

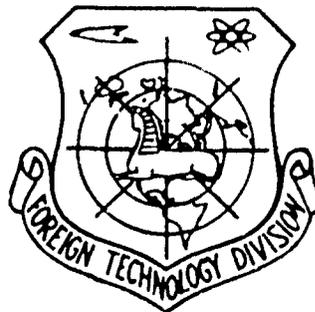
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NEW ELECTROPLATED BLACK COATING -- BLACK CHROMIUM

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EDITED TRANSLATION

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By: Hsu, Hsiao-feng

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ABSTRACT

The author describes electroplating of black chromium coating adopted by the Shanghai Electric Meter Plant for use on instrument components to eliminate glare and to prevent corrosion. Plating is conducted in a solution of chromic anhydride and sodium nitrate for a period of 20 minutes at a current density of 30-60 amp/dm (to the second power) and a temperature of 15-40C. The temperature is maintained by a cooling water jacket enveloping a plating bath made of welded aluminum sheets 2 mm thick. Distilled water is used in the solution, with barium carbonate added to remove sulfate radical. A lead-tin alloy (7 percent tin) is used as the anode, and the chromium oxide content in the solution is regularly checked by the Hull cell test for replenishment. Coating thickness determined by metallographic method is 4.8 microns at a 20 min period and current density of 60 amp/dm (to the second power). The coating, containing a mixture of 75 percent chromium and 25 percent chromium oxide can be directly plated on aluminum and stainless steel components, and on iron components with undercoats of low tin-containing bronze. Results from humid heat tests and salt fog tests showed that the black chromium coating exhibits a better quality than the black nickel coating or bluing. Defects likely to occur in plating and their remedies are also given in a table. Orig. art. has: 2 tables.

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BLACK CHROME---A NEW TYPE OF BLACK-COLORED PLATING

Hsu Hsiao-feng

I. Introduction

To prevent diffuse reflection and to increase their corrosion-resistant capacity, optical components of light-beam instrument are plated with black nickel or developing blue which serves as a working protective coating. Observation has shown that black nickel and developing blue do not perform ideally in corrosion resistance and generally develop white spots and rust when subject to a 24 hr humidheat test. Besides, black nickel plating is not wearproof and often rubs off along the edges and surface during transportation and installation, exposing the base metal, spoiling appearance and affecting the corrosion-resistance characteristic.

After a year or more of searching and experimentation, we succeeded in using black chrome for plating, and satisfactory results have been obtained through a long period of application in actual production.

II. Corrosion-Resistant Performance of Black Chrome Plating

Black chrome plating contains a mixture of 75% chromium and 25% chrome oxide. It is wear-resistant and can be polished. It

has been proved by actual application to be able to withstand 150°C temperatures for long periods in vacuum without changing color and peeling off. The plating has a satisfactory corrosion-resistant property, and is suitable for application on components made of steel, iron, stainless steel, and other metals.

Results of comparative tests on corrosion-resistant performance of black chrome with black nickel and developing blue are as follows:

1) Humid-heat test (temperature 40°C, humidity 98%):

Steel with a black chrome coating 2 μ in thickness retained its original luster after 6 hr and even after 48 hr. Steel with a 6 μ thick zinc coating followed by black nickel plating developed a few white spots occupying 10% of the area after 6 hr and a large amount of white spots occupying 90% of the area after 48 hr. Iron with a 16 μ thick low tin coating followed by black chrome plating showed no change in luster after 6 hr or even after 48 hr. Iron with a 15 μ thick zinc coating followed by black nickel plating showed no change after 6 hr but produced white spots and complete corrosion after 48 hr. Developing blue on iron components showed rust spots around the holes after 6 hr and serious corrosion after 48 hr. Iron with a 2 μ thick low tin coating followed by black chrome plating showed no change after 6 hr and no apparent change even after 48 hr.

2) Brine-fog test (sea water solution; temperature, 35°C; humidity, 95%; fog sprayed 15 min every hour):

Steel with a 2 μ thick black chrome coating showed no change after 6 hr or 48 hr. Steel with a 6 μ thick zinc coating followed by black nickel plating produced a few white spots after 6 hr and showed complete corrosion after 48 hr. Iron with a 16 μ thick low tin coating followed by black chrome plating showed no change after 6 hr and no apparent change after 48 hr. Iron with a 15 μ thick zinc coating followed by black nickel plating produced a large amount of white spots after 6 hr and showed serious corrosion after 48 hr. Iron with a 2 μ thick low tin coating followed by black chrome plating showed no change after 6 hr and no apparent change

after 48 hr. Developing blue on iron components produced a large amount of rust spots after 6 hr and showed serious corrosion throughout after 48 hr.

As observed from the above two sets of comparative tests, the quality of black chrome plating is superior to black nickel plating and developing blue coating.

III. Formula and Operating Conditions

Formula: Chromic anhydride (CrO_3), 250 ~ 300 g/l; sodium nitrate (NaNO_3), 7 ~ 11 g/l.

Operating conditions: Temperature, 15 ~ 40°C; cathode current density, 30 ~ 60 amp/dm²; plating time, 20 min.

The solution must be prepared with distilled water, and the sulfate radical (SO_4^{--}) must be removed with barium carbonate (BaCO_3).

Items to be noted:

1) Variation of the chromic anhydride content in the electrolyte has a rather great effect on plating thickness. A high chromic anhydride content produces thicker plating with fine crystals. Hence, chromic anhydride is maintained in a rather high range (or 250 ~ 300 g/l) in the working formula.

2) Variation of the sodium nitrate content has a great effect on plating. The lower the sodium nitrate content, the higher the electrolytic electric resistance and the higher the bath voltage will be. No black plating can be obtained in a normal current density range. When sodium nitrate content reaches 40 g/l or higher, the electrolytic electric resistance is reduced, thus affecting the plating depth. In a normal current density range, only the edges of a component receive black-colored plating. Therefore, care should be taken not to add sodium nitrate in excess amounts.

3) The solution temperature will spontaneously rise during electrolysis. The temperature cannot be higher than 40°C, otherwise the plating will not have a black color and will contain suspended ashes. Therefore, the plating tank must be provided with a water cooling jacket.

4) Effect of current density on the luster of plating: Plating becomes dark gray (burned) at a current density higher than 70 amp/dm², normal black at 30 ~ 60 amp/dm², yellowish brown at 30 amp/dm² or lower, and a dark rainbow color at 15 amp/dm² or lower. No plating is obtained at a value lower than 10 amp/dm².

5) When the solution contains sulfate radicals, plating becomes bean gray. Plating is light gray when sulfate radicals reach a concentration of 1.5 g/l.

6) When the solution contains chlorine radicals, plating is yellowish brown with suspended ashes, and has a poor protection capacity, causing the base metal to rust.

7) Barium carbonate and solution turbidity have no great effects on plating.

8) Poor quality black chrome plating can be removed by concentrated hydrochloric acid treatment.

IV. Anode and Electroplating Bath

Lead used as anode in all black chrome electroplating baths has a short life and dissolves easily. We used lead-cadmium alloy (containing 7% Cd) as the anode with satisfactory results. It has good conductivity and will not dissolve.

It is rather difficult to select materials for tank constructions. A lead tank will dissolve chemically, and it is not easy to cool a tank made of polyvinyl chloride. After many tests, we selected

a tank made of 2 mm aluminum sheet by welding, with low cost and satisfactory results. The tank was protected outside with [illegible] and cooled by running water.

V. Solution Preservation

The composition of chromic anhydride in the solution can be determined by a hydrometer or a conventional method for analyzing the chromic acid content in a electrolyte. At present there is no simple and accurate method to determine sodium nitrate content. In our plant, we determine the required amount of sodium nitrate to be added by Hull tank experimentation.

We clean the tank once a month by draining, and it is not necessary to remove the sediment completely.

VI. Thickness of Black Chrome Plating

At present neither the spot-out method nor the liquid flow method can be applied to determine the thickness of black chrome plating. The metallographic method has been employed many times at out plant to determine electroplating at a cathode current density of 60 amp/dm². The results are shown in Table 1.

Table 1.

Time (min)	5	10	15	20
Thickness (μ)	2.5	3.3	3.9	4.3

VII. Scheme for Black Chrome Plating

- 1) Silver components can be black chrome plated directly for 20 min.
- 2) Iron components are first plated with low tin bronze 16 ~ 20 μ

3) Iron components to meet high dimensional requirements are first plated with low tin bronze 2 μ thick as a base layer, followed by black chrome plating for 20 min.

4) Stainless steel components can be black chrome plated directly for 20 min.

Black chrome plating can be preserved with wax or oil [illegible].

VIII. Various Technological Processes for Black Chrome Plating of Metals

1) Iron and steel components for black plating: Gasoline degreasing \rightarrow chemical degreasing \rightarrow water cleaning \rightarrow rust removal in HCl \rightarrow water cleaning \rightarrow cathodic \rightarrow electrolytic degreasing \rightarrow water cleaning \rightarrow dilute acid cleaning \rightarrow water cleaning \rightarrow low tin bronze plating (Formula: Cu, 30 g/l; Sn, 9 g/l; Na₂O, 18 g/l; and water, 1 l. Temperature, 60 \sim 70°C; $D_E = 1 \sim 2$ amp/dm²) \rightarrow water cleaning \rightarrow black chrome plating \rightarrow water cleaning \rightarrow drying \rightarrow oiling (spindle oil) \rightarrow inspection.

2) Technological process for black chrome plating of steel and steel alloy components: Gasoline degreasing \rightarrow water cleaning \rightarrow chemical degreasing \rightarrow water cleaning \rightarrow cathodic \rightarrow electrolytic degreasing \rightarrow water cleaning \rightarrow oxidic film removal by pickling in acid water cleaning \rightarrow acid washing for luster (1 part nitric acid, 1 part sulfuric acid, and 10 ml hydrochloric acid) \rightarrow water cleaning \rightarrow black chrome plating \rightarrow water cleaning \rightarrow drying \rightarrow oiling \rightarrow inspection.

3) Technological process for black chrome plating of stainless steel components: chemical degreasing \rightarrow water cleaning \rightarrow acid cleaning (hydrochloric acid, 270 ml; sulfuric acid, 230 ml; and water, 500 ml. Temperature, 40 \sim 50°C) \rightarrow activation (1 part hydrochloric acid and 1 part water) \rightarrow black chrome plating \rightarrow water cleaning \rightarrow drying \rightarrow oiling inspection.

IX. Possible Defects Discovered During
Operation and Remedial Action

(See Table 2)

Table 2. Part 1

Defect discovered	Cause	Remedial action
No plating or plating of yellowish brown color with suspended ashes.	<ol style="list-style-type: none"> 1) Current density too low. 2) NaNO_3 insufficient. 3) Temperature too high. 	<ol style="list-style-type: none"> 1) Adjust to specified value. 2) Add 2 to 4 g/l NaNO_3. 3) Reduce temperature to 40°C or lower.
Conductivity of solution satisfactory, poor deposition with no plating even in the middle.	<ol style="list-style-type: none"> 1) Excess NaNO_3. 2) Temperature too high. 	<ol style="list-style-type: none"> 1) Dilute solution. 2) Reduce temperature.
Electric resistance of the electrolyte too high, and burned appearance (dark gray) in the normal current density range.	Sodium nitrate insufficient.	Add NaNO_3 .
Plating dark red.	Current density too low.	Adjust current density.

Table 2. Part 2

Defect discovered	Cause	Remedial action
Plating contains ashes and very white, poor protection.	Presence of sulfate radical in solution.	Remove with barium carbonate.
Plating yellowish brown throughout, poor protection, appearance of corrosion on steel components.	Presence of chlorine radical.	Treat with silver nitrate.
Electrolyte has small electric resistance, plating shows brown streaks.	Copper content 0.5 g/l. or higher.	
Appearance of large steel-wire streaks, no plating on some areas or on hollow places.	1) Poor contact. 2) No auxiliary anode.	1) Change to hooks. 2) Install an auxiliary anode.
Surface with suspended ashes, plating not black but slightly brown.	1) Solution temperature too high. 2) Solution turbid.	1) Reduce temperature. 2) Clean electrolyte.
Plating not black and seemingly transparent.	Plating time too short.	Increase plating time.