RECOVERY OF MIXED PLATING RINSES


Filed Apr. 8, 1971, Ser. No. 132,416

Int. Cl. B01J 1/04; C02b 1/42, 1/60

U.S. Cl. 204—35 R

10 Claims

ABSTRACT OF THE DISCLOSURE

A method and system for treating mixed rinse waters used to rinse workpieces removed from chromium and other metal treating baths provides for reducing hexavalent chromium ions carried by the workpieces prior to rinsing and mixing the rinse waters from a plurality of different rinses prior to passage thereof through cation and anion exchangers. The method and system also provide for the immediate removal of CN from the anion regenerant while it has a high pH value and then combining the cation and anion regenerants prior to neutralization.

The present invention relates to a new and improved method and system for simultaneously treating toxic water resulting from the rinsing of workpieces carrying different metal plating solutions, and it relates more particularly to a method and system for recovering water used to rinse workpieces in a metal plating or treating line carrying, for example, solution containing chromium and cyanide ions.

The common practice in the metal plating industry is to remove the metal plating solution carried by the workpieces from the plating bath by rinsing, spraying, or washing the workpieces with water. Not only does this water become toxic, thereby necessitating treatment before its disposal, but it also contains sufficient quantities of the metal plating solution used to make the treatment economical if such metal is recovered.

Generally speaking, two or more different metals will be sequentially plated on the same workpiece in a single plating line, and in some cases different plating lines are operated in the same general location or at least at the same plant. In order to minimize the cost of operating such plating lines and to ensure that no toxicity is released into the water, it would be desirable to provide a completely closed rinse water system. Such a system would have the added advantage of minimizing the use of water which is consumed in extremely large quantities in plating systems of the prior art. It would be further desirable to provide a system wherein all of the rinse water from each metal plating line including the acid dip and alkaline cleaning stations as well as the water from several plating lines could be mixed and simultaneously deionized prior to recirculation to the various rinsing stations.

An object of the present invention is, therefore, to provide a new and improved method and system for recovering rinse water used in metal plating systems.

Another object of the present invention is to provide a new and improved system for recovering the water used to rinse workpieces removed from a chromium plating solution.

A further object of the present invention is to provide a new and improved system for recovering water used to rinse workpieces carrying various metal plating solutions.

A still further object of the present invention is to provide a new and improved method and system for simultaneously deionizing the rinse water used for removing different metal plating solutions from workpieces.

Briefly, the above and further objects of the present invention may be realized by moving the workpieces from a chromium plating solution directly into a reducing bath prior to rinsing, thereby to convert the hexavalent chromium ions carried by the workpieces to trivalent chromium ions. The workpieces are then moved through water rinse baths or sprays wherein the liquid carried by the workpieces is transferred to the water. Inasmuch as the rinse water does not contain any hexavalent chromium, it may then be mixed or combined directly with the rinse water from other metal plating stations such, for example, as nickel plating, copper plating, or zinc plating stations, when the mixed waters subjected to the usual deionization treatment by passing them sequentially through cation and anion exchange resin columns.

Further objects and advantages and a better understanding of the present invention may be had from the following detailed description taken in connection with the accompanying drawing which is a schematic flow diagram of a typical chrome plating line as used, for example, in plating automobile bumpers.

Referring now to the drawing, there is shown a chrome plating line comprising a plurality of adjacent tanks generally arranged in the shape of a horseshoe with the workpieces traveling in a clockwise direction as it is carried from one tank to the next in the system. As will be understood by those skilled in the art, the exact arrangement of the various solutions through which workpieces are moved during a plating operation is subject to substantial variation, and therefore, the plating line shown in the drawing is merely by way of illustration of a typical system with which the present invention finds application.

As shown, the workpieces are first immersed in an alkaline cleaning bath 10 and then rinsed in a cold water rinse tank 12 before moving into an electrolytic cleaning bath 14. The workpieces are again cleaned in a cold water rinse tank 16 and lightly dipped in an acid bath 18 before again being washed in a cold water rinse tank 20. The parts are then electro-plated with copper while immersed in a copper plating solution in the tank 22. Typically, this solution will contain CuCl₂, KCl, and KCN. After removal from the copper plating bath tank 22, the workpieces are washed in a cold water rinse tank 25 and again in a second cold water rinse tank 26. In accordance with common plating practices, the fresh water enters the cold water rinse tank 26 and flows over a weir between the tanks 24 and 26 into the tank 24 at the same rate as water enters the tank 26. The workpieces are then immersed in a nickel plating solution contained in a tank 28 wherein a layer of nickel is electroplated over the copper layer previously plated onto the workpieces. The nickel plating bath will typically contain Ni, NiCl₂, boric acid, sodium formate, cobalt formate, formaldehyde and brighteners.

After being plated with the desired thickness of nickel, the workpieces are moved from the bath 28 into a first cold water rinse tank 30, then into a second cold water rinse tank 32 and into a third cold water rinse tank 34. As shown, fresh water enters the rinse tank 34 and flows over suitable weirs first into the tank 32 and then into the tank 39 from which it exits at a rate equal to the rate at which water enters the third tank 34.

After being thus thoroughly washed, the nickel plated workpieces are now immersed in a chromium plating solution contained in the tank 36 wherein a layer of chromium is electroplated thereon over the nickel. The chromium plating solution typically includes H₂CrO₄ and H₂SO₄. This solution will contain a substantial number of hexavalent chromium ions as well as a substantial number of trivalent chromium ions which are generated during the plating operation. The workpieces after leaving the chromium plating tank 36 are immersed in a drag-out
bath contained in a tank 38. The solution in the tank 38 is essentially the same as the solution in the tank 36 although at a substantially lower concentration. Accordingly, the tanks 36 and 38 both contain a solution including both hexavalent and trivalent chromium ions.

In accordance with an important feature of the present invention the workpieces leaving the chromium plating solution contained in the tank 38 are immediately immersed in a reducing solution contained in the tank 40. The reducing agent may, for example, be NaHSO₃ and its purpose is to reduce or convert the hexavalent chromium ions to trivalent chromium ions before the workpieces are washed. When the workpieces are removed from the tank 40, they move through a pair of cold water rinse tanks 42 and 44 wherein the solution carried by the workpieces is substantially completely washed therefrom. As shown, fresh water is supplied to the tank 44 and passes over a weir into the tank 42 before exiting at a rate substantially equal to the rate at which fresh water enters the tank 44. After leaving the tank 44, the workpieces may be immersed in a hot water rinse contained in the tank 46 to minimize dry out time.

In accordance with the present invention, the rinse waters from the rinse tanks 42, 30 and 24 are combined or mixed and supplied via a line 50 to a cathode exchange column 52 containing a cathode exchange resin which removes the trivalent chromium ions and any other elements contained in the rinse water. For example, in the system illustrated and described above, sodium ions will also be removed from the rinse water by the cathode exchange resin in the tank 52. The solution then passes through a line 54 to an anion exchange column 56 containing an anion exchange resin. The various contaminants contained in the solution are removed by the anion exchange resin in the column 56 and completely deionized water flows out of the column 56 from which it is recirculated to the various cold water rinse tanks 26, 34 and 44. It will be realized by those skilled in the art that it is not necessary to use deionized water for rinsing the workpieces after the copper plating and nickel plating operations. Nevertheless, with the present invention it is economically possible to use deionized water at all rinse stations in the plating system, thereby providing better washing than has been achieved with any other process. Any make up water to be added to replace that water which has evaporated may be added just prior to the cation exchange resin or if desired it can be added at either the tank 26 or the tank 34.

The cation exchange resin in the column 52 will be regenerated by passing an acid such, for example, as H₂SO₄ therethrough and the anion exchange resin will be regenerated by passing a hydroxide such as NaOH therethrough. The regeneration solution coming off the cation exchange resin will thus contain Na₂SO₄, Ca₃(SO₄)₂ at a low value of pH e.g. approximately 3. The regenerant coming off the anion exchange resin will contain NaCN, NaCl at a pH of approximately 10. This latter regenerant may be immediately treated with chlorine while at the high pH value to remove the CN ions and then blended directly with the regenerant from the cation exchange resin prior to the addition of an acid or alkali to neutralize the combined regenerant solutions. Accordingly, the expense of repeatedly altering the pH level of the regenerant solutions in order to remove the cyanide ions from the anion exchange resin and then to remove the hexavalent chromium ions therefrom is obviated with the present invention.

The process of the invention is illustrated in greater detail in the drawings set forth below. It is to be understood however, that the examples are illustrative only and that the proportions of reagents, the specific acids, bases and salts employed therein can be changed within the general description of the method of the invention.

In this example, the work process line comprising, for example, a continuous mechanical conveyor carrying racked workpieces such as automobile bumpers is passed through a copper plating bath containing 8 oz. per gal. of copper cyanide, from 0.75 to 1.5 oz. per gal. of potassium cyanide and from 4 to 7 oz. per gal. of gelatin hydroxide. Generally, it will be necessary to clean the workpieces in a preliminary plating preparation process utilizing conventional treatment tanks providing alkaline cleaning, electrolytic cleaning, acid cleaning and appropriate cold water rinses.

After the work line leaves the copper plating bath, the workpieces are rinsed in cold water and then passed into an electroplating bath containing from 9 to 10 oz. per gal. of metallic nickel, 7 oz. per gal. of nickel chloride, 4.75 oz. per gal. of boric acid, 5.6 oz. per gal. of sodium formate and 2.5 oz. per gal. of cobalt formate. Thereafter, the nickel plated workpieces are thoroughly rinsed with cold water and immersed in a chrome plating solution containing 33 oz. per gal. of chromic acid (H₂CrO₄) and 0.33 oz. per gal. of sulfuric acid.

The workpieces upon leaving the chrome plating bath carry out a substantial quantity of chromium solution containing hexavalent chromium ions as well as trivalent chromium ions generated during the plating operation. Therefore, in this example a drag out bath is employed to reduce the concentration of Cr⁶⁺ and Cr³⁺ ions in the solution carried by the plated workpieces as they leave the chroming plating station. By this method, the concentration of chromic acid in the carried out solution will vary from zero to about approximately three percent by weight.

The workpieces are immediately immersed in a reducing solution of sodium bisulfite (NaHSO₃) at a pH of approximately 2.0-3.0 wherein all chromium present as Cr⁶⁺ ions is reduced and converted to Cr³⁺ ions. The solution containing trivalent chromium ions carried by the workpieces from the reducing bath is washed from them in a cold water rinse tank and the rinse water mixed with the rinse water from the previous rinses following the copper and nickel plating steps, is recovered by passing it across the surfaces of an anion exchange resin and then across the surfaces of an anion exchange resin.

As has already been mentioned above, in accordance with the present invention, waste water from one or more other plating lines can be mixed with the waste water from the copper-nickel-chromium work process line of the invention above described. And simultaneously deionized prior to recirculation to the various rinsing stations, the waste water from a zinc plating station can be combined with the waste water coming from the copper-nickel-chromium plating line. In this example the zinc plating bath contains 8 oz. per gal. of zinc cyanide, 5.6 oz. per gal. of sodium cyanide, 10.5 oz. of caustic soda and 4.5 oz. per gal. of metallic zinc. Rinse water from workpieces coming from the zinc plating bath is then mixed with the rinse water from the copper, nickel and chrome plating steps and simultaneously recovered by passing the combined rinse waters across the surfaces of a cation exchange resin and then across the surfaces of an anion exchange resin.

From the above it will be readily seen that by moving the workpieces directly from a chromium plating bath into a tank containing a strong reducing agent, all chromium ions entering the rinse recirculation system have been converted to the trivalent state and therefore all such ions are removed from the rinse water on the cation resin of a rinse recirculating demineralization station. Accordingly, by this process, the possibility of the presence of hexavalent chromium on an anion resin and the expensive anion regenerant effluent treatment problem attendant thereto, is completely eliminated.

While the present invention has been described in connection with particular embodiments thereof, it will be understood that many changes and modifications of this invention may be made by those skilled in the art without departing from the true spirit and the scope thereof. Accordingly, the appended claims are intended to cover
all such changes and modifications as fall within the true spirit and scope of the present invention.

What is claimed is:

1. A method of recovering water used in a chromium plating system, comprising the steps of moving the workpieces directly from a chromium plating solution containing hexavalent chromium into a reducing bath wherein hexavalent chromium carried by the workpieces from the plating solution is converted to trivalent chromium, then rinsing said workpieces in water, flowing the water in which said workpieces have been rinsed across the surface of a cation exchange resin to remove the trivalent chromium ions therefrom, then flowing the effluent from said cation exchange resin through an anion exchange resin to remove anions therefrom to provide an effluent of substantially purified water, and recirculating said purified water to rinse said workpieces.

2. A method according to claim 1 comprising the additional steps of regenerating said cation exchange resin by passing an acid regenerant across the surfaces thereof, regenerating said anion exchange resin by passing a hydroxide regenerant across the surfaces thereof, treating the regenerant passed across said anion exchange resin to remove the cyanide ions therefrom while said regenerant has a high pH value, then blending said treated regenerant with the regenerant passed across said cation resin, and neutralizing said blended regenerants.

3. A method according to claim 2 wherein said step of treating the regenerant from the anion exchange resin is carried out by adding chlorine to said regenerant.

4. A method according to claim 3 wherein said chlorine is added to said regenerant while said regenerant has a pH value of about ten.

5. A method of recovering rinse water used in a metal plating system which includes a chromium plating bath and at least one other metal plating bath, comprising the steps of moving the workpieces directly from the chromium plating bath into a reducing bath wherein hexavalent chromium carried by the workpieces is converted to trivalent chromium, then rinsing said workpieces in deionized water, combining said water in which said workpieces have been rinsed with the water in which workpieces removed from said other plating bath have been rinsed, passing the combined rinse waters through cation and anion exchange resin beds, and then recirculating the water to rinse workpieces being plated in said system.

6. A method according to claim 5 wherein said other metal plating bath contains nickel ions.

7. A method according to claim 5 wherein said other metal plating bath contains copper ions.

8. A method according to claim 5 wherein said other metal plating bath contains zinc ions.

9. A method of recovering rinse water used in a plating system wherein workpieces are immersed in the nickel and chromium plating baths, comprising the steps of moving workpieces from a nickel plating bath into a reducing water rinse bath, moving workpieces from a chrome plating bath directly into a reducing bath wherein hexavalent chrome carried by the workpieces is converted to trivalent chrome, then rinsing the chrome plated workpieces in a running water bath, combining the water from both said rinse baths and passing it first across the surface of a cation exchange resin and then across the surface of an anion exchange resin, and reusing said water to rinse said workpieces.

10. A method according to claim 9 further comprising the steps of immersing said workpieces in a copper plating bath and then rinsing said workpieces in a running water bath before immersing said workpieces in said nickel plating bath; and combining the water in which said workpieces have been rinsed prior to immersion thereof in said nickel plating bath with the water from the other of said rinse baths prior to passing said water across said resins.

References Cited

UNITED STATES PATENTS

2,733,204 11956 Costa 210—38 X
3,417,016 12/1966 Yagishita 210—37 X
3,552,993 11/1971 Buchanan 204—35 R X

OTHER REFERENCES


GERALD L. KAPLAN, Primary Examiner

U.S. Cl. X.R.

117—102 A; 204—45 R, 49, 51, 1 R, 52 Y, 55 Y, 232, 237; 210—37, 38