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Report No. NADC-91114-60

NONCYANIDE CADMIUM PLATING BATHS

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4 OCTOBER 1991

FINAL REPORT

Approved for Public Release; Distribution is Unlimited.

Prepared for
Air Vehicle and Crew System Technology Department (Code 60)
NAVAL AIR DEVELOPMENT CENTER
Warminster, PA 18974-5000

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Reviewed By: Arthur Fletcher Date: 1/13/92
Branch Head

Reviewed By: D S Shaffer Date: 1/21/92
Division Head

Reviewed By: J H Frost Date: 3 Mar 92
Director/Deputy Director

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE 4 Oct. 1991

3. REPORT TYPE AND DATES COVERED Final

4. TITLE AND SUBTITLE

NONCYANIDE CADMIUM PLATING BATHS

5. FUNDING NUMBERS

6. AUTHOR(S)

F. Pearlstein and V. S. Agarwala

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Vehicle and Crew Systems Technology Department
(Code 6062)
NAVAL AIR DEVELOPMENT CENTER
Warminster, PA 18974-5000

8. PERFORMING ORGANIZATION REPORT NUMBER

NADC-91114-60

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

NAVAL CIVIL ENGINEERING LABORATORY
Code L 74A
Port Hueneme, CA 93043-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for Public Release; Distribution is Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

One approach to minimizing toxic wastes is to eliminate the use of cyanide plating baths. Non-cyanide zinc plating baths have been successfully developed and have found widespread use. An investigation was conducted in an attempt to accomplish similar results with cadmium plating baths. The focus of this study was on additives to a near neutral cadmium bath, free of complexing agents. A Hull cell was used to enable visualization of deposits over a broad range of cathode current densities. Experimental design (Taguchi Method) was used to optimize bath parameters and constituent concentrations. Bath have been developed which indicate promise for producing dense deposits with good covering power, and relatively low tendency for hydrogen embrittlement

14. SUBJECT TERMS

Electroplated Cadmium, Noncyanide Plating, Cadmium Plating, Hull Cell Test, Taguchi Methods, Dicyanobis Compounds

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	SAR

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ACKNOWLEDGMENT

The spectrophotometric analysis work of Christine M. Dickey is gratefully acknowledged by the authors. The financial support by the Naval Civil Engineering Laboratory is highly appreciated.

1. BACKGROUND

For many years, cadmium has been used by the Navy for coating of steels to provide the following:

a. corrosion resistance in naval environments
b. sacrificial protection to steel substrates
c. galvanic compatibility with aluminum alloy aircraft structures
d. favorable torque-tension characteristics of plated aircraft fasteners.

However, owing to the toxic nature of cadmium and the adverse environmental impact associated with deposition and service, alternatives to cadmium have been explored.

1.1 ALTERNATIVES TO CADMIUM

Ion vapor deposited (IVD) aluminum [1] has found applications to naval aircraft, particularly the F/A-18 by McDonnell-Douglas Corp. IVD aluminum has found an important niche where electrodeposited cadmium is unsuitable, e.g., when temperatures in excess of 450^{o} C may be encountered, when contact of plated parts with titanium is expected (cadmium can cause embrittlement of titanium) and when cathodic processes are precluded for very high strength steels. However, the IVD process falls short as a viable universal alternative to cadmium because frictional properties of the aluminum are inferior and the process is quite expensive and not readily available. Zinc deposits are approximately equal (or superior) in corrosion resistance to cadmium during outdoor industrial environmental exposure but cadmium is far superior at the marine environments that comprise major Navy interest. In addition, zinc has the characteristic of forming voluminous corrosion products which can result in serious binding of close-fitting parts. However, for many commercial and military applications, zinc is a viable alternative to cadmium when applied at approximately double the thickness suitable for cadmium. Zinc - 10 to 15% nickel alloy electrodeposits [2] offer corrosion resistance superior to cadmium in most environments but the possibility of dezincification, and leaving a nickel rich surface, would preclude its use on components in contact with aluminum alloys because of adverse galvanic effects. The tin-20 to 25% zinc alloy electrodeposits are produced from cyanide-based baths (3); they offer good corrosion resistance but have found little commercial interest over the years. It is therefore concluded that, at this time, continued utilization of cadmium coatings is necessary for many Navy applications.

1.2 NONCYANIDE CADMIUM PLATING BATHS

Cadmium is readily and effectively plated from cyanide-based baths which offer ease of control, excellent throwing power and ability to produce dense, fine-grained or bright deposits. However, the cyanide baths present a serious health hazard to plating personnel when proper safety measures are not heeded; inadvertent mixing of acids with cyanide baths releases deadly hydrocyanic acid vapors. For this reason, there has been a governmental initiative established to replace cyanide baths used by the plating and surface finishing industry. The cost of waste treatment of cyanide is an additional factor to consider.

1.2.1 Acid Fluoborate

Acid fluoborate-cadmium plating baths have been widely used by the military, in place of cyanide baths, to help alleviate hydrogen embrittlement problems as the acid bath has a considerably lower tendency to embrittle plated high strength steels. However, the bath is highly corrosive and poor in throwing and/or covering power. The fluoborate bath cannot be considered as an alternative to cyanide baths for most applications.

1.2.2 Mechanical Plating

Mechanical (peen) plating of cadmium is accomplished by tumbling parts with glass beads in a special solution with the calculated amount of cadmium powder added to provide the desired thickness. The deposit is formed by the sliding and tumbling actions of the glass beads. Recent studies indicated that mechanically plated zinc - 25% cadmium was superior to 100% cadmium in corrosion resistance and had satisfactory torque-tension drive characteristics [4]. This process produces little or no embrittlement to high strength steels; however, the process, while well suited to batch treatment of small parts, is usually not appropriate for coating large or heavy objects.

1.2.3 Proprietary Baths

Three proprietary noncyanide cadmium plating bath (two acid-sulfate and one alkaline ammonium sulfate-chloride) were studied by Boeing Aircraft Corp [5]. One of the acid baths "was ruled out because of poor appearance and cathode efficiency." The other acid bath, pH @ 0.5, had some performance deficiencies as plated parts were smutty and the cadmium content rose owing to anode dissolution during bath inactivity. The alkaline bath (pH 7 to 9) performed well on tests covering 59 ampere hours using a seven liter bath. However, the high concentration of ammonium salts in the bath (>1.5 molar) prevented precipitation of cadmium and other metals that may enter the waste treatment process; thus, ammonium ions must be decomposed, usually by chlorination. Alkaline cadmium plating baths, based upon EDTA complexation, have been reported but EDTA complexes present essentially the same order of waste treatment problems as ammonium compounds.

It was considered that the most useful cadmium baths for Navy operations would be near-neutral (slightly acidic) and essentially free of complexing agents. This report concerns the efforts to achieve this goal.

2. EXPERIMENTAL WORK AND RESULTS

2.1 SELECTION OF INITIAL BATH - HULL CELL TESTS

The main bath composition was selected based on the considerations of essential ingredients, and prepared from analyzed reagent grade chemicals:

80 g/l $CdSO_4.8/3H_2O$
40 g/l Na_2SO_4
10 g/l $NaC_2H_3O_2$

Plating tests were conducted on polished steel panels using a 267 ml Hull Cell with reciprocating paddle agitation. The Hull Cell [6] is a miniature plating unit designed to produce metal deposits over a wide range of cathode current density (CCD); the current density at any point along the cathode is predicted by the equation (1)

$$i = I (27.7 - 48.7 \log L) \qquad (1)$$

where $\underline{i}$ is CCD in A/ft^2 (mA/cm^2). I is the total current applied in amperes and L is distance in inches along the cathode from the high current density edge. This relationship is generally valid, though there can be variations in specific baths where cathode polarization is particularly high. The electrodeposited metal coatings were evaluated for their appearance, covering power and "burning." For screening tests, 0.5 A were applied for five minutes with baths at pH 5.8 ± 0.1 and temperature 31 ± 1^o C.

2.1.1 Bath Additives

The simple bath as described above, produced little or no deposit at less than 2 mA/cm^2, thin and highly porous deposit at less than 25 mA/cm^2 and dense matte deposit only at greater than about 25 mA/cm^2. Variations in bath concentration or substitution of potassium for sodium, chloride for sulfate or borate for acetate did little to improve deposits. Consideration was then given to applying additives which are known to have beneficial effects in plating baths of various types. Sulfur-containing compounds, as a class, had the most beneficial effects on improving cadmium deposit characteristics. Of these, 2-mercaptothiazoline (MTA) was the most effective and at 0.1 g/l, dense, white matte deposits were produced at CCD greater than about 1 mA/cm^2. At lower CCD, deposits were thin and porous and did not extend below about 0.2 mA/cm^2.

Other additives that showed some beneficial effects were thiourea, diethylthiourea, sulfonated mercaptobenzothiazole, 1,10-phenanthroline-iron, cetyltrimethylammonium bromide, hydroxyethylcellulose, 1,2-dimethylimidazole or 1-allyl-2-thiourea (ATU).

Since deposits from the bath containing 0.1 g/l MTA were considered inadequate in covering power for practical use, the effect of additional agents was considered for enhancing this characteristic as well as for improving deposit luster. Agents which showed some promise in these regards are: 1,10-phenanthroline-iron, dicyanobis 1,10-phenanthroline iron II (DCPhI), dicyanobis 2,2'-bipyridine iron II (DCbPyI), polyethylene glycols, polyethylene oxides, quaternary ammonium chloride compounds, sulfonated mercaptobenzothiazole (SMBT). Interestingly, agents which improved covering power, usually also improved deposit lustre. Of these, DCPhI, DCbPyI or SMBT was most effective for improved covering power and with potential for yielding semi-bright to bright deposits. DCPhI or DCbPyI was considered most promising and behaved similarly but the latter was selected for additional testing as it was substantially more soluble. Approximately 0.04 g/l DCbPyI yielded good results and addition of 0.3 g/l ATU was beneficial for improving appearance and reducing the tendency for formation of dendrites/nodules at the high CCD edge. A bath formulation showing promise was comprised as follows:

80 g/l $CdSO_4.8/3H_2O$
40 g/l Na_2SO_4
10 g/l $NaC_2H_3O_2$
0.08 g/l 2-Mercaptothiazoline (MTA)
0.04 g/l Dicyanobis 2,2'-bipyridine Iron II (DCbPyI)
0.3 g/l Allyl-2-thiourea (ATU)
pH 5.8; Temperature 31° C

2.2 TAGUCHI METHOD OF EXPERIMENTAL DESIGN

It was decided to subject this formulation to the Taguchi Method of Experimental Design [7,8] which is effective for screening a large number of variables with minimum number of experiments. The L_8 (2^7) design matrix was selected to determine the effects of plating bath variables, each at two levels (higher or lower) from the initial bath composition shown above. Table 1 shows the eight experiments (baths) when the selected six variables were changed in accordance with the Taguchi method. It is apparent that with six variables, each at two levels, a total number of 2^6 or 64 experiments would be required to cover all possible test combinations. The conductive salt (sodium sulfate) and the buffer (sodium acetate) were kept at constant concentration for these tests. In the case of MTA, the high value was not increased above 0.1 g/l as the agent was difficultly soluble above this level. It was found that ultrasonic agitation helped speed dissolution of the compound.

Table I - Composition of Experimental Baths Using the Taguchi Experimental Design L_8 (2^7).

Bath No.	Concentration, g/l				pH	Temp., °C
	DCbPyI	ATU	MTA	$CdSO_4.8/3H_2O$		
1	0.02	0.15	0.04	60	5.3	27
2	0.02	0.6	0.04	120	6.3	27
3	0.02	0.15	0.1	60	6.3	37
4	0.02	0.6	0.1	120	5.3	37
5	0.08	0.15	0.1	120	5.3	27
6	0.08	0.6	0.1	60	6.3	27
7	0.08	0.15	0.04	120	6.3	37
8	0.08	0.6	0.04	60	5.3	37

The eight formulations were allowed to stand for one week prior to conducting Hull Cell tests, as described above, with 0.5 amperes applied for five minutes.

2.2.1 Criteria for Evaluation of Deposits

Deposit Appearance. Deposit appearance was subjectively evaluated over the CCD range 4 to 20 mA/cm^2 (roughly between 1.5 to 6.5 cm from the high CCD edge). Numerical values were arbitrarily assigned as follow:

Deposit Appearance	Assigned Numerical Value
Bright	- 100
Semi-bright to bright	- 80
Semi-bright	- 60
Matte with some reflectivity	- 40
Matte, nonlustrous	- 20

Covering Power. Covering power (CP) is normally determined by the lowest CCD at which deposit forms. However, in some instances, deposits at low CCD were extremely thin and porous. It was therefore decided to neglect these very porous deposits as unacceptable quality and instead to determine the lowest CCD to which "sound" nonporous deposits are judged to extend; this criteria will be called "sound-deposit" covering power. Numerical values were assigned as follow:

Extent of Sound Deposit from Low CCD End, mm	Assigned Numerical Value
0-1	100
>1-2	80
>2-4	60
>4-8	40
>8-16	20
>16	0

2.2.2 Evaluation of Hull Cell Panels

Based upon the criteria established above, the plated Hull Cell cathodes from each of the eight experimental baths were evaluated and numerical scores assigned as shown in Table II.

Table II - Hull Cell Deposits from Experimental Baths with Numerical Scores Assigned Based upon Deposit Appearance and Sound-Deposit Covering Power.

Bath No.	Deposit Appearance (4-20 mA/cm^2)	Sound-Deposit CP
1	20	0
2	40	40
3	60	20
4	20	0
5	40	40
6	80	60
7	50	40
8	20	0
Overall average	**41**	**25**

It is evident that the deposit from Bath #6 was best in appearance and sound-deposit CP. It should also be noted that dendrites were produced at the high CCD edge from Bath #1 (0.5 mm long dendrites) and Bath #7 (4mm long dendrites). After the eight experiments were run and the appearance and covering power evaluations were compiled, the data were subjected to analysis by the Taguchi method. The experimental design array is orthogonal, or balanced, which allows for the calculation of the effect of each variable independently. For any pair of columns, all combinations of levels will occur an equal number of times. As a result, it is possible to compare the average for the results of the high setting of any variable to its low setting; the effects of all of the other variables will cancel out.

The sum of the above numerical scores was determined for the four baths representing a low value of bath variable and the four containing a high value of bath variable. For example, low DCbPyI concentration was in Baths #1, 2, 3 and 4 for a total score of 140; high DCdPy I in Baths #5, 6, 7 and 8 for a total score of 190. Each total was divided by four to yield an average score of 35 and 48 respectively. These scores were then compared to the overall average; namely, 41. Likewise, appearance scores for low ATU concentration were obtained from deposits of Baths #1, 3, 5 and 7; high ATU from Baths # 2, 4, 6 and 8. The results were 170 and 160 with averages at 43 and 40 respectively. The results for all bath variables calculated in this way are shown in Table III.

Table III - Total and Average Scores for Four Baths Containing Low or High Bath Variable.

Bath Variable	Deposit Appearance				Sound-Dep. Covering Power			
	Low Bath Var		High Bath Var		Low Bath Var		High Bath Var	
	Total	Avg	Total	Avg	Total	Avg	Total	Avg
DCbPyI	140	35	190	48	60	15	140	35
ATU	170	43	160	40	100	25	100	25
MTA	130	33	200	50	80	20	120	30
CdSO4	180	45	150	38	80	20	120	30
pH	100	25	230	58	40	10	160	40
Temp	180	45	150	38	140	35	60	15

The average appearance and sound-deposit CP scores for each bath variable (high or low) was compared to the overall average scores of 41 for appearance and 25 for sound-deposit CP. The degree of improvement in % over the average overall score effected by either high or low variable value is shown in Tables IV and V, for ease of evaluating the results.

Table IV - Effect of Low and High Values of Bath Variables on Percent Improvement in Deposit Appearance.

Bath Variable	Low Value	High Value	% Improvement in Deposit Appearance
DCbPyI	----	0.08 g/l	17
ATU	0.15 g/l	-----	5
MTA	----	0.1 g/l	22
$CdSO_4.8/3H_2O$	60 g/l	----	10
pH	----	6.3	41
Temp	27 C	----	10

It can be seen from Table IV that deposit appearance is affected most strongly by the higher value of pH and moderately by the higher value of DCbPyI and MTA. From Table V, sound-deposit CP was most strongly affected by higher pH, higher DCbPyI and lower temperature; moderate improvement resulted from higher MTA or CdSO4 concentration. Beneficial effects on both appearance and sound-deposit CP resulted from the higher values of DCbPyI, MTA, pH and from the lower temperature. ATU had little or no effect on the deposit criteria. The higher concentration of $CdSO_4$ improved sound-deposit CP somewhat but the lower concentration improved the deposit appearance. It was considered more beneficial to keep the cadmium content at the lower value to reduce the quantities dragged out during plating which would require waste treatment.

Hull Cell tests were conducted on a bath containing 0.1 g/l MTA and various concentrations of DCbPyI; deposits improved in appearance and CP up to 0.12 g/l though improvement was only marginal between 0.08 and 0.12 g/l. Increasing the MTA level from 0.1 to 0.2 g/l in the bath containing 0.12 g/l DCbPyI, somewhat improved deposit appearance but not CP.

Table V - Effect of Low and High Values of Bath Variables on Percent Improvement in Sound-Deposit Covering Power.

Bath Variable	Low Value	High Value	% Improvement in Sound-Deposit CP
DCbPyI	----	0.08 g/l	40
ATU	0.15 g/l	0.60 g/l	0
MTA	----	0.1 g/l	20
$CdSO_4.8/3H_2O$	----	120 g/l	20
pH	----	6.3	60
Temp	27 C	----	40

Based upon these results, the following bath was considered an appropriate compromise for providing good deposit appearance and reasonable CP while minimizing the chemical additives used:

60 g/l $CdSO_4.8/3\ H_2O$
40 g/l Na_2SO_4
10 g/l $NaC_2H_3O_2$
0.1 g/l MTA
0.08 g/l DCbPyI
0.15 g/l ATU
pH 6.3; Temp 27°C

Figure 1(a) shows, diagrammatically, Hull Cell deposit from the above bath without MTA and DCbPyI. Addition of 0.1 g/l MTA greatly improved deposit characteristics but CP was poor; see Figure 1(b). Addition of 0.08 g/l DCbPyI, along with the MTA, resulted in semi-bright deposit over a wide CCD range. See Figure 1(c). The Hull Cell deposit of Figure 1(c) was superior in both appearance and covering power to that of any of the original eight bath combinations of Table I, indicating the value of the Taguchi method for optimizing compositions.

2.3 DECOMPOSITION OF DICYANOBIS

Three weeks after make-up of the eight Taguchi design baths, it was noted that the amber color of the baths from dissolution of the DCbPyI was noticeably lighter than when freshly prepared. Decreased DCbPyI in the cadmium plating bath was confirmed by spectrophotometric analysis at 500 nm wavelength. The final bath formulation was then prepared with and without cadmium salts. Various agents were added to samples of the complete bath to ascertain whether the rate of DCbPyI decomposition could be reduced substantially; the agents were 0.5 g/l $K_4Fe(CN)_6$, 2-2' bipyridine, Na_2SO_3 or EDTA. A bath sample was deaerated by bubbling with nitrogen and another sample stored in the dark. All samples were sealed during storage and samples withdrawn periodically for spectrophotometric analysis.

In the absence of cadmium salts, but containing all other bath constituents, the peak for detection of DCbPyI occurred at 520 nm vice 500 nm for the complete bath. It is thus evident that the cadmium salts interact with the DCbPyI. A shift in wavelength in the direction observed is to be expected in conformance with ligand field theory. The bath without cadmium salts showed no visual loss in color or reduction of absorbance value after standing 74 days. Even after many months, no perceptible change in color was evident. On the other hand, when cadmium salts were also present in the bath, the peak for DCbPyI showed gradual loss of color with time and decrease in peak absorbance value at 500 nm with time. Based upon peak absorbance values, the following approximate reduction of DCbPyI was indicated:

Storage Time, days	0	14	49	74
% Reduction DCbPyI	0	37	70	86

Of the additives, only 2-2' Bipyridine (bPy) had a significant effect on DCbPyI decomposition rate at up to 49 days storage but had little benefit with longer storage times. The results are shown below:

Storage Time, days	0	14	49	74
% Reduction DCbPyI (0.5 g/l bPy added)	0	19	45	81

Even so, addition of bipyridine reduced deposit quality and particularly increased high CCD "burning". Aged baths, largely depleted of DCbPyI, lost ability to produce lustrous deposits. Replenishment of DCbPyI restored deposit luster though there was somewhat increased tendency for "burning" at high CCD, presumably from presence of decomposition products. Neither deaeration with nitrogen nor storage in the dark had any significant effect on DCbPyI decomposition rate. It was found that the freshly prepared final bath could be decolorized rapidly and completely by heating at 90 to 95 C with the same apparent results as long-term aging.

When dicyanobis 1,10-phenanthroline iron II (DCPhI) was dissolved in the Cd bath in place of the bipyridine compound (DCbPyI), similar deposition results were obtained and the DCPhI was also subject to decomposition (decolorization) with bath aging. Although the decomposition mechanism has not been determined, it is obviously related to reaction with cadmium. It is apparently not an oxidation process and free iron is not detected in the decomposed bath. It is considered likely that the dissolved cadmium gradually replaces iron in the compound (see Fig. 2) possibly forming cadmium bipyridine and releasing $Fe(CN)_2$. A pale yellow precipitate forms in the aged bath but has not yet been analyzed for composition. Unless means can be found to retard, prevent or reverse the decomposition process, practical use of the bath will be limited as the cost of the agents is considerable. It is possible that the dicyanobis compounds would be useful additives in baths for plating other metals that may not behave similarly to cadmium in enhancing decomposition. For example, the dicyanobis compounds may be useful additions for iron plating baths since decomposition would not be expected in the presence of ferrous ions. Dicyanobis compounds of metals other than iron may be more stable and resistant to decomposition. For instance, if dicyanobis compound of cadmium could be prepared, it should be stable in the cadmium plating bath. A ruthenium analog is known but this compound may be prohibitive in cost even if it should prove effective and stable.

2.4 CATHODE CURRENT EFFICIENCY (CCE)

The final bath was tested for CCE based upon weight gain measurements using Faraday's law calculation. Deposits were applied in a rectangular cell with anode at one end and cathode at the other. The CCE was found to be 90 and 88% at 5 and 25 mA/cm^2 respectively.

2.5 HYDROGEN EMBRITTLEMENT

Preliminary tests were conducted to determine the tendency for producing hydrogen embrittlement in steel during plating from the newly developed bath compared to a bright cyanide-cadmium plating bath using the Barnacle Cell method [9]. The amount of hydrogen pick-up was about 25% of that from the cyanide bath.

3. CONCLUSIONS

The Taguchi method of experimental design permits rapid evaluation of the effects of six bath variables since only eight plating baths were required. A bath formulation was developed which is considered potentially useful; however, aging of the baths results in serious decomposition of a critical and expensive agent, DCbPyI or DCPhI. Additional investigation of the decomposition phenomenon and possible means for avoidance is indicated.

4. ADDITIONAL STUDIES

4.1 BATH WITHOUT DICYANOBIS COMPOUNDS

Noncyanide cadmium bath of the following composition was found to provide semi-bright deposits over a wide cathode current density range:

60 g/l	$CdSO_4 \cdot 8/3\ H_2O$
40 g/l	Na_2SO_4
16 g/l	H_3BO_3
0.4 g/l	Allyl - 2 - thiourea (ATU)
0.3 g/l	Sulfonated mercaptobenzothiazole (SMBT)
0.1 g/l	Pluracol E1000 (BASF Corp)
0.06 g/l	Mercaptothiazoline (MTA)

pH 5.8 ; 27°C

An approximation of Throwing Power (TP) was made by measuring the thickness of cadmuim at several locations on the Hull Cell panel; 33% TP was found over the range of 10 to 40 mA/cm^2 cathode current density.

Extended use of the bath resulted in a gradual increase in pH indicative of higher anode current efficiency (ACE) than cathode current efficiency (CCE). When the pH increased to above about 6.2, deposit adhesion problems were encountered; the pH must, therefore, be kept below about 6.0.

4.2 PROPRIETARY BATH (PAVCO INC)

The Ameribrite Neutra-Cad bath developed by Pavco Inc., Cleveland, Ohio 44104, was investigated as an alternative to cyanide cadmium baths. Hull Cell tests were conducted and deposits were quite bright but pitted. The efficiency of deposition (ACE) was determined using a Haring-Blum cell with the results shown in the Table VI.

Table VI - Cathode Current Efficiency (CCE) of Proprietary Ameribrite Neutra-Cad Bath at Various Cathode Current Densities (CCD)

CCD, mA/cm^2	CCE, %	Deposit Appearance
10	99.8	Dull, somewhat powdery
20	61.6	Bright, some pitting
40	44.9	Bright, badly pitted

The ACE ranged from 102 to 112% with the higher values at the higher current densities. Cadmium can therefore be expected to build up in the bath with usage and would require use of inert anodes such as graphite or lead.

The TP was calculated to be 64% over the 10 to 40 mA/cm^2 CCD range. This is considered excellent and may be comparable to the TP of typical cyanide - cadmium bath. Further investigation of this bath, in conjunction with the supplier, is believed warranted. The proprietary bath is currently being used, apparently satisfactorily, at a large commercial plating facility.

5. RECOMMENDATIONS

5.1 Near-Neutral Cadmium

Conduct additional studies on the bath containing ATU, SMBT, MTA and Pluracol E1000. The bath composition should be optimized by utilizing Taguchi experimental design $L_{16}(4^5)$ orthogonal array which entails preparation of 16 baths and five variables, each at four levels. Baths should be aged to ensure that all agents are stable. Determine ACE, CCE and TP.

5.2 Fluoborate Baths

Conduct tests with cadmium fluoborate baths at pH 4 to 5 with additives to improve deposit appearance and throwing power.

5.3 Alkaline Bath

Conduct tests with alkaline - cadmium baths which entail use of complexing agents. Complexing agents of moderate strengths, e.g., gluconates, quadrol, may be effective without jeopardizing successful waste treatment. Alkaline baths are normally excellent in TP.

5.4 Pulse Plating

Pulse plating (current interrupt or reversal) has been reported to produce the following beneficial effects on deposits from certain plating baths:

(1) smoother, denser, less porous deposits
(2) increased deposition rate
(3) improved current distribution (throwing power)
(4) increased hardness and wear resistance
(5) higher purity deposits
(6) reduced hydrogen embrittlement

However, these effects have been noted for plating baths of specific composition using particular pulse wave forms. Most previous investigations have been carried out with pulse interruption; relatively little with pulse reversal. Pulse plating is an evolving technology and much more research and development work is required to effect advances in metal deposit characteristics to meet the needs of the military.

Pulse plating investigations are being considered in the following areas of specific interest to NADEP plating facilities:

(1) Cadmium plating of improved properties from non-cyanide baths
(2) Improved throwing power of silver, copper, gold and nickel plating baths
(3) Alternatives to chromium plating:
    (a) Electroless nickel-phosphorus at increased rate & hardness
    (b) Hard nickel
    (c) Hard cobalt
    (d) Tungsten-nickel alloy
    (4) Tungsten or molybdenum deposition (not achieved by normal electrodeposition techniques)

The above areas will be investigated for feasibility and technology transfer to the NADEP's. Pulse plating equipment has been procured which is admirably suited for the proposed experimental work because of the flexibility of the pulse formation and control and current capacity suitable for laboratory or pilot lot studies.

5.5 Closed Loop Plating

Electroplating and other surface finishing operations at Navy Depots utilize hazardous/toxic chemicals such as cadmium, chromates and cyanides. The dragout in rinse waters must be waste treated prior to discharge. However, restrictions on the level of contamination of effluents entering waterways or sewage treatment plants are becoming ever more stringent and, limited landfill areas remain for disposal of sludges formed during waste treatment operations.

Waste treatment of dragout chemicals in rinse waters is expensive and represents a loss of nonrenewable resources; subsequent disposal of sludges represent substantial expenses and responsibility.

Technologies are currently available for economic recovery of metal values for reuse or sale and/or for recycling (closed-loop) of the chemicals back to the metal treatment tanks.

The following approach will be considered critically:

(1) Develop counterflow rinse requirements for cyanide-cadmium and chromium plating operations at selected Navy Depots.
(2) Construct appropriate counterflow rinse system at a selected Navy Depot.

(3) Determine minimum rinse water flow rate to achieve desired degree of parts cleanliness and the concentration of chemicals in effluent.
(4) Determine practicability of recovery of cadmium by electrodeposition along with anodic cyanide decomposition.
(5) Determine degree of evaporation of treatment tank (cadmium and chromium plating baths) to enable return of all counterflow rinse waters; i.e., closed-loop plating.
(6) Procure appropriate atmospheric evaporators to effect closed-loop plating (consideration will also be given to vacuum distillation or advanced reverse-osmosis for concentrating chemicals in the rinse water).
(7) Conduct Navy Depot evaluation of process.
(8) Evaluate process for cost savings and intangible benefits.

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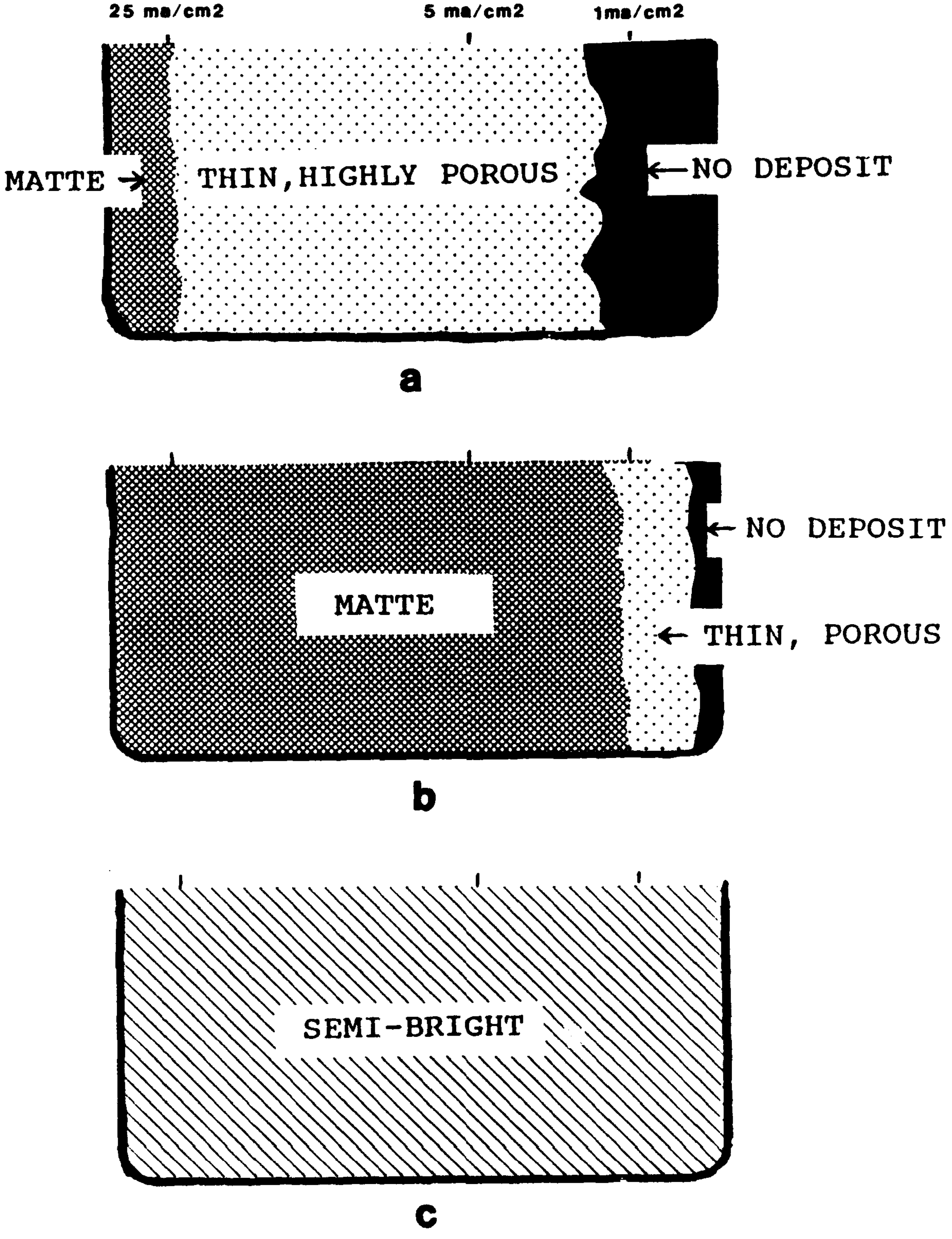
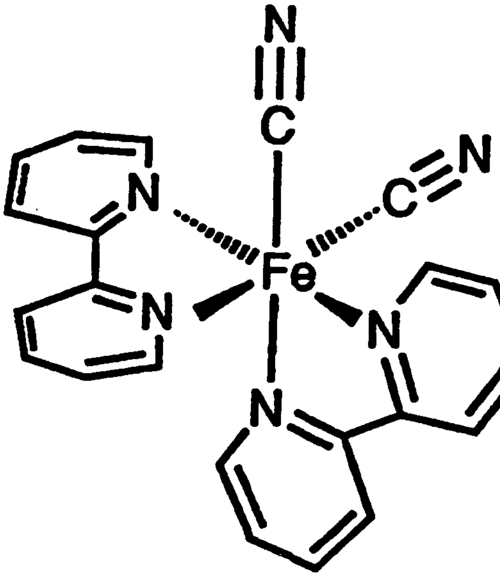


Figure *1* - Graphical representation of Hull Cell cadmium deposits obtained at 0.5 A for 5 minutes in baths of pH 6.1 at 27^{0} C: (a) base bath composition; (b) base bath + 0.1 g/l MTA; and (c) base bath + 0.1 g/l MTA + 0.08 g/l DCbPyI.



DICYANOBIS(BIPYRIDYL)IRON(II)

Figure 2 - Structural representation of dicyanobis 2,2'-bipyridine iron II.

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