This invention relates to the prevention of etching of metal articles that are to be chromium plated. Etching of metal articles during plating in chromic acid baths is undesirable because it involves a dissolution of the metal with consequent damage to the metal surface, and it results in the contamination of the plating solution. Sometimes etching produces discoloration of an article, which is a disadvantage wherever the appearance of the plated article is important. Etching is particularly a problem in the plating of articles having recessed or unprotected areas where no chromium is deposited.

It is commonly known that chromic acid chromium plating baths having a high catalyst acid radical content tend to produce etching on unprotected areas which are exposed to the plating solution. For example, in conventional CrO₃-SO₃ bath etching may occur at chromic acid/sulphate ratios of 7:1 and lower, with the etching becoming more pronounced at the lower ratios. When other catalyst acid radicals such as chloride, fluoride or fluoro-containing radicals are used, the tendency to etch is increased. A commonly used fluoride-containing radical is the silicofluoride, as in the well-known CrO₃-SO₃-SiF₆ bath.

A principal object of the invention is to minimize or eliminate the tendency of chromic acid plating baths to etch by providing a method of preparing or pretreating the article to be plated so as to coat it with an etch-resistant film on at least those exposed areas that will not receive any chromium plate. The filmed article is then plated, it having been found that the film so protects the article against the effects of the bath as to reduce or eliminate etching on the areas covered by the film.

Filming of the article is done by immersing it, or at least that portion of it which is to be protected against etching, in an aqueous solution containing about 100 to 1000 g/l. of chromic acid maintained at a temperature of about 50 to 110°F. and substantially free of catalyst acid radicals. A current density in the range of 0.05 to 2 a. s. i. is passed from an anode through the solution to the article as a cathode for a period of time ranging from 0.5 to 10 minutes. In these ranges, higher current densities are used with lower times and CrO₃ concentrations, and vice versa. Preferred filming conditions comprise the use of an aqueous solution of about 300 to 500 g/l., particularly about 400 g/l. of CrO₃ at room temperatures and a current density of 0.1 to 1.0, particularly 0.5 a. s. i. for a time of 2 to 5 minutes. No chromium is plated on the article during this treatment and to ensure that none is plated and that the required film is formed on the article, it is desirable to have the chromic acid solution free of substantially free of catalyst acid radicals. However, in some cases the use of phosphoric acid in amounts ranging from 75 to 300 g/l. in the chromic acid filming solution is desirable.

The filming solution may be conveniently prepared, for example, by dissolving in water ordinary chromic acid of technical grade. If it is known that the chromic acid, from whatever source, contains more than about 0.1% sulfate (the usual amount in the technical grade chromic acid is about 0.1% by weight), the sulfate is removed by chemical precipitation as barium sulfate; and such removal is also done in regard to the filming solution if the sulfate concentration builds up during use. Any other catalyst acid radicals which may be present as impurities are also removed.

The film that is produced on the article may be almost invisible when wet; it may vary from one that is thin and transparent to one that is thicker and has a colored cast, such colors as brown, olive drab, yellow, green, and grey being found. The colored films are usually iridescent. Besides affording protection against etching, the film improves the covering or throwing power in the chromium plating operation. In effect, it acts to extend the current density range of the plating bath. If it is desired, the film may be removed from the article following the plating step, and this may be done, for example, by means of a quick dip in dilute hydrochloric acid, or by an anodic treatment in alkali or chromic acid solution, or by an abrasive action as by wiping on a polishing wheel.

Prior to filming, the article is cleaned by the usual methods and subjected to a conventional anodic treatment, the latter, as is apparent, also being a cleaning step. Then the article is filmed and plated. It is preferred, but not necessary, to perform the anodic treatment and the filming in the same filming solution.

Examples 1, 2, 3, 4 and 5 illustrate how films may be produced, and Examples 2, 3, 4 and 5 show that they are protective; Example 4 further demonstrates the protective nature of the films in terms of weight loss.

Example 1

Three solutions were made up, identified as Nos. 1, 2, and 3, containing, respectively, 100, 300 and 600 g/l. of CrO₃. A flat steel strip 1" x 6" was immersed in each of Nos. 1, 2 and 3 at 80°F. and a current density of 0.05 a. s. i. passed from an anode to the strip as cathode for 5 minutes. The strips were then rinsed, washed, dried, and inspected. The strip from solution No. 1 had no film, that from No. 2 had a very thin, transparent film, and that from No. 3 had a yellowish-green iridescent film. The foregoing tests were repeated using 0.1 a. s. i., and it was found that the strip from No. 1 had a light olive drab iridescent film, that from No. 2 was the same as the latter except that its film was thicker, and that from No. 3 had a dark olive drab film. A repetition of the tests using 0.50 a. s. i. produced strips having olive drab films in the case of Nos. 1 and 2 and a light grey film in the case of No. 3. In another series of tests using 0.05 a. s. i. and a temperature of 110°F., no films were produced on any of the strips, indicating that the higher temperature had decreased the tendency for a film to form. A further series of tests at 110°F. but with 0.10 a. s. i. produced on the strip from No. 1 a very thin, olive drab, iridescent film; on the strip from No. 2 an olive drab, iridescent film; and on the strip from No. 3 an olive drab, non-iridescent film.

Example 2

In another series of tests, steel panels 3" x 4" were filmed on both sides in an aqueous solution of 400 g/l. of CrO₃ at 0.25 a. s. i. for 5 minutes at 85°F., and then plated at 130°F. in a chromium plating solution of the chromic acid-sulfate-silicofluoride type with only one side of each panel facing the anode so that while chromium deposited on the front side of the panel, the back side did not receive any plate but remained exposed to the etching action of the plating solution. Nevertheless, the unplated back side of each panel was not etched and was
thus protected by the film. An unfilmed control panel, plated under identical conditions, became etched on its unplated back side.

**Example 3**

Two solutions, identified as Nos. 4 and 5, were made up containing 200 g./l. of CrO3 and 100 cc. per liter of phosphoric acid, and 400 g./l. CrO3 and 100 cc. per liter phosphoric acid. Ordinary, commercial grade phosphoric acid was used, 100 cc. of which weighed 143.6 g. A steel tube 4%" long x 2%" diameter was immersed in each solution at 75° F. and treated as cathode using a current density of 0.5 a. s. i. for 5 minutes. The surfaces of the tube from No. 4 had a semi-bright metallic appearing film inside and outside, while the tube from No. 5 had a dull olive drab film. When plated in a chromium plating solution of the chromic acid-sulfate-silicofluoride type using only an inside anode for 2 hours at 135° F. and 2 a. s. i., both tubes were plated with chromium on the inside but not on the outside. Although the outside of each tube was exposed to the etching action of the plating solution, it was not etched. An unfilmed control tube, plated under the foregoing conditions, was etched on the outside.

**Example 4**

Two flat steel strips 1" x 6" were immersed for 5 minutes at 80° F. in a chromic acid solution containing 400 g./l. CrO3 and a current density of 0.5 a. s. i. was passed to produce a film on the strips. In a second step, the filmed strips were successively subjected as cathode to the action of a chromium plating solution of the chromic acid-sulfate-silicofluoride type for one hour at 130° F. at current densities of 0.02 and 0.05 a. s. i., respectively. The loss in weight of the strips is tabulated below. For comparison, the losses obtained in treating two identical but unfilmed strips only according to the above second step are also given.

<table>
<thead>
<tr>
<th>Current density, a.s.i.</th>
<th>0.02</th>
<th>0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight loss, grams:</td>
<td>0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>Filmed strip</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Unfilmed strip</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

As is apparent, the filmed strips have very substantially reduced losses compared to the control.

**Example 5**

Two steel panels 3" x 4", one of them filmed using the filming conditions set forth in Example 4 and the other unfilmed, were subjected as cathode to the action of a chromic acid-sulfate type chromium plating bath at 140° F. for 1 hour, using 0.1 a. s. i. The unfilmed panel was etched on both sides while the filmed panel was not etched on either side.

The invention is suitable for articles made of steel, particularly of plain carbon steels of low, medium, and high carbon content, and of steels commonly used in tools. It is beneficial for alloy-treated steels in which the additional element or elements comprises aluminum, copper, chromium, manganese, molybdenum, silicon, titanium, tungsten, vanadium; also for complex alloy special purpose steels in which the alloying element may be manganese, nickel, chromium, tungsten, silicon, molybdenum, vanadium, chrome-nickel, chrome-vanadium, chrome-molybdenum, chrome-tungsten-vanadium, chrome-tungsten, and cast iron. The invention is applicable also to non-ferrous metals like nickel, zinc, copper, brass, and bronze.

In the light of the foregoing description the following is claimed:

1. Method of preventing etching of a metal article to be chromium plated in a chromic acid plating bath containing acid radicals, said bath tending to etch non-plated, exposed areas of the article which comprises immersing at least that portion of the article to be protected against etching in an aqueous solution consisting essentially of 100 to 1000 g./l. of CrO3 for a period of time ranging from 0.5 to 10 minutes and at a temperature ranging from 50 to 110° F., passing current in the range of 0.05 to 2 amperes per square inch from an anode to said article as a cathode during said time, thereby forming an etch-resistant film on the article, said filming step being ineffective to deposit chromium plate on the article, then placing the article in said chromic acid chromium plating bath and plating chromium thereon, said film protecting non-plated exposed areas of the article against etching by said chromic acid plating bath.

2. Method according to claim 1 in which the metal article is a steel article.

3. Method of preventing etching of a metal article to be chromium plated in a chromic acid plating bath containing catalyst acid radicals, said bath tending to etch non-plated, exposed areas of the article which comprises immersing at least that portion of the article to be protected against etching in an aqueous solution consisting essentially of 100 to 1000 g./l. of CrO3 and 75 to 300 g./l. of phosphoric acid for a period of time ranging from 0.5 to 10 minutes and at a temperature ranging from 50 to 110° F., passing current in the range of 0.05 to 2 amperes per square inch from an anode to said article as a cathode during said time, thereby forming an etch-resistant film on the article, said filming step being ineffective to deposit chromium plate on the article, then placing the article in said chromic acid chromium plating bath and plating chromium thereon, said film protecting non-plated exposed areas of the article against etching by said chromic acid plating bath.

4. Method of protecting a metal article against etching during chromium plating of the article in a chromic acid-sulfate-silicofluoride type chromium plating bath that tends to etch non-plated, exposed areas of the article which comprises immersing at least that portion of the article to be protected against etching in an aqueous solution consisting essentially of 300 to 500 g./l. of CrO3 for a period of time ranging from 2 to 5 minutes and at room temperature, passing current in the range of 0.1 to 0.5 amperes per square inch from an anode to said article as a cathode during said time, thereby forming an etch-resistant film on the article, said filming step being ineffective to deposit chromium plate on the article, then placing the article in said chromic acid chromium plating bath and plating chromium thereon, said film protecting non-plated exposed areas of the article against etching by said plating bath.

5. Method according to claim 1 in which the plating bath is of the chromic acid-sulfate type.

6. Method according to claim 1 in which the plating bath is of the chromic acid-sulfate-silicofluoride type.

7. Method of preventing etching of a metal article to be chromium plated in a chromic acid plating bath containing catalyst acid radicals, said bath tending to etch non-plated, exposed areas of the article which comprises immersing at least that portion of the article to be protected against etching in an aqueous solution consisting essentially of 100 to 1000 g./l. of CrO3 for a period of time ranging from 0.5 to 10 minutes and at a temperature ranging from 50 to 110° F., said solution being substantially free of catalyst acid radicals, passing current in the range of 0.05 to 2 amperes per square inch from an anode to said article as a cathode during said time, thereby forming an etch-resistant film on the article, said filming step being ineffective to deposit chromium plate on the article, then placing the article in said chromic acid chromium plating bath and depositing chromium plate thereon, said film protecting non-plated, exposed areas of the article against etching by said chromic acid plating bath.

8. Method of protecting a metal article against etching during chromium plating of the article in a chromic acid plating bath containing catalyst acid radicals, said bath tending to etch non-plated, exposed areas of the article
which comprises immersing at least that portion of the article to be protected against etching in an aqueous solution consisting essentially of 100 to 1000 g./l. of CrO₃ for a period of time ranging from 0.5 to 10 minutes and at a temperature ranging from 50 to 110° F., said solution being substantially free of catalyst acid radicals to help avoid deposition of chromium from said solution on said article, passing current in the range of 0.05 to 2 a. s. i. from an anode to said article at a cathode during said time to form an etch-resistant film but not deposit chromium on said portion of the article during the passage of said current, then placing the filmed article in said chromic acid chromium plating bath and depositing chromium plate thereon, said non-plated filmed portion receiving no plate but being exposed to said plating bath, and recovering the chromium plated article having said non-plated portion in unetched condition with said film thereon.

9. Method of claim 8 in which said article, prior to said film forming step, is cleaned by a conventional anodic cleaning step.

10. Method of claim 9 in which said anodic cleaning step is performed in said aqueous, film forming solution.

11. Method of claim 8 in which, following said chromium plating step, the film on said non-plated portion of the article is removed.

References Cited in the file of this patent

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Inventor</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,774,269</td>
<td>Haueisen</td>
<td>Aug. 26, 1930</td>
</tr>
<tr>
<td>1,815,081</td>
<td>Sohn et al.</td>
<td>July 21, 1931</td>
</tr>
<tr>
<td>1,827,247</td>
<td>Mason</td>
<td>Oct. 13, 1931</td>
</tr>
<tr>
<td>1,953,484</td>
<td>Drebell</td>
<td>Apr. 3, 1934</td>
</tr>
<tr>
<td>2,182,244</td>
<td>Beall</td>
<td>Dec. 5, 1939</td>
</tr>
<tr>
<td>2,623,847</td>
<td>Gilbert</td>
<td>Dec. 30, 1952</td>
</tr>
<tr>
<td>2,635,993</td>
<td>Snively</td>
<td>Apr. 21, 1953</td>
</tr>
</tbody>
</table>

OTHER REFERENCES