BARREL CHROMIUM PLATING FROM A TRIVALENT CHROMIUM ELECTROLYTE

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ABSTRACT

ecorative chromium plating from trivalent chromium solutions is gaining commercial cceptance. The advantages of plating chromium from the trivalent state are numerous nd have been discussed in detail in other articles. One of the major advantages of lating chromium from the trivalent state is the ability to tolerate current interruption ithout causing passivation to the chromium plate. Barrel plating can maximize the dvantage of tolerating current interruption.

he history of barrel chromium plating from hexavalent chromium solution is reviewed. olution composition, barrel design, anode configuration, cathode contact and quality f chromium plate will be discussed for successful trivalent chromium barrel plating.

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INTRODUCTION

Since the first commercial development of chromium plating in 1924, barrel chromium plating has attracted numerous investigators, most of whom believed design of the barrel would be the key to success. The results obtained were frequently encouraging, but none of the barrels offered remained on the market and gained widespread acceptance. [1]

Developments in barrel design coordinated with hexavalent chromium plating solution especially regulated for barrel plating will be described. Knowledge gained from this was used to develop the trivalent chromium barrel. Next, developments in barrel design coordinated with trivalent chromium plating will be discussed.

GENERAL REQUIREMENTS FOR BARREL CHROMIUM PLATING

The chromium plating of small parts in a rotating barrel has many points of similarity to still tank plating with chromium and also to barrel plating with other metals. Knowledge gained in those fields is helpful here. Thus, too little current causes lack of coverage or no plate, and too much current causes burning in hexavalent chromium and "tinseling", thick macrocracked deposits, in trivalent chromium. The principle differences between chromium and other metals plated in barrels is the solution composition and operation, the barrel construction required for barrel chromium, as well as the intrinsic differences between chromium and other types of plating.

Chromium plating requires a high average current density. In barrel plating the average current density is usually one forth the normal current density found in rack plating. Normal trivalent or hexavalent chromium solutions do not produce deposits that are acceptable under those conditions. In addition the throwing power and plating range for chromium plating is more narrow than with other types of plating.

These differences limit barrel chromium plating to a thin layer of work only, parts cannot be heaped up in a thick layer or mass as in barrel plating nickel, copper, zinc, or cadmium. The term "barrel plating" loosely applies to barrel chromium plating operations and does not mean large production volume plating such as comes to mind when one talks of barrel plating.

BARREL TYPES USED IN CHROMIUM ELECTRODEPOSITION

This is a brief overview of some of the designs that were proposed or used for hexavalent chromium plating small parts in a barrel.

- Kruppa's oblique chromium plating barrel.[2] The design of this barrel requires circulation of solution and cooling, anode area, and a perforated cylinder with inside and outside anodes, but very few details are given.

- Butziger and W. Canning & Co. rocking cradle.[3,4] The parts were placed in the cradle and rocked back and forth in the solution. Literature states that this process had many flaws. These flaws were poor contact with the parts, white wash and poor throwing power.

- Dreyfus modified oblique barrel with eccentric rotation.[5] Actually three different barrel designs were developed, two had both inside and outside anodes and the third barrel design involved rotation on the horizontal axis with eccentric rotation.

- Walker oblique barrel.[6] The design of this barrel incorporated an oblique barrel with an inside and outside anode. The work pieces maintained contact with the cathode due to high speed rotation or magnetically applied force or both.

- Price's totally enclosed barrel.[7] This barrel design consisted of a perforated ceramic container with cathode buttons with an exterior lead sheet anode enclosed in a container with valves to release the hydrogen.

- Siemen and Halskis' rocking basket.[8] This consisted of a flat perforated sheet that was submersed in the plating tank and rocked back and forth. Similar to the cradle type apparatus developed by Butziger and W. Canning & Co.

- Langbein-Phanhauser automatic barrel.[9] The layout of this apparatus incorporated a helical wall on the inside of the barrel wall. Parts were fed in on one end through a hopper and the parts traveled uniformly, while being plated, through the hexavalent chromium solution and were discharged into baskets.

Very limited information has been published on the chemistry and operating parameters of a barrel chromium solution. The data available on the hexavalent chromium solution, see Table 1,[10] shows a high chromium/sulfate ratio with fluorides.

TRIVALENT CHROMIUM PLATING

Recently, decorative chromium plating from the trivalent state has been gaining commercial acceptance. The advantages of plating chromium from the trivalent state are numerous and have been discussed in detail in other articles.[11-13]

One of the major advantages of plating chromium from the trivalent state is the ability to tolerate current interruption without causing passivation to the chromium plate. This ability to tolerate current interruption makes trivalent chromium plating unique to chromium plating. Unlike past work that focused on barrel design for hexavalent chromium plating initial work on the trivalent chromium barrel process focused on the chemistry of the solution.

EXPERIMENTAL SECTION

A two level factorial design experiment with three variables was designed. Table 2 lists the variables, temperature, pH and compound D, and the ranges, 80-120°F, 2.3-3.0 and 0-80 g/L respectively. The factors evaluated were efficiency and covering power.

Two replicates of a 2^3 factorial design matrix was used, Table 3, plus four center points giving a total of 20 data points for each factor. The center points were placed at runs numbered 1,6,13, and 20 to spread them throughout the design but the factorial points were randomized into the remaining 16 runs.

Tables 4A and 4B lists the experimental results of the efficiency and covering power experiments respectively. Tables 5A and 5B shows the computation of the factor effects. When analyzing a small factorial experiment it is helpful to plot them graphically as a first step in analysis. Figure 1A and 1B show the data averages on the three-dimensional cube and the center point for the efficiency and covering power experiments respectively.

In the efficiency experiment only pH has a positive effect whereas temperature and compound D have negative effects. Also, there is one significant positive interaction, temperature and compound D. This interaction between temperature and compound D is important to know for barrel plating. This interaction shows that the negative effect of temperature and compound D on efficiency is decreased at low concentration. Increased efficiency will allow you plate faster thereby decreasing the plating time in the barrel. With longer plating time in the barrel you are more prone to have problems. There is also one significant negative interaction between pH and compound D on efficiency. That the positive effect of pH on efficiency is decreased in magnitude at high concentration of compound D.

In the covering power experiment only temperature has a negative effect, whereas pH and compound D have positive effects. There is only one significant positive interaction between temperature and compound D. This positive interaction shows that the negative effect of temperature and compound D on covering power is decreased at low concentration. The numbers are reversed on the covering power experiment. High values indicate poor covering power, whereas low values indicate good covering power. The covering power was measured on a bent cathode; a special jig is used to bend the brass cathode producing a deep recess, and the misplate in the deep recess is measured. Therefor a positive interaction is negative and a negative interaction is positive.

From the above work a trivalent chromium solution was formulated to incorporate the experimental optimum conditions. These conditions are low temperature, median pH and low compound D. Using this solution in the laboratory barrel showed excellent results, Table 6. This information shows us that not only does current density have an effect on acceptable plated parts but also load size. Also the type of parts plated have a significant effect on the quality of work.

DESIGN OF THE TRIVALENT CHROMIUM BARREL

The design of the barrel did not seem very critical on final product yield in the laboratory barrel. The most important feature in the barrel is the type of contact. Three types of contacts were tried in the laboratory barrel: danglers, center bar and baffles attached to the center bar.

The results of these barrel tests shows danglers as the cathode contact, Table 7, are not acceptable since not enough cathode contact with the parts is obtained and therefore not enough current carrying capacity. The best result with dangler contact was 60% whereas with either a center bar or modified center bar, Table 8, the best result was 98% at the same current density. The contact with the parts is increased with the center bar or modified center bar also the current carrying capacity of the center bar and modified center bar is greater than that of danglers. Anode placement and rotation of the barrel appear very important also.

In the laboratory set-up and in the 50 gallon pilot tank anodes were placed under the barrel. The rotation of the laboratory barrel was approximately 14 RPM and the rotation of large barrel for the pilot line was 7 RPM. The cathode contacts in the pilot barrel had the following types of contacts: modified center bar, straps and straps with wire mesh.

Results from the large barrel in the 50 gallon pilot line were not very promising, Table 9. The best results obtained in this evaluation was 50%. Rejected parts consisted mainly from misplate and dark patches on the work. Decrease in the misplate and dark patches were accomplished by periodically stopping and reversing the barrel rotation.

This method only increased the yield to 60% acceptably plated parts.

COMPARISON OF HEXAVALENT BARREL CHROMIUM PLATING TO TRIVALENT CHROMIUM BARREL PLATING

Scale up from the laboratory barrel to a production barrel failed. Results from the laboratory barrel were usually greater than 95% whereas the production barrel only 35-40% of the work was successfully plated. The next step of the experiment was to compare characteristics of hexavalent chromium barrel designs and choose what features were similar to the successfully operated barrels.

The main features of past barrels consisted of the following:

- Conforming Anode
- Inside Anode
- Small layer of parts

Conforming anodes would help get the current to the parts at the bottom of the barrel. In addition the current distribution on the parts would be more uniform. The inside anode probably would work but was too expensive to manufacture and also had other problems associated with that design. In addition we were trying to develop a system where you would use the same barrel from the cleaner through the nickel plate than chromium plate. The key to most successfully barrel plated chromium parts was the fact that you only had a small layer of parts.

If the parts are piled high in the barrel they tend to bunch up and you cannot obtain good chromium coverage of the parts in the middle of the barrel. What was needed was a way to plate a small layer of parts but in significant quantity to be practical and economical?

The barrel design that we came up with was a compartmental barrel with three compartments. This barrel fulfilled the following characteristic, thin layer of parts and significant quantity to be practical and economical. Also we incorporated the conforming anode.

Results from this barrel in our application laboratory showed a range from 50% to greater than 95% acceptable plated parts, Table 10, with the compartmental barrel. The key to successfully plate small objects is to balance the load size to the compartment size. You have to have enough space inside the barrel so that the parts tumble but also small enough layer so the parts do not nest together.

SUMMARY AND CONCLUSION

A brief review on the development of barrel chromium plating from hexavalent chromium solutions over the past 60 years is outlined here. With this information we were able to achieve a barrel design that would allow us to plate from trivalent chromium electrolytes. With this barrel design you need only one barrel to both nickel and chromium plate. You do not need to operate a separate nickel barrel and batch chromium plate. Experimental work was performed also to optimize the chemistry of rack trivalent chromium plating solutions to allow us to barrel plate. This experimental work included anode design and a statistical design experiment to optimize the plating chemistry for barrel plating.

In conclusion a process for barrel plating chromium from the trivalent electrolyte has been developed. This process utilizes a unique compartmental barrel in conjunction with conforming anodes. In addition, a special trivalent chromium electrolyte is used. More work is needed on this process to increase the yield of the plated parts and also produce consistent quantity and quality plated parts.

BIBLIOGRAPHY

1. 34th ASF PROCEEDINGS
2. British Patent 298,225
3. British Patent 342,477
4. Metal Industry London 40, 248-249
5. French Patent 672,742 678,720
6. French Patent 682,908
7. British Patent 375,991
8. British Patent 366,401
9. British Patent 351,168
10. Metal Finishing Guide Book 1984
11. D.L. Snyder, Plating and Surface Finishing 1979, June, 66, 60-65
12. D.L. Snyder, Product Finishing, December 1990
13. D.L. Snyder, Product Finishing, March 1988

Table 1

BARREL HEXAVALENT CHROMIUM SOLUTION

Chromic Acid	(oz/gal)	53
Fluosilicate	(oz/gal)	0.8
Sulfate	(oz/gal)	0.13
Temperature	(°F)	Room to 95
Voltage		6-18
Current Density		Wide variation
Time of Plating		Approximately 10 minutes

Table 2

VARIABLE	RANGE	0
X1 Temperature	80-120°F	95°F
X2 pH	2.3 - 3.0	2.8
X3 Compound D	0 - 80 g/L	50 g/L
Factor Coding	(-) (+)	

Table 3

DESIGN MATRIX

ORDER	TRIAL	X1	X2	X3
1	9	0	0	0
2	6	+	-	+
3	7	-	+	+
4	4	+	+	-
5	3	-	+	-
6	9	0	0	0
7	5	-	-	+
8	1	-	-	-
9	8	+	+	+
10	2	+	-	-
11	1	-	-	-
12	4	+	+	-
13	9	0	0	0
14	8	+	+	+
15	5	-	-	+
16	3	-	+	-
17	7	-	+	+
18	2	+	-	-
19	6	+	-	+
20	9	0	0	0

Table 4A

SUMMARY OF DATA - EFFICIENCY EXPERIMENT

TRIAL	Y OBSERVATIONS		$\bar{Y}$
1	24	28	26
2	4	5	4.5
3	30	32	31
4	22	25	23.5
5	8.4	11	9.7
6	4.5	4.9	4.7
7	8	7.2	7.6
8	9.6	12.4	11
9	13	15	
	13.4	13.9	14.1

Table 4B

SUMMARY OF DATA - COVERING POWER

TRIAL	Y OBSERVATIONS		$\bar{Y}$
1	21	27	24
2	54	50	52
3	12.8	15.2	14
4	50	46	48
5	17	16	16.5
6	39.5	36.5	38
7	14.5	14.5	14.5
8	18	14	16
9	24	27	27.75
	29	31	

Table 5A

COMPUTATION OF FACTOR EFFECTS EFFICIENCY EXPERIMENT

AVE = 14.94
X1 = -7.8
X2 = 7.4
X1X2 = 5.5
X3 = -13.4
X1X3 = 7.0
X2X3 = -5.3
X1X2X3 = -1.3

TABLE 5B

COMPUTATION OF FACTOR EFFECTS COVERING POWER

AVE = 27.9
X1 = 21.3
X2 = -9.5
X1X2 = -3.5
X3 = -13.3
X1X3 = -9.75
X2X3 = 2.5
X1X2X3 = -6.5

Figure 1A

EFFICIENCY EXPERIMENT

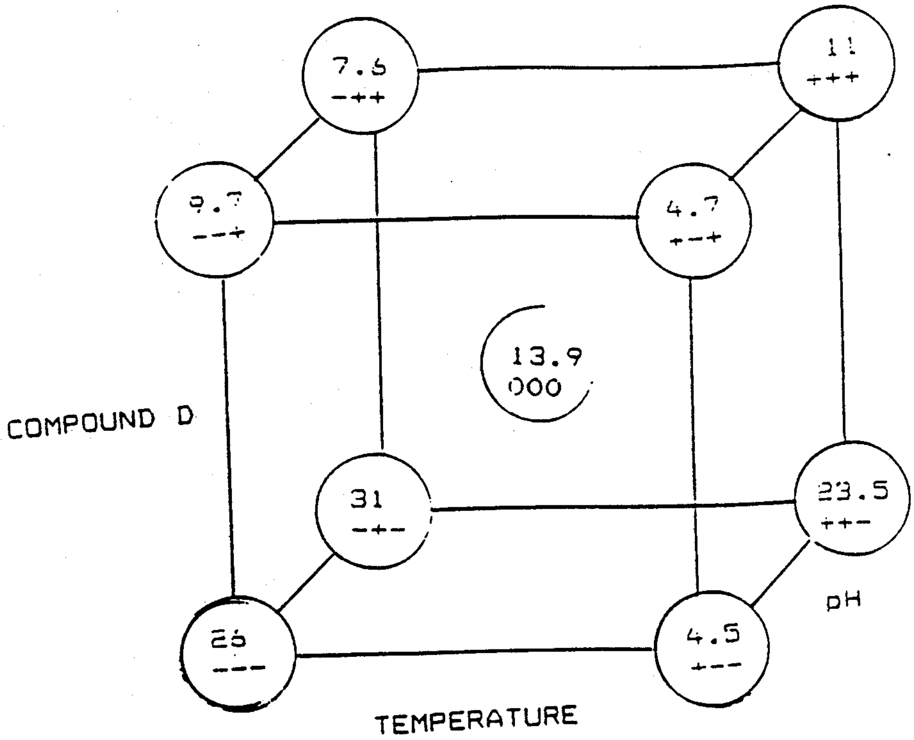

Figure 1B

COVERING POWER EXPERIMENT

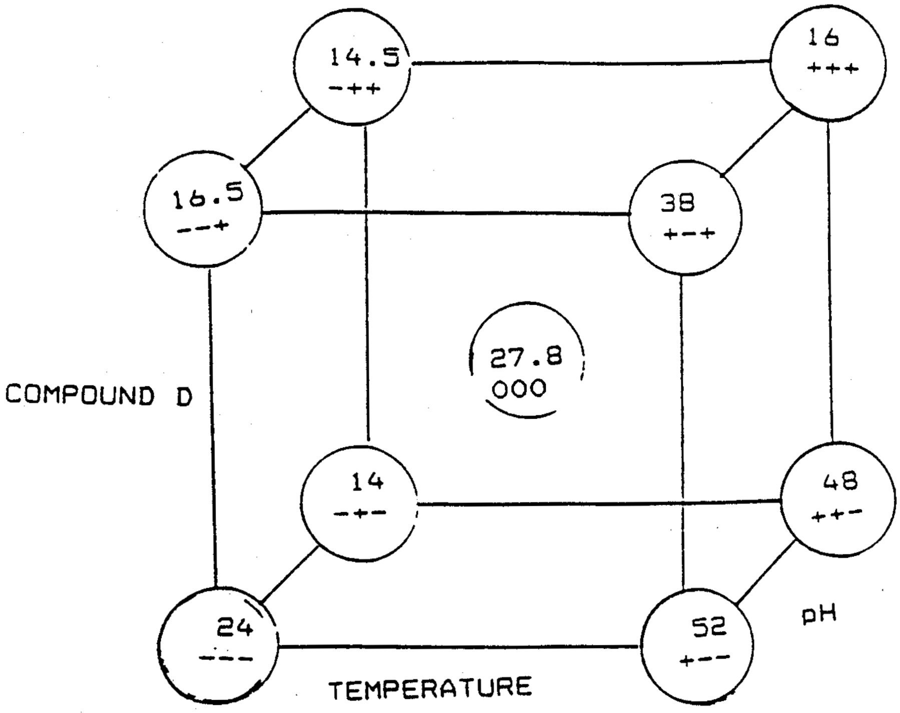

Table 6

Results From Laboratory Barrel

Wt. of Pieces (g)	*Type of Pieces*	*Current Density (ASF)*	*% Plated*
220	screws	60	98
220	screws	80	99
220	wrenches	60	85
144	wrenches	80	97

Table 7

Laboratory Barrel With Dangler Contact

Wt. of Pieces (g)	*Type of Pieces*	*Current Density (ASF)*	*% Plated*
220	screws	80	50
144	screws	80	60
144	wrenches	80	40
100	wrenches	80	55

Table 8

Laboratory Barrel With Center Bar Or Modified Center Bar

Wt. of Pieces (g)	*Type of Pieces*	*Type of Contact*	*Current Density*	*% Plated*
220	screws	center bar	60	98
220	wrenches	modified center bar	60	90
144	wrenches	modified center bar	60	95
144	wrenches	center bar	60	97

Table 9

Laboratory Barrel With Center Bar Of Modified Center Bar

Wt. of Pieces (lbs.)	*Type of Pieces*	*Type of Contact*	*Current Density (ASF)*	*% Plated*
5	screws	straps	60	25
5	screws	straps	80	40
5	wrenches	straps	80	35
3	wrenches	modified center bar	80	50
3	wrenches	straps with wire mesh	80	30

Table 10

Compartmental Barrel Results

Wt. of Parts (lbs.)	*Type of Parts*	*Current Density (ASF)*	*% Plated*
6.6	wrenches	80	50
4.3	wrenches	80	98
4.3	wrenches	60	99
6.6	screws	80	60
4.3	screws	80	95