

# United States Patent

Shepard et al.

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[54] **ANODIC TREATMENT FOR STAINLESS STEEL**

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[56] **References Cited**

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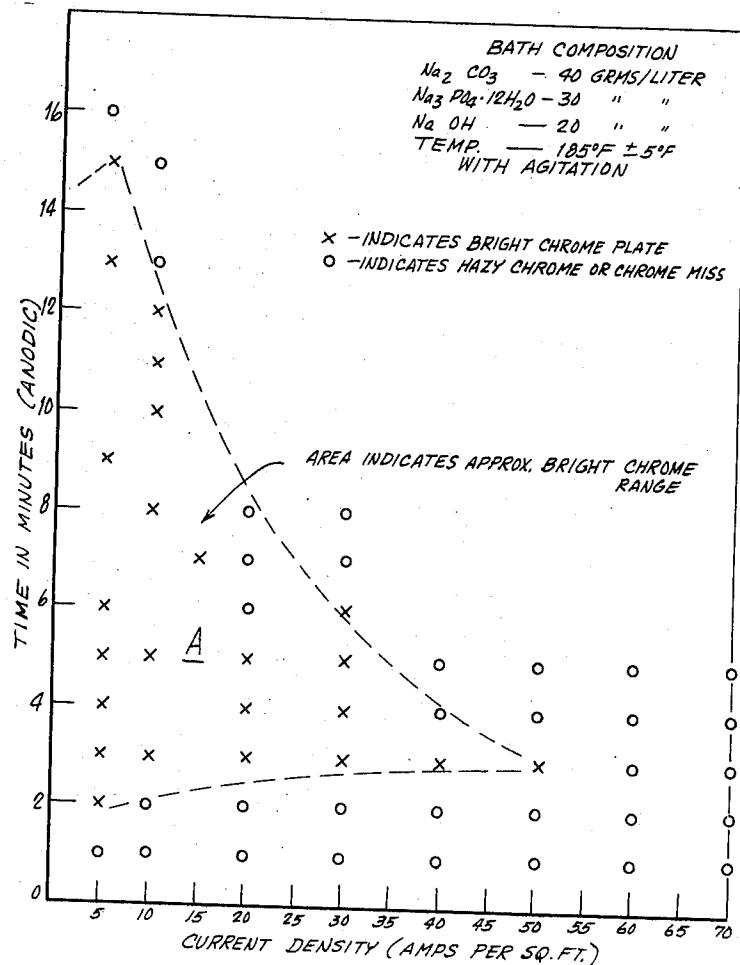
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[57]

## ABSTRACT

A method of treating bright-annealed stainless steel of the AISI-type 400 series. The treatment method is particularly suitable for preparing the steel for subsequent plating with chromium while obviating the need for buffing prior to the chromium plating step. The article is treated in an electrolytic bath maintained above about 180° F. with an electrical current for a time of at least about 1 minute and at a current density which ranges below about 50 amperes per square foot of article surface (current density varies inversely with treatment time). The article is rendered anodic during the electrical treatment, and the bath consists essentially of an aqueous solution of alkali metal hydroxide or hydroxides and an agent or agents of the class consisting of alkali metal phosphates and carbonates so that pH is maintained between about 12 and 13.5.

19 Claims, 2 Drawing Figures



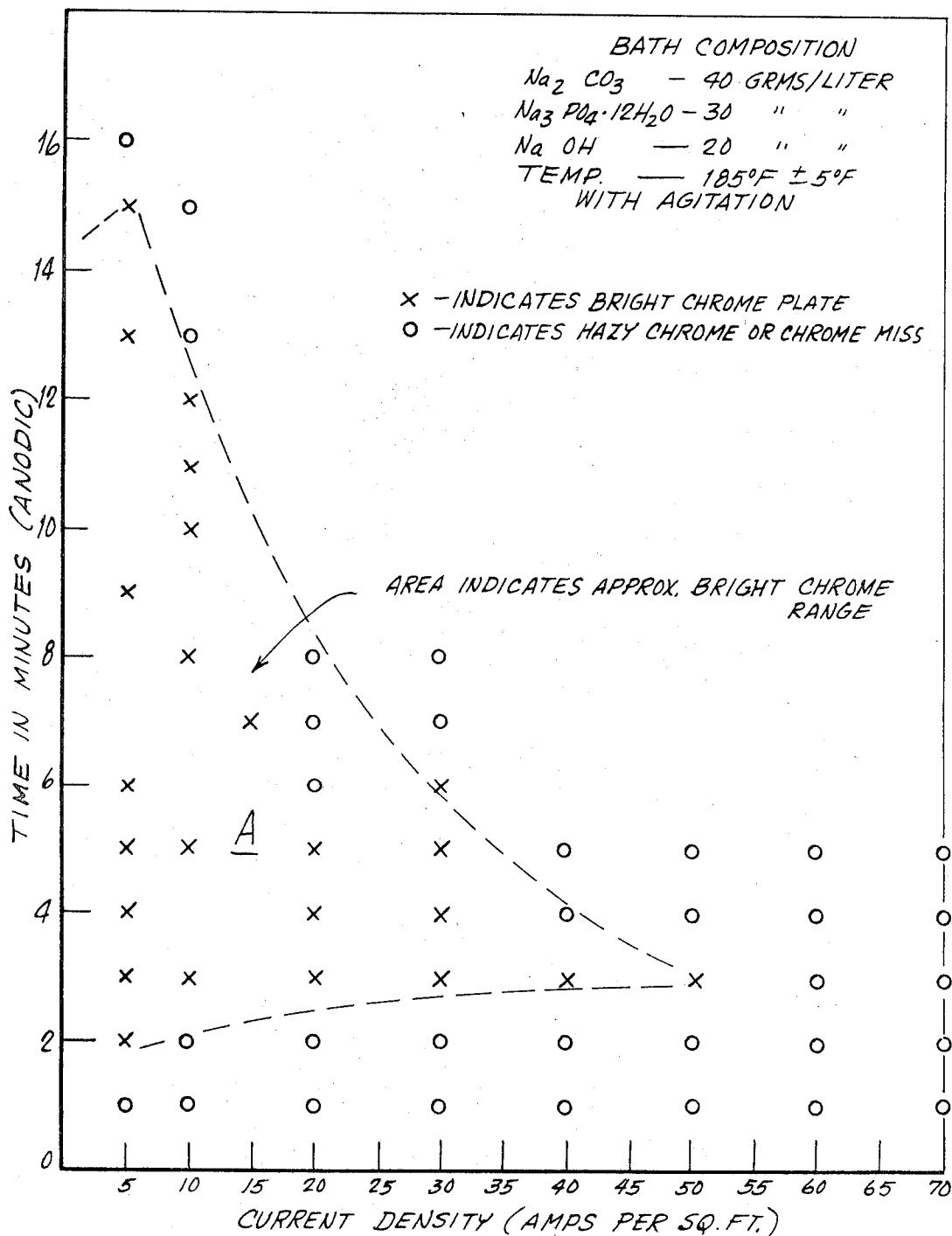


Fig. 1.

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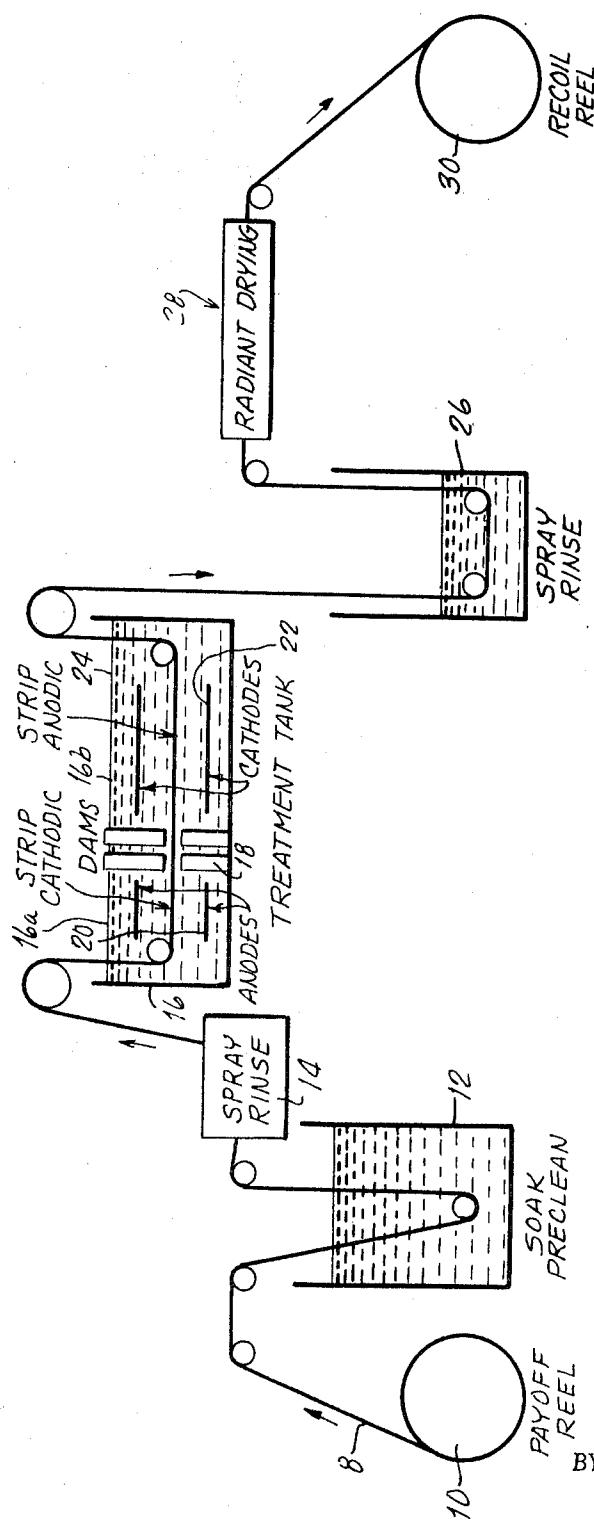


Fig. 2.

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## ANODIC TREATMENT FOR STAINLESS STEEL

## BACKGROUND AND BRIEF DESCRIPTION OF THE INVENTION

This invention relates to the treatment of stainless steel, and particularly to the treatment of bright-annealed stainless steel of the AISI type 400 series. The treatment method disclosed herein is particularly suitable for preparing such steel for subsequent plating with chromium while obviating the need for buffing prior to the chromium plating step. The treatment is also suitable as a replacement for the conventional nitric acid pickle-washing of this type of stainless steel.

There are two methods of annealing stainless steel strip after cold rolling. The first is conventional or open air annealing. In this procedure the stainless steel strip is heated to annealing temperature in air. An oxide scale forms during this procedure, and a subsequent descaling operation is necessary. The usual practice is to remove the oxide scale by acid pickling with or without an electrolytic assist. The pickling is aggressive in its attack on the scale and on the underlying metal and results in a duller surface. After the pickling step the strip is given a further rolling (skin pass) which tempers and brightens the stainless steel. The major drawback of the air annealing and pickling process is that the surface is left deficient in chromium to a depth of several microinches, and the chromium-deficient surface is vulnerable to corrosional attack.

The second method is to anneal the stainless steel in a protective atmosphere which prevents the formation of an oxide scale. The most commonly used atmosphere is hydrogen containing, such as dissociated ammonia. This procedure is known as "bright-annealing" since no oxide scale is formed and the steel surface is left clean and bright (although a very thin mixed oxide film no more than about 150 angstroms thick is formed on the steel surface). The acid pickling step is obviated, and the resultant surface is not deficient in chromium; it therefore has a superior corrosion resistance compared with air annealed stainless steels. A second benefit is that the subsequent skin pass further enhances the specularity of the steel.

Bright-annealed stainless steel AISI type 434 is preferred for automotive trim applications because of its corrosion resistance properties and relatively low cost. Because there are slight but noticeable differences in color from coil to coil of this material, and between it and chromium plated parts, auto trim fabricators often plate the formed trim pieces with a few microinches of chromium. This gives uniform color to all the trim parts. It has been found, however, that when bright-annealed stainless steel of the AISI type 400 series is chromium plated without special treatment of the surface, the chromium deposits have a displeasing dull gray or hazy appearance. To overcome this problem, the bright-annealed surface is usually buffed prior to the chromium plating of that surface. After the buffing operation, the subsequent chromium plating is bright. The problem with buffing the steel prior to chromium plating is twofold: (1) the procedure is relatively expensive and (2) unsightly buffing lines are generally left on the stainless steel strip.

The present invention is directed to the treatment of bright-annealed stainless steel of the AISI type 400 series by which the steel may be plated with chromium, without first buffing the steel and yet retaining the bright appearance of the chromium-plated steel. This is achieved by treating the bright-annealed steel in an electrolytic bath in which the steel is anodic, or at least is anodic during the terminal portion of the treatment. The treatment bath consists essentially of an aqueous solution of alkali metal hydroxide or hydroxides which is buffered to a pH between about 12 and 13.5 with a buffering agent that does not yield an ion which attacks the stainless steel. Conveniently sodium hydroxide may be employed as an alkali metal hydroxide in the solution and the buffering agent may be an alkali metal phosphate or carbonate or both. A suitable electrolytic bath is 2 percent sodium hydroxide (NaOH), 3 percent sodium phosphate, tribasic (Na<sub>3</sub>PO<sub>4</sub>·12 H<sub>2</sub>O) and 4 percent sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). The bath

should be maintained at a temperature of at least about 180° F., and typically about 190° F. It has been found that the anodic treatment should be for a time of at least about 1 minute and practically may range up to about 4 minutes. The current density should range below about 50 amperes per square foot of steel surface, and varies inversely with treatment time. For a treatment time varying from 1 to 4 minutes, the current density varies from about 50 to about 8 or less amperes per square foot of steel surface.

10 The anodic treatment of the steel should be employed with a clean steel surface. If the steel has been soiled prior to treatment, it may be cleaned with any suitable soak-type commercial cleaner, as long as that cleaner is free from silicates. It has been found that cleaners containing silicates are difficult to rinse, and leave a residue which may prevent successful anodic treatment. It has been found that the anodic treatment of the invention is compatible with the conventional nitric acid pickle-washing treatment of stainless steel. The conventional pickle-washing treatment involves passivation of the stainless steel surface, is an electrolytic process and involves bipolar treatment, i.e., periodic reversal of polarity. Generally, no other electrolytic process can be used in conjunction with the anodic treatment of this invention, either before or after the anodic treatment, without affecting the steel surface.

15 The present invention is thus directed to the alteration of the surface properties of the relatively thin (probably between 70 and 150 angstroms thick) and colorless mixed oxide film that the bright-annealing process leaves on steel. This film, 20 whose composition is unknown although it is believed to be composed of approximately 60 to 65 percent oxides of chromium and iron, in about the proportion of these elements in the base metal, with the balance believed to be water of hydration, is to be distinguished from the relatively thick and colored scale composed of iron and chromium oxides that remains on stainless steel after air annealing. Bright-annealed stainless steel of the AISI type 400 series, when treated anodically in accordance with the invention, has been found to 25 remain passive in sulfuric acid (room temperature) virtually indefinitely, while the same steel, bright-annealed but not so anodically treated, has been found to lose its passivity rather quickly.

30 Accordingly, although the invention is particularly directed to the treatment of stainless steel for subsequent chromium plating, nonetheless the present invention is applicable to the passivation of stainless steel not necessarily to be followed by chromium coating. Thus anodic treatment of the present invention may be employed to passivate stainless steel of the 35 AISI type 400 series in place of the conventional nitric acid pickle-washing passivation technique that is now followed.

40 Accordingly, an object of the present invention is to provide for the treatment of bright-annealed stainless steel of the AISI type 400 series.

45 Another object of the invention is to provide for the treatment of such stainless steel specifically to prepare that steel for subsequent plating with chromium and to obviate the need for buffing prior to the chromium plating step.

50 A further object of the invention is to provide a bright-annealed anodically treated article, both with and without a chromium plate.

55 In the prior art, Goldstein et al. U.S. Pat. No. 3,247,086 discloses an electrolytic treatment of stainless steel designed to enhance the corrosion resistance of the steel. The patent is directed to the problem of pit corrosion in particular, and utilizes an anodic treatment carried out preferably in an acid bath. A basic solution such as of sodium hydroxide is disclosed in the patent. It has been found that such a basic solution is unsuitable for the treating of stainless steel, particularly to be subsequently coated with chromium, unless that solution is buffered to a pH between about 12 to 13.5 utilizing a buffering agent that does not release ions during electrolysis that attack the stainless steel surface. Such a buffering of the solution is in 60 no way suggested by Goldstein et al.

Hahn U.S. Pat. No. 2,973,307 is directed to a method of treating stainless steel. The problem of removing oxide scale from air annealed stainless steel is dealt with in this patent, as distinguished from the treatment of bright-annealed steels. Further, Hahn speaks of the buffering of the stainless steel surface, a step which is obviated in the practice of the present invention.

Hammond et al. U.S. Pat. No. 2,776,255 discloses an alkaline and anodic cleaning of steel, utilizing a cleaning solution containing  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_3\text{PO}_4$ . This is a typical alkaline solution electrolytic cleaning operation and is not suggestive of the passivation or prechrome plating anodic treatment carried out in accordance with the present invention, suitable specifically for stainless steels of the AISI type 400 series. The Hammond et al. cleaning solution has been found to have a pH of 11.7, as distinguished from a pH between about 12 and 13.5 as in the present invention.

#### BRIEF DESCRIPTION OF DRAWING

FIG. 1 is a plot of experimental data from beaker tests showing the relationship between anodic treatment time and current density in practicing the invention.

FIG. 2 is a flow diagram of the treatment of a stainless steel strip in accordance with the invention.

#### DETAILED DESCRIPTION

The invention is directed to the treating of stainless steel of the AISI type 400 series, which has been bright-annealed. (In the type 400 series, both 414 and 431 are martensitic-type stainless steels, and are not normally manufactured in sheet or strip form for decorative purposes. These two types would generally not be either bright-annealed or require an anodic treatment for chrome plating, and hence the invention is principally directed to the treatment of the other types of stainless steels within the 400 series.) Bright-annealing leaves a mixed oxide film which is relatively thin and which is between about 70 and 150 angstroms thick. In the event that such steel is not clean, it should be precleaned. Precleaning may be carried out with any conventional soak-type cleaner, as long as it does not contain silicates. Silicate-containing cleaners are difficult to rinse and leave a residue which is inimical to a successful anodic treatment. The bright-annealed stainless steel may also be pretreated by conventional nitric acid pickle-washing. However, pickle-washing may microscopically etch the steel surface, and may be undesirable for that reason. In any treatment, no other electrolytic process other than the conventional pickle-washing treatment just mentioned should be used, inasmuch as the anodic treatment of the invention will be adversely affected.

An electrolytic bath is prepared including an alkali metal hydroxide or hydroxides in aqueous solution. Typically these hydroxides are sodium and potassium hydroxide, to name two of the alkali metals most used commercially out of those alkali metals that constitute Group Ia of the Periodic Table of elements. "Alkali metal hydroxide" thus is intended to mean a hydroxide formed from an alkali metal found in Group Ia of the Periodic Table. Sodium hydroxide has been found to be a suitable alkali metal hydroxide and has been employed in an aqueous solution in a concentration of 20 grams per liter, or 2 percent. A buffering agent is added to the solution to buffer the pH to between about 12 and 13.5. The buffering agent should be one that does not yield an ion which attacks the stainless steel, and thus halogen-containing compounds are to be avoided in particular. The buffering agent typically is an alkali metal phosphate and/or alkali metal carbonate. It has been found that  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$  are suitable in aqueous solution, along with  $\text{NaOH}$ , as specified above, when added respectively in the concentrations of about 40 grams per liter (4 percent) and 30 grams per liter (3 percent).

After the formation of such a solution, a bright-annealed stainless steel article which, if necessary, has been precleaned, as noted above, is scrubbed and rinsed (cold water is

adequate) and then is immersed in the electrolytic bath just described. The bath should be maintained at a temperature above about 180° F. and the steel article should be treated electrolytically. Specifically, the steel article is rendered an electrical anode. Suitable cathode materials have been found to be stainless steel of AISI type 430 or 434. An electrical current is passed between the cathode and the article-anode for a time of at least about 1 minute. The time of treatment may range upwardly from 1 minute, although relatively long treatment times are impractical from a commercial standpoint. It is believed that a suitable range of treatment times is from about 1 to about 4 minutes. The current density varies inversely with treatment time, and is a maximum of about 50 amperes per square foot of article surface for a treatment time of 1 minute. The current density thus ranges downwardly from about 50 amperes, for example, to about 8 amperes or less (a lower current density of 5 amperes has been successfully employed) corresponding to a treatment time of about 4 minutes.

The bath should be agitated during the time that the article within the bath is being electrolytically treated. In the case of stainless steel strip undergoing electrolytic treatment, the movement of the strip through the bath is generally sufficient to provide the necessary bath agitation.

After the anodic treatment, as noted above, the article may be rinsed in water and then dried. As has been noted above, the surface of the anodically treated article is passivated by the treatment. Thus this treatment may serve as a replacement for the conventional nitric acid pickle-washing electrolytic treatment commonly used in the processing of stainless steels of the AISI type 400 series. However, the anodic treatment of the present invention is particularly suitable for the subsequent plating of the steel with chromium, and is generally done in the case of automotive trim. Chromium metal is generally deposited electrolytically (cathodic coating) through the use of a solution containing 33 ounces per gallon of chromic acid ( $\text{CrO}_3$ ) in combination with a sulfate that provides a sulfate ion ( $\text{SO}_4^{2-}$ ) so that the following ratio is achieved:  $\text{CrO}_3 : \text{SO}_4 = 100 : 1$ . Typically 10 to 20 microinches of chromium are coated on the anodically treated steel utilizing a current density of about 1 ampere per square inch of surface for a treatment time of about 3 minutes. The chromium coating of the anodically treated steel may take place immediately after the anodic treatment or following a time lapse of days or even months following such anodic treatment.

As has been noted above, the anodic treatment of the present invention obviates the need for buffing the bright-annealed stainless steel surface prior to the chromium plating operation. The specularity or brightness of the chrome-coated article, anodically treated and not buffed, is excellent, and no buffing lines, of course, are evident inasmuch as buffing is eliminated. It has been found that for any given current density or any given treatment time in the anodic treatment, the specularity of the subsequent chromium-plate increases with total coulomb treatment until optimum brightness is achieved over a range of coulomb treatments. Prolonged treatment beyond this range renders the steel surface too passive to accept a chromium plate, and thus a steel article which has been

"over treated" usually contains "spotty" chromium. To explain, for any given current density (or treatment time), as the time (or current density) of treatment increases the brightness of the subsequently chromium-coated product varies from a noticeably hazy appearance uniformly through less haziness in appearance ultimately to optimum or uniform brightness that is achievable over a range of treatment times (or current densities). Once this range of treatment times (or current densities) is exceeded for this particular current density (or treatment time), the platability of chromium on the anodically treated surface is adversely affected.

It has been found that a minimum treatment time of about 1 minute is required to avoid a hazy appearance of the chromium-coated product. For a treatment time of about 1 minute, the current density in amperes per square foot may be about 50 amperes. Any greater current density will result in a

product for which chromium platability is nonuniform; a lesser current density results in a somewhat hazy appearing product. As the treatment time increases over 1 minute, the current density is lowered from 50 amperes to provide a resultant bright chrome-coated product. For any treatment time (or current density) there is generally a range of current densities (or treatment times) for which the resultant chrome-coated product will be bright and not hazy in appearance and yet exhibit uniform chromium platability. For any commercial process, it is desirable to retain the treatment time as small as possible. However, it should be noted that, as the treatment time approaches the limit of 1 minute, the variation possible in current density is slight in order to still achieve a bright chromium-coated product. Steel strip has been successfully coated in accordance with the invention moving through a solution and electrolytically anodically treated for a treatment time of about 73 seconds. However, individual samples of steel have been successfully anodically treated for a treatment period of about 8 minutes and a current density of about 3.7 amperes per square foot of substrate.

The range of current densities permissible for any given treatment time (and the range of treatment times for any given current density) may vary as to different stainless steel types, and may also vary as to different heats of the same type of stainless steel. It has been found that, using the NaOH,  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$  solution specified above, the treatment time may vary from about 1 to 4 minutes, and current density from about 48 to 8 amperes per square foot, and consistently good results will be obtained, particularly for AISI type 434 stainless steel. What is essential is that total coulomb treatment be greater than that resulting in a hazy chrome-coated product and less than that resulting in a poorly platable chrome coating. The appropriate range may be easily determined.

FIG. 1 is a plot of experimental data showing the relationship between anodic treatment time and current density. It will be noted that the range is rather broad at lower current density values; at current densities in excess of 50 amps per sq. ft., hazy chrome plates were obtained. The area designated A is generally the range within which acceptable (bright) chrome plates are obtained. It should be noted that the area A is approximate. Some of the plates that fall outside the area might be acceptable, depending on specularity desired. There may be variations from coil to coil; the particular data in FIG. 1 are from one coil. The test samples were done in beaker tests; some variations in treatment have been found when strip is done on a continuous basis.

As has been noted above, the temperature of the electrolytic solution used for the anodic treatment of the present invention should be maintained at above about 180° F. For temperatures less than about 180° F., the resultant chrome coating following such treatment has evidenced a hazy appearance.

As noted above, the pH of the solution should be maintained between about 12 and 13.5. Pure caustic solutions, such as those suggested by Goldstein et al. in the patent noted above, are considerably more basic and do not provide a suitable passivation of the stainless steel surface. If the solution is too basic, i.e., pH above about 13.5, the stainless steel surface plates hazy or becomes so passive that it will not accept a chrome plate. On the other hand, if the coating solution tends toward acidity, i.e., its pH is less than about 12, the chrome plate is hazy and streaked.

As noted above, the electrolytic treatment solution utilizes an alkali metal hydroxide. The hydroxides formed from elements of Group Ia of the Periodic Table of Elements are believed eminently suitable, particularly sodium hydroxide and potassium hydroxide from the standpoint of commercial availability. The concentration of NaOH may range from about 1 to 3 percent. As to the buffering agent, to maintain pH at a level between about 12 and 13.5, sodium phosphate (tribasic) and sodium carbonate have been specifically employed with sodium hydroxide. The ranges of concentrations

may be 2 to 6%  $\text{Na}_2\text{CO}_3$  and 1.5 to 4.5%  $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ . Any of the alkali metal phosphates and/or carbonates are believed suitable. For example, potassium carbonate and potassium phosphate are believed useful as buffering agents.

5 The bath is operable over a wide range of concentrations as long as the pH remains between about 12 and 13.5. From actual concentration values the bath can operate at approximately one-half the original concentration or double the concentration.

10 With respect to the electrolytic bath, the solution should be such as not to liberate ions that attack the stainless steel surface or the bright-annealed film on the surface. Although the electrolytic action is not exactly known, the response of the bright-annealed film to its environment is changed by this action. There is believed to be some buildup of the bright-annealed film during the electrolytic anodic treatment of the present invention. It is believed that oxygen liberation at the surface of the steel article is involved in the electrolytic action, and hence substances which release such oxygen (and yet do not release ions which attack the steel surface) would be suitable in the practice of the invention.

#### EXAMPLE

25 Samples of AISI type 434 bright-annealed stainless steel of a configuration  $9 \times 2 \times 0.020$  inch were placed in a solution of pH 13.5 (4%  $\text{Na}_2\text{CO}_3$ , 3%  $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$  and 2% NaOH) of approximately 4 liters and electrolytically treated, with bath agitation and with the samples rendered anodic. Following the 30 anodic treatment, the samples were chromium plated with chromium metal by cathodic electrolytic deposition in a solution of 33 oz./gal.  $\text{CrO}_3$  and 0.3 oz./gal.  $\text{SO}_4^{2-}$  ion, to give a ratio of 100:1.  $7 \times 2 \times 10$  to 20 microinches of chromium were plated, utilizing a current density of 1 amp/in.<sup>2</sup> and a treatment 35 time of 3.0 min. The plating bath temperature was 125° F.

The following table gives the effect of temperature variations on specularity of the chromium-plated articles for varying current densities and treatment times. The need to maintain temperature above about 180° F. is apparent.

TABLE 1

Temp., ° F.	Current density, amps./ft. <sup>2</sup>	Treatment time, minutes	Coulomb treatment	Specularity after Cr plating
45	100	3.7	8	1,776 Hazy.
	120	3.7	8	1,776 Hazy/with streaks.
	140	3.7	8	1,776 Slight haze.
	160	3.7	8	1,776 Very slight haze.
	180	3.7	8	1,776 Excellent.
	200	3.7	8	1,776 Do.
50	100	3.7	4	888 Very hazy.
	120	3.7	4	888 Hazy.
	140	3.7	4	888 Do.
	160	3.7	4	888 Do.
	180	3.7	4	888 Excellent.
	200	3.7	4	888 Do.
55	100	7.2	8	3,456 Hazy.
	120	7.2	8	3,456 Do.
	140	7.2	8	3,456 Slight haze.
	160	7.2	8	3,456 Very slight haze.
	180	7.2	8	3,456 Excellent.
	200	7.2	8	3,456 Do.
60	100	7.2	4	1,728 Very hazy.
	120	7.2	4	1,728 Hazy.
	140	7.2	4	1,728 Do.
	160	7.2	4	1,728 Slight haze.
	200	7.2	4	1,728 Excellent.

Samples of bright annealed type 434 stainless steel from different coils were cut into  $2 \times 8$  inch samples and given an 65 anodic pretreatment for chrome plating (8 amps/ft.<sup>2</sup>, 4 minutes in 40 g./l.  $\text{Na}_2\text{CO}_3$ , 30 g./l.  $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ , 20 g./l. NaOH at 180° F.). The chrome plating was done immediately after the treatment. The results were as follows:

Sample No.	Chrome plate
1	Bright
2	Bright
3	Bright
4	Bright
5	Bright
6	Bright

The effect of pH on the chrome platability of anodically treated 434 stainless steel is demonstrated by the following table. All samples were treated anodically in a treatment solution as described above for 5 minutes at 10 amps per square foot with a bath temperature of 180° F.

TABLE II

The Effect of pH on the Chrome Platability of Anodically treated 343 Stainless Steel

Treatment bath pH	Chrome Plate
11.0	Hazy
11.5	Slight haze
12.0	Excellent
12.5	Excellent
13.0	Excellent
13.5	Excellent
>13.5	Hazy, streaks, chrome miss

It is apparent that pH should range between about 12 and 13.5 for good specularity.

Continuous Plating of Strip

FIG. 2 is a flow diagram illustrating the treatment of a stainless steel strip 8 in accordance with the invention. The strip is typically stored on a payoff reel 10 and is then transported through a soak-precleaning operation designated 12. After the soak-precleaning, the strip is spray rinsed as indicated at 14. After spray rinsing, the strip is passed through a treatment tank 16 which may be advantageously divided into two sections 16a and 16b through the use of conventional dam structure 18. An anode structure 20 and a cathode structure 22 are respectively located within the sections 16a and 16b of the treatment tank, and each structure may be positioned on both sides of the steel strip within the respective tank sections to achieve electrolytic treatment of one or both sides of the strip. The treatment tank is filled with an electrolytic solution 24 of the type described above in practicing the present invention. 40 The strip exits from the treatment tank and is given a spray rinse in section 26, is then dried in a drying section 28, and is finally recoiled on a recoil reel 30.

Within the treatment tank 16 positive current flows from the anode structure 20 to the strip 8 and thence through the 45 strip to the cathode structure 22. The dam structure 18 prevents any substantial current from flowing directly from anode structure 20 to cathode structure 22. Thus the stainless steel strip is treated cathodically in the first treatment section 16a and is then treated anodically in the second treatment section 16b. It should be noted that the present invention involves the anodic treatment in the second section 16b of the treatment tank. The procedure of first cathodically treating and then subsequently anodically treating is employed so that no direct electrical connection need be made to the stainless steel strip, thereby avoiding any arcing that might take place between strip and electrical connections thereto. It has been found that the ratio of cathodic to anodic treatment should range between about 1:2 and 2:3 in order to produce a bright 50 chromium plate on the steel strip. The ratio may be defined as the length (in the direction of strip movement) of the strip 8 within the tank section 16a (when it is cathodic) to the length of the strip within the tank section 16b (when it is anodic). The effect of the cathode-to-anode ratio is given in the following table:

TABLE III.—THE EFFECT OF THE CATHODE TO ANODE RATIO ON THE CHROME PLATABILITY OF ANODICALLY TREATED MATERIAL

Current density, amps/sq. ft.	Chrome plate appearance cathode to anode ratio (strip)					
	1:1	2:3	1:2	1:3	1:4	1:5
8	Hazy	Hazy	Hazy	Hazy	Hazy	Hazy
12	do	do	do	do	do	do
18	do	Slightly hazy	do	do	do	do

TABLE III.—THE EFFECT OF THE CATHODE TO ANODE RATIO ON THE CHROME PLATABILITY OF ANODICALLY TREATED MATERIAL.—Continued

24	do	Slightly hazy	do	do	do	do
30	do	Bright	Bright	do	do	do
36	do	Slightly hazy	do	do	do	do

It was found that discoloration of the steel surface sometimes resulted from bipolar operation as in FIG. 2. Reducing the width (the dimension in a direction transverse to strip movement) of the cathode structure 22 reduced discoloration. The reduction in discoloration is believed to be due to a more uniform current density across the width of the strip when a 15 narrower cathode structure is used (less edge effect).

EXAMPLE

A tank 63 inches wide by 27 feet, 2 inches long by 14 inches deep was employed as treatment tank 16. A double dam 18 with sheet neoprene curtains was used between the anode and cathode sections. The anodic treatment length was 139 inches and the cathodic treatment length was 69.5 inches (strip polarity). Five electrodes were used above and below the strip. The tank was lined with 6-mil thick polyethylene sheet. 20 The solution 24 comprised 300 pounds  $\text{Na}_2\text{CO}_3$  (4%), 225 pounds  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (3%), and 150 pounds  $\text{NaOH}$  (2%). The treatment temperature was 190° F. and the solution was heated with steam. A 25-inch wide coil of Type 434 bright annealed stainless steel was run at a line speed of 9 feet per minute; the anodic treatment time for strip speed and anodic treatment length given was thus slightly over 1 minute. A current density of 30 amps per sq. ft. was maintained on the anodic side (section 16b) of the double dam. After treatment 25 the strip was rinsed, hot air dried, and coiled with interleaved paper.

Samples were cut from the front and back of each coil and were chrome plated. Both top and bottom sides of the treated coil plated bright.

We claim:

1. A method of preparing a bright-annealed stainless steel article of the AISI type 400 series for subsequent plating with chromium and obviating the need for buffing prior to the chromium plating step, comprising treating the article in an electrolytic bath which is maintained above about 180° F. with an electrical current for a time sufficient to provide a total coulomb treatment that renders the article bright plateable with chromium without requiring buffing, the total coulomb treatment being greater than that which results in a hazy chromium coating and less than that which results in a poorly adherent chromium coating, with the article being rendered anodic during said electrical treatment, and with said bath consisting essentially of an aqueous solution of alkali metal hydroxide or hydroxides and an agent or agents of the class consisting of alkali metal phosphates and carbonates, at a pH between about 12 and 13.5.

2. A method of treating a bright-annealed stainless steel article of the AISI type 400 series, comprising treating the article in an electrolytic bath maintained at a temperature above about 180° F. with an electrical current of no more than about 50 amperes per square foot of article surface for a time of at least about 1 minute, with current density varying inversely with treatment time, with the article being rendered anodic during such electrical treatment and with said bath consisting essentially of an aqueous solution of alkali metal hydroxide or hydroxides buffered to a pH between about 12 and 13.5 with a buffering agent that yields no ion which attacks the stainless steel.

3. A method of preparing a bright-annealed stainless steel article of the AISI type 400 series for subsequent plating with chromium and obviating the need for buffing prior to the chromium plating step, comprising treating the article in an electrolytic bath which is maintained above about 180° F. with an electrical current of no more than about 50 amperes per square foot of article surface for a time of at least about 1 minute, with current density varying inversely with treatment

time, with the article being rendered anodic during said electrical treatment, and with said bath consisting of essentially of an aqueous solution of alkali metal hydroxide or hydroxides and an agent or agents of the class consisting of alkali metal phosphates and carbonates, at a pH between about 12 and 13.5.

4. A method according to claim 3, in which the solution includes about 30 grams per liter of  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  and about 40 grams per liter of  $\text{Na}_2\text{CO}_3$ .

5. A method according to claim 3, in which the electrolytic bath includes by weight about 4% of  $\text{Na}_2\text{CO}_3$ , about 3%  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  and about 2%  $\text{NaOH}$ .

6. A method according to claim 3, in which the electrolytic bath is agitated during the electrical treatment.

7. A method according to claim 3, in which the article is cleaned in a soak-type cleaning solution free from silicates prior to said electrolytic treatment.

8. A method according to claim 3, in which the temperature of the bath is about 190° F.

9. A method according to claim 3, in which the PH of the electrolytic bath is about 13.0.

10. A method according to claim 3, in which the steel article is steel strip which is moved through the bath, the movement of the strip through the bath providing agitation of the bath.

11. A method according to claim 3, in which the electrolytic bath is a solution of  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , and  $\text{NaOH}$  respectively in concentrations of about 40, 30 and 20 grams per liter.

12. A method according to claim 3, in which the article is a

strip of steel which is moved through a treatment tank divided into two sections, the first section being one in which the strip moves past an anode structure, and the second section being one in which the strip moves past a cathode structure, such that the strip is rendered cathodic with respect to the anode structure in the first section and is rendered anodic with respect to the cathode structure in the second section, and with the ratio of cathodic-to-anodic treatment of the strip ranging between about 1:2 and 2:3.

13. A bright-annealed anodically treated article produced by the method of claim 3.

14. A method according to claim 3, in which the alkali metal hydroxide is  $\text{NaOH}$ .

15. A method according to claim 14, in which the concentration of  $\text{NaOH}$  in solution is about 20 grams per liter.

16. A method according to claim 3, in which the anodically treated article is subsequently plated with a chromium coating.

17. A bright-annealed anodically treated and chromium-plated article produced by the method of claim 16.

18. A method according to claim 3, in which the electrical treatment time ranges from about 1 minute to about 4 minutes.

19. A method according to claim 18, in which the current density ranges from about 50 amperes per square foot of article surface, corresponding to a treatment time of about 1 minute, to about 8 amperes per square foot of article surface, corresponding to a treatment time of about 4 minutes.

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