# THE SUBSTITUTION OF CADMIUM CYANIDE ELECTROPLATING WITH ZINC CHLORIDE ELECTROPLATING

by

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### **FOREWORD**

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, Superfund-related activities, and pollution prevention. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

Passage of the Pollution Prevention Act of 1990 marked a significant change in the U.S. policies concerning the generation of hazardous and nonhazardous wastes. This Act implements the national objective of pollution prevention by establishing a source reduction program at the EPA and by assisting states in providing information and technical assistance about source reduction. In support of the emphasis on pollution prevention, the "Waste Reduction Innovative Technology Evaluation (WRITE) Program" has been designed to identify, evaluate, and/or demonstrate new techniques and technologies that lead to waste reduction. The WRITE Program emphasizes source reduction and on-site recycling. These methods reduce or eliminate transportation, handling, treatment, and disposal of hazardous materials in the environment. The project discussed in this report evaluated the success of substituting zinc chloride electroplating for cadmium cyanide electroplating processes. The project determined hazardous waste reduction, economic benefits, and change in product quality resulting from the process substitution.

E. Timothy Oppelt, Director Risk Reduction Engineering Laboratory U.S. Environmental Protection Agency

#### **ABSTRACT**

This project evaluated the substitution of zinc chloride for cadmium cyanide in electroplating at Aeroquip Corporation, Van Wert, Ohio. The evaluation looked at product quality, waste volume and pollutant reduction benefits, and economic benefit resulting from the process change. Battelle obtained data on the zinc-plating process by sampling and analyzing waste streams and conducting corrosion tests on zinc-plated production parts. Aeroquip provided data on the older cadmium-plating process for comparison with the zinc data.

It was concluded that the newer process is successful on the quality and the waste volume/pollutant reduction aspects. It results in products whose quality satisfies customer requirements for corrosion resistance. The process change greatly reduces worker hazards and environmental pollution because it eliminates 12,132 lb of cadmium and 835 lb of cyanide annually from the waste streams and chlorine from the wastewater treatment process. The change also reduced annual oil and grease waste from 14,615 lb to 5,123 lb by reducing the oil concentration in the water-soluble oil bath by a factor of approximately ten. However, the change had two negative impacts on waste generation. Wastewater and wastewater treatment sludge increased by approximately 12 and 36 percent, respectively, because the plating bath concentration increased from about 3 oz/gal in the older cadmium process to about 3.5 oz/gal in the newer zinc process. The change also increased total chromium in treated wastewater and sludge from 677 lb/yr to 4,421 lb/yr, because there was a fivefold increase in the chromate bath concentration.

The process substitution was less clearly beneficial from an economic standpoint. For a company with existing cadmium process lines, the substitution of zinc cannot be justified on economic grounds and must be weighed with other factors, such as market, environmental, health, and safety considerations. At Aeroquip, capital cost was estimated to be \$1,972,000, of which approximately 72 percent was the cost of cleaning old equipment and disposing of wastes generated by plant modifications. The process change reduced operating costs by \$17,000/yr, for a simple payback period of about 115 years to recover the capital cost of the process substitution. However, because the cadmium and the zinc-plating lines have similar equipment requirements, the capital costs for new plating lines can be expected to be about equal for either process. Thus, for a new installation, the zinc-plating process offers an economic advantage of lower operating cost.

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The U.S. Environmental Protection Agency and Battelle wish to thank Aeroquip Corporation for providing the site for this evaluation. The authors appreciate the cooperation and assistance provided by the Aeroquip staff, particularly Mr. James Bookman in the Metal Finishing Department. Mr. Bookman arranged the salt-spray corrosion tests, provided assistance to Battelle project staff during collection of wastewater and sludge samples, and collected and supplied data from Aeroquip files for inclusion in the evaluation.

#### **SECTION 1**

#### INTRODUCTION

### **GENERAL OVERVIEW**

The objective of the U.S. Environmental Protection Agency's (U.S. EPA) Waste Reduction Innovative Technology Evaluation (WRITE) Program is to evaluate in the work place prototype technologies that have potential for reducing wastes at the source (also referred to as preventing pollution). In general, each technology is evaluated on three issues.

First, the new technology's effectiveness is assessed, in terms of maintaining product quality. Pollution prevention or waste reduction technologies usually recycle or reuse materials, or use alternative materials or techniques. Therefore, it is important to verify whether the quality of the feed materials and the quality of the products are acceptable for the intended purpose.

Second, the impact of the new technology on waste generation is measured. The new technology is compared with the existing technology (baseline) or the process that it replaces. The wastes generated from each technology are determined and compared.

Third, the economics of the new technology are quantified and compared with the economics of the existing technology.

This study evaluated the zinc chloride electroplating process as a substitute for cadmium cyanide electroplating in the manufacture of industrial connectors and fittings at Aeroquip Corporation. The process substitution eliminates certain wastes, specifically cadmium and cyanide, which are listed among the 17 priority toxic pollutants designated by the U.S. EPA, although as will be seen, zinc and chromium wastes increased with the process change.

# DESCRIPTION OF THE SITE AND TECHNOLOGY STUDIED

The site for this study was Aeroquip Corporation, in Van Wert, Ohio. Aeroquip manufactures industrial connectors such as hose fittings. The specific area studied was the zinc chloride plating operation, which includes a rack plating line and two barrel plating lines.

Plating operations at Aeroquip previously used cadmium cyanide plating baths to deposit a 0.005-0.010-mm (0.0002-0.0004-inch) cadmium coating to provide protection against corrosion. Both cadmium and cyanide, however, are toxic chemicals targeted for reduction by the U.S. EPA. In December 1990 and January 1991, Aeroquip modified its plating process to substitute zinc chloride plating for cadmium cyanide plating. This substitution eliminated hazardous cadmium and cyanide wastes.

The zinc chloride plating processes for the rack plating and the two barrel plating lines (single-hoist and double-hoist) are illustrated in Figures 1, 2, and 3, respectively. Each step in the automated plating operation is carried out in a tank with racks or barrels of pieces progressing through each step in sequence. The tanks are open at the top to allow the racks or barrels to enter from above. Rinse water and chemicals are added continuously or intermittently to appropriate tanks to maintain the desired tank levels and concentrations of chemicals.

Comparisons of the cadmium cyanide and the zinc chloride plating processes for the rack plating and the barrel plating lines are shown in Tables 1, 2, and 3 respectively. Hydrochloric acid is used to condition parts (shown as step 12 in Table 1 and step 10 in Tables 2 and 3) prior to plating in the zinc chloride process whereas sodium cyanide is used in the cadmium cyanide process. The cadmium cyanide lines had separate tanks to apply either clear chromate or yellow chromate coatings (e.g., steps 18 and 20 in Table 1). Aeroquip used clear chromate coating on the majority (90-95 percent) of cadmium-plated parts. Currently, Aeroquip use yellow chromate coating on all zinc-plated parts. The reasons for the change were: (a) Aeroquip has adopted a worldwide standardization of yellow as the color their fittings and (b) the corrosion protection of the zinc-plated fittings vastly improves when the fittings are coated with yellow chromate. The yellow chromate solution used by Aeroquip contained approximately five times greater chromium concentration than the clear chromate solution. In the water-soluble oil application step (e.g., step 22 in Table 1), the concentration of the oil was substantially reduced by a factor of approximately ten in the zinc

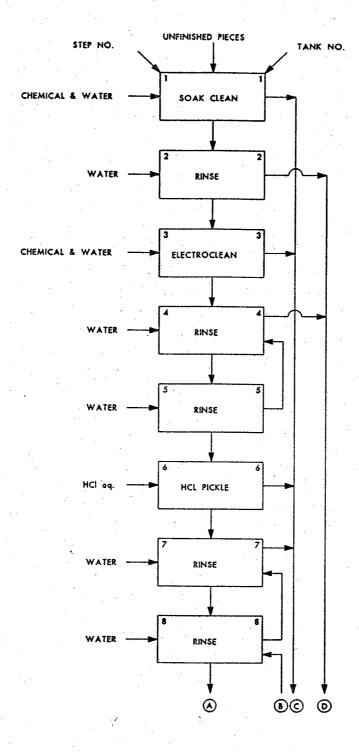


Figure 1. Flowsheet of zinc chloride rack plating line (continued).

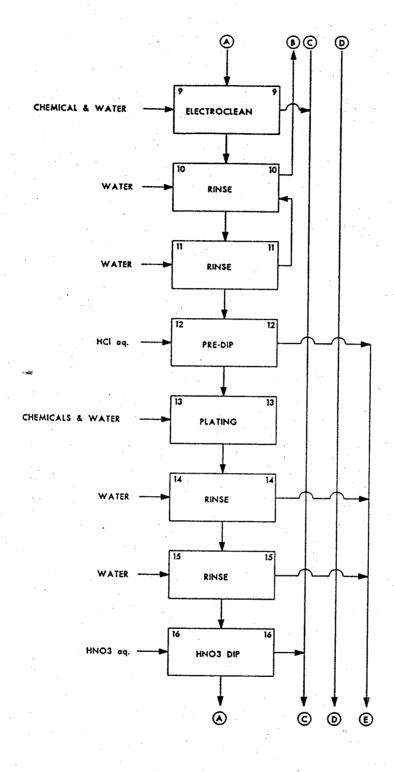


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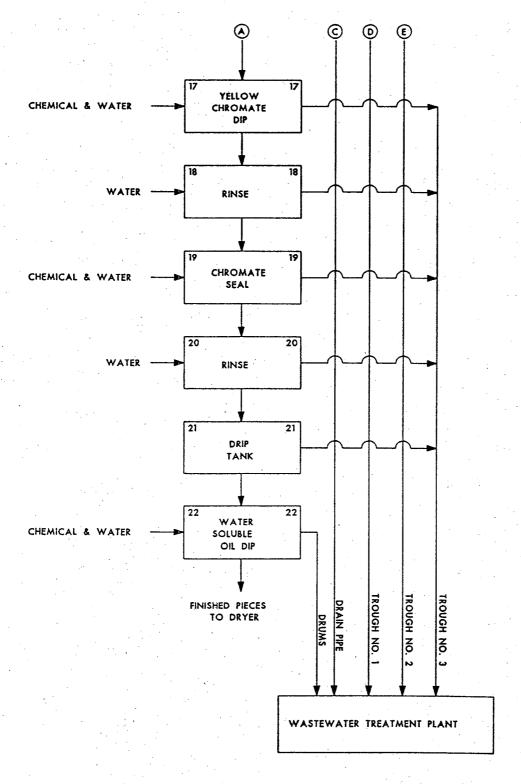


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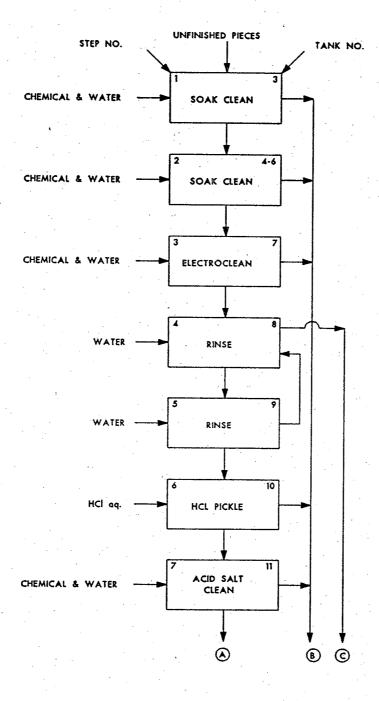


Figure 2. Flowsheet of zinc chloride single hoist barrel plating line (continued).

Note: Letters A, B, C, and D refer to continuation of flow lines

between successive pages.

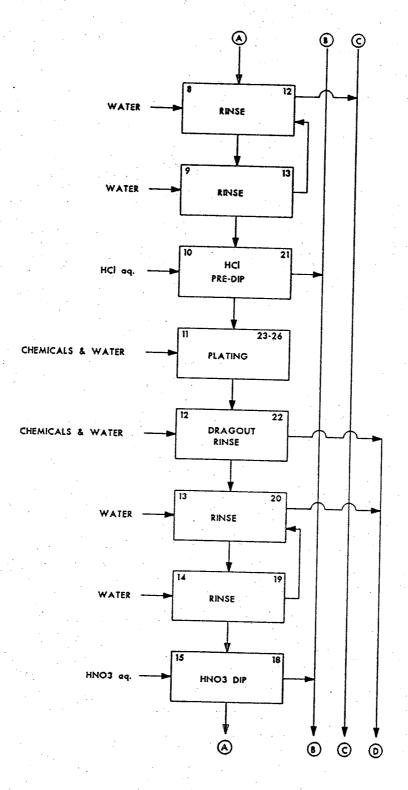


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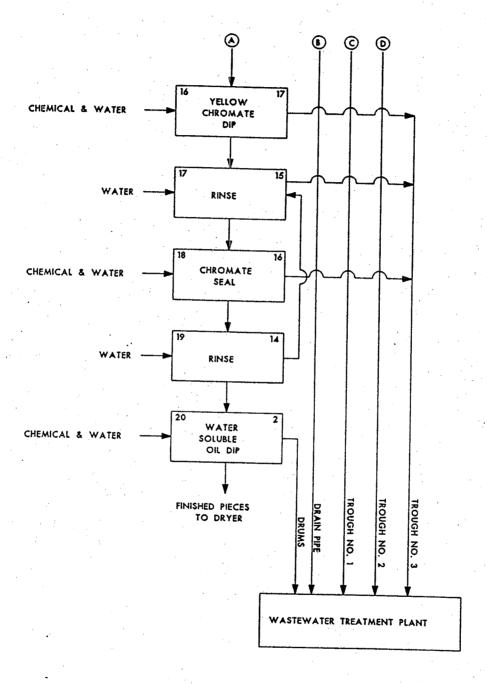


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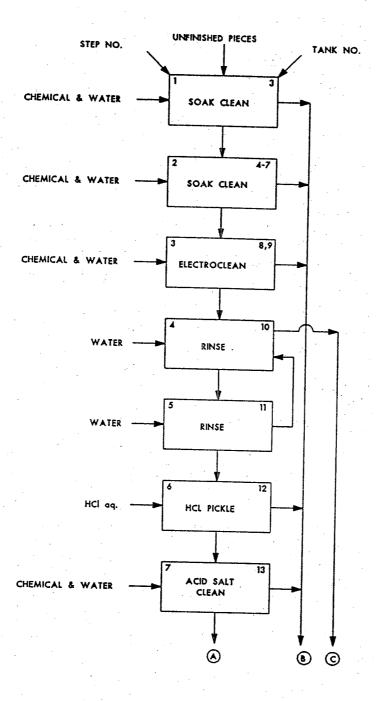


Figure 3. Flowsheet of zinc chloride double hoist barrel plating line (continued).

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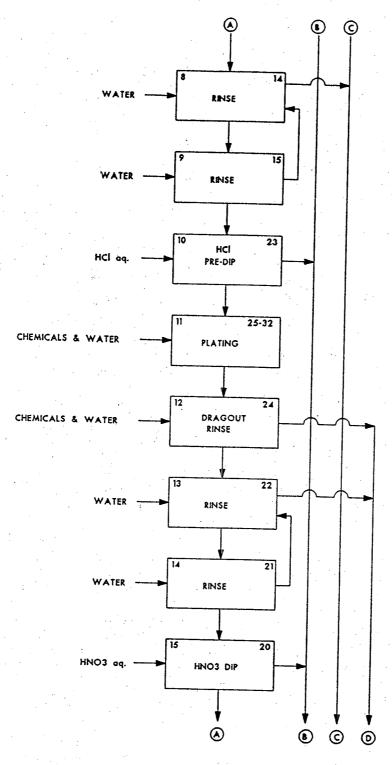


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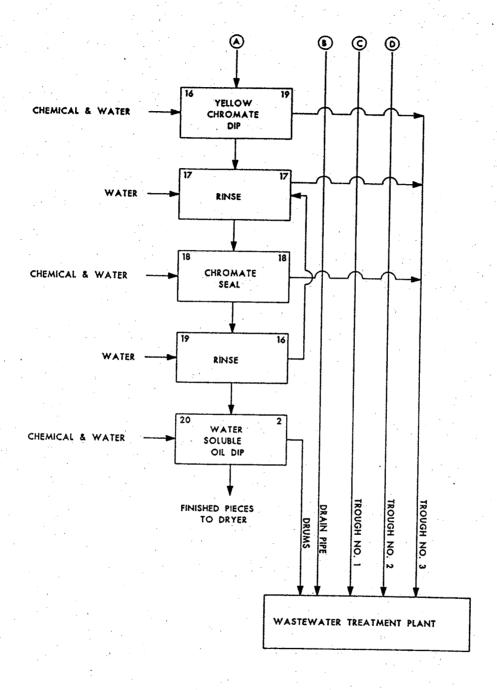


Figure 3. (continued).

TABLE 1. COMPARISON OF ZINC CHLORIDE AND CADMIUM CYANIDE RACK PLATING PROCESSES

		Operation		
Process Step	Tank No.	Zinc Chloride Plating Line	Cadmium Cyanide Plating Line Soak clean	
. 1	1	Soak clean		
2	2	Rinse	Rinse	
3	3	Electroclean	Electroclean	
4	4	Rinse	Rinse	
5	5	Rinse	Rinse	
6	6	Hydrochloric acid pickle	Hydrochloric acid pickle	
7	7	Rinse	Rinse	
8	8	Rinse	Rinse	
9	9	Electroclean	Electroclean	
10	10	Rinse	Rinse	
11	11	Rinse	Rinse	
12	12	Hydrochloric acid pre-dip	Sodium cyanide pre-dip	
13	13	Zinc plating	Cadmium plating	
14.	14	Rinse	Rinse	
15	15	Rinse	Rinse	
16	16	Nitric acid dip	Rinse	
17	17	Yellow chromate dip <sup>(a)</sup>	Nitric acid dip	
18	18	Rinse	Clear chromate dip <sup>(a)(b)</sup>	
19	19	Chromate seal	Rinse <sup>(b)</sup>	
20	20	Rinse	Yellow chromate dip <sup>(b)</sup>	
21	21	Drip tank dip	Rinse <sup>(b)</sup>	
22	22	Water-soluble oil dip <sup>(c)</sup>	Water-soluble oil dip(c)	

<sup>(</sup>a) The Cr concentration in the yellow chromate bath was approximately five times the Cr concentration in the clear chromate bath.

<sup>(</sup>b) Approximately 90-95 of the cadmium-plated parts were coated with clear chromate, and the remainder coated with yellow chromate.

<sup>(</sup>c) The oil concentration in the water-soluble oil bath in the zinc-plating process was approximately 1/10 of the concentration used in the cadmium-plating process.

TABLE 2. COMPARISON OF ZINC CHLORIDE AND CADMIUM CYANIDE SINGLE HOIST BARREL PLATING PROCESSES

		Operation		
Process Step	Tank No.	Zinc Chloride Plating Line	Cadmium Cyanide Plating Line	
1	3	Soak clean	Soak clean	
2	4-6	Soak clean	Soak clean	
3 .	7	Electroclean	Electroclean	
4	8	Rinse	Rinse	
5	9	Rinse	Rinse	
6	10	Hydrochloric acid pickle	Hydrochloric acid pickle	
7	11	Acid salt clean	Acid salt clean	
8	12	Rinse	Rinse	
9	13	Rinse	Rinse	
10	21	Hydrochloric acid pre-dip	Sodium cyanide pre-dip	
11	23-26	Zinc plating	Cadmium plating	
12	22	Dragout rinse	Dragout rinse	
13	20	Rinse	Rinse	
14	19	Rinse	Rinse	
15	. 18	Nitric acid dip	Nitric acid dip	
16	17	Yellow chromate dip <sup>(a)</sup>	Clear chromate dip <sup>(a)(b)</sup>	
17	15	Rinse	Rinse <sup>(b)</sup>	
18	16	Chromate seal	Yellow chromate dip <sup>(b)</sup>	
19	14	Rinse	Rinse <sup>(b)</sup>	
20	2	Water-soluble oil dip(c)	Water-soluble oil dip <sup>(c)</sup>	

<sup>(</sup>a) The Cr concentration in the yellow chromate bath was approximately five times the Cr concentration in the clear chromate bath.

<sup>(</sup>b) Approximately 90-95 of the cadmium-plated parts were coated with clear chromate, and the remainder coated with yellow chromate.

<sup>(</sup>c) The oil concentration in the water-soluble oil bath in the zinc-plating process was approximately 1/10 of the concentration used in the cadmium-plating process.

TABLE 3. COMPARISON OF ZINC CHLORIDE AND CADMIUM CYANIDE DOUBLE HOIST BARREL PLATING PROCESSES

_		Operation		
Process Step	Tank No.	Zinc Chloride Plating Line	Cadmium Cyanide Plating Line Soak clean	
1	3	Soak clean		
2	4-7	Soak clean	Soak clean	
3	8-9	Electroclean	Electroclean	
4	10	Rinse	Rinse	
5	11	Rinse	Rinse	
6	12	Hydrochloric acid pickle	Hydrochloric acid pickle	
7	13	Acid salt clean	Acid salt clean	
8	14	Rinse	Rinse	
9	15	Rinse	Rinse	
10	23	Hydrochloric acid pre-dip	Sodium cyanide pre-dip	
11	25-32	Zinc plating	Cadmium plating	
12	24	Dragout rinse	Dragout rinse	
13	22	Rinse	Rinse	
14	21	Rinse	Rinse	
15	. 20	Nitric acid dip	Nitric acid dip	
16	. 19	Yellow chromate dip <sup>(a)</sup>	Clear chromate dip <sup>(a)(b)</sup>	
17	17	Rinse	Rinse <sup>(b)</sup>	
18	18	Chromate seal	Yellow chromate dip(b)	
19	16	Rinse	Rinse <sup>(b)</sup>	
20	2	Water-soluble oil dip <sup>(c)</sup>	Water-soluble oil dip(c)	

<sup>(</sup>a) The Cr concentration in the yellow chromate bath was approximately five times the Cr concentration in the clear chromate bath.

<sup>(</sup>b) Approximately 90-95 of the cadmium-plated parts were coated with clear chromate, and the remainder coated with yellow chromate at.

<sup>(</sup>c) The oil concentration in the water-soluble oil bath in the zinc-plating process was approximately 1/10 of the concentration used in the cadmium-plating process.

chloride plating process from the level used in the cadmium cyanide plating process. The change was necessary to obtain improved adhesion of chromate coating during the subsequent heat-curing step.

Rinse water and various cleaning and plating solutions are discharged continuously or periodically dumped from the tanks and treated in an on-site wastewater treatment plant. Wastewater bearing chromium is collected separately and treated with sulfur dioxide to convert hexavalent chromium to trivalent chromium, after which it is combined with the rest of the wastewater for further treatment. The combined wastewater is treated with sodium hydroxide to precipitate heavy metals as hydroxides. In the cadmium cyanide plating process, cyanide-bearing wastewater was collected separately and treated with chlorine gas to destroy cyanide; sodium sulfide was used to precipitate cadmium as a sulfide.

The wastewater with precipitated metal hydroxides is sent first to a gravity settler. The overflow from the gravity settler is clarified further in a sand filter before discharge to a sanitary sewer. The underflow from the gravity settler and the sand filter are sent to a sludge thickener, from which the sludge is pumped every 3 working days and dewatered in a filter press. The water-soluble oil is collected separately and treated with hydrochloric acid to form an insoluble oil phase, which subsequently is separated from water by decantation. The water is returned to the wastewater treatment plant. Material flows around the plating process and the wastewater treatment plant are illustrated in Figure 4.

All wastes from the plating operations eventually end up in three waste streams (treated water, dewatered sludge, and waste oil) that are discharged from the wastewater treatment plant. The treated water is discharged to a sanitary sewer and sent to the municipal wastewater treatment plant. The dewatered sludge is collected in a 20-cubic-yard hopper and sent to an off-site hazardous landfill once a month. The waste oil is collected in drums and sent to an off-site hazardous waste incinerator every 3 months.

Because the cadmium cyanide process is no longer in operation, its evaluation was based entirely on information provided by Aeroquip from their historical files. Evaluation of the present zinc chloride process was based on information provided by Aeroquip and on data generated in this study from Battelle's sampling and analysis of selected waste streams and from testing of zinc-plated parts for corrosion resistance. Aeroquip's analyses were not subject to the same QA/QC as were the analyses by Battelle's subcontractor for analytical work. The only waste analysis data available from Aeroquip for the cadmium cyanide process

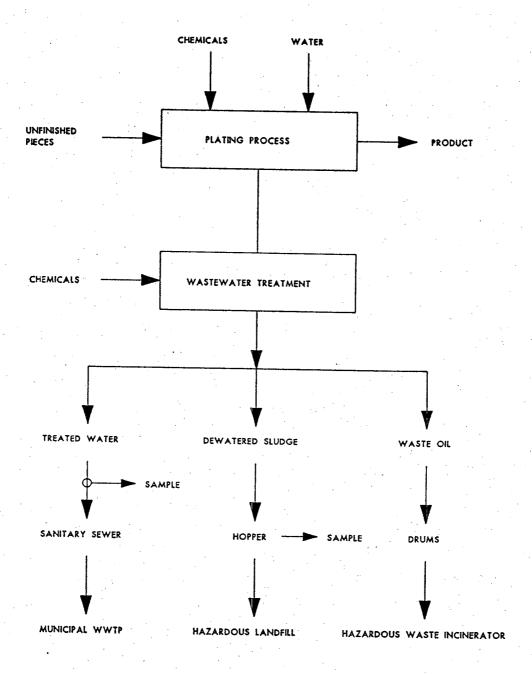


Figure 4. Material flows around electroplating and wastewater treatment processes.

were on the dewatered sludge and the treated water discharged from the wastewater treatment plant. Therefore, these same two streams were sampled and analyzed for the existing zinc chloride process so that the two processes could be compared.

### LITERATURE SURVEY

The literature survey conducted on this project indicates that the search for alternative processes for cadmium electroplating started in the 1970s. For example, the U.S. EPA and seven other government agencies sponsored a government-industry workshop on "Alternatives for Cadmium Electroplating" at the National Bureau of Standards (NBS) in Gaithersburg, Maryland, during October 2-4, 1977 (Journal of Plating and Surface Finishing, 1977). At this workshop, the Food and Drug Administration presented the results from a survey study indicating that the average human intake of cadmium in the U.S. was estimated at 72 micrograms per day from food and water and was approaching the maximum level recommended by the World Health Organization. NBS estimated that the majority of cadmium water pollution in the U.S. was caused by cadmium electroplating and stripping.

International Business Machines (IBM) reported at the workshop that they had begun to look for an alternative to cadmium plating in 1973 for 2,500 IBM parts plated with cadmium. After an eight-month engineering study, IBM had successfully switched from cadmium to zinc plating over a five-month period for all but 60 out of 2,500 parts that required corrosion protection only. The other IBM parts formerly plated with cadmium for properties other than corrosion protection were switched to zinc plating followed by a water-emulsion post treatment for parts requiring lubricity, to tin or tin-lead alloy for parts requiring good solderability, and to electroless nickel for a few remaining parts.

Other alternatives to cadmium plating reported at the workshop included: zinc-nickel alloy plating by Sandia Laboratories., a tin alloy containing about 35 percent zinc by Tin Research Institute, and ion vapor deposited (IVD) aluminum by McDonnell Aircraft Co. and by Air Force Materials Laboratory. Dini and Johnson (1979) from Sandia Laboratories describe results from salt-spray corrosion tests performed on steel panels electroplated with zinc-nickel alloy, cadmium and zinc. The data obtained at 2.5-micron coating thickness indicate the appearance of red rust after 72 hours for zinc coating (with chromate treatment) and

192 hours for cadmium coating (with chromate treatment), but no red rust after 500 hours for zinc-nickel coating (with chromate treatment).

Hsu (1984) from Boeing describes another zinc-nickel plating process, which produced coatings that were better than cadmium-titanium coatings for corrosion protection. Salt-spray corrosion tests showed a steel panel plated with a 12.5-micron Boeing zinc-nickel coating showed no corrosion after 7,604 hours whereas a steel specimen plated with cadmium-titanium coating corroded completely in the center after 1,848 hours. Rizzi et al. (1986) describe a new zinc based coating containing phosphates and silicon that outperformed cadmium and zinc in salt-spray corrosion tests. The time to appearance of red corrosion was 100 hours for commercial electrodeposited zinc, 300 hours for cadmium, and 1,150 hours for the new zinc coating. Evaluation of alternative coatings for bearings prepared by the Kaydon Bearing Div., Keene Corp. (Iron Age, 1980) shows zinc plating to be equal to cadmium plating in corrosion resistance.

Donakowski and Morgan (1983) from Ford Motor Co. describe the development of zinc/graphite composite coatings to achieve the anti-galling properties of cadmium desired for fasteners. Relative coefficients of friction determined by using the Ford Portable Joint Analyzer were 0.13 for zinc/graphite and 0.12 for cadmium. Salt-spray corrosion tests on nuts electroplated with a 12.7-micron coating showed first appearance of white corrosion after 120 hours for zinc/graphite (with chromate treatment) and no corrosion after 288 hours for cadmium (with chromate treatment).

The findings from the literature survey suggest that zinc or zinc-based coatings are the most widely used alternatives to cadmium coating.

### STATEMENT OF OBJECTIVES

The goal of this project was to evaluate the substitution of cadmium cyanide electroplating with zinc chloride electroplating. This study had three primary objectives.

- Evaluate the effects of the process substitution on product quality.
- Evaluate the waste reduction/pollutant reduction effects of the process substitution.
- Evaluate the economics of implementing the process substitution.

#### **SECTION 2**

# **CONCLUSIONS AND RECOMMENDATIONS**

Based on the product quality evaluation performed in this study and data provided by Aeroquip, it was concluded that zinc-plated parts meet customer requirements of 96 hours of corrosion test (ASTM Method B117-90) before the appearance of white corrosion products. Further, the zinc-plated parts meet the Aeroquip process requirements of 360 hours of corrosion test before the appearance of red rust. Cadmium-plated parts are superior in their corrosion resistance properties (i.e., appearance of white corrosion products and red rust in salt-spray tests) to zinc-plated parts. However, as indicated above, the corrosion resistance of zinc-plated parts was considered satisfactory for Aeroquip's customer requirements. The process substitution also satisfied the requirements of some domestic and foreign customers for cadmium-free products.

The changes in waste generation from the process substitution were: (a) reduction of cadmium by 12,100 lb/yr, (b) reduction of cyanide (as CN) by 835 lb/yr, (c) reduction of oil and grease waste, including waste oil, from 14,600 lb/yr to 5,120 lb/yr, (d) increase of zinc by 22,300 lb/yr, (e) increase of chromium from 677 lb/yr to 4,420 lb/yr, (f) increase of treated wastewater from 40,000,000 gal/yr to 44,900,000 gal/yr, and (g) increase of wastewater treatment sludge from 282,000 lb/yr to 383,000 lb/yr. Table 4 shows the pollutant generation from each process. The process substitution eliminated cadmium and cyanide, which are priority pollutants. The increases in wastewater and sludge were due increase in plating bath concentration from approximately 3 oz/gal cadmium in the cadmium-plating baths to approximately 3.5 oz/gal zinc in the zinc-plating baths. The decrease in oil and grease was due to approximately tenfold decrease in the concentration of oil used in the water-soluble oil dip tank. The increase in chromium was due to approximately fivefold increase in the chromate bath concentration. The chromium, which also is a priority pollutant, is effectively converted from the toxic hexavalent form to a much less toxic trivalent form in the wastewater treatment plant; therefore, it does not pose as great a health risk as cadmium.

The overall hazard level of the waste, therefore, was substantially reduced by eliminating cadmium and cyanide. The process substitution also eliminated the use of chlorine (96,500 lb in 1989) for cyanide destruction in the wastewater treatment plant. The process substitution, therefore, significantly reduced personnel health risks from handling hazardous materials, such as cadmium, cyanide and chlorine. Consequently, the process substitution has reduced the company's potential liability for accidental worker exposure to and environmental release of these hazardous materials.

TABLE 4. POLLUTANTS GENERATED FROM CADMIUM- AND ZINC-PLATING PROCESSES (LB/YEAR BASED ON PRODUCTION RATE OF 3.39 MILLION SQ FT)

Pollutant	Cadmium Plating	Zinc Plating	
Cd	12,100	. 0	
Total CN	835	• . • . • . • . • . • . • . • . • . •	
Total Cr	677	4,420	
Zn	0	22,300	
Oil & Grease	14,600	5,120	

The capital cost for the process change at Aeroquip was estimated to be \$1,972,000. About 72 percent of the capital cost was for expenses associated with cleaning up the process equipment contaminated with cadmium and cyanide, and for disposal of the waste generated from the cleanup activity, and the remaining 28 percent was for new equipment. The annual operating cost reduction that resulted from the process change was estimated to be \$17,100. Based on these costs, the estimated payback period is 115 years. The process change, therefore, cannot be justified on economic grounds alone. Justification would be based on the improved worker and environmental safety considerations plus the market's requirements for zinc-plated rather than cadmium-plated parts in many applications. However, in comparing the two for a new installation, the zinc chloride-plating process offers obvious advantages over the cadmium cyanide-plating process.

#### SECTION 3

## **MATERIALS AND METHODS**

### PRODUCT QUALITY

Product quality was measured by the corrosion resistance of plated parts determined by salt-spray (fog) tests. Salt-spray tests were carried out in accordance with the ASTM Method B117-90 [Standard Test Method of Salt Spray (Fog) Testing]. Test specimens are suspended in a chamber and exposed to a salt-spray (fog) under controlled conditions of temperature, salt solution concentration and pH, and spraying rate. For the duration of the test period, test specimens are visually inspected at 24-hour intervals (except weekends) for the initial appearance of corrosion products on part surfaces and the subsequent progress of corrosion.

# Corrosion Resistance Requirements at Aeroquip

As part of their quality acceptance criteria for zinc-plated parts, Aeroquip's engineering process specification has adopted the ASTM Method B633-85 (Standard Specification for Electrodeposited Coatings of Zinc on Iron and Steel) requirement of 96 hours of freedom from white corrosion products in salt-spray testing. Most Aeroquip customers require 96 hours before the first appearance of white corrosion on zinc-plated parts. ASTM Method B633-85 requires the corrosion resistance of zinc-plated specimens to be determined in accordance with ASTM Method B117-90. ASTM Method B633-85 states that zinc coatings with Type II treatment (i.e., with colored chromate conversion coating) shall show corrosion products of neither zinc nor the substrate metal after 96 hours, when tested by continuous exposure to salt spray in accordance with ASTM B117-90. The first appearance within 96 hours of corrosion products visible to the unaided eye at normal reading distance

shall be cause for rejection, except that white corrosion products at the edges of specimens shall not constitute failure.

The process specification for some of Aeroquip's products has an additional acceptance criterion of 360 hours of salt-spray exposure before the first appearance of red rust.

Thus the salt-spray test requirements for Aeroquip zinc-plated (plus yellow chromate) parts are as follows:

Appearance of White Corrosion: 96 hr (all parts)
Appearance of Red Rust: 360 hr (designated parts).

# ASTM Method B117-90: Apparatus and Operating Conditions

The apparatus required for salt-spray (fog) testing, in accordance with ASTM Method B 117-90, consists of a fog chamber, a salt solution reservoir, a supply of suitably conditioned compressed air, one or more atomizing nozzles, specimen supports, and the necessary means for control. The size and construction details of the apparatus are optional, provided the conditions obtained meet the requirements of this method.

According to ASTM Method B 117-90, the fog shall be such that, for each  $80 \text{ cm}^2$  of horizontal collecting area, there will be collected in each collector from 1.0 to 2.0 ml of solution per hour, based on an average of at least 16 hours. B 117-90 states also that: (1) the sodium chloride concentration shall be  $5 \pm 1$  weight percent (specific gravity, 1.027-1.041) and (2) the pH of the collected solution shall be 6.5 to 7.2. Other data on chamber operation are provided later in this report in the section that covers the salt-spray tests carried out by Detroit Testing Laboratory on zinc-plated specimens.

It should be noted that ASTM Method B117-90 prescribes neither the type of test specimen and exposure periods to be used for a specific product nor the interpretation to be given the results. It should be noted further that there seldom is a direct relation between resistance to salt spray and resistance to corrosion in other media. This is because the chemistry of the reactions, including the formation of films and their protective value, frequently varies greatly with the precise conditions encountered by parts during use.

The reader should be aware also of possible wide variations in the quality and thicknesses of coatings on plated items produced on the same racks at the same time and the consequent need to use multiple specimens for testing.

# **Experimental Corrosion Property Evaluation Program**

For the salt-spray corrosion tests, 12 pieces each of four representative types of zinc-plated parts were obtained for use as test specimens. Each group of 12 pieces was split into two smaller groups of six specimens each. This was done to provide two sets (consisting of four groups each) for testing. One set was retained by Aeroquip for testing in its laboratory; the other set was given to Battelle, which in turn sent the set to an independent testing laboratory [Detroit Testing Laboratory, Inc. (DTL), Warren, Michigan]. Thus, the salt-spray tests were conducted in parallel by Aeroquip and DTL. The parts evaluated in the salt-spray test are shown in Figure 5.

All of the above parts were rack plated with zinc (thickness: 0.0002-0.0004 inch), followed by a yellow chromate coating.

## DTL Salt-spray Tests

A total of 24 zinc-plated specimens, comprising six pieces each of four representative Aeroquip fittings (Figure 5), were subjected to 5-percent salt-spray (fog) corrosion testing by DTL, in accordance with procedures designated in ASTM B 117-90.

Tests were carried out in a Singleton Corrosion Test Chamber. The specimens were mounted with the significant surface inclined approximately 15 degrees from the vertical and exposed for 360 hours, with evaluations every 24 hours (excluding weekends). After 360 hours, the test specimens were rinsed in running water (not warmer than 100°F) and dried. During the 360-hour (14 day) test period, the 11 readings (daily except for weekends) showed that cabinet temperature was 95 ± 1°F, tower temperature was 120-121°F, and tower pressure was 10 psi. All of these readings were in accordance with B117-90 test requirements. Four separate solution collectors were employed in the cabinet. Examination of the data for each of the four collectors showed that (1) the collection volume rates all were within a range of 1.0 to 1.2 ml/hr; (2) the pH values of the collected solution were within a range of 6.6 to 6.8; and (3) the specific gravities of the collected solutions were all within a range of 1.031 to 1.032 (4.6 to 4.8 percent NaCl). These collection volumes, solution pH values, and concentrations were all within the required ranges of B 117-90, as described above.

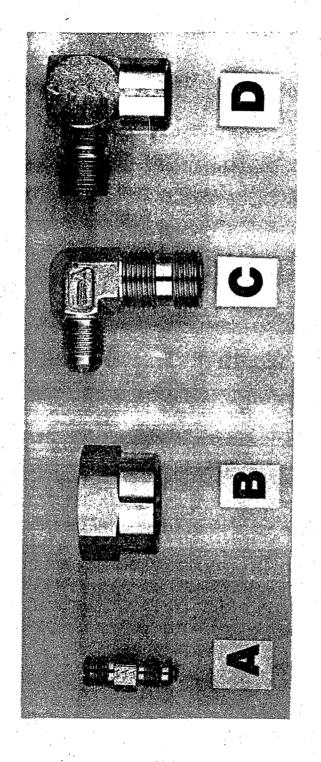


Figure 5. Zinc-plated parts salt-spray tested by Detroit Testing Laboratory and Aeroquip (rack plated).

Group A: Part No. 2021-2-35; pipe to 37° male flare adapter Group B: Part No. 210204-12s; swivel nut (crimp type) Group C: Part No. 2206204-8-6s; SAE male to 37° male flare adapter Group D: Part No. 2089-6-6s; 90° male to female pipe adapter

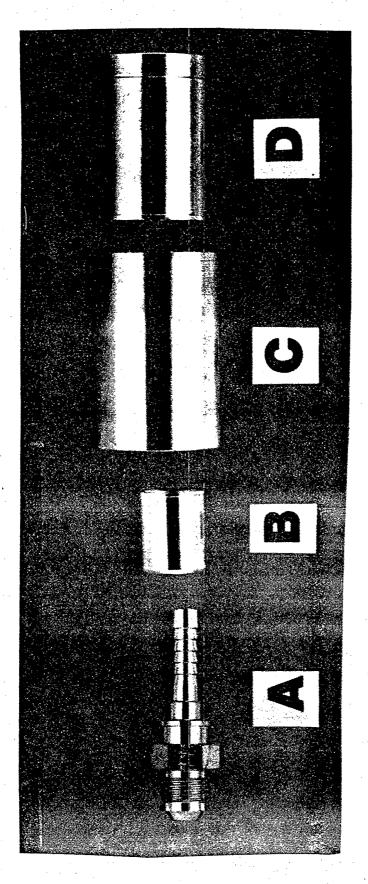


Figure 6. Zinc-plated parts salt-spray tested by Aeroquip (barrel plated).

Group A: Part No. FC1044; nipple Group B: Part No. FC3596-08s; crimp socket Group C: Part No. FC1006-12s; socket Group D: Part No. FC1130-08s; socket

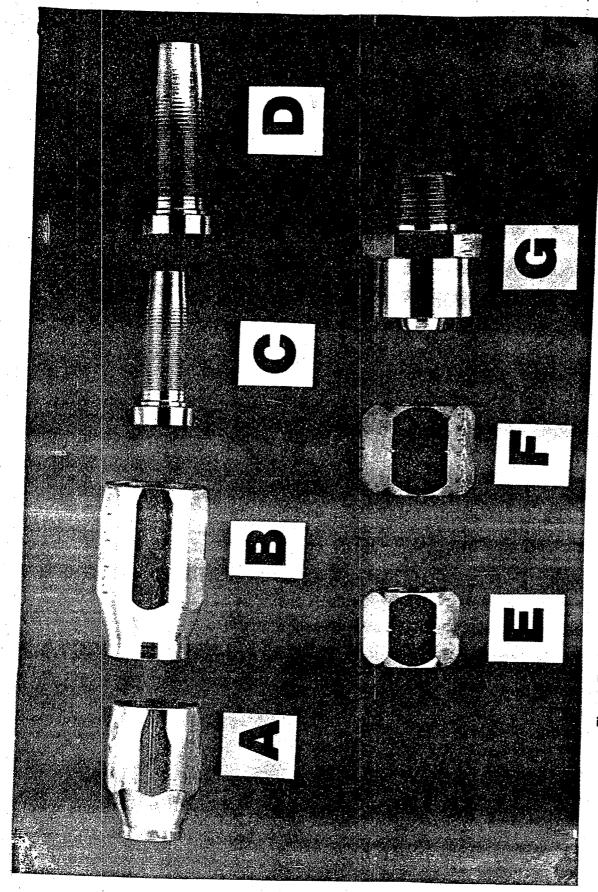


Figure 7. Cadmium- and zinc-plated parts salt-spray tested by Aeroquip.

Group A: Part No. 1210-6s; reusable socket (barrel plated) Group B: Part No. 1210-82; reusable socket (barrel plated) Group C: Part No. 1241-6s; reusable nipple (barrel plated) Group D: Part No. 1251-8s; reusable nipple (harrel plated) Part No. 1241-6s; reusable nipple (barrel plated) Part No. 1251-8s; reusable nipple (barrel plated)

Group E: Part No. 1285-6s; nut (barrel plated) Group F: Part No. 1285-8s; nut (rack plated) Group G: Part No. FC5192-0606s; crimp fitting (rack plated)

The concentrations of zinc and total chromium in the dewatered sludge and the treated water, and the total solids and the concentration of oil and grease in the dewatered sludge discharged from the zinc chloride process.

The historical data supplied by Aeroquip included: (a) wastewater and sludge generation data from 1989 and 1991; (b) waste oil generation data from 1989 and 1991; (c) treated wastewater analysis data from 1989, 1991, and 1992; and (d) sludge analysis data from 1987, 1988, and 1991.

Battelle collected additional samples of sludge and treated wastewater to determine zinc, total chromium, and oil and grease (for sludge only) for comparison with the analysis data provided by Aeroquip. Table 5 shows the samples collected by Battelle. The samples collected by Battelle were analyzed by a subcontractor (Zande Environmental Service). The generation of all pollutants, in lb/yr, including cadmium, cyanide, zinc, total chromium, and oil and grease, was calculated from the waste volume and analysis data received from Aeroquip.

Zande analyzed the sludge samples for zinc and total chromium using EPA Methods 3050 and 6010, for oil and grease using EPA Method 9071, and for total solids (moisture content) using ASTM Method D2216. Zande analyzed the treated wastewater and tap water samples for zinc and total chromium using EPA Methods 3010 and 6010. Battelle collected and determined the pH of the water samples at the time the samples were collected, using EPA Method 150.1.

Battelle collected all samples over a 2-week period. Battelle collected dewatered sludge samples as grab samples from the sludge hopper located at the discharge of the filter press. The sludge samples were taken from various locations in the hopper and mixed in a glass beaker to obtain composite samples. Battelle collected all sludge samples within a week after filter press operation.

TABLE 5. SUMMARY OF PRIMARY AND QUALITY CONTROL SAMPLES FOR CHEMICAL ANALYSIS AND CHARACTERIZATION

Sample Location	Sample Matrix	Time of Sampling	Number of Samples <sup>(b)</sup>	Measurements
Outlet of sand filter	Treated water	During the same week the sludge was sampled	4	Zn, total Cr, pH
Sludge hopper	Sludge	Within a week after filter press operation	6	Zn, total Cr, oil & grease, total solids
Tap water line	Tap water <sup>(a)</sup>	During the same week the sludge was sampled	2	Zn, total Cr

<sup>(</sup>b) Including one reserve sample for each sample matrix. Samples collected in the field did not include samples prepared in the laboratory for QA, such as duplicates, matrix spikes, and method blanks.

Battelle collected the treated wastewater samples continuously over a 24-hour period by means of the existing sampling pump in the plant, which is used at Aeroquip to collect composite water samples. The sample collection rate was varied in each shift in proportion to the discharge rate of each shift; i.e., at a ratio of 2.6:1.9:1.0 corresponding to first:second:third shifts. Battelle collected tap water samples as grab samples from a tap water faucet. These served as field blanks. A laboratory blank was provided by Zande Environmental Service, who performed the chemical analyses of treated wastewater and sludge samples.

# **ECONOMIC EVALUATION**

Economic evaluation of the process substitution was based on a simple payback period analysis, using the cost data provided by Aeroquip. The evaluation included estimation of capital costs for the process conversion and of the reduction, if any, in operating costs resulting from the process substitution. Capital costs included:

- plant modifications
- removal and disposal of the old cadmium cyanide plating solution
- the cost of a fresh zinc chloride plating solution
- cleanup of process tanks, piping and equipment.

## Operating costs included:

- operating and maintenance labor
- utilities
- plating chemicals
- wastewater treatment chemicals
- waste disposal costs.
- miscellaneous items, such as blood tests, environmental monitoring, record keeping, washdown of plating department, and treatment of washdown water

#### **SECTION 4**

## RESULTS AND DISCUSSION

## PRODUCT QUALITY

# **Experimental Corrosion Property Evaluation Program**

For the salt-spray corrosion tests, 12 pieces each of four representative types of zinc-plated parts were obtained for use as test specimens. Each group of 12 pieces was split into two smaller groups of six specimens each. All of the above parts were rack plated with zinc (thickness: 0.0002-0.0004 inch), followed by a yellow chromate coating. Detailed data and results of the salt-spray tests performed by DTL and Aeroquip are presented and discussed below.

# DTL Salt-Spray Test Data and Results

A total of 24 zinc-plated specimens, comprising six pieces each of four representative Aeroquip fittings (Figure 5), were subjected to 5-percent salt-spray (fog) corrosion testing by DTL, in accordance with procedures designated in ASTM B 117-90. Data and results of the DTL salt-spray tests are shown in Table 6.

As can be seen from the DTL salt-spray test results shown in Table 6, all of the Group A, B, and D specimens were free of white corrosion (WC) products at 120 hours, so that the 96-hour requirement of no WC for zinc-plated (plus yellow chromate) parts was met. Very slight WC was noted on some Group C specimens at 120 hours; therefore, no definitive statement can be made as to whether all the Group C specimens met the no-WC requirement for 96 hours. (Through an oversight, the observation at 96 hours (which occurred over the weekend) was not made as had been planned.) However, because results of the Aeroquip salt-spray tests, which had been run on comparable specimens (Table 7), showed no WC at 96 and

120 hours and small WC at 144 hours on the Group C specimens, it is likely that the DTL Group C specimens would have met the 96-hour requirement.

TABLE 6. RESULTS OF CORROSION RESISTANCE TESTS ON VARIOUS PARTS RACK PLATED WITH ZINC USING 5-PERCENT SALT SPRAY; TESTS PERFORMED BY DETROIT TESTING LABORATORY USING ASTM B117-90(a)

		· .	Corrosion Te	est Ratings <sup>(b)</sup>	
		Group A	Group B	Group C	Group D
Date	Elapsed Hours	2021-2-35 Adapter	210204-12s Swivel Nut	206204-8-6s Adapter	2089-6-6s Adapter
07/09/92	24	0	О	0	0
07/10/92	48	0	0	0	0
07/13/92	120	0	0	1 WC	0
07/14/92	144	0	1 WC	2 WC	1 WC
07/15/92	168	1 WC	1 WC	3 WC	2 WC
07/16/92	192	1 WC	1 WC	3 WC	2 WC
07/17/92	216	1 WC	2 WC	4 WC	3 WC
07/20/92	288	2 WC	2 WC	5 WC	4 WC
07/21/92	312	2 WC	4 WC	6 WC	5 WC
07/22/92	336	3 WC	6 WC	6 WC/2 RR <sup>(c)</sup>	5 WC
07/23/92	360	3 WC	6 WC	6 WC/4 RR <sup>(c)</sup>	5 WC

<sup>(</sup>a) Four different parts, which had been rack plated with zinc, were tested. Each group of parts consisted of six specimens.

(b) The following corrosion rating system was employed by DTL:

WC = White Corrosion

RR = Red Rust

0 = No corrosion

1 = Very slight

2 = Slight

3 = Slight to moderate

4 = Moderate

5 = Moderate to heavy

6 = Heavy

7 = Very heavy.

<sup>(</sup>c) Two of the six specimens in Group C exhibited red rust (RR) at the 336-hour and 360-hour observation times.

TABLE 7. RESULTS OF CORROSION RESISTANCE TESTS ON VARIOUS PARTS RACK PLATED WITH ZINC USING 5-PERCENT SALT SPRAY; TESTS PERFORMED BY AEROQUIP USING ASTM B117-90(a)

11			Corrosion 1	Test Results	
		Group A	Group B	Group C	Group D
Date	Elapsed Hours	2021-2-35 Adapter	210204-12s Swivel Nut	206204-8-6s Adapter	2089-6-6s Adapter
07/10/92	0	***			
07/13/92	72	No signs of white corrosion (WC)	No signs of WC	No signs of WC	No signs of WC
07/14/92	96	No change	No change	No change	No change
07/15/92	120	WC on threads and near braze joint	WC on threads and cones	No change	WC on threads and cones
07/16/92	144	No change	No change	Small WC, small specks on corners	No change
07/17/92	168	No change	No change	No change	No change
07/20/92	240	No change	No change	More WC	No change
07/21/92	264	No change	No change	No change	One part of six has red rust (RR)
07/22/92	288	More WC; black areas	No change	More WC	No change
07/23/92	312	No change	No change	No change	No change
07/24/92	336	No change	No change	No change	No change
07/27/92	408	No change	One part RR on ext. threads, RR on ID; parts removed	No change	No change; parts removed
07/28/92	432	RR starting on two parts; parts removed		No change	
07/29/92	456	74+		No change	
07/30/92	480	+++		No change	
07/31/92	504	# 4 ···	***	No change	4
08/03/92	576			No change	
08/04/92	600	***		More WC	
08/05/92	624		***	No change	
08/06/92	648			Small discolored spots on flats of hex.	
08/07/92	672			RR spots; parts re-	

<sup>(</sup>a) Four different parts, which had been rack plated with zinc, were tested. Each group of parts consisted of six specimens. Readings of cabinet temperatures and pressures and salt-spray conditions were generally in compliance with B117-90 requirements for the overall test period. Some problems with the D.I. water supply and pH meter were encountered from 07/07/92 to 07/23/92, so that salt solution pH values were below 6.5. The effect of lower solution pH values or corrosion results was not considered significant. If anything, the lower pH would have resulted in a more corrosive salt-spray solution.

In the DTL tests, all specimens in Groups A, B, and D were free of red rust (RR) at the end of the 360-hour observation period. Two of the six specimens in Group C showed

RR at the 336-hour and 360-hour observation periods. In comparison, the Aeroquip tests (Table 7) on the Group C specimens showed no RR until the observation at 672 hours.

## Aeroquip Salt-Spray Test Data and Results

As was done at DTL, four comparable groups of six pieces each (Figure 5) were subjected to 5 percent salt-spray (fog) corrosion testing at the Aeroquip Laboratory in accordance with procedures designated in ASTM B117-90. Data and results of the Aeroquip salt-spray tests are presented in Table 7.

Because there was no sign of white corrosion products on any of the specimens in any of the groups at the 96-hour observation period, all specimens met the no WC requirement at 96 hours. One of the six parts in Group D showed red rust (RR) at the 264-hour observation point, but no other parts in Group D exhibited RR at the 408-hour observation point, at which time all Group D specimens were removed from the test chamber. Specimens in Groups A, B, and C exhibited good resistance to red rust; the first signs of red rust for specimens in the three groups were as follows:

Group A: 432 hours Group B: 408 hours Group C: 672 hours.

The Aeroquip salt-spray test results (Table 7) showed that the zinc (plus yellow chromate) plated parts exhibited very good performance with regard to freedom from white corrosion products for 96-hours. Further, the extended-exposure tests showed that only one of six specimens in Group D exhibited RR at 264 hours. Thus, of a total 24 specimens, only one specimen definitely would not have met the Aeroquip internal requirement of freedom from RR at 360 hours. One specimen in Group B exhibited RR at 408 hours; at 336 hours, no specimens in this group showed RR. Whether that one specimen exhibited RR at 360 hours is not known, as no observation was made at 360 hours, which occurred on a weekend.

# Comparison of DTL and Aeroquip Salt-Spray Test Results

The data and results shown in Tables 6 and 7 and discussed above demonstrate very good agreement in results of the salt-spray tests conducted by the two laboratories on the zinc-plated parts. In general, very good agreement and full compliance with the requirement for absence of white corrosion products for 96 hours was noted for the groups of specimens tested at both laboratories. Further, there was generally good agreement in results with respect to the appearance of red rust. At both laboratories, only 3 of 48 specimens did not meet Aeroquip's internal requirement of freedom from red rust for 360 hours of exposure to salt spray.

## Additional Aeroquip Salt-Spray Test Data and Results

In addition to the salt-spray testing of the rack-plated parts, carried out in parallel by DTL and Aeroquip and reported above in Tables 6 and 7, Aeroquip also tested four groups of barrel-plated parts. Each group of parts consisted of six specimens plated with zinc. Corrosion data and results of these latter tests are presented in Table 8. As can be seen from Table 8, all specimens in all four groups met the requirement of freedom from white corrosion (WC) products at 96 hours. WC had started to appear on most of the specimens at the 168-hour observation point.

All parts also met the requirement of no red rust (RR) at 360 hours. One specimen in Group A exhibited RR at 432 hours. At 504 hours, RR was present on Group A and Group C parts, but Group B and Group D specimens showed no RR. The tests were terminated at 504 hours. The above data and results show that excellent resistance to both white corrosion and red rust was exhibited by all 24 specimens in the four groups of parts that had been barrel plated with zinc.

# Comprehensive Program of Salt-Spray Testing of Zinc- and Cadmium-Plated Parts at Aeroquip

From October 15 to November 5, 1991, Aeroquip carried out corrosion tests to compare the salt-spray corrosion resistance of zinc-plated parts with cadmium-plated parts. These tests were done in accordance with ASTM Method B117-90. Seven groups of representative parts plated with zinc and seven groups of identical parts plated with cadmium

were subjected to 5 percent salt-spray (fog) testing at Aeroquip. Barrel and rack plated parts were included in the program. Data and results of the salt-spray tests on the zinc- and cadmium-plated parts are presented in Tables 9 and 10, respectively.

TABLE 8. RESULTS OF CORROSION RESISTANCE TESTS ON VARIOUS PARTS BARREL PLATED WITH ZINC USING 5-PERCENT SALT SPRAY; TESTS PERFORMED BY AEROQUIP USING ASTM B117-90<sup>(a)</sup>

			Corrosion	Test Results	
	Elapsed	Group A	Group B	Group C	Group D
Date	Hours	FC1044 Nipple	FC3596-08s Crimp Socket	FC1006-12s Socket	FC1130-08 Socket
10/05/92	0				Sucket
10/06/92	24	No corrosion	No corrosion		
10/07/92	48	No corrosion	No corrosion	No corrosion	No corrosion
10/08/92	72	No corrosion	1	No corrosion	No corrosion
10/09/92	96	No corrosion	No corrosion	No corrosion	No corrosion
10/12/92	168		No corrosion	No corrosion	No corrosion
10/13/92		WC starting	WC starting	WC starting	WC starting
10/13/92	192	No change	No change	No change	No change
	216	No change	No change	No change	No change
10/15/92	240	Slightly more WC	Slightly more WC	Slightly more WC	Slightly more
10/16/92	264	No change	No change	No change	WC .
10/21/92	384	No change	More WC		No change
0/22/92	408	No change	No change	More WC	:More WC
0/23/92	432	Red rust (RR) on		No change	No change
		one part	No change	No change	No change
0/26/92	504	Red rust	No change	RR in I.D.	No change

<sup>(</sup>a) Four different parts, which had been barrel plated with zinc, were tested. Each group of parts consisted of six specimens.

TABLE 9. RESULTS OF CORROSION RESISTANCE TESTS ON VARIOUS PARTS PLATED WITH ZINC USING USING 5-PERCENT SALT SPRAY; TESTS PERFORMED BY AEROQUIP USING ASTM B117-90 IN 1991(a)

					Salt-spray Test Results	lits			- 11
ć	î	Group A	Group B	Group C	Group D	Group E	Group F	Group G	
<u> </u>	Elapsed Time, hr	1210-6s Barrel Plated Reusable Socket	1210-8s Barrel Plated Reusable Socket	1241-6s Barrel Plated Reusable Nipple	1241-8s Barrel Plated Reusable Nipple	1285-6s Barrel Plated Nut	1285-8s Rack Plated Nut	FC5192-0606s Rack Plated Crimp Fitting	
10-15-91	0	-	1			1			
10-16-91	24	Yellow chromate white corrosion ()	present; no (WC)	Yellow chromate corrosion (WC)	Yellow chromate present; no white corrosion (WC)	Yellow chromate present; no white corrosion (WC)	esent; no white c	orrosion (WC)	1
10-17-91	48	Slight color chang	ge in yellow chro	Slight color change in yellow chromate (lighter yellow); no corrosion	w); no corrosion	Slight color change in yellow chromate (lighter yellow); no corrosion	in yellow chroma	te (lighter yellow);	
10-18-91	72	Slight color change in yellow chromate (lighter yellow), no corrosion	ge in yellow yellow), no	Slight areas of W root of threads <sup>(b)</sup>	Slight areas of WC developing in the root of threads <sup>(b)</sup>	No change from 48-hr observation	hr observation	s.	1
10-19-91	<b>9</b>	Slight color chang chromate (lighter corrosion; sample	ge in yellow yellow), no ypulled	Slight areas of WC devel threads <sup>(b)</sup> ; sample pulled	Slight areas of WC developing on threads <sup>(b)</sup> ; sample pulled	No change from 48-hr observation; sample pulled	hr observation;	Slight WC developing on threads;(e)	
10-20-91	120	Slight areas of WC developing on edges and flats; sample pulled	C developing s; sample	Slight WC develo tending beyond the	Slight WC developing in size and ex- tending beyond thread region; sample pulled	Slight WC developing on edges and flats; sample pulled	on edges and	(No record of ob-	
10-21-91	144	Similar to the 120-hr observations; sample pulled	)-hr observations;	sample pulled	Similar to the 120-hr observations; sample pulled	Similar to the 120-hr observations; sample pulled	observations;	Similar to the 120-hr observations; no sample	
10-22-91	168	Near in appearance sample pulled	e to 120-hr observations;	vations;	Near in appearance to 120-hr observations; sample pulled	0-hr observations; sam	pelled bulled		
10-23-91	192	WC developing further in size/area; no sample pulled	rther in size/area;		WC developing further in size/area; no sample pulled	size/area; no sample p	pelln		7
									=

(continued)

TABLE 9. (Continued)

	1	T===					
	Group G	FC5192-0606s Rack Plated Crimp Fitting				WC more evident in thread area and hex area; round skirt portion is not as affected; sample pulled	
	Group F	1285-8s Reck Plated Nut	pelled s	nples pulled		present at hex ippears that RR levelop;	
iults	Group E	1285-6s Berrel Plated Nut	in size/area, no sample	ise in size/area; no san		WC and black areas present at hex corners and edges; appears that RR is just beginning to develop; sample pulled	
Salt-spray Test Results	Group D	1241-8s Barrel Pleted Reusable Nipple	WC developing further in size/area, no samples pulled	WC continuing to increase in size/area; no samples pulled		Results basically the same as for 1210-6s; sample pulled	
	Group C	1241-6s Barrel Plated Reusable Nipple	a, no samples	/area, no		WC on seat OD in thread region and at nose end; ap- pears that RR is developing; some yellow chromate still	nipple shank ramp angle; sample pulled
	Group B	1210-8s Barrel Plated Reusable Socket	WC developing further in size/area, no samples pulled	g further in size/area, no sam y to increase in size/area, no	WC predominant on one side and skirt end of socket; black area showing on exterior, but no RR;		
	Group A	1210-6s Barrel Plated Reusable Socket	WC developing pulled	WC continuing to samples pulled	•	WC present on exterior to various degrees, yellow invisible; no red rust (RR);	
	Elapsed	Time, hr	216 240 264 288 312	336 360 384 408	432 456 480	504	
	Date		10-24-91 10-25-91 10-26-91 10-27-91 10-28-91	10-29-91 10-30-91 10-31-91 11-01-91	11-02-91 11-03-91 11-04-91	11-05-91	

<sup>(</sup>a) Each group of parts consisted of six specimens.

According to ASTM B633-85, the first appearance of WC visible to the unaided eye at normal reading distance shall be cause for rejection except that WC products at the edges of specimens shall not constitute failure. Threads were considered to be the equivalent of edges.

TABLE 10. RESULTS OF CORROSION RESISTANCE TESTS ON VARIOUS PARTS PLATED WITH CADMIUM USING 5-PERCENT SALT SPRAY; TESTS PERFORMED BY AEROQUIP USING ASTM B117-90<sup>(4)</sup>

			·	Sa	Salt-epray Test Results	9		
į	i	Group A	Group B	Group C	Group D	Group E	Group F	Group G
Çağ	Time, hr	1210-6e Berrel Plated Reusable Socket	1210-8s Barrel Plated Reusable Socket	1241-6e Barrel Plated Reusable Nipple	1241-8e Barrel Plated Rousable Nipple	1286-8e Barrel Plated Nut	1285-8e Rack Plated Nut	FC5 192-0606a Reck Pleted Crime Fitting
10-15-91	0	•••				•		
10-16-91	24	No change observed	No change observed	No change observed	No change observed	No change observed	No change observed	No change observed
10-17-91	48	Parts starting to dull no corrosion	dull, losing sheen;	Parts starting to dull, losing sheen; no corrosion	II, fosing sheen;	Parts starting to c	Parts starting to dull, losing sheen; no corrosion	o corrosion
10-18-91	72	Same as 48-hour ob	observations	Same as 48 hour observations	bsorvations	Same as 48 hour observations	observations	Same as 48 hour observations
10-19-91	98	Parte turning grey in appearance; no corrosion	n appearance; no	Parts turning grey in appearance; no corrosion	n appearance; no	Parts turning grey	Parta turning grey in appearance; no corrosion	corrosion
10-20-91	120	Same as 96-hr obse	bservations	Same as 96-hr observations	ırvations	Same as 96-hr observations	servations	
10-21-91	144	Same as 96-hr obse	bservations	Same as 96-hr observations	rvations	Same as 96-hr observations	servations	
10-22-91	168	Parts continus to gre no corrosion	grey;	Parts continue to grey; no corrosion	ey; no corrosion	Parts continue to	Parts continue to gray; no corrosion	
10-23-91	192	Parts continue to gre no corrosion	grey;	Parts continue to grey; no corrosion	øy; no corrosion	Parts continue to grey; no corrosion observed	grey; no d	Some white corrosion (WC) developing on threads <sup>(b)</sup>
10-24-91	216	Parts continue to gre no corrosion	groy;	Parts continus to gray; no corrosion	ey; no corrosion	Parts continue to grey; no corrosion observed	gray; no d	Some WC developing on threads

(continued)

TABLE 10. (Continued)

	·			Sal	Salt-spray Test Results				
į	í	Group A	Group B	Group C	Group D	Group E	Group F	S. Group	T
Oa(e	Flapsed Time, hr	1210-6s Barrel Piated Reusable Socket	1210-8s Barrel Piated Reusable Socket	1241-6s Barrel Plated Reusable Nipple	1241-8s Barrel Plated Reussble Ninnle	1285-6s Barrel Plated	1285-8s Rack Plated	FC5192-0606s Rack Plated	T
10-26-91	264	Parts continue to gruno corrosion	grey;	Parts continue to grey; no corrosion	ey; no corrosion	Parts continue to grey; no corrosion observed	rey; no	Some WC developing on	
10-27-91	288	Parts continue to gre no corrosion	grey;	Parts continue to grey; no corrosion	ey; no corrosion	Parts continue to grey; no corrosion observed	rey; no	Some WC developing on	<del></del>
10-28-91	312	Parts continue to grey; no corrosion	9 <b>火</b> ;	Parts continue to grey; no corrosion	ey; no corrosion	Parts continue to grey; no corrosion observed	rey; no	Some WC developing on threads	
10-29-91	336	Parts continue to grey; no corrosion	;\e	White corrosion (WC) appears to be developing in threads	s appears to be	Parts continue to grey; no corrosion	:Ае	WC on threads appears to be increasing	
10-30-91	360	Parts continue to grey; no corrosion		WC appears to be developing in threads	veloping in	Parts continue to grey, no corrosion	θy,	WC on threads appears to be	
10-31-91	384	Parts continue to grey; no corrosion	λ;	WC appears to be developing in threads	veloping in	Parts continue to grey, no corrosion	ø,,	WC on threads appears to be increasing	
11-01-91	408	Parts continue to grey; no corrosion		WC appears to be developing in threads		Parts continue to grey, no corrosion	37,	WC on threads appears to be increasing	
11-02-91	432	Parts continue to grey no corrosion	rey;	WC appears to be developing in threads		Parts continue to grey, no corrosion	34,	WC on threads appears to be	
								ALICE COROLLES	

(continued)

TABLE 10. (Continued)

				Be	Sait-Spray Test Results	8	į	
Date	Elabsed	Group A	Group B	Group C	Group D	Group E	Group F	o another
	Time, hr	1210-6s Barrel Plated Reusable Socket	1210-8s Barrel Plated Reusable Socket	1241-6s Barrel Plated Beusable Nimie	1241-8s Barrel Plated	1285-6s Barrel Plated	1285-8s Rack Plated	FC5192-0606s Rack Plated
11-03-91	456	Dorte continue		Biddin propos	neusable Nipple	Nut	Nut	Crimp Fitting
		no corrosion	grey;	WC appears to be developing in threads	leveloping in	Parts continue to grey, no corrosion	эгөу,	WC on threads appears to be
1,000								increasing
2	480	Parts continue to gre no corrosion	ľey;	WC appears to be developing in threads	eveloping in	Parts continue to grey, no corrosion	ırey,	WC on threads appears to be
11-05-91	203	1800 111						increasing
	}	WC alid blackening o	continue	WC and blackening continue particularly in threads and nipple	· .	WC developing on edges/corners	edges/corners	WC and
				nose area				threads continue

- (a) Each group of parts consisted of six specimens.
- According to ASTM B633-85, the first appearance of WC visible to the unaided eye at normal reading distance shall be cause for rejection except that WC products at the edges of specimens shall not constitute failure. Threads were considered to be the equivalent of edges. 9

The results of the salt-spray tests on the zinc-plated parts (Table 9) are summarized below:

- All specimens in the seven groups of parts passed the requirement of 96 hours before the first appearance of white corrosion products.
- No red rust appeared on any of the specimens in the seven groups at the 360-hour observation time, so that all specimens met the requirement of freedom from RR for 360 hours.
- All specimens in Groups A, B, D and G were still free of red rust after 504 hours of salt-spray exposure. Red rust was beginning to develop on specimens in Groups C, E, and F at 504 hours, at which point all tests were terminated.

The results of the salt-spray tests on cadmium-plated parts (Table 10) are summarized below:

- All specimens in the seven groups passed the requirement of 96 hours before the first appearance of white corrosion products. The appearance of white corrosion products in any of the seven groups was delayed to 336 hours and beyond.
- No red rust was observed on any of the cadmium-plated specimens after 504 hours of exposure, at which point the tests were terminated.

The above results demonstrate that the cadmium-plated parts exhibit superior corrosion resistance to zinc-plated parts with regard to the appearance of white corrosion products and red rust in salt-spray tests.

## <u>Summation Comments on Adequacy of Corrosion</u> <u>Resistance Properties of Zinc-Plated Parts</u>

In view of the results of salt-spray tests carried out on zinc-plated parts by the Detroit Testing and the Aeroquip Laboratories during this project, along with the results from earlier Aeroquip tests on zinc- and cadmium-plated parts, the following generalized comments can be made:

Zinc plating produces a coating that satisfies customer requirements of 96 hours before the appearance of white corrosion products.

- These same zinc-plated parts also comply with Aeroquip process requirements of 360 hours before the appearance of red rust.
- Cadmium-plated parts are superior in their corrosion resistance properties (i.e., appearance of white corrosion products and red rust) to zinc-plated parts.

In light of the above evaluations, the corrosion resistance properties of zinc-plated parts are considered satisfactory to allow use of zinc as a substitute for cadmium in many plating applications. The Aeroquip Corporation, after extensive evaluation, switched over to acid zinc chloride plating to replace their existing cyanide cadmium-plating operations in early 1991. The Aeroquip acid zinc chloride plated coatings comply with ASTM and many industrial company specifications for corrosion resistance.

#### WASTE AND POLLUTANT REDUCTION

Environmental effects of the process change were evaluated on the basis of waste volume reduction and pollutant reduction. Waste volume reductions were estimated for the treated wastewater and the dewatered sludge, which affect conservation of water and landfill space, respectively. Pollutant estimates focused mainly on toxic pollutants, such as cadmium, cyanide, and chromium.

#### Waste Reduction

The quantities of treated wastewater and dewatered sludge from the cadmium-plating process generated in 1989 and from the zinc-plating process generated in 1991 were estimated from the data provided by Aeroquip and shown in Table 11. The production rate (i.e., number of parts or pieces plated) in 1989 was 31 percent higher than the production rate in 1991. Therefore, the waste generation for 1991 was adjusted upward by a factor of 1.31 for direct comparison with the 1989 waste generation. The adjusted 1991 wastewater generations were 40.0 million gallons from the cadmium-plating process and 44.9 million gallons from the zinc-plating process was, therefore, 12 percent higher than the wastewater generated from the cadmium-process was, therefore, 12 percent higher than the wastewater generated from the cadmium-

plating process. The adjusted sludge generations were 282,000 lb from the cadmium-plating process and 383,000 lb from the zinc-plating process, an increase of 36 percent due to the process substitution. The increases in wastewater and sludge generations were due to increase in plating bath concentration from approximately 3 oz/gal cadmium in the cadmium-plating baths to approximately 3.5 oz/gal zinc in the zinc-plating baths. The increased zinc metal concentration in the zinc chloride plating bath increased the dragout and rinse water and thereby increased the wastewater and sludge generation. The waste oil generation data provided by Aeroquip were 26 drums/year from the cadmium-plating process in 1989 and 6 drums/year from the zinc-plating process in 1991, or 9,542 lb/year and 2,202 lb/year, respectively, based on a specific gravity of the waste oil at 0.8. The decrease in the waste oil generation was probably due to approximately tenfold reduction in the concentration of oil in the water-soluble oil dip tank used in the zinc chloride plating process compared with the oil concentration used in the cadmium cyanide plating process.

TABLE 11. ANNUAL GENERATION OF TREATED WASTEWATER AND SLUDGE FROM CADMIUM- AND ZINC-PLATING PROCESSES (AEROQUIP DATA)

Year	Plating Process	Treated Wastewater, gal	Sludge, lb
1989	Cd	40,000,000	282,000
1991 <sup>(a)</sup>	Zn	44,900,000	383,000

<sup>(</sup>a) Adjusted to the 1989 production rate of the electroplating process.

#### **Pollutant Reduction**

Tables 12 and 13 show chemical analyses of treated wastewater discharged from the plant. Table 12 includes the data obtained by Aeroquip during July-December 1989 for the cadmium-plating process, and during July-December 1991 and June-August 1992 for the zinc-plating process. The change from cadmium to zinc plating occurred during December 1990 and January 1991. The Aeroquip data shown in Table 12 indicate that all pollutant concentrations are below the effluent discharge limits set by the municipal wastewater treatment plant that receives the wastewater. The changes in the average wastewater ana-

TABLE 12. CHEMICAL ANALYSIS OF TREATED WASTEWATER FROM CADMIUM- AND ZINC-PLATING PROCESSES (AEROQUIP DATA)

			Co	ncentration,	mg/L	
Month	рН	Cd	Total Cr	Total CN <sup>(a)</sup>	Amenable CN <sup>(a)</sup>	Zn
1989 Cd Plating						
Jul	10.51	0.011	0.07	1.23	0.14	< 0.003
Aug	10.21	0.060	0.025	2.99	<0.18	0.017
Sep	10.05	0.045	0.008	3.25	0.13	< 0.007
Oct	9.75	0.04	0.018	3.49	0.17	<0.008
Nov	9.44	0.06	0.46	1.68	0.12	< 0.003
Dec	9.91	0.04	0.09	2.37	0.19	0.008
Average	9.98	0.043	0.11	2.50	0.16	<0.008
1991 Zn Plating	**************************************					•
Jul	7.87	0.011	0.161	< 0.02	< 0.02	0.366
Aug	8.59	0.012	0.042	0.030	<0.01	0.345
Sep	7.83	0.053	0.111	< 0.02	< 0.02	0.510
Oct	8.46	0.079	1.01	< 0.02	< 0.02	0.580
Nov	8.52	0.038	0.249	< 0.02	< 0.02	0.659
Dec	8.15	0.015	0.104	< 0.002	< 0.002	0.264
Average	8.24	0.035	0.28	< 0.019	< 0.015	0.454
1992 Zn Plating			÷ .			
Jun	8.14	0.006	0.104	< 0.02	< 0.02	0.515
Jul	8.29	0.011	0.065	< 0.02	< 0.02	0.322
Aug	8.01	0.008	0.092	< 0.02	< 0.02	0.356
Average	8.15	0.008	0.087	< 0.02	< 0.02	0.398
Discharge Limits	<10.50	0.26	1.71	(a)	0.32	1.00

<sup>(</sup>a) Aeroquip is required to report total cyanide but is regulated by the amenable cyanide limit of 0.32 mg/L.

TABLE 13. CHEMICAL ANALYSIS OF TREATED WASTEWATER FROM ZINC-PLATING PROCESS (BATTELLE DATA)

			Concentra	tion, mg/L
Sample No.	Date of Sampling	рН	Total Cr	Zn
46325-05-05	06/23/92	8.41	0.025	0.330
46325-06-28	06/24/92	8.21	0.129	0.466
46325-10-07	06/25/92	8.44	0.079	0.384
46325-13-21	06/30/92	8.61	0.042	0.340
Average		8.42	0.069	0.380

lyses from July-December 1989 to July-December 1991 shown by the Aeroquip data were: (a) decrease in pH from 9.98 to 8.24, (b) decrease in Cd concentration from 0.043 to 0.035 mg/L, (c) increase in total Cr concentration from 0.11 to 0.28 mg/L, (d) decrease in total CN concentration from 2.50 to less than 0.019 mg/L, (e) decrease in amenable CN from 0.16 to less than 0.015 mg/L, and (f) increase in Zn concentration from less than 0.008 to 0.454 mg/L. The changes in pollutant concentrations were consistent with the process substitution. The higher pH was used in the cadmium cyanide plating process to optimize removal of Cd by sulfide precipitation. Increase in total Cr concentration was due to approximately fivefold increase in the Cr concentration in the yellow chromate solution used in the zinc chloride plating process compared with the Cr concentration in the clear chromate solution used in the cadmium cyanide plating process. The Aeroquip data in Table 12 show further decrease in Cd concentration from 0.035 mg/L during June-December 1991 to 0.008 mg/L during June-August 1992, indicating the residual Cd left in the process tanks (mainly in the sludge thickener in the wastewater treatment plant) continued to decline. Table 13 shows the wastewater analysis data for the samples collected by Battelle from the zinc-plating process during June 1992. The Battelle data generally agreed with the Aeroquip data reported for June-August 1992.

Table 14 shows the sludge analysis data obtained by Aeroquip for the cadmiumplating process during November 1987 and February 1988 and from the zinc-plating process during July 1991. The historical data provided by Aeroquip for the cadmium-plating process included one analysis each for moisture content (67 percent), Cd (43,000 mg/kg), hexavalent Cr (below detection limit, 0.1 mg/kg), and oil and grease (18,000 mg/kg). The historical data provided by Aeroquip for the zinc-plating process included one analysis each for total Cr (5,900 mg/kg) and hexavalent Cr (below detection limit, <0.1 mg/kg). No data were available on total Cr concentration of the sludge from the cadmium-plating process. The extremely low concentration of hexavalent Cr in the sludge from either process indicates very efficient operation of the chemical treatment step, which converts the toxic hexavalent Cr to much less toxic trivalent Cr.

TABLE 14. CHEMICAL ANALYSIS OF SLUDGE FROM CADMIUM- AND ZINC-PLATING PROCESSES (AEROQUIP DATA)

			Concentra	tion, mg/kg	
Date of Sampling	Moisture, percent	Cd	Total Cr	Cr(+6)	Oil & Grease
Nov/87 <sup>(a)</sup>	67	(c)	(a)	(d)	18,000
Feb/88 <sup>(a)</sup>	(c)	43,000	(a)	(c)	(c)
Jul/91 <sup>(b)</sup>	71	(c)	5,900	(d)	(c)

<sup>(</sup>a) From cadmium plating.

Table 15 shows the sludge analysis data obtained by Battelle for the zinc-plating process. Comparison of the data shown in Tables 14 and 15 indicate that the concentration of oil and grease decreased from 18,000 mg/kg in the Cd plating process in November 1987 to 7,630 mg/kg (averaged for 6 samples) in the Zn plating process in June 1992. The decrease in oil and grease concentration was probably due to approximately tenfold reduction in the oil concentration used in the water-soluble oil dip tank in the zinc chloride plating process. The concentration of total Cr in the sludge determined by Battelle in June 1992 (16,800 mg/kg) was significantly higher than the value determined by Aeroquip in July 1991 (5,900 mg/kg). The increase could be due to more efficient removal of Cr from the wastewater to sludge as indicated by the much lower Cr concentration in the treated

<sup>(</sup>b) From zinc plating.

<sup>(</sup>c) Not analyzed.

<sup>(</sup>d) Not detected (<0.1 mg/kg).

wastewater analyzed by Battelle in June 1992 (shown as 0.069 mg/L in Table 13) than the Cr concentration in the treated wastewater analyzed by Aeroquip in July 1991 (shown as 0.161 mg/L Table 12).

TABLE 15. CHEMICAL ANALYSIS OF DEWATERED SLUDGE FROM ZINC-PLATING PROCESS (BATTELLE DATA)(a)

			Concentration, mg/kg		
Sample No.	Date of Sampling	Moisture, percent	Total Cr	Zn	Oil & Grease
46325-01-12	06/22/92	67.5	20,700	55,100	7,580
46325-03-24	06/23/92	72.8	14,700	55,600	5,520
46325-06-22	06/24/92	70.4	15,800	59,000	8,040
46235-08-26	06/25/92	69.6	15,300	61,700	9,140
46235-12-08	06/26/92	69.1	17,500	59,600	9,110
46325-13-07	06/30/92	70.6	16,900	56,400	6,410
Average		70.1	16,800	57,900 😹	7,630

<sup>(</sup>a) Sludge samples were collected as grab samples.

Pollutant generations, estimated from the quantities of treated wastewater and sludge and pollutant concentrations in each waste stream, are summarized in Table 16 for the cadmium- and the zinc-plating processes. For example, the quantity of Cd generated in the sludge was estimated by multiplying the annual sludge generation (281,820 lb/yr from Table 11) and the Cd concentration in the sludge (43,000 mg/kg from Table 14) as follows: 281,820 x 43,000/1,000,000 = 12,118 lb/yr. The pollutant generations were based on the 1989 production rate of the electroplating process. The 1989 production rate, expressed as sq ft of electroplated surface area of production parts, was estimated from the quantity of Cd metal coated and the coating thickness. The quantity of Cd metal coated was estimated as 44,400 lb by subtracting the waste Cd metal (12,100 lb from Table 16) from the actual Cd consumption in 1989 reported by Aeroquip as 56,500 lb. Based on an average coating thickness of 0.0003 inches (the mean of the 0.0002- to 0.0004—inch coating thickness specification) and the specific gravity of Cd metal at 8.64,the total surface area of production

TABLE 16. POLLUTANT GENERATION IN LB/YR FROM CADMIUM-AND ZINC-PLATING PROCESSES BASED ON 1989 PRODUCTION RATE OF 3.29 MILLION SQ FT<sup>(a)</sup>

	Wastewater	Sludge	Waste Oil	Total
Cadmium-Plating Process				
Cd	14 <sup>(b)</sup>	12,100 <sup>(c)</sup>	_(d)	12,100
Total CN	835 <sup>(b)</sup>	0	_(d)	835
Total Cr	37 <sup>(b)</sup>	640 <sup>(e)</sup>	_(d)	677
Zn	0	O	0	· 0
Oil & Grease	_(d)	5,070 <sup>(c)</sup>	9,540 <sup>(f)</sup>	14,600
Zinc-Plating Process			5	
Cd	O <sub>(a)</sub>	O(a)	_(d)	0
Total CN	O(a)	O <sup>(g)</sup>	_(d)	0
Total Cr	75 <sup>(h)</sup>	4,350 <sup>(i)</sup>	_(d)	4,420
Zn	161 <sup>(h)</sup>	22,200 <sup>(j)</sup>	_(q)	22,300
Oil & Grease	_(d)	2,920 <sup>(j)</sup>	2,200 <sup>(f)</sup>	5,120

- (a) Pollutant generation calculated from the wastewater and sludge generation shown in Table 11 and pollutant concentrations as noted below.
- (b) Based on pollutant concentrations shown in Table 12 for July-December 1989: Cd, 0.043 mg/L; total Cr, 0.11 mg/L; total CN, 2.5 mg/L.
- (c) Based on pollutant concentrations shown in Table 14: Cd, 43,000 mg/kg; oil & grease, 18,000 mg/kg.
- (d) Not available.
- (e) Based on Cr concentration estimated as 1/5 of the average of the two Cr concentrations shown in Tables 14 and 15: Cr, (1/5)x(5,900+16,800)/2 = 2,270 mg/kg.
- (f) Based on waste oil generation of 26 drums/yr from the Cd plating process and 6 drums/yr from the Zn plating process and specific gravity of oil at 0.8; e.g., 26 x 55 x 8.34 x 0.8 = 9,540 lb/yr.
- (g) Assuming continuous decline of residual Cd and CN in the process tanks after the process substitution.

  (h) Based on average values (obtained by prorating the monthly data) of pollutant concentrations shown in Table 12 for July-December 1991 and June-August 1992, and in Table 13 for June 1992: Cr,
- (1/10)x(0.28x6+0.087x3+0.069) = 0.201 mg/L; Zn, (1/10)x(0.454x6+0.398x3+0.430 = 0.430 mg/L.(i) Based on average value of the two Cr concentrations shown in Tables 14 and 15: Cr, (5,900+16,000)/2 = 11,350 mg/kg.
- (j) Based on the Zn and oil & grease concentrations shown in Table 15: Zn, 57,900 mg/kg; oil & grease, 7,630 mg/kg.

parts electroplated in 1989 was estimated as 3.29 million sq ft. The estimated pollutant generations were based on the following assumptions:

- Zero discharge of Cd and CN from the Zn plating process.
- Zero discharge of Zn from the Cd plating process.
- The concentration of CN in sludge was assumed to be equal to that in wastewater. This assumption will result in overestimating CN in the sludge because CN is present in both media in a soluble form.

In the cadmium cyanide plating process, Cd and Cr were predominantly discharged in the sludge and the CN in the treated wastewater. In the zinc chloride plating process, Zn and Cr are also discharged predominantly in the sludge stream. A complete comparison of Cr discharges from the two processes was not possible due to lack of data on Cr analysis of sludge from the Cd plating process. Since the Cr concentration in the clear chromate solution used in the Cd plating process was approximately 1/5 of the Cr concentration in the yellow chromate solution used in the Zn plating process, the quantity of Cr in the sludge from the Cd plating process (shown as 640 lb/yr in Table 16) was estimated by assuming that the Cr concentration in the sludge from the Cd plating process was 1/5 of the Cr concentration of the sludge from the Zn plating process.

Chemical analysis of the field blank (tap water) and the laboratory blank are shown in Table 17. The Cr and Zn levels in the blanks appeared to be low enough that they have negligible effect on estimation of the Cr and Zn discharges from the Zn plating process.

#### **ECONOMICS**

Table 18 shows the capital cost for converting the plating lines at Aeroquip from cadmium plating to zinc plating. The cost data were provided by Aeroquip and were adjusted to 1992 dollars using a 5 percent/year escalation. Approximately 72 percent of the total cost was for expenses related to cleaning up the Cd process equipment and for disposal of the waste generated from the cleanup operation; the remaining 28 percent was for installation of the new equipment. The work involved in converting the plating lines included: (a) removal and off-site destruction of the cadmium cyanide plating bath, (b) cleanup of the plating areas and the cyanide destruction tanks in the wastewater treatment plant, (c) stripping and relining

of the plating and rinse tanks with a new resin liner, (d) replacement of process piping, (e) installation of a continuous filter for the new zinc chloride bath, (e) installation of new heat exchangers to dissipate additional heat generated from the zinc-plating process, (f) installation of a new air agitation system for the zinc-plating bath, (g) installation of an acid resistant epoxy liner on the concrete pit used in emergencies when the plating tanks need to be cleaned of sludge, (h) replacement of the dryers on the barrel plating lines, and (i) extension of the dryer on the rack plating line.

TABLE 17. CHEMICAL ANALYSIS OF FIELD BLANK AND LABORATORY BLANK (BATTELLE DATA)

					ntration, g/L
Sample	Sample No.	Date Sampled	рН	Total Cr	Zn
Field Blank (Tap Water)	46325-06-12	06/23/92	7.57	0.019	0.027
	46325-11-26	06/24/92	7.77	0.041	0.032
	Average		7.67	0.030	0.030
Laboratory Blank		06/24/92	(a)	0.017	0.021

(a) Not determined.

TABLE 18. CAPITAL COST

Parameter	Barrel Plating Lines	Rack Plating Line	Subtotal
Expense (clean-up of old equipment and waste disposal)	\$ 428,000	\$ 999,000	\$ 1,427,000
New equipment	\$ 424,000	\$ 122,000	\$ 546,000
Subtotal	\$ 852,000	\$ 1,121,000	
Total			\$ 1,973,000

Table 19 shows the annual operating cost data provided by Aeroquip, adjusted to 1992 dollars. The data for the cadmium-plating process were from actual 1989 expenses, except for the cadmium anode cost, which was based on the actual amount of the anode consumed in 1989 (56,500 lb) and the 1992 price of cadmium anode at \$0.99/lb. Consumption of zinc anode was estimated as 59,000 lb by adding the amount of Zn coated (36,668 lb based on 0.0003 inch coating thickness, 3.29 million sq ft of coating, and specific gravity of Zn metal at 7.14) and the amount of Zn wasted (22,300 lb from Table 16). The cost for zinc anode was based on the above estimate and the 1992 price of the zinc anode at \$0.78/lb.

The cost of wastewater treatment chemicals for the zinc-plating process included savings of \$38,300, primarily due to elimination of chlorine for cyanide destruction, and an increase of \$13,900 due to increased consumption of sulfur dioxide for reduction of hexavalent chromium. These changes resulted in a net cost savings of \$24,400. The labor cost was based on the number of operators (which has not changed between the two processes) and a unit cost of \$25/hr, including supervision and overhead. The cost of electricity for the plating processes was estimated from the voltage and current data provided by Aeroquip. Details of the electrical power consumption and cost calculations are provided in the Appendix.

Incremental maintenance costs for the cadmium-plating process over the zinc-plating process were listed under miscellaneous expenses, which included the costs for the washdown of the plating department, treatment of the washdown water, blood tests for workers, environmental monitoring, and record keeping. The cost of sludge disposal was estimated from the sludge volumes (shown in Table 7) and a sludge disposal unit cost of \$178.50/ton, as provided by Aeroquip. The cost of waste oil disposal was estimated from the waste oil generation (Table 16) and disposal cost of \$600/drum for hazardous waste incinerator charge estimated by Battelle.

The reduction in annual operating cost resulting from substitution of zinc plating for cadmium plating was estimated to be \$17,200. For a new installation, therefore, the zinc chloride plating process has an economic advantage of lower operating cost over the cadmium cyanide plating process. The payback period for the capital investment of \$1,973,000 for process substitution was estimated as 115 years. The process substitution, therefore, cannot be justified solely on economic grounds. It should be based on improving worker safety and

environmental pollution, as well as on greater acceptance of the zinc-plated components in domestic and foreign industrial and consumer markets. However, in comparing the two for a new installation, the zinc chloride plating process offers obvious advantages over the cadmium cyanide plating process.

TABLE 19. COMPARISON OF OPERATING COSTS FOR CADMIUM-AND ZINC-PLATING PROCESSES<sup>(a)</sup>

	Cadmium Plating	Zinc Plating
Electroplating Chemicals		
Clear chromate	\$ 3,840	
Brightener	3,180	\$ 49,800
NaOH flakes	3,330	
Yellow chromate	16,900	28,900
Sodium cyanide Cadmium anode @ \$0.99/lb	42,800	
Potassium chloride	55,900	
Boric acid		6,680
Wetter		18,200 4,050
Zinc anode @ \$0.78/lb		46,000
Wastewater Treatment Chemicals	÷ 045 000	
Trastewater Treatment Chemicals	\$ 215,000	\$ 190,000
Operating Labor, 14 persons @ \$2-5/hr	\$ 728,000	\$ 728,000
Electricity, @ \$0.08/kwh	\$8,920	\$ 7,880
Miscellaneous	•	
Blood Tests	\$ 3,240	
Environmental monitoring Record Keeping	2,320	
Washdown of Plating Dept.	463 6,370	
Treatment of washdown	4,050	
water	4,000	
Sludge Disposal Cost, @ \$178.50/ton	\$ 25,200	\$ 34,200
Waste Oil Disposal, @ \$600/drum	\$15,600	\$ 3,600
Total	\$ 1,135,000	\$ 1,118,000
Net Cost Reduction		\$ 17,200
		,250

<sup>(</sup>a) Adjusted to 1992 dollars.

#### **SECTION 5**

#### **QUALITY ASSURANCE**

A Quality Assurance Project Plan (QAPP, Battelle, 1992) was prepared and approved by the EPA before testing began. This QAPP contained a detailed procedure for conducting this study. Collection and analyses of samples were performed according to the QAPP.

#### **ON-SITE SAMPLE COLLECTION**

All samples were collected as outlined in the QAPP. The original sampling plan proposed in the QAPP is shown in Table 20. All samples were collected over a 2-week period. Dewatered sludge samples were collected as grab samples from the sludge hopper located at the discharge of the filter press. The sludge samples were taken from various locations in the hopper and mixed in a glass beaker to obtain composite samples. All sludge samples were collected within a week after filter press operation.

Treated wastewater samples were collected continuously over a 24-hour period by means of the existing sampling pump in the plant, which is used at Aeroquip to collect composite water samples. The sample collection rate was varied in each shift in proportion to the discharge rate of each shift (i.e., at a ratio of 2.6:1.9:1.0, corresponding to first:second:third shifts). Tap water samples were collected as grab samples from a tap water faucet. These served as field blanks. A laboratory blank was provided by Zande Environmental Service, who performed the chemical analyses of treated wastewater and sludge samples.

TABLE 20. SUMMARY OF PRIMARY AND QUALITY CONTROL SAMPLES FOR CHEMICAL ANALYSIS AND CHARACTERIZATION

Sample Location	Sample Matrix	Time of Sampling	Number of Samples <sup>(b)</sup>	Measurements
Outlet of Sand Filter	Treated Water	During the same week the sludge was sampled	4	Zn, Total Cr, pH
Sludge Hopper	Sludge	Within a week after filter press operation	6	Zn, Total Cr, Oil & Grease, Total Solids
Tap Water Line	Tap Water <sup>(a)</sup>	During the same week the sludge was sampled	2	Zn, Total Cr

<sup>(</sup>a) Field blank.

## CHEMICAL ANALYSIS

All analyses were performed as planned in the QAPP. The pH of the treated wastewater and tap water was determined at the time of sample collection. The precision of the chemical analysis of the sludge and the treated wastewater are presented in Tables 21 and 22, respectively. All precision data were in the acceptable range of 25 percent.

TABLE 21. PRECISION OF SLUDGE ANALYSIS

Parameter	Sample No.	Regular Sample	Duplicate	Precision (%)
Oil & Grease	46325-6-22	8040 mg/kg	8500 mg/kg	5.6
Total Chromium	46325-6-22	15800 mg/kg	15800 mg/kg	0.0
Zinc	46325-6-22	5900 mg/kg	5800 mg/kg	1.7
Total Solids	46325-6-22	70.4 %	70.3 %	0.1

<sup>(</sup>b) Including one reserve sample for each sample matrix. Samples collected in the field did not include samples prepared in the laboratory for QA, such as duplicates, matrix spikes, and method blanks.

TABLE 22. PRECISION OF TREATED WASTEWATER ANALYSIS

Parameter	Sample No.	Regular Sample	Duplicate	Precision (%)
Total Chromium	46325-6-28	0.129 mg/L	0.117 mg/L	9.8
Zinc	46325-6-28	0.466 mg/L	0.434 mg/L	7.1
рН	46325-6-28	8.21	8.16	0.6

The accuracy of the chemical analysis of the sludge and the treated wastewater is presented in Tables 23 and 24, respectively. All matrix spike recoveries were in the acceptable range of 75 to 125 percent.

TABLE 23. ACCURACY OF SLUDGE ANALYSIS

Parameter	Sample No.	Regular Sample (mg/kg)	Matrix Spike Level (mg/kg)	Matrix Spike Measured (mg/kg)	Accuracy (% Recovery)
Oil & Grease	46325-8-26	9810	50000	64150	107
Total Chromium	46325-8-26	15300	16600	32600	102
Zinc	46325-8-26	61700	33200	97500	103

TABLE 24. ACCURACY OF TREATED WASTEWATER ANALYSIS

Parameter	Sample No.	Regular Sample (mg/L)	Matrix Spike Level (mg/L)	Matrix Spike Measured (mg/L)	Accuracy (% Recovery)
Total Chromium	46325-10-7	0.079	1.000	0.980	91
Zinc	46325-10-7	0.384	1.000	1.342	97

All samples collected and analyzed in accordance with the QAPP were judged to be valid to achieve a 100 percent completeness. The detection limits of the methods used for all chemical analyses were equal to or smaller than the minimum required detection limits specified in the QAPP.

## LIMITATIONS AND QUALIFICATIONS

Based on the above QA data, the results of the on-site and laboratory testing can be considered valid for drawing conclusions about the chemical compositions of the sludge and of the treated wastewater discharged from the wastewater treatment plant at Aeroquip.

#### **SECTION 6**

#### REFERENCES

- Battelle. 1992. Quality Assurance Project Plan for the Substitution of Zinc Chloride Electroplating for Cadmium Cyanide Electroplating. Prepared for the U.S. Environmental Protection Agency Risk Reduction Engineering Laboratory, Cincinnati, Ohio.
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#### **APPENDIX**

# COMPARISON OF POWER CONSUMPTION VALUES FOR THE ZINC VERSUS CADMIUM PLATING OPERATIONS

Aeroquip has indicated that the thickness of the zinc coating being applied now is the same as the thickness of the cadmium coating applied previously; this thickness is 0.0002 to 0.0004 in. Therefore, comparison of power consumptions for the two processes was based on the same coating thickness.

## REPRESENTATIVE PLATING CONDITIONS

Representative electroplating conditions currently employed on the various lines at Aeroquip for the deposition of zinc coatings from the zinc chloride bath and those used earlier for deposition of cadmium from the cadmium cyanide bath are as follows:

	Zinc Chloride Bath	Cadmium Cyanide
Rack Plating Line		
	Cell Voltage: 2.5 - 3.0 volts Current: 3200 amp	Cell Voltage: 5.0 volts Current: No data provided
Single Hoist Barrel	<u>Line</u>	
	Cell Voltage: 5-6 volts Current: 1100 amps	Cell Voltage: 6 to 8 volts Current: No data provided
Twin Hoist Barrel I	<u>_ine</u>	
	Cell Voltage: 5-6 volts Current: 1300 amps	Cell Voltage: 6 to 8 volts Current: No data provided

The current values shown for the various lines are typical values employed in production at Aeroquip; these values depend on the area of the work pieces being plated. No amperage data for the cadmium plating operations were available from Aeroquip.

## **ELECTROCHEMICAL EQUIVALENCE AND OTHER DATA**

The following are other data related to the electrodeposition of zinc and cadmium:

## Electrochemical Equivalent (Theoretical):

Zinc: 2.6886 lb/1000 amp-hr Cadmium: 4.6226 lb/1000 amp-hr

## Specific Gravity or Density:

Zinc: 7.14 g/cc Cadmium: 8.64 g/cc

#### Electrodeposition Factor (Theoretical):

Zinc: 13.7 amp-hr to deposit 0.001 inch/sq ft Cadmium: 9.73 amp-hr to deposit 0.001 inch/sq ft.

Based on the electrochemical equivalence data, more pounds of cadmium theoretically are deposited per 1000 amp-hr than for zinc by a factor of 4.6226/2.6886 or 1.719. However, based on the metal density values, it requires more (i.e., a greater weight) cadmium than zinc to provide an equivalent coating thickness by a factor of 8.64/7.14 = 1.21. The theoretical electrodeposition factor data indicate that it requires more amp-hrs to deposit 0.001 inch/sq ft of zinc than of cadmium by a ratio of 13.7:9.73 or 1.4:1.

## POWER CONSUMPTION CALCULATION FOR ZINC ELECTROPLATING OPERATIONS

Using the plating line data provided above, the estimated annual power consumption data for the zinc electroplating operations were calculated.

The following plating schedule was assumed:

2 shifts/day; 8 hrs/shift 5 days/week; 50 weeks/year

Total annual hours of plating operation: (2)(8)(5)(50) = 4000Rack plating line: (3200 amp)(2.8 v) = 8,960 watts or 8.96 kW

Combined barrel lines: (2400 amp)(5.5 v) = 13,200 watts or 13.20 kW

Combined rack and barrel lines = 22,160 watts or 22.16 kW

## **Estimated Annual Power Consumption:**

Rack plating: (8.96)(4000) = 35,840 kWh Barrel plating: (13.20)(4000) = 52,800 kWh Combined plating: (22.16)(4000) = 88,640 kWh.

The lack of current (amperage) data for the cadmium-plating operations precluded similar direct calculation of power consumption data for cadmium plating. The method employed to determine power consumption data for cadmium for comparison purposes is described below.

## POWER CONSUMPTION VALUES FOR ZINC AND CADMIUM PLATING OPERATIONS

To estimate the power requirements for depositing an equivalent coating thickness of zinc compared to cadmium, it is necessary to take into account the respective cell voltages and current efficiencies for the zinc chloride and cadmium-cyanide plating operations. Data in the literature indicate that typical cathode current efficiency (CE) values for plating zinc from zinc chloride are near 100 percent (Dini and Johnson, 1979); Geduld (1988) states 95 to 98 percent. For the cadmium cyanide bath, typical CE values are generally in the range of 85 to 95 percent (Dini and Johnson, 1979). For calculation purposes herein, a CE value of 97 percent was assumed for zinc plating; a CE value of 90 percent was assumed for cadmium plating.

The comparative power consumption values for the zinc and cadmium plating operations were calculated using the data on electrodeposition factors, cell voltages, and current efficiencies cited above. The results of these determinations are as follows:

#### **Rack Plating Power Consumption:**

Zinc: 13.7(2.8)/0.97 = 39.5 watt-hr to deposit 0.001 inch/sq ft Cadmium: 9.72(5.0)/0.90 = 54.0 watt-hr to deposit 0.001 inch/sq ft

## **Barrel Plating Power Consumption:**

Zinc: 13.7(5.5)/0.97 = 77.7 watt-hr to deposit 0.001 inch/sq ft Cadmium: 9.72(7.0)/0.90 = 75.6 watt-hr to deposit 0.001 inch/sq ft.

From the above, it can be seen that power consumption values for deposition of equivalent thicknesses on work pieces are significantly higher for the barrel plating operations than for the rack plating operations for both zinc and cadmium coatings. This is primarily because of the higher cell voltages required for the barrel plating operations. About 27 percent less power is required for the rack plating of zinc as compared to that for cadmium. For barrel plating, about 3 percent more power is required for the plating of zinc as compared to that for cadmium.

Assuming that the same proportional amounts of rack and barrel plating occurred in the cadmium plating operations as in the zinc-plating operations, the estimated annual power consumption data for deposition of cadmium coatings were calculated as follows:

## Annual Power Consumption:

Zn Rack Plating = 35,840 kWh Cd Rack Plating = 35,840 (54.0/39.5) = 49,000 kWh

Zn Barrel Plating = 52,800 kWh Cd Barrel Plating = 52,800 (75.6/77.7) = 51,370 kWh

Zn Combined Rack and Barrel Plating = 88,640 kWh Cd Combined Rack and Barrel Plating = 100,370 kWh.

The above data show that, for the combined rack and barrel operations, the power expenditure is about 10 percent less for the electroplating of zinc from the zinc chloride bath as compared with the previous electroplating of parts with cadmium from a cadmium cyanide bath.

## ESTIMATED POWER COSTS OF ELECTROPLATING OPERATIONS

The above calculations of power consumption were based on direct current (DC) amperage values. Assuming a rectifier efficiency of 90 percent for converting alternating current (AC) to direct current, the power consumption values for the combined rack and barrel operations are as follows:

Zinc: 88,640/0.90 = 98,490 kWh

Cadmium: 100,370/0.90 = 111,520 kWh.

At an electricity charge of \$0.08/kWh, the estimated annual cost for the electrodeposition of the coatings is as follows:

Zinc: 98,490(0.08) = \$7879

Cadmium: 111,520(0.08) = \$8922.

#### **SUMMATION COMMENTS**

The switch to plating parts at Aeroquip with zinc from a zinc chloride bath instead of cadmium from a cadmium cyanide bath has resulted in a small (about 10 percent) reduction in the consumption and consequent cost of electricity.

#### **REFERENCES**

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