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CHROMIUM PLATING

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The invention relates to chromium plating and is more particularly concerned with improved methods of depositing chromium upon a chromium surface.

There are various instances where it is desired to deposit chromium upon an article which has been previously plated with chromium. Many industrial applications require articles plated with hard and dense chromium of substantial thickness. Existing methods of depositing hard chromium from chromic acid plating baths, however, do not permit deposition of more than a few thousandths in thickness before the deposit begins to show signs of cracking. Continued plating results in paths or openings in the chromium surface layer which lead to the underlying or base metal. Where the underlying metal is not corrosion resistant, a chromium layer having such openings therein does not impart the desired corrosion resistance to the article. If, before undue cracking occurs, the deposition of chromium can be interrupted and the plated article subsequently plated with an additional layer of chromium, the fresh or additional deposit will cover cracks or incipient cracks in the initial deposit, and thereby furnish increased resistance to corrosion. Whatever lines of cracking may appear in the overlying chromium deposit generally are not in alignment with cracks or openings in the initial chromium deposit.

It is frequently desirable to deposit chromium upon an object to very close dimensional tolerances. However, if upon removal from the chromium plating bath, the article is undersize, then it becomes necessary to deposit an additional thickness of chromium on the chromium plated surface. If the thickness of chromium is over-size, the excess amount can be buffed or ground off if the characteristics of the chromium surface layer and its adherence to the initially deposited chromium are such as to permit such subsequent operations.

Where the surface layer of a chromium plated article has become worn, it is highly desirable to deposit a fresh coating of chromium directly on the article without resorting to the painstaking, costly and difficult to control procedure of stripping the initial chromium deposit.

In each of the foregoing instances involving the deposition of chromium upon a previously chromium plated surface, the chromium surface layer must be strongly adherent, particularly if the rigid requirements of various industrial applications are to be met.

Prior to my invention, great difficulties have been encountered in endeavors to satisfactorily deposit chromium upon an object or article which had been previously plated with chromium. The solid surface structure of the initial chromium deposit does not accept the new or additional chromium deposit. A zone of weakness or line of cleavage occurs between the initial and subsequent chromium deposits so that adequate adhesion of the new deposit has been difficult to obtain. Moreover, where it has been desired to deposit chromium upon a worn chromium surface, the metals underlying the worn chromium surface have further complicated the problem. Any preliminary or conditioning treatment designed to make the worn

chromium receptive to the deposition of an additional thickness of chromium must be of a nature and character which will not adversely affect, or be unduly reactive with, the metal in the areas beneath the worn or unduly thin chromium. In addition, the chromium deposit must not only be tightly adherent to the underlying chromium, it must also be strongly adherent to the metal other than chromium at areas which may be worn.

One of the primary objects of the present invention is to simply and effectively treat or condition an object having a chromium surface to permit direct plating thereof with chromium to provide a strongly adherent deposit.

Another object of the invention is to prepare a previously plated chromium surface for the deposition of a strongly adherent layer of chromium in a manner which permits the utilization of standard or common hard chromium plating baths under normal or ordinary plating conditions in a minimum amount of time.

Still another object of the invention is to provide a conditioning treatment for the strong adhesion of a chromium deposit to a chromium surface which permits wide latitude in time of treatment, thereby eliminating exacting and costly procedural controls.

Still a further object of the invention resides in depositing chromium directly upon a worn chromium surface to provide a strong bond with the underlying chromium which may be exposed at the worn or thin chromium coated areas.

These, and other objects and advantages of the invention will be apparent from the following and more detailed description.

I have found that articles having a chromium surface or a chromium plate thereon may be simply and effectively prepared for direct plating with chromium by subjecting the articles to the action of hydrogen chloride in the form of the gas, vapor or fumes. After chromium plating, the deposited metal is strongly adherent and will withstand severe mechanical abrasion and distortion encountered in many rigid industrial applications. The hydrogen chloride gas preferably is in a heated state when the chromium surfaced article being prepared for chromium plating is subjected to its action. The hydrogen chloride gas may be supplied in any suitable manner and piped into the chamber in which the article is suspended for treatment. It is preferred, however, to provide the hydrogen chloride gas, vapor or fumes by heating or boiling hydrochloric acid in the same chamber or vessel in which the article is suspended to receive the conditioning treatment. The acid may be fully concentrated or diluted, and commercial muriatic acid having a concentration of 18° Bé. will furnish satisfactory results. Whatever concentration of acid is used, upon heating the acid under atmospheric conditions, the concentration of the acid soon reaches a point of stabilization or equilbirium where the concentration of the acid is approximately 20.4%. A gas temperature at approximately 140° F. to 170° F. in the vicinity of the article is preferred. If the article being conditioned has a worn chromium surface coating which exposes an underlying metal such as zinc, lead, or aluminum, care should be exercised to prevent the article from coming in direct contact with the heated acid.

Describing the invention in greater detail, the chromium surfaced article to be conditioned and plated with chromium is first cleaned in any suitable manner as by immersion in a hot caustic soda bath or by liquid honing (a pressure blast of chemical emulsion and fine abrasive in solution). The article is then suspended in a chamber or vessel and subjected to the action of the hydrogen chloride gas formed by heating hydrochloric acid in the same chamber until the chromium surface shows a green color. The time of treatment depends upon the tempera-

ture of the gas in the vicinity of the article, the surface area of the article and the rate of flow of the gas over the surface to be conditioned. A gas temperature of approximately 140° F. to 170° F. in the vicinity of the article has been found to furnish satisfactory results. The time of treatment may vary from just a few seconds to several minutes, and is not critical. There are no adverse effects if the article is subjected to activation for an extended period of time. In any event, activation is indicated as completed when the chromium assumes the aforementioned green color. The article is then removed from the gaseous medium, given a thorough rinse in cold water, which preferably is followed by immersion in a hot aqueous chromic acid solution. This solution preferably contains 28 ounces per gallon of chromic acid maintained at a temperature of approximately 175° F. The time of immersion in the hot chromic acid solution is approximately one minute. Then, without further rinsing, the article is made the cathode in a chromium plating bath.

Any commercial chromium plating bath may be used to deposit chromium upon the article conditioned in the manner above described. A chromium plating bath which has been found particularly suitable for the deposition of hard, dense or industrial chromium contains 33 ounces per gallon of chromic acid and 0.33 ounce per gallon of sulphate in the form of sulphuric acid. The bath is maintained at a temperature of approximately 132° F., and a current density of approximately 3 amperes per square inch is used. The bath composition and conditions described will provide a chromium deposit of 0.001 inch per hour. Plating may be extended for as long as 20 hours, and the plate is strongly adherent.

Another bath which has provided hard, dense and tightly adherent chromium deposits upon a chromium surfaced article after conditioning in the manner above described is a bath containing 54 ounces per gallon of chromic acid and 0.54 ounce per gallon of sulphate in the form of sulphuric acid. With a bath of this composition, a temperature of approximately 122° F. is maintained with a current density of approximately 1.5 amperes per square inch. The bath composition and plating conditions described will furnish 0.0005 inch of deposit per hour.

The metal underlying the initial chromium deposit may be ferrous, aluminum, zinc, lead, titanium, copper, nickel. "Ferrous," "aluminum," "zinc," "lead," "titanium," "copper," and "nickel" as used in the claims are intended in a generic sense to include both a commercially pure metal and alloys of the metal which are predominantly, or contain a substantial amount of, iron, aluminum, zinc, lead, titanium, copper and nickel, respectively. Even if portions of the chromium are worn, and areas of the base metal are partially exposed, or covered with only a very thin coating of chromium, the hydrogen chloride gas treatment to activate the article for the subsequent deposition of chromium does not deleteriously affect the base or underlying metal. In fact, the underlying or base metal is also activated to permit excellent bonding with a subsequent chromium deposit.

While as previously stated, the chromium plated article may be given a suitable cleaning prior to the hydrogen chloride gas treatment, I have found that the gas treatment possesses a cleaning function in addition to its function of making the chromium surface receptive to subsequent plating with chromium with strong adherence. The same is true where the initial chromium deposit is worn and another metal is exposed in spots. Thus, it is within the scope of the invention to eliminate preliminary cleaning operations prior to treatment with the hydrogen chloride gas.

It will be apparent that the deposition of chromium on a worn chromium surface involves deposition upon a surface which is not linearly smooth, and therefore may result in a final chromium deposit which may require buffing or grinding. The chromium deposited upon an article conditioned in the manner above described is so tightly adherent that the mechanical abrasion incident to grinding will not result in chipping, peeling or flaking of the chromium. Such subsequent operation is much less costly and laborious than is involved in a stripping procedure.

In lieu of the hydrogen chloride gas, hydrogen bromine, hydrogen fluorine, or hydrogen iodine gas, vapor or fumes may be used. Hydrogen chloride gas, however, is preferred, because of the advantages of cost and handling.

It is believed that the novel process of the present invention, as well as the advantages thereof, will be apparent from the foregoing detailed description. It also will be apparent that while the invention has been described in its preferred form, changes may be made without departing from the spirit and scope of the invention as sought to be defined in the following claims.

I claim:

1. A process of chromium electroplating an article having a chromium plated surface comprising subjecting said surface to a treatment with a hydrogen halide gas, removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on the chromium surface of the article.

2. A process of chromium electroplating an article having a chromium plated surface comprising subjecting said surface to a treatment with a heated hydrogen halide gas, removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on the chromium surface of the article.

3. A process of chromium electroplating an article having a chromium plated surface comprising subjecting said surface to a treatment with a heated hydrogen halide gas, the temperature of the gas in the vicinity of the article being approximately 140° F. to 170° F., removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on the chromium surface of the article.

4. A process of chromium electroplating an article having a chromium plated surface comprising subjecting said surface to a treatment with a heated hydrogen halide gas, said gas being formed by heating a hydrogen halide solution in the same chamber in which the article is suspended for treatment, the temperature of the gas in the vicinity of the article being approximately 140° F. to 170° F., removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on the chromium surface of the article.

5. A process of chromium electroplating an article having a chromium plated surface comprising subjecting said surface to a treatment with a heated hydrogen halide gas, removing the article from the gaseous medium when the chromium surface assumes a green color, rinsing the article in water, immersing the article in a heated aqueous chromic acid solution, making the article a cathode in a chromium plating bath, and electroplating chromium on the chromium surface of the article.

6. A process of chromium electroplating an article having a chromium plated surface comprising subjecting said surface to a treatment with hydrogen chloride gas, removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on the chromium surface of the article.

7. A process of chromium electroplating an article having a chromium plated surface comprising subjecting said surface to a treatment with heated hydrogen chloride gas, removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on the chromium surface of the article.

8. A process of chromium electroplating an article

having a chromium plated surface comprising subjecting said surface to a treatment with heated hydrogen chloride gas, the temperature of the gas in the vicinity of the article being approximately 140° F. to 170° F., removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on the chromium surface of the article.

9. A process of chromium electroplating an article having a chromium plated surface comprising subjecting said surface to a treatment with heated hydrogen chloride gas, said gas being formed by heating hydrochloric acid in the same chamber in which the article is suspended for treatment, the temperature of the gas in the vicinity of the article being approximately 140° F. to 170° F., removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on the chromium surface of the article.

10. A process of chromium electroplating an article having a chromium plated surface comprising subjecting said surface to a treatment with heated hydrogen chloride gas, removing the article from the gaseous medium when the chromium surface assumes a green color, rinsing the article in water, immersing the article in a heated aqueous chromic acid solution, making the article a cathode in a chromium plating bath, and electroplating chromium on the chromium surface of the article.

11. A process of chromium electroplating an article having a chromium plated surface comprising subjecting said surface to a treatment with heated hydrogen chloride gas, the temperature of the gas in the vicinity of the article being approximately 140° F. to 170° F., said gas being formed by heating hydrochloric acid in the same chamber in which the article is suspended for treatment, removing the article from the gaseous medium when the chromium surface assumes a green color, making the article a cathode in a chromic acid plating bath comprising 33 ounces per gallon of chromic acid and 0.33 ounce per gallon of sulphate, and plating the article at a current density of approximately 3 amperes per square inch with the temperature of the bath at approximately 132° F.

12. A process of chromium electroplating an article having a worn chromium plated surface which exposes the underneath metal, the metal beneath said worn chromium surface being selected from the group consisting of ferrous, aluminum, zinc, lead, titanium, copper, and nickel, said process comprising subjecting said surface to a treatment with a hydrogen halide gas, removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on said worn chromium surface and underneath metal of the article.

13. A process of chromium electroplating an article having a worn chromium plated surface which exposes the underneath metal, the metal beneath said worn chromium surface being selected from the group consisting of ferrous, aluminum, zinc, lead, titanium, copper, and nickel, said process comprising subjecting said surface to a treatment with a heated hydrogen halide gas, removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on said worn chromium surface and underneath metal of the article.

14. A process of chromium electroplating an article having a worn chromium plated surface which exposes the underneath metal, the metal beneath said worn chromium surface being selected from the group consisting of ferrous, aluminum, zinc, lead, titanium, copper, and nickel, said process comprising subjecting said surface to a treatment with hydrogen chloride gas, removing the article from the gaseous medium when the chromium surface assume a green color, and electroplating chromium on said worn chromium surface and underneath metal of the article.

15. A process of chromium electroplating an article having a worn chromium plated surface which exposes the underneath metal, the metal beneath said worn chromium surface being selected from the group consisting of ferrous, aluminum, zinc, lead, titanium copper, and nickel, said process comprising subjecting said surface to a treatment with heated hydrogen chloride gas, removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on said worn chromium surface and underneath metal of the article.

16. A process of chromium electroplating an article having a worn chromium plated surface which exposes the underneath metal, the metal beneath said worn chromium surface being selected from the group consisting of ferrous, aluminum, zinc, lead, titanium, copper, and nickel, said process comprising subjecting said surface to a treatment with heated hydrogen chloride gas, the temperature of the gas in the vicinity of the article being approximately 140° F. to 170° F., removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on said worn chromium surface and underneath metal of the article.

17. A process of chromium electroplating an article having a worn chromium plated surface which exposes the underneath metal, the metal beneath said worn chromium surface being selected from the group consisting of ferrous, aluminum, zinc, lead, titanium, copper, and nickel, said process comprising subjecting said surface to a treatment with heated hydrogen chloride gas, said gas being formed by heating hydrochloric acid in the same chamber in which the article is suspended for treatment, removing the article from the gaseous medium when the chromium surface assumes a green color, and electroplating chromium on said worn chromium surface and underneath metal of the article.

18. A process of chromium electroplating an article having a worn chromium plated surface which exposes the underneath metal, the metal beneath said worn chromium surface being selected from the group consisting of ferrous, aluminum, zinc, lead, titanium, copper, and nickel, said process comprising subjecting said surface to a treatment with heated hydrogen chloride gas, removing the article from the gaseous medium when the chromium surface assumes a green color, rinsing the article in water, immersing the article in a heated aqueous chromic acid solution, making the article a cathode in a chromium plating bath, and electroplating chromium on said worn chromium surface and underneath metal of the article.

References Cited in the file of this patent

UNITED STATES PATENTS

1,608,694	Cain	Nov. 30, 1926
1,774,901	Piersol	Sept. 2, 1930
2,028,312	Bornhauser	Jan. 21, 1936
2,091,386	Viers	Aug. 31, 1937
2,096,434	Lukens	Oct. 19, 1937
2,285,549	Wesley et al.	June 9, 1942
2,293,810	Domm	Aug. 25, 1942
2,574,305	Wagner	Nov. 6, 1951
2,728,719	Tucker et al.	Dec. 27, 1955

FOREIGN PATENTS

503,008	Great Britain	Mar. 29, 1939

OTHER REFERENCES

Metal Industry, May 12, 1944, pages 299–300, "Chromium Plating on Steel."