the articles at very different rates, so that the zinc has been corroded at certain portions prior to significant removal of the outermost layer of other zones. Even with articles having a shape permitting exceptionally uniform stripping, the zinc was corroded when attempts were made to electrolytically remove portions of the chromium and nickel layers and thereafter to abrade off the copper layer and splotches of nickel and chromium. Heretofore no commercial method has been available for stripping all of the plating without attacking the zinc. The fact that in the electromotive series of metals zinc is much higher than the plated metals partially explains why extreme difficulties have been encountered in stripping chromium-plated zinc articles.

It is an object of the present invention to provide a process of electrolytically stripping metals such as chromium, nickel and copper from zinc articles in such a manner that the articles are not adversely affected or significantly dissolved.

An important feature of the present invention is the provision of a process whereby a protective layer consisting of a film formed by the joint cooperation of both zinc phosphate and zinc chromate is deposited upon the zinc surface at the moment that the zinc surface is exposed to the stripping bath by the removal of the overlying layer of metal. Accordingly, the provision of a stripping bath containing water, phosphoric acid, chromic acid, and sulphuric acid, is an important feature of the present invention.

A further feature of the present invention is the use of a process in which the electrolytic operation is conducted for a sufficient period of time that oxygen is evolved at the anode prior to the removal of the articles from the stripping bath.

In carrying out the process of the present invention, a lead-lined tank can be employed for the electrolytic bath. This lead lining can be employed as the cathode in the cell. If a ceramic tank is utilized, lead cathodes are desirably utilized, but carbon cathodes or other cathodes not corroded under operating conditions may be used. The chromium, nickel and copper stripped from the articles and deposited upon the cathode adhere loosely thereto, and can be readily removed periodically.

As previously explained, the stripping bath contains water, phosphoric acid, chromic acid, and sulphuric acid, the concentrations of which are referred to in parts by weight or weight percent. The stripping bath is an

aqueous solution containing from 10% to 30% phosphoric acid. This corresponds to approximately 11.8% to 35.3% of the 85% orthophosphoric acid available commercially. The phosphoric acid cooperates with the chromic acid, and possibly other ingredients, in forming a protective film on the zinc as soon as any zinc surface is exposed by the stripping of all overlying metal layers. It was established that both phosphoric acid and chromic acid are necessary for forming a suitable protective film. Some kind of a complex of zinc chromate and zinc phosphate might explain the remarkable corrosion resistance of the protective film of the present invention.

The stripping bath can be saturated with chromic acid. For example, salts such as potassium dichromate or an anhydride such as chromium trioxide can be added to the bath. The bath preferably contains at least 3% chromic acid. Certain advantages are achieved by keeping the bath at least one-half saturated with chromic acid. Under some circumstances the amazing corrosion resistance was imparted to small amounts of zinc by baths containing approximately 0.1% chromic acid. Although for most convenient operation the lower limit of chromic acid concentration is 3%, the lower limit for some purposes can be set at 0.1% chromic acid.

The bath contains from 30% to 55% of sulfuric acid, which corresponds to about 32.3% to 59.1% of the commercially available 60° Baumé acid. The high concentration of acid is effective in preventing the dissolving of the protective film formed on the surface of the zinc. The water concentration should be kept within the range of from about 20% to 45%, which corresponds to about 15.9% to 35.6% water when the bath is prepared from commercially available phosphoric acid and sulfuric acid. It is particularly important that the water concentration of the stripping bath be kept sufficiently low as to prevent the attack of the acid upon the zinc, inasmuch as the protective film is effective only in the relatively concentrated acid. During the operation of the stripping bath, moisture may be absorbed from the air, or water may enter the bath accidentally by other methods. Concentrated acid should be added to overcome any such dilution.

The bath may contain zinc sulfate up to the solubility limit thereof, together with nickel sulfate, copper sulfate, and chromic sulfate. Salts of nickel, chromium and copper appear in the stripping solution as these metals are removed from the anode and deposited on the cathode. No significant amounts of zinc are deposited on the cathode. Small amounts of zinc are removed at the anode immediately after the zinc is exposed to the acid and before the protective film is formed. Although the zinc sulfate is formed very slowly, the zinc accumulates in the stripping bath. For example, after a stripping bath had been used for several weeks, it would contain measurable amounts of zinc salts. It is sometimes desirable to add salts of chromium, copper, nickel, and especially zinc so that the bath initially will have concentrations thereof approximately equal to those of a bath used for several weeks. A bath might be prepared containing the required concentrations of acids, and then adding approximately 0.1% nickel sulfate, 0.1% copper sulfate and 5% zinc sulfate thereto.

In the operation of the process of the present invention, the articles to be stripped, for example, chromium-plated cigarette lighters, nickel-plated rings, or other articles made from an alloy consisting principally of zinc, and plated with chromium, nickel, copper or mixtures thereof, are made the anode of an electrolytic cell containing a bath having the proportions previously indicated. It is important that the electrical contact to the articles be very secure, inasmuch as a loose connection might decrease the current density below the optimum level.

It is ordinarily desirable to conduct the stripping at a rapid rate, thereby inhibiting the competitive chemical reactions which might produce adverse results. This stripping speed is regulated by controlling such factors as temperature and current density.

The bath should be heated to a temperature between 60° and 190° F., and preferably maintained at a temperature of approximately 180°. Relatively high current

densities are preferred. For example, the current density may be regulated to provide from 1 to 300 amperes per square foot of article surface. In maintaining such current densities, the cell is operated at a potential of at least 2 volts and not more than 40 volts. In the course of stripping multicomponent platings, the current density will vary by reason of the changing composition of the mixture of metals being stripped. Nickel is readily stripped; hence, a higher current density prevails when the operation is removing predominantly nickel.

The passage of the electric current through the bath causes, first the chromium, then the nickel, and finally all of the copper to be electrolytically stripped off the zinc articles and deposited in a loosely adherent condition upon the corrosion-resistance cathode. All of the chromium, nickel and copper are removed from certain portions of the articles prior to the completion of the removal of even the first layer of chromium from other portions of the articles, as a result of the electrical effects attributable to the peculiar shapes of the articles. Almost as soon as any of the zinc is exposed to the bath by the final stripping of the last layer of copper therefrom, and before significant amounts of the zinc are dissolved, a protective coating is immediately formed upon that portion of the zinc by the reaction of the zinc with the phosphate and chromate content of the bath. The electrolytic action occurring at the anode may also assist in the formation of the protective coating but is not essential thereto. Sheet zinc can be immersed in the hot acid bath of the present invention and left immersed for weeks without any corrosion except that resulting during the few seconds during which the protective film is formed on the zinc.

The current is passed through the bath, not merely long enough to remove all of the chromium and nickel, but also long enough to remove electrolytically all of the underlying copper. In removing the plating from test sheets, the current density is moderate during the stripping of the chromium, high during the stripping of the nickel, low during the stripping of the copper, and very low after the stripping of the copper. The protective film renders the zinc so passive that almost no current flows with such an anode. Some oxygen may be evolved from the film-protected zinc, but the zinc is not dissolved even by prolonged electrolytic treatment. It is ordinarily not desirable to unduly prolong the electrolysis after all of the copper has been stripped from the articles, inasmuch as the bath is more profitably utilized in stripping platings from other articles. In the operation of the process of the present invention, the timing of the removal of the articles from the stripping bath is not extremely critical by reason of the effectiveness of the protective film formed upon the zinc articles. In commercial practice, the basket of many articles being stripped can be periodically lifted from the bath, and the completely stripped articles can be removed. Thus visual inspection provides a convenient method for determining the removal of the articles from the stripping bath. The removal of the articles from the stripping bath after the beginning of the evolution of oxygen at the anode expresses the precaution that ordinarily the articles should not continue to serve as anodes in the stripping bath for a period of hours after the removal of the last layer of metal stripped therefrom. In commercial practice, completely stripped zinc articles have fallen from the racks and been immersed for weeks in the stripping bath without adverse corrosion thereof. Although the protective film of chromate and phosphate deposited upon the zinc is effective in inhibiting corrosion so long as the articles are immersed in the bath, the protective film is less effective when the bath-wetted articles are exposed to the air. The film of adhering acid on the articles absorbs moisture from the air, increasing the water concentration in the film sufficiently to bring about galvanic corrosion action. Hence, the articles are promptly rinsed with wash water immediately after being removed from the stripping bath. Because there is so much danger of corrosion of the zinc by delay in adequate rinsing, it is frequently desirable to rinse the articles first in a solution of sodium bicarbonate and then in water. It has been established that good results are obtained by the use of a preliminary rinse solution having a concentration of 8 ounces of sodium bicarbonate per gallon of solution (approximately 1.2 molar) as the preliminary rinse. Other slightly alkaline rinses such as solution of sodium acetate or ammonium carbonate could be employed.

Periodically during the weeks of use of a bath, the cathode is cleaned to remove the loosely adherent mixture of metals, such as chromium, nickel and copper, deposited thereon. The alloy thus deposited is substantially free from zinc.

Example 1

A stripping bath was prepared consisting of chromic oxide, phosphoric acid, sulfuric acid and water, by mixing:

	G.
CrO_3	5
H_3PO_4	20
H_2SO_4	40
H_2O	35

The solution was heated to 180° F. and then placed in a lead-lined tank which was made the cathode of a stripping cell. An assortment of 50 imperfectly plated cigarette lighter parts, originally formed by die-casting an alloy consisting principally of zinc, were securely clipped to wires connected with the positive pole of a source of direct current, The chromium-plated cigarette lighters were immersed in the stripping bath. The cell was then connected with a source of electricity which provided an average of approximately 100 amperes per square foot of article surface. During the course of the stripping the current density varied considerably, dropping nearly to zero at the end. The chromium, nickel and copper were satisfactorily stripped from the imperfectly plated cigarette lighters, and the mixture of metals was deposited in a loosely adherent form upon the lead lining of the tank, which served as a cathode. The articles were periodically inspected after the low current density measurements indicated that most of the copper had been stripped. After the copper was completely stripped, the articles were removed from the stripping bath and promptly rinsed in a spray of a 1.2 M. solution of sodium bicarbonate, and then with a spray of water. The articles were found to be free from any kind of pitholes or other evidences of corrosion, and were dimensionally so nearly the same as zinc articles which had never been subjected to plating and stripping that it was feasible to re-use the articles for first quality merchandise after satisfactory replating. The cost of salvaging imperfectly plated articles was low. The order of magnitude of the cost of removing platings 0.001 inch thick was about four cents per square yard, or about one cent per square foot for 0.002 inch thick platings.

The concentration ranges for the various ingredients were set by determining the operable limits of commercial stripping baths. It was established that the concentration of chromic acid should preferably be within the range from 3% to about one half the saturation value under operating conditions. Alternatively, the stripping bath may be saturated with chromic acid, with an excess or reserve maintaining the saturation. Usually the chromic acid concentration is not in excess of 10%. If very low concentrations such as 0.1% chromic acid are used, frequent additions of the reagent should be made. It was also established that the concentration of the phosphoric acid should be within the range of from 10% to 30%. The concentration of the sulfuric acid should be within the range of from 30% to 55%. Water should be present in a concentration within the range of from 20% to 45%. The values for the commercially available liquid acids correspond to from 32.3% to 59.1% commercial sulfuric acid of 66° Baumé strength, and from 11.8% to 35.3% of 85% phosphoric acid.

The data hereinabove include examples which are used only for purposes of illustration and not of limitation, the invention being defined by the claims.

What we claim is:

1. The process of electrolytically stripping off metal platings of the group consisting of chromium, nickel, copper and mixtures thereof, from articles made of alloys consisting principally of zinc, which includes the steps of: preparing a bath consisting essentially of from 10% to 30% phosphoric acid by weight, from 30% to 55% sulfuric acid by weight, chromic acid in a concentration from 0.1% by weight to saturation, and the balance water; making the articles anodes in said bath; and subjecting the articles to electrolytic stripping to remove all of the

metal platings therefrom and to form a protective film on the zinc effectively protecting the zinc from corrosion during its immersion in said bath.

2. The process of electrolytically stripping off metal platings of the group consisting of chromium, nickel, copper and mixtures thereof, from articles made of alloys consisting principally of zinc, which includes the steps of: preparing a bath consisting essentially of from 10% to 30% phosphoric acid by weight, from 30% to 55% sulfuric acid by weight, a concentration of chromic acid from 0.1% by weight to saturation, and the balance water; making the articles anodes in said bath; passing through said bath an electric current for a period of time sufficient to remove the metal platings, whereby the zinc alloy articles are preserved in an uncorroded condition by reason of a protective film thus imparted to the zinc upon its exposure to the bath by the stripping off of the plating, no significant amount of the zinc alloy being dissolved in the bath; then removing the articles from the bath; and then promptly rinsing the articles.

3. The process of electrolytically removing chromium, nickel and copper platings from alloys made principally of zinc, which process includes the steps of: preparing a bath consisting essentially of approximately 20% phosphoric acid by weight, 40% sulfuric acid by weight, 5% chromic acid by weight, and the balance water; heating the bath to a temperature of 180° F. in a tank having a cathode; making the articles anodes in a stripping cell; passing an electric current through the stripping bath, thereby removing the plating from the articles and forming on the zinc articles a protective film substantially preventing dissolution of said zinc articles; removing the articles from said bath; and then promptly rinsing the articles.

4. The process of claim 1, in which the bath is maintained at approximately 175° F.

5. The method of claim 2 in which the articles are first rapidly rinsed by a solution having an alkalinity and neutralizing equivalency of a solution of approximately 1.2 molar sodium bicarbonate and are then rinsed by water.

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