March 22, 1932. W. A. TYRRELL 1,850,426

PROCESS FOR ELECTRODEPOSITING CHROMIUM AND THE LIKE

Filed July 15, 1926 5 Sheets-Sheet 1

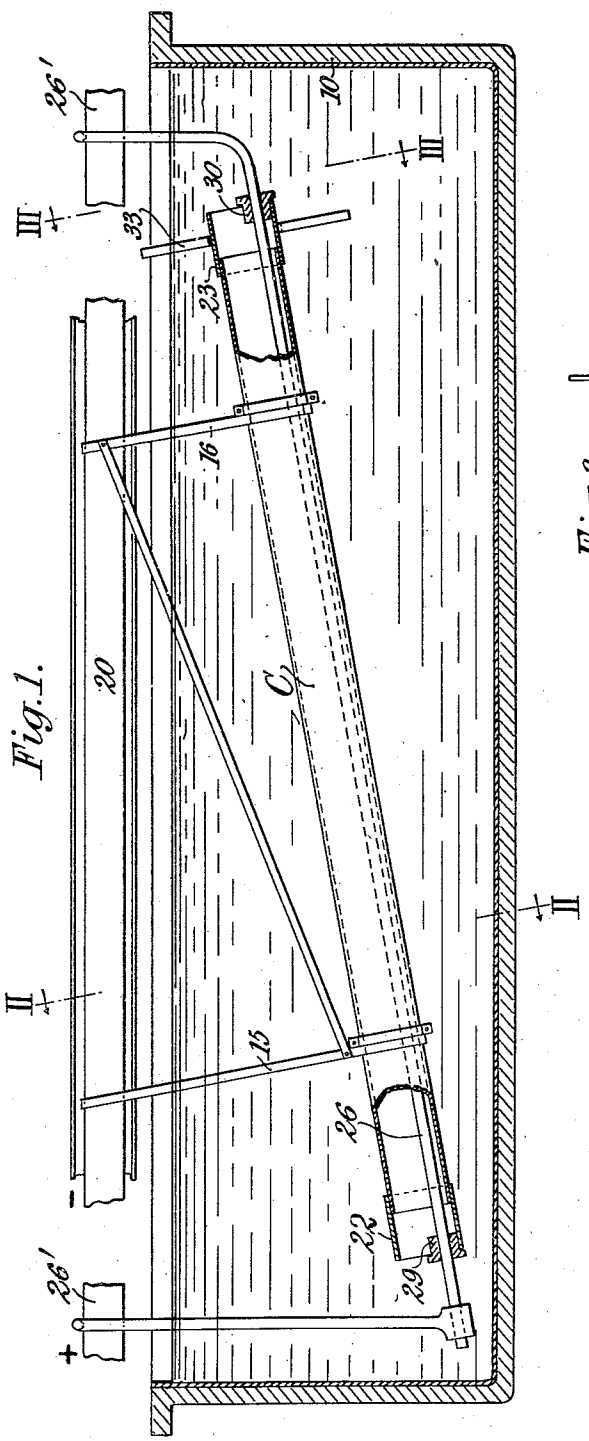


Fig. 1.

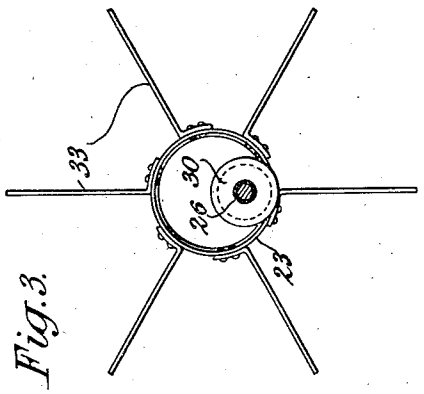


Fig. 3.

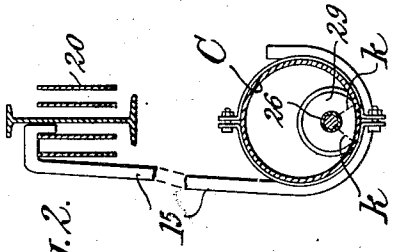


Fig. 2.

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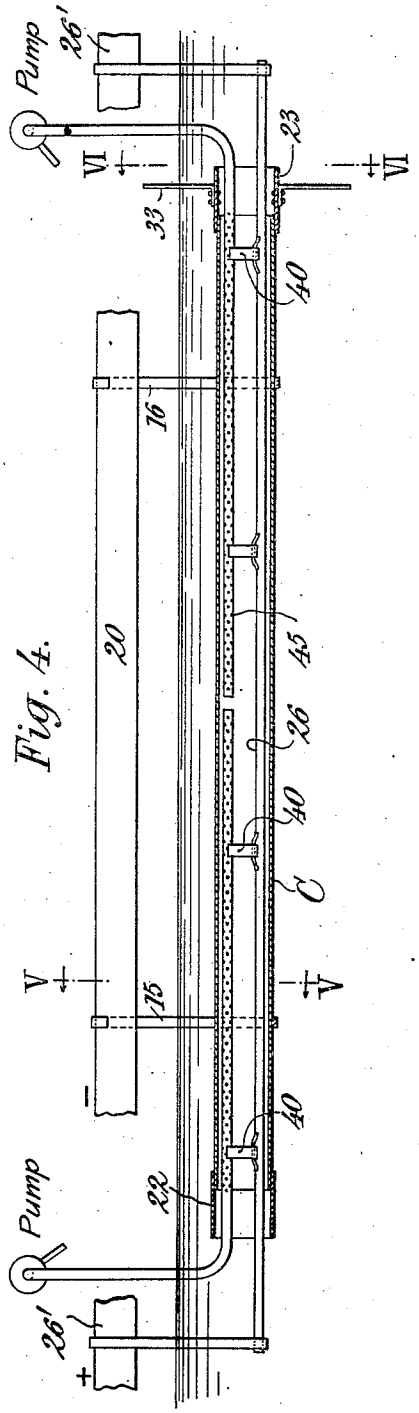


Fig. 4.

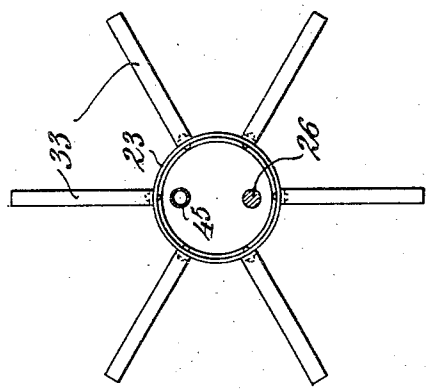


Fig. 6.

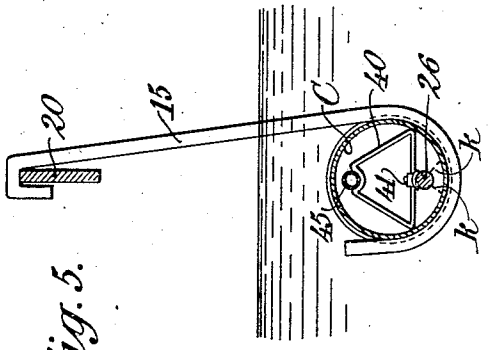


Fig. 5.

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PROCESS FOR ELECTRODEPOSITING CHROMIUM AND THE LIKE

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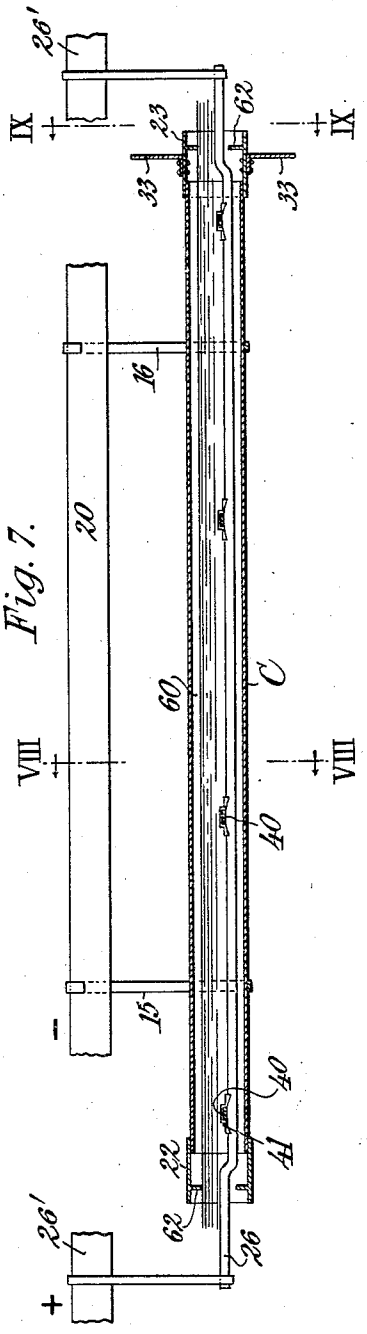


Fig. 7.

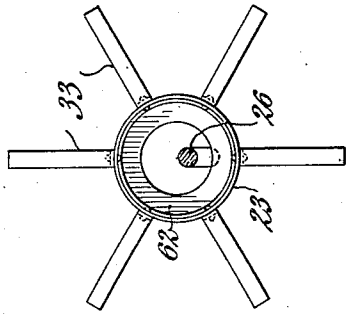


Fig. 9.

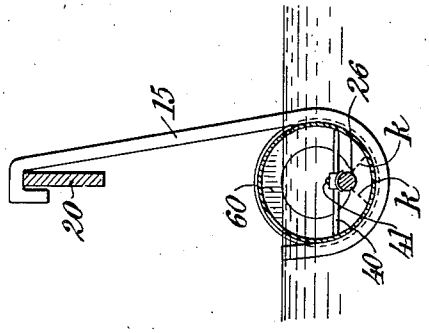


Fig. 8

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Fig. 10.

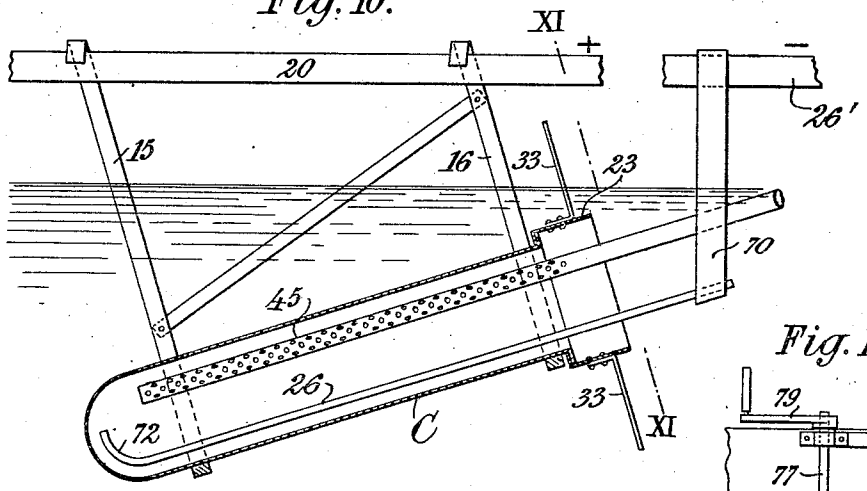


Fig. 12.

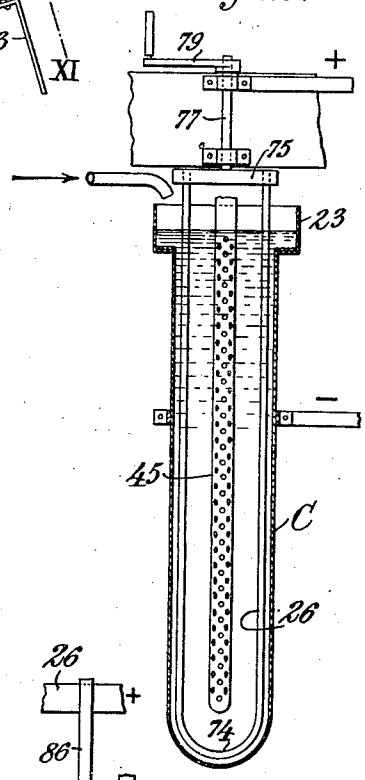


Fig. 11.

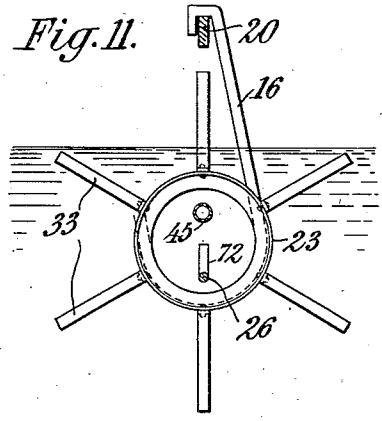
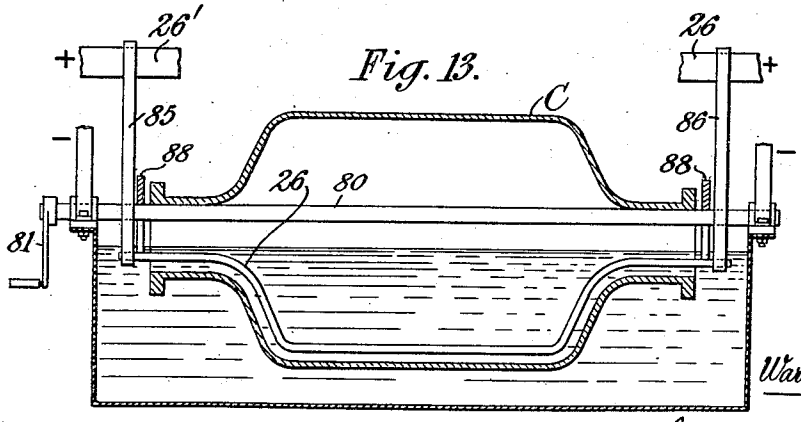


Fig. 13.



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PROCESS FOR ELECTRODEPOSITING CHROMIUM AND THE LIKE

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Fig. 14.

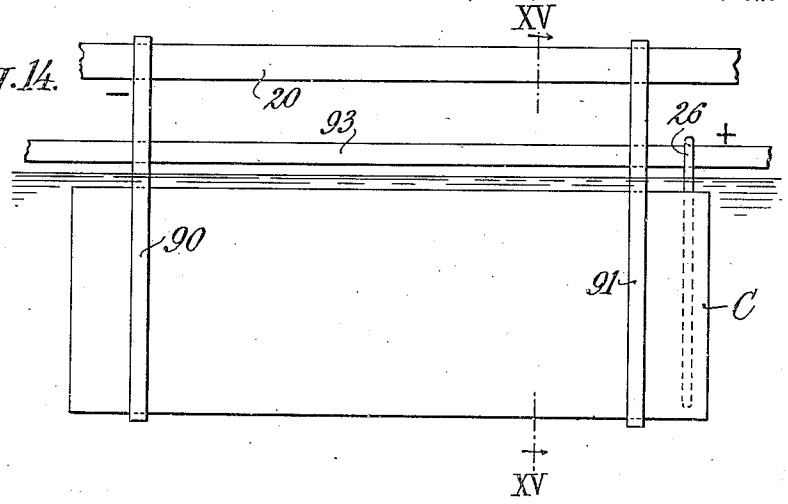


Fig. 15.

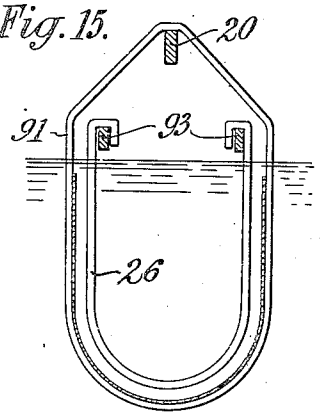
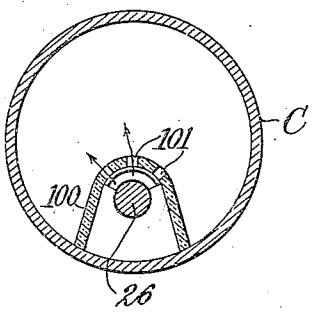


Fig. 16.



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UNITED STATES PATENT OFFICE

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PROCESS FOR ELECTRODEPOSITING CHROMIUM AND THE LIKE

Application filed July 15, 1926. Serial No. 122,513.

This invention relates to electrodepositing chromium or the like on the interiors of vessels, tubular articles, pipes and the like, and to apparatus therefor. It further relates to a process and apparatus for electrolytic cleaning.

The invention provides a convenient, practical, and effective process of electrodepositing chromium or the like on the interior of vessels, tubes, pipes, and the like, and particularly upon the interiors of elongated articles; it also provides an improved process and apparatus for effecting electrolytic cleaning.

The accompanying drawings illustrate several modes of carrying the process into practice.

Figure 1 is a longitudinal sectional view through a plating tank, showing one mode of carrying out the process.

Fig. 2 is a cross section on the line II—II, Fig. 1.

Fig. 3 is a detail view, looking at one end of the apparatus in the direction of the arrows III—III, Fig. 1.

Fig. 4 is a view similar to Fig. 2, showing a longitudinal section of a chromium plating tank, and showing another mode of carrying the process into practice.

Figs. 5 and 6 are detail views, Fig. 5 being a section on the line V—V, Fig. 4, and Fig. 6 being an end view looking in the direction of the arrows VI—VI, Fig. 4.

Fig. 7 is a longitudinal view through the chromium plating tank, and illustrating a third mode of applying the process.

Figs. 8 and 9 are detail views, Fig. 8 being a section on the line VIII—VIII, Fig. 7, and Fig. 9 being an end view looking in the direction of the arrows IX—IX, Fig. 7.

Fig. 10 is a longitudinal sectional view through a chromium plating bath, and illustrates a mode of carrying the invention into practice somewhat similar to that illustrated in Fig. 1, the object being a tube closed at one end. Fig. 11 is a cross-sectional view on line XI—XI, Fig. 10.

Fig. 12 is also a longitudinal sectional view through a chromium plating bath and illustrates a mode of carrying the invention into practice similar to that illustrated in Fig. 10.

Fig. 13 is a longitudinal sectional view through a chromium plating bath and illustrates a mode of carrying the invention into practice somewhat similar to that illustrated in Fig. 7.

Fig. 14 is a longitudinal sectional view through a chromium plating bath, and illustrates a fourth mode of carrying the invention into practice.

Fig. 15 is a cross-sectional view on the line XV—XV, Fig. 14.

Fig. 16 is a detail view illustrating a shield between the anode and portions of the cathode.

According to the present invention, the article to be plated, as for example a long pipe or tube such as shown in Figs. 1 to 9, inclusive, or a vessel, as shown in Figs. 13 and 14, or a tube closed at one end, as shown in Figs. 10 and 12 has a suitable plating solution introduced into the inside thereof. The process of electrodeposition will be described with particular reference to chromium plating, though the process may be used to advantage in plating such metals from baths where relatively large quantities of hydrogen are evolved, and where current densities of considerable amount are required before plating is initiated or is effective. The solution is most conveniently introduced into the article by supporting the object horizontally or slightly inclined, immersed, or partially immersed, in the solution in a long tank. The article itself may however in some cases be made to serve as a tank, as shown in Fig. 12.

The plating solution is preferably a solution of chromic acid containing sulphate radicals as a catalyst, as described in the Fink Patent No. 1,581,188, granted April 20, 1926, and the plating is carried on according to the conditions as to temperatures, current density, etc. described in said patent.

The anode is placed lengthwise of the article, on the inside thereof, and the article is made cathode by suitable connections.

A current of sufficient density to deposit chromium is passed from the anode to the cathode, and the relatively large volume of

hydrogen which is evolved is removed in a suitable manner. This removal may be effected by inclining the cathode article in the bath, as illustrated in Fig. 1, in such manner that the hydrogen flows by gravity through the upper end of the article. Where the article is open at both ends, a circulation is induced which assists in the removal of the hydrogen. The removal of the hydrogen may also be effected by placing a pipe inside of the article and drawing off the hydrogen from one or both ends. The hydrogen may be drawn off through the pipe, or the pipe may be used to introduce solution into the article and force the hydrogen out at any desired rate. The article may be horizontal, or inclined to any desired extent.

Hydrogen may also be removed by so immersing the article in the bath or filling the article that a space is left above the level of the bath, to which the hydrogen may escape, and in which space it may flow to an outlet or point of escape.

In long articles where the disengagement of hydrogen gas would be excessive, the electrodeposition is preferably effected along a longitudinal strip, whereby the plating is effected progressively, and not all at once.

Where the plating is effected progressively in longitudinal strips, the portions of the surface which are as yet unplated are protected from oxidation, so that when plating later takes place thereon, the chromium plate will adhere, and an integral adherent plate produced all around the inside of the article. This protection is afforded by covering the unplated surfaces with the bath solution, as by wetting or by complete immersion, or by hydrogen. Where the unplated surface is to be protected by the hydrogen, its escape is preferably retarded.

A current of appropriate density for electrodepositing chromium along a strip may be effected by locating the anode closer to the strip of surface to be plated than to the other portions of the surface, or by shielding the anode from the other portions of the surface, or otherwise. Moreover, it is preferable to shield the anode from the portions of the cathode on which plating is not being effected at the time, in order to conserve current, inasmuch as all that part of the current flowing to the cathode below the necessary current density for electrodepositing chromium, is ineffective and therefore lost.

On inside surfaces cleaning is frequently very difficult. A strong cleaning action, resulting in excellent cleaning may be effected by concentrating the current at portions of the surface and effecting a progressive cleaning, the apparatus being similar to that described for plating, and an acid bath, preferably concentrated sulphuric acid used instead of the plating solution. The article is made cathode.

Referring to the illustrated examples of the process and apparatus, and first to Fig. 1, numeral 10 designates a tank containing suitable chromium plating solution (such for example as described in the Fink patent referred to above), and the cathode article, here shown as a long pipe C, is immersed in the bath, and suspended in an inclined position by means of suitable hangers 15, 16, these hangers conveniently making connection with a cathode bus bar 20, which thereby places said bus bar and cathode article in electrical connection. Sleeves or other suitable extensions 22, 23 are preferably placed on the ends of the pipe or article, this having been found to insure good plating at the ends of the pipe or article.

The anode, conveniently in the form of a long rod 26, is passed through the pipe, and its ends conveniently supported as by means of insulating rollers 29, 30, or porcelain for example, bearing on the ends of the pipe, or the pipe extensions, and thereby permitting of the pipe to be turned without changing the position of the anode. 26′ designates an anode bus-bar.

The cathode C preferably has thereon means for progressively turning it on its longitudinal axis, as for example a series of radial arms 33, which are conveniently attached to one of the extensions 23. The hangers 15, 16 permit of the cathode pipe turning therein.

In very long articles, the hydrogen gas released in plating the entire inside of the pipe under ordinary conditions would be so great as to prevent the deposition of chromium at and toward the ends of the pipe, and even where means were provided for carrying off the hydrogen it would still be difficult in many cases to prevent the excess hydrogen interfering with the plating. Moreover, in such cases, the use of a large amount of current will have a heating effect which would make it difficult to maintain the proper limits of temperature for chromium plating. Under these conditions the quantity of current flowing from the anode is reduced by passing only enough current at a proper current density for depositing the chromium along a longitudinal strip on the inside of the pipe. This is conveniently effected by locating the anode relatively close to the strip on which the deposition is to be effected and remote from the other portions of the surface, as illustrated most clearly in Fig. 2. As here shown, current at a proper density for plating passes from the anode to the cathode along a narrow strip, having a width for example of the arc between the lines *k*—*k*.

Current may be saved by shielding the anode from the cathode at those parts of the cathode surface where the current density is below that between the lines *k*—*k*. This shielding may be effected by glass or porce-

lain plate or plates 100 having hydrogen vents 101, as illustrated in Fig. 16.

The total current passing is confined to an amount which, together with the circulation, will release only such an excess of hydrogen gas as can be carried off without interfering with the plating at the end or ends of the article. As shown in Fig. 1, the hydrogen gas rises to the upper inside and part of the cathode, and flows toward and out from the upper end, the flow being assisted by the circulation of the plating solution through the pipe, which circulation may be natural, as shown, or forced.

The solution (and hydrogen) acts to protect the unplated portions while the plating is going on at the other portions of the inside of the pipe or article. When the pipe along one longitudinal strip has received the proper deposit of chromium, it is turned so that deposition may be effected along another longitudinal portion. The turning may be either intermittent or continuous, and the turning is continued until the entire surface to be plated has received a chromium deposit.

Referring to Fig. 4, the article C is shown as a long pipe, which is immersed in the electrolytic solution, and which, as here shown, may be suspended in a horizontal position. The sleeves or extensions 22, 23 may be placed on the ends of the cathode pipe, radial arms 33 for turning the cathode pipe, and hangers 15, 16, similar to those shown in Figs. 1 to 3, inclusive, may be provided.

An anode 26 is run through the pipe, and has suitable connections at its end to the anode bus 26′. The anode may be supported by suitable means inside the pipe. These means may be conveniently a series of glass plates or frames 40 making contact with the inside of the pipe, placed at intervals along the inside of the pipe, and having strips 41 or other suitable means connecting the anode thereto. These inside supports facilitate the placing of the anode inside of the pipe without coming into contact with the inner prepared walls, it being preferable to avoid such contact in the case of anodes such as are usually used, viz. lead or lead-covered anodes. An imperfect plate usually results where such anodes touch the inside walls.

Means, as a perforated pipe 45, is introduced into the cathode pipe, preferably at its upper side, being conveniently supported by the insulating brackets 40. This pipe 45 is provided with openings or perforations therein, and the excess hydrogen, or the solution containing the greater portion of such excess hydrogen, is drawn off through the pipe 45. Alternatively, portions of the above solution can be introduced into the interior of the cathode pipe through the pipes 45, and thereby produce a forced circulation through the pipe, and thus reducing the concentration of hydrogen in the bath solution inside the pipe.

Preferably the hydrogen is drawn off (or the fresh solution introduced) from each end of the pipe, so that the amount of hydrogen, or solution containing hydrogen, passing out through each end is one-half of what it would be if it all passed out through one end. This materially increases the amount of current which may be used for depositing the chromium over similar conditions where all of the introduction of liquid or withdrawal of hydrogen is through one end.

In case of long relatively narrow articles, the current, at a sufficient density for depositing chromium, is preferably passed from the anode to a longitudinal strip or portion only of the cathode pipe, and the cathode pipe turned successively to provide for electrodeposition of chromium over the entire surface, in practically the same manner as heretofore described with reference to Fig. 1.

Referring to Fig. 7, the cathode article C is again shown as a long pipe, and it is immersed in the plating solution, preferably in such manner as to leave a space 60 between the upper level of the solution in the pipe, and the upper surface. The cathode pipe may be suspended from the cathode bus 20 by hangers 15, 16 as described in reference to Fig. 1, and sleeves or extensions 22, 23 may be placed on its ends, and radial arms 33 be provided for turning the same, also as heretofore described with reference to Fig. 1. The anode 26′ is passed through the cathode pipe, and may be supported by glass plates 40 and strips 41 similar to those illustrated in Fig. 5.

In the case of long articles of relatively small diameter, the current at a proper density for electrodepositing chromium is passed from the anode 26 to the cathode C along a strip or longitudinal portion of the inner surface, as for example between the lines *k*—*k*, Fig. 8. The excess hydrogen finds a short path to the space 60, at the upper inside of the pipe, and can flow along said space 60 unopposed by having to pass through the body of the plating solution, and thereby enables a relatively large quantity of excess hydrogen to be evolved without interfering with the perfect plating of the inside of the pipe. To retard the flow of the hydrogen from the space 60, and to maintain an atmosphere of hydrogen in said space 60, suitable means are placed at the end or ends of the pipe. These means are conveniently flanges 62, which extend inward to about the solution level, or even slightly below it, so that the hydrogen gas has a confined passage to the atmosphere, or has to overcome the resistance of a slight depth of the solution in passing out. The hydrogen protects the part of the surface which is not immersed from oxidation, and this is assisted by the liquid splashed upward by the rising

bubbles of hydrogen. The pipe is turned on its longitudinal axis (as by means of radial arms 33, Fig. 9) one or more times to complete the plating of the inside surface.

Referring to Figs. 10, 11 and 12, the cathode article C is shown as a flanged tube, closed at one end.

The cathode article, Fig. 10, is suspended in a bath by hangers 15, 16 similarly to the cathode article in Fig. 1, the article being inclined and having its open end uppermost, whereby excess hydrogen is removed by gravitation, assisted by the flow of electrolyte induced by the outflow of the hydrogen. If desired, a perforated pipe 45 may be introduced into the cathode article, through which hydrogen may be withdrawn, or fresh electrolyte introduced into the article to force the circulation and thereby reduce the concentration of hydrogen.

As shown in Fig. 12, the cathode article itself may be made the tank or container for the electrolyte.

The anode 26 extends lengthwise of the article, and is arranged in a manner to concentrate the current (at a sufficient strength for electrodepositing chromium) along a longitudinal strip.

As shown in Fig. 10, the anode 26 is held in a fixed or stationary support 70, and the cathode article turned in relation thereto. One end of the anode, as indicated at 72, near the closed end, is turned up or inward to insure plating to the center of the closed end.

As shown in Fig. 12, the anode 26 may be arranged in the form of a loop 74, attached to a suitable head 75, carried by shaft 77, and turned in any suitable manner, as by means of a handle 79. In this mode of carrying out the process the anode is rotated progressively either continuously or step by step whereby to plate longitudinal strips on the inside of the cathode. With the loop or double arrangement, two strips are simultaneously plated.

A perforated pipe 45 may be employed for withdrawing the excess hydrogen, so as to avoid an excessive concentration at the upper end of the tube.

Sleeves or extensions 23 are preferably placed at the open ends of the cathode articles. This permits of the solution level being carried above the upper edge of the tube in both Figs. 10 and 12, and assures plating at the open ends of the tube, as heretofore explained. Radial arms 33, may be placed on the extension 23, Fig. 10, as means for turning the cathode article.

Referring to Fig. 13, the cathode article C is shown as a hollow or tubular article having reduced ends.

The cathode article C is conveniently supported in the bath by passing a shaft 80 through its two ends, which shaft 80 may be mounted in journals, and turned, by means of a handle 81, for example, to rotate the article, and it may also serve as a means of carrying the cathode current to the cathode article.

The anode 26 is conveniently rod shaped to conform generally with the longitudinal contour of the cathode article, and extends lengthwise thereof, and may be suspended from the anode bus 26′ by means of conducting strips 85, 86, or the like.

The solution level is preferably on a line which passes through the open ends of the cathode article.

The excess hydrogen gas disengaged in the process of the plating flows upward through the solution, as described in reference to Fig. 7, and flows laterally toward the open ends without having to pass through the liquid. Suitable means, such as disks 88, may be placed at the open ends of the cathode article so as to partially close the same, and thereby restrict the escape of gas from the interior of the cathode article, thereby maintaining a protective atmosphere of hydrogen gas on those portions of the interior surface not being plated at the time, plating taking place, as heretofore explained, along a longitudinal strip, and the cathode article being turned to obtain progressively a plating extending entirely around the inside surface of the article.

In Figs. 14 and 15 there is illustrated a mode of applying the process to articles of other than cylindrical form. The article C as shown is a trough-like article having straight sides and a curved body. The ends may or may not be closed. Large sheets may be bent in the form of a U, and thereby plated in a bath which is more shallow than would be required for immersing the sheet to a depth corresponding to its full width.

The cathode article C is conveniently suspended from a cathode bus 20 by means of loops or straps 90, 91.

The anode 26 is conveniently in the form of a loop suspended at each end from a pair of anode bus bars 93. The anode could, however, be otherwise arranged to extend to the center line of the bottom of the cathode article, similarly to the arrangement shown in Fig. 10.

The plating is effected in strips parallel to the anode, which, for uniformity of expression, will be described as longitudinal strips. The U (or J) shaped anode is slid continuously or step by step from end to end of the cathode article, thereby laying down a continuous chromium plate on the article. The surface not being plated at the time being immersed, and being cathode, is protected against oxidation, or other influence which would inhibit a good adherent plate of chromium being later applied thereto.

In Fig. 16 there is shown a means of shielding the parts of the cathode C not being plated at the time, which means is also a means for concentrating current on parts of

the cathode to be plated. As here shown, the means may be an insulating plate 100 placed around the anode except at the portions opposite the strip or area to be plated. This insulating plate may conveniently be of porcelain or glass, and is provided with openings 101 of any suitable nature at its upper side to enable hydrogen to readily escape.

The apparatus for electrolytic cleaning may be similar to that used for deposition. The removal of the hydrogen gas from the solution is advantageous, as it reduces the resistance of the solution. However, with acid (used as the bath) which does not have an oxidizing effect on the parts not undergoing the concentrated treatment at the time, the confining means 62, Fig. 7 and 88, Fig. 13 may conveniently be omitted, as the copious hydrogen evolution will usually serve to prevent atmospheric oxidation.

The invention may be carried out in other modes of procedure than those herein specifically illustrated and described.

What is claimed is:—

1. In a method of electrodepositing a metal such as chromium accompanied by the disengagement of large quantities of hydrogen, on the inside of hollow articles, removing hydrogen from the solution at localities intermediate the ends whereby the concentration of hydrogen in the plating solution at the end or ends is reduced.

2. In a method of electrodepositing a metal such as chromium accompanied by the disengagement of large quantities of hydrogen, on the inside of hollow articles, removing hydrogen from the plating solution at localities intermediate the ends, toward each end, whereby the hydrogen passing out through each end is reduced.

3. In a method of electrodepositing a metal such as chromium accompanied by the disengagement of large quantities of hydrogen, on the inside of hollow articles, forcing a circulation of the solution in opposite directions on the interior of said article.

4. In a method of electrodepositing a metal such as chromium accompanied by the disengagement of large quantities of hydrogen, on the inside of hollow articles, passing into an anode extending longitudinally of said article less current than the amount required to furnish current at the required current density for plating to the entire inside surface, and concentrating the current, at the required current density for plating, along a longitudinal strip.

5. The process set forth in claim 1 in which extensions are placed on the end or ends of said articles and then passing current from the anode extending longitudinally of said article.

6. The process set forth in claim 1 in which extensions are placed on the ends of the articles and then current passed from the anode extending longitudinally of said article and making the plating current effective on a longitudinal strip of relatively narrow width therein.

In witness whereof, I have hereunto signed my name.

WARREN AYRES TYRRELL.