Preliminary Testing of Perchlorate Cadmium Plating Solutions

By S. Sriveeraraghavan, R.M. Krishnan, S.R. Natarajan & K. Balakrishnan

A study was initiated to investigate various aspects of electrodeposition of cadmium from perchlorate-based electrolytes. Specific goals were to study the effects of metal concentration and current density on current efficiency, the extent of hydrogen permeation in different electrolytes, the embrittlement characteristics of perchloric acid cadmium plating on high-strength steel, and to compare the results with those of cyanide cadmium plating.

Cadmium is frequently used as a protective coating for iron and steel to prevent rusting and corrosion, and is better than zinc in this respect. Because of its low contact resistance, cadmium is also widely used in the electrical and electronics industries. Cadmium can be electroplated from cyanide,[1-4] sulfate,[5-10] polyamine,[11] fluoborate,[12] sulfamate and sulfate[13,14] and chloride solutions. Because of certain advantages, such as good throwing power and covering power, cyanide baths have been favored for commercial use. They give rise, however, to unacceptably high hydrogen intake by plated components of high-strength steel, leading to hydrogen embrittlement. Also, cyanide waste treatment is costly. Consequently, efforts have been made world-wide to develop non-cyanide baths for cadmium plating, based upon sulfamate, fluoborate[15] and neutral chloride.[16] Although fluoborate baths are gaining in popularity, they are limited because of toxicity. Published literature mentions the superiority of perchlorate baths without giving details of practical importance, such as bath compositions and operating conditions.

Experimental Procedure

Hull Cell Studies

Hull Cell experiments were carried out on cold-rolled steel and copper cathodes at a current of 1 A for 5 min. Specimens were degreased with trichloroethylene, electrocleaned in an alkaline electrocleaner and given a dip in 5-percent (V/V) H_2SO_4. The test panels were rinsed in tap water, then in distilled water prior to the Hull Cell tests.

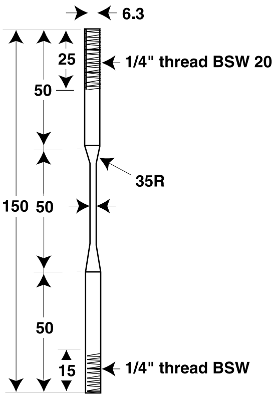


Fig. 1—Unplated specimen of notched high-tensile-strength steel.

Current Efficiency Studies

Mild steel, as well as copper specimens, 7.5 x 2.5 x 0.04 cm, were degreased, weighed,

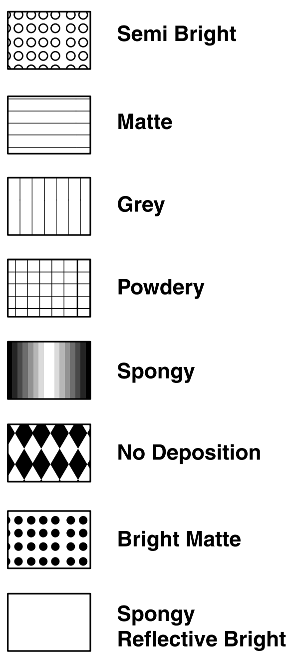
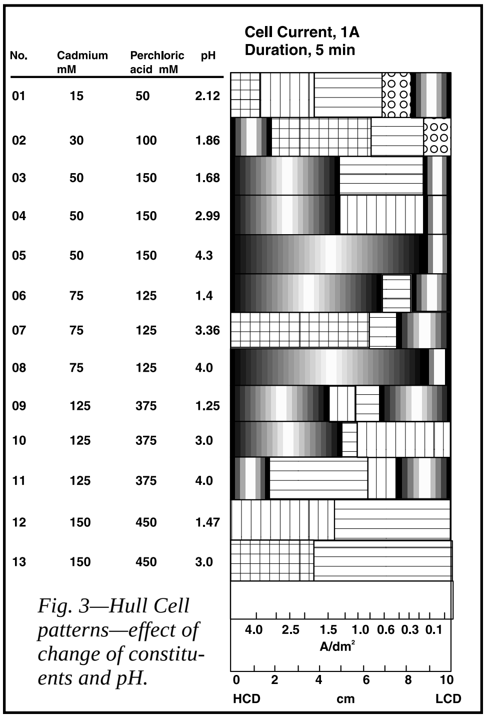
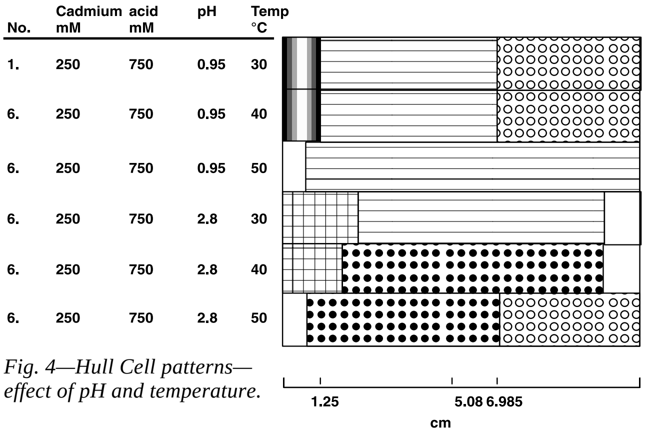


Fig. 2—Legend for Hull Cell patterns.



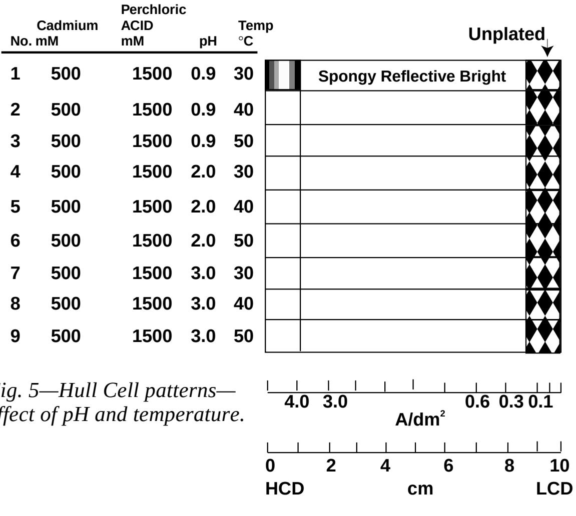
No.	Cadmium mM	Perchloric acid mM	pH
01	15	50	2.12
02	30	100	1.86
03	50	150	1.68
04	50	150	2.99
05	50	150	4.3
06	75	125	1.4
07	75	125	3.36
08	75	125	4.0
09	125	375	1.25
10	125	375	3.0
11	125	375	4.0
12	150	450	1.47
13	150	450	3.0

Fig. 3—Hull Cell patterns—effect of change of constituents and pH.



No.	Cadmium mM	Perchloric acid mM	pH	Temp °C
1.	250	750	0.95	30
6.	250	750	0.95	40
6.	250	750	0.95	50
6.	250	750	2.8	30
6.	250	750	2.8	40
6.	250	750	2.8	50

Fig. 4—Hull Cell patterns—effect of pH and temperature.



No.	Cadmium mM	Perchloric ACID mM	pH	Temp °C
1	500	1500	0.9	30
2	500	1500	0.9	40
3	500	1500	0.9	50
4	500	1500	2.0	30
5	500	1500	2.0	40
6	500	1500	2.0	50
7	500	1500	3.0	30
8	500	1500	3.0	40
9	500	1500	3.0	50

Fig. 5—Hull Cell patterns—effect of pH and temperature.

Table 1
Bath Compositions

No.	Cadmium mmol	Cadmium g/L	Perchloric Acid mmol	Perchloric Acid g/L	Ammonium Fluoborate g/L	Boric Acid g/L	Dextrin g/L	Sodium Cyanide g/L
1	15	1.69	50	5.02	-	-	-	-
2	30	3.38	100	10.04	-	-	-	-
3	50	5.63	150	15.06	-	-	-	-
4	75	8.45	225	22.60	-	-	-	-
5	125	14.10	350	35.14	-	-	-	-
6	150	16.90	450	45.20	-	-	-	-
7	250	28.10	750	75.35	-	-	-	-
8	500	56.20	1500	150.68	-	-	-	-
9	900	101.2	2700	271.25	-	-	-	-
10		240.0	-	-	60	20	2	-
11	45 (as CdO)	-	-	-	-	-	-	120

electrocleaned, washed, acid-dipped and rinsed in tap water, followed by a final rinse in distilled water. Cadmium was plated from different baths, using a cadmium anode, under different conditions. The cathode efficiency, thickness, rate of build-up, etc., were calculated from the weights of deposits obtained and coulombs of current.

Porosity Tests

Cadmium deposits of different thicknesses obtained from different baths on mild steel substrates were tested for their porosity by the Ferroxyl Test.[17-19]

Hydrogen Permeation Studies

The cell set-up used by Venkatesan *et al.*[20] and, as subsequently modified by Nityanandan *et al.*,[21] was employed. A double-walled glass vessel with thermostatic provision to circulate water at the required temperature served as the cell. Teflon™ bushings held the specimen (3.0 x 2.0 cm), plated on one side with palladium. The steel membrane was made to function as a bipolar electrode in the cell. The palladium coating on the anodic side of the membrane was produced by electrodeposition from a solution containing palladium chloride (0.8 g/L) and sodium hydroxide (60 g/L), at 12 µA/cm^2, at room temperature, for 2 min, with a stainless steel anode.

The Teflon bushings were provided with a hole of approx. 1 cm^2 inner area. Both compartments were constructed for insertion of a platinum auxiliary electrode and a HgO/Hg/0.2N NaOH reference electrode. The palladium-coated steel membrane was placed between the Teflon bushings and clamped in place. The compartment facing the palladium-plated side was filled with 0.2N NaOH and purified by pre-electrolyzing at a current of 10 µA for 24 hr, using a platinum foil as the cathode and a HgO/Hg/NaOH reference electrode. Hydrogen permeation studies were begun only after a steady current was achieved during the anodic treatment of the Pd-coated steel membrane, at a potential of 310 mV.

The cell was connected to a potentiostat and a constant potential of -300 mV was applied to the specimen.[20] When the initial current decreased and reached a steady value, the compartment facing the unplated side of the specimen was filled with the experimental solution and the permeation current of hydrogen was recorded at 1 A/dm^2 and at an ambient temperature of 88 ±2 °F (30 ±1 °C) for 15 min. The experiments were repeated for different cadmium plating solutions.

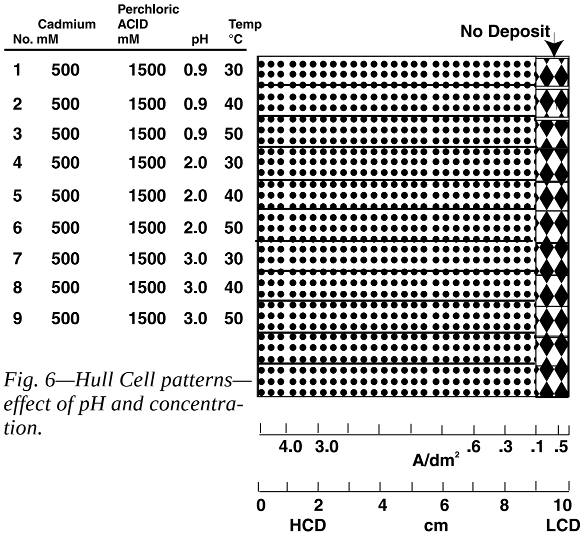


Fig. 6—Hull Cell patterns—effect of pH and concentration.

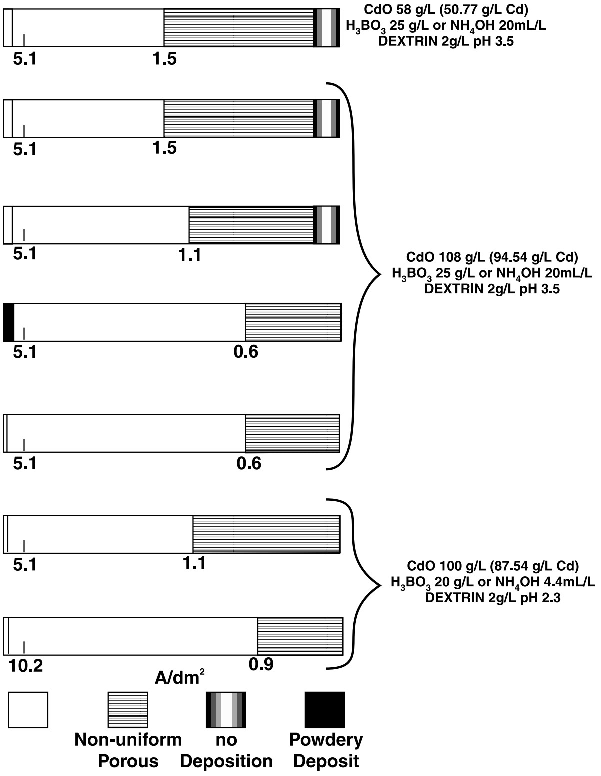


Fig. 7—Hull Cell patterns for a fluoborate bath—effect of pH and concentration.

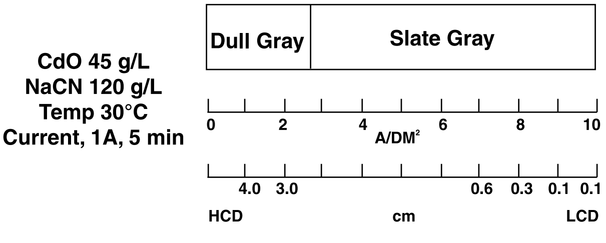


Fig. 8—Hull Cell pattern for cadmium cyanide bath.

Table 2
Results of Current Efficiency Studies
(Substrate: H-S Steel/Copper)
at pH 2

No.	Bath Comp. & Solution Conditions	Current Density A/dm^2	Rate of Build-up µm/hr	Current Efficiency %	Appearance of Deposit
1	Cadmium 16.9 g/L Perchlor. acid 45.2 g/L Temp 30 °C	1	20.9	86.2	matte
2	Same	1.5	30.5	83.8	matte
3	Cadmium 28.5 g/L Perchlor. acid 75.35 g/L Temp 30 °C	1.0	24.2	100.0	velvety white
4	Same	2.0	48.5	100.0	velvety white
5	Same	3.0	74.7	100.0	velvety white
6	Cadmium 56.2 g/L Perchlor. acid 150 g/L Temp 30 °C	1.0	24.2	100.0	satin
7	Same	2.0	48.5	100.0	satin
8	Same	3.0	72.7	100.0	satin
9	Cadmium 101.2 g/L Perchlor. acid 45.2 g/L Temp 30 °C	1.0	24.2	100.0	satin
10	Same	2.0	48.5	100.0	satin
11	Same	3.0	72.7	100.0	satin
12	Cadmium 16.9 g/L Perchlor. acid 45.2 g/L Temp 40 °C	1.0	24.2	100.0	satin
13	Same	1.5	36.4	96.0	satin
14	Cadmium 28.1 g/L Perchlor. acid 75.35 g/L Temp 30 °C	1.0	24.2	100.0	satin
15	Same	2.0	48.5	100.0	satin
16	Same	3.0	65.4	97.4	satin
17	Cadmium 56.2 g/L Perchlor. acid 150.7 g/L Temp 40 °C	1.0	24.2	100.0	satin
18	Same	2.0	48.5	100.0	satin
19	Same	3.0	72.7	100.0	satin
20	Same	4.0	96.9	100.0	
21	Cadmium 101.2 g/L Perchlor. acid 271.25 g/L Temp 40 °C	1.0	24.2	100.0	satin
22	Same	2.0	48.5	100.0	satin
23	Same	3.0	72.7	100.0	satin
24	Same	4.0	96.9	100.0	satin
25	Same	5.0	121.2	100.0	satin
26	Cadmium 240 g/L fluoborate Ammonium 60 g/L fluoborate Boric acid 20 g/L Dextrin 2-2.5 g/L pH 2-3.5 Temp 30°C	0.5	10.5	100.0	matte
27	Same	1.0	24.2	100.0	matte
28	Same	2.0	48.5	100.0	matte
29	Same	3.0	72.7	100.0	matte
30	Cadmium oxide 45 g/L Sodium cyanide 120 g/L pH 13 Temp 30 °C	0.5	10.15	96.9	slate gray
31	Same	1.0	24.2	100.0	slate gray
32	Same	3.0	-	78.0	slate gray

Hydrogen Embrittlement

The relative extent of hydrogen embrittlement, in comparison with unplated high-strength steel of 179.9 kg/mm^2 tensile strength, was assessed by measuring the stress required to fracture plated, notched specimens. Because such stresses are lower, the higher the hydrogen content, the higher the extent of hydrogen embrittlement.[22] Specimens of standard diameter and length (shown as unplated in Fig. 1), plated with 10 µm of cadmium from different baths, were subjected to stress by applying a 20 kN load and the breaking point load observed.

Results and Discussion

Hull Cell Studies

Table 1 lists the various cadmium baths used. In Fig. 2, the legend is given for the Hull Cell patterns of the subsequent figures. Figures 3-8 show the patterns obtained for these baths under different conditions. Figures 3-6 illustrate patterns obtained for cadmium perchlorate baths under different conditions, while Fig. 7 shows the patterns for cadmium deposits from fluoborate baths. Finally, Fig. 8 shows the pattern for a conventional cadmium cyanide bath under standard conditions.

From the figures and patterns obtained for cadmium perchlorate baths, it can be seen that at a cadmium concentration below 14.1 g/L, no useful current density range for obtaining satisfactory, smooth matte layers is indicated. With an increase in concentration of cadmium from 16.9 g/L (0.15 M), there is a change, with formation of a matte layer for any pH from 0.9 to 3.0, which predominates with still higher concentrations of cadmium, especially beyond 28.1 g/L, with com-

Table 3
Results of Current Efficiency Studies (Substrate: H-S Steel/Copper) at pH 3

No.	Bath Comp. & Solution Conditions	Current Density A/dm^2	Rate of Build-up µm/hr	Current Efficiency %	Appearance of Deposit
1	Cadmium 16.9 g/L Perchlor. acid 45.2 g/L Temp 30-50 °C	1.0	20.9	100	white matte
2	Same	2.0	48.5	100	white matte
3	Cadmium 28.1 g/L Perchlor. acid 75.35 g/L Temp 30-50 °C	1.0	24.2	100	velvety
4	Same	2.0	48.5	100	velvety
5	Cadmium 56.2 g/L Perchlor. acid 150.7 g/L Temp 30-50 °C	1.0	24.2	100	velvety
6	Same	2.0	48.5	100	velvety
7	Same	3.0	74.7	100	velvety
8	Same	4.0	97.0	100	velvety
9	Same	5.0	121.2	100	velvety
10	Cadmium 101.2 g/L Perchlor. acid 271.25 g/L Temp 30-50 °C	1-5		100	velvety

Table 4
Results of Current Efficiency Studies (Substrate: Med.-S Steel/Copper)

No.	Bath Comp. & Solution Conditions	Current Density A/dm^2	Rate of Build-up µm/hr	Current Efficiency %	Appearance of Deposit
1	Cadmium 28.1 g/L Perchlor. acid 75.35 g/L Temp 30 °C	1	19.1	79.0	matte
2	Same	2	47.2	97.3	matte
3	Cadmium 56.2 g/L Perchlor. acid 150.7 g/L Temp 30 °C	1 to 5		100.0	velvety
4	Cadmium 101.2 g/L Perchlor. acid 271.2 g/L Temp 30 °C	1 to 5		100.0	velvety
5	Cadmium 28.1 g/L Perchlor. acid 75.35 g/L Temp 40 °C	1	24.2	100	spongy gray
6	Same	2	40.7	83.8	spongy gray
7	Same	3	63.2	86.8	spongy gray
8	Cadmium 56.27 g/L Perchlor. acid 150.7 g/L Temp 40 °C	1 to 5		100	matte
9	Cadmium 101.2 g/L Perchlor. acid 271.2 g/L Temp 40 °C	1 to 5		100	satin, spongy at edges
10	Cadmium 28.1 g/L Perchlor. acid 75.35 g/L Temp 50 °C	1 and 2		100	matte
11	Same	3	74.7	100	spongy gray
12	Cadmium 56.2 g/L Perchlor. acid 150.7 g/L Temp 50 °C	1 to 5		100	matte

Table 5
Results of Studies of Hydrogen Permeation Characteristics

	Bath g/L		CD A/dm^2	i_{max} µm	i_{max} sec	i µA	QH coulombs
	Cd	$HClO_4$					
1	16.9	45.2	1	49.4	13	1.96	13.56
2	56.2	150.7	1	10.0	5	0.7	0.78
3	101.3	271.25	1	10.8	5	0.01	0.24
4	240 NH_4BF_4, 60 g/L H_3BO_3, 60 g/L		1	26.4	5	1.32	1.80
5	Cadmium oxide 45 g/L Sodium cyanide 120 g/L		1	90.64	5	80.25	64.20

plete coverage of the Hull Cell panel, and with still better-looking layers possible for 28, 56, and 101 g/L of cadmium, at any pH value up to 3.0 and up to any temperature from 30 to 50 °C (Figs. 4-6).

For the effect of pH, the results are satisfactory up to 3.5, but beyond 4 and at higher concentrations of cadmium, especially at 101 g/L, the deposit becomes spongy, more so at higher current densities and at higher temperature (50 °C).

For the patterns obtained for cadmium deposits from fluoborate baths (Fig. 7), it may be observed that a sufficiently wide range of matte white cadmium deposition is possible only at a cadmium concentration of 87.54 g/L, in the presence of dextrin and ammonia, at a pH of 2 to 3 and at room temperature.

From Fig. 8, it is clear that from an additive-free cyanide bath, only a slate-gray deposit can be produced at current densities of up to 2.5 A/dm^2 at room temperature.

The Hull Cell studies indicate that perchlorate solutions are superior to other baths and suggest the need for further studies of the same bath with concentrations of cadmium ranging from 16.9 to 101.5 g/L under varying conditions.

Current Efficiency Studies

Tables 2-4 list the results obtained with different baths and different conditions. The current efficiency is almost 100% in all the perchloric acid-based cadmium baths except the one with 16.9 g/L cadmium, in which the cathode current efficiency is approximately 86% at the lower pH (2) and at lower temperature (30 °C), irrespective of current density. This trend continues up to pH 3.0. At pH 4, the current efficiency values are not consistent for a cadmium concentration of 28.1 g/L and are lower at lower temperatures (Table 4). The values are always 100 percent, however, for cadmium concentrations of 56.2 g/L and 101.2 g/L respectively, regardless of pH, temperature and current density.

The current efficiency values are almost 100 percent with the fluoborate baths, also at all current densities from 0.5 to 3 A/dm^2 only when the temperature is 30 °C and the pH is 2.5 to 3.0. The results are not satisfactory for the other conditions of operation (Table 2).

Plain cyanide baths have an efficiency of 100 percent, either at 0.5 A/dm^2 or 1 A/dm^2, but with poor quality (slate gray) deposits being produced (Table 2).

Nature of Deposits

The nature of deposits studied, from all the baths based on perchlorate and fluoborate, are uniform, smooth, adherent and matte. The deposits from perchlorate baths, however, are brighter than those from either fluoborate or cyanide baths.

The color of the deposits generally improves with an increase of metal concentration, pH, temperature and current density. In the case of perchloric acid-based electrolytes, they are of better appearance at the highest concentration of cadmium studied, *viz.*, 101.2 g/L, at pH 3 and at 40 °C and at the highest current density of 5 A/dm^2. The nature of the deposit is unaltered under different conditions with fluoborate and cyanide baths.

Porosity Tests

The results of the ferroxyl tests, carried out with deposits of different thickness (4.5 to 30.0 µm) from different baths, show that deposits of 4.8 and 7.9 µm thickness from cyanide baths have 3- and 1-percent porosity respectively, whereas all other deposits are pore free.

Adhesion

All the deposits were found to adhere well to the steel substrate, as determined by the bend test.

Hydrogen Permeation Studies

The results show that hydrogen permeation is very low in the case of perchlorate-based cadmium, especially with 56.2 and 101.2 g/L cadmium, with values of 0.78 QH and 0.28 QH coulombs respectively (Table 5). The values are higher with the fluoborate and cyanide baths, *viz.*, 1.8 QH and 64.2 QH respectively. It is clear that perchlorate cadmium plating is unlikely to cause hydrogen embrittlement of processed high-tensile steel items, in view of too little or no hydrogen absorbed during the plating operation, unlike the other cases.

Hydrogen Embrittlement Studies

From the studies carried out with notched specimens of high-strength steel plated with different baths, those from perchlorate baths have a break load of 179.9 kg/mm^2, the same value as the unplated notched specimen. This shows the unembrittled nature of perchlorate cadmium plating. Specimens plated with fluoborate and cyanide baths, however, have break load points lower than that of the control specimen (Table 6).

Table 6
Values of Ultimate Tensile Strength for
High-strength Steel Specimens

g/L	UTS, kg/mm^2
1. Unplated	179.9
2. Cd, 16.9 $HClO_4$, 45.2	179.9
3. Cd, 56.20 $HClO_4$, 150.68	179.9
4. Cd, 101.2 $HClO_4$, 271.25	179.9
5. Cd, 240 (as fluoborates) NH_4BF_4, 60 H_3BO_3, 20 Dextrin 2	179.4
6. Cadmium oxide, 45 Sodium cyanide, 120	117.9

Conclusions

From the investigations carried out with different baths, the following composition, based on perchloric acid, is useful for unembrittled cadmium plating of high-strength steels with 100 percent cathode current efficiency over a wide range of solution pH, current density and temperature, and with pure cadmium anodes:

Cadmium	17 - 100 g/L
Temperature	30 - 50 °C
Perchloric acid	45 - 270 g/L
pH	1.0 - 3.5
Current density	0.5 - 5 A/dm^2

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