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NONCYANIDE PLATING AND DERUSTING PROCESSES FOR POLLUTION ABATEMENT

FRANK TESTROET

JULY 1982

U.S. ARMY ARRCOM

TECHNICAL REPORT

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This project was undertaken to eliminate pollution of wastewater effluent caused by electroplating operations using cyanide based plating solutions. Noncyanide derusting and plating baths were investigated to compare their ability to perform as well as the cyanide based counterparts. Suitable materials were found and noncyanide derusting as well as noncyanide cadmium and copper plating were implemented in Rock Island Arsenal's production plating facility. All cyanide based baths were removed from the plating production area and were properly disposed of in compliance with pertinent regulations.

FOREWORD

The work was authorized as part of the Manufacturing Methods and Technology Program of the US Army Materiel Development and Readiness Command and was administered by the US Army Industrial Base Engineering Activity.

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1.0 INTRODUCTION

The objective of this work was to improve the quality of industrial wastewater effluent by eliminating the use of cyanide based cadmium and copper plating and derusting baths at Rock Island Arsenal (RIA).

At RIA a constant effort is made to identify and eliminate pollutants which are known to be hazardous to health and/or environment at minimum cost.

At the present time, RIA wastewater is treated by the City of Rock Island, Illinois, at their waste treatment plant. Because the City of Rock Island imposed an ordinance that limits amounts of cyanide for disposal through the sewer system, a major effort was directed to eliminate all cyanide from RIA's wastewater effluent.

The plating facility of the Arsenal Operations Directorate was a potential source of excessive cyanide pollution. In this facility, parts are cleaned in cyanide-based derusting solution and plated in cyanide based cadmium or copper plating baths. During these operations, normal "dragout" occurs when work pieces from derusting or plating baths are rinsed with water and causes the wastewater to approach limits established by the City of Rock Island. Since an increase in production would result in even more dragout, work was directed to insure that RIA did not exceed city limits for cyanide.

Two methods to produce cyanide-free wastewater effluent were considered. One method would be to construct separate sewers to collect only cyanide wastes and divert them to holding tanks for chemical destruction when sufficient quantities were accumulated to warrant operation of the destruction process. This system of sewers, holding tanks, and destruction equipment would require costly construction work estimated at $150,000. Furthermore, use of the cyanide destruction system would be operational only during the warm months of the year and its use would be a recurring costly process ($475.00 per 55 gallon drum).

The second method would be to replace conventional cyanide based derusting solutions and cadmium and copper plating baths with appropriate noncyanide solutions. This appeared to be the most efficient and cost effective approach for resolution of all potential problem areas.

2.0 PROCEDURE

A literature search was conducted to find suitable, noncyanide based chemicals to replace the cyanide based electroplating solutions. Only two cadmium and one copper cyanide-free plating solutions were found which appeared suitable for production use. Candidate solutions were acquired and used to plate test specimens. The resultant coatings were tested to confirm their conformance to required specifications. Those tested were:

a. Cadvert cadmium: Minnesota Mining & Manufacturing (3M) Company.

b. Kadizid cadmium: Lea Ronal Incorporated.

c. Cupure copper: Lea Ronal Incorporated.

Compositions and operating conditions of the cadmium and copper plating baths are listed in Tables 1 and 2, respectively. Pure cadmium and phosphorized copper anodes were required for the respective baths. Acid and alkali resistant Dynel anode bags, zirconium anode baskets, and plastisol coated plating racks were required to prevent contamination of the baths.

Steel and brass Hull Cell panel specimens were prepared for testing the efficiency of cadmium and copper baths, respectively. Steel panels were dipped in dilute hydrochloric acid to remove a protective zinc coating, rinsed in running water, and swabbed with a paper towel. Brass panels used for copper plating had a protective seal material that was stripped off just prior to being dipped in dilute hydrochloric acid. They were also rinsed in running water and swabbed with a paper towel.

The cadmium baths were poured into a 267 ml Hull Cell and panels were plated at 75°F for five minutes at two amperes. The Cupure bath was tested in a 267 ml Model WT Hull Cell equipped with a quartz heater to maintain bath temperature. The brass specimens were plated at 140°F for five minutes at two amperes.

Metal panels measuring 1" x 2" x 0.125" and 2" x 3" x 0.125" were prepared from AISI 1009 steel for plating in a laboratory plater. The plater consists of seven chemical resistant polyvinyl chloride tanks, each with 3.8 gallons capacity. One five ampere and one 10 ampere rectifier, both with dual range ammeters provided the necessary electric current.

Steel specimens were cleaned by glass grit blasting and vapor degreasing in 1,1,1 Trichloroethane. The specimens were then activated by immersion for 30 seconds in a 50 percent solution of hydrochloric acid. They were then rinsed in water and gently blown dry with air.

Test panels were cadmium plated at room temperature and copper plated at 150°F to prepare them for testing as specified by Federal Specification QQ-P-416C(1) and Military Specification Mil-C-14550A, respectively. Similar panels were plated in production baths for comparison. Some of the cadmium coated panels were given supplementary chromate or phosphate treatments. The supplementary chromate treatment is applied for improved corrosion resistance and the phosphate treatment also offers added corrosion resistance and is used as an undercoat for paint.

Coating adhesion was evaluated by the knife test where the coating is cut through to the basis metal with a sharp knife and then examined under 4X magnification to determine any evidence of non-adhesion. The 180° bend test was also used. In this test, a portion of a panel is clamped in a vise and the projecting portion is bent back and forth until rupture occurs. Following rupture, attempts were made to scrape or peel away any loose portion of the adherent coating.

Supplementary treatments were applied in accordance with Federal Specification QQ-P-416C. Cadmium plated panels were dipped in Type II supplementary chromate treatment. Other cadmium plated panels were dipped in Type III phosphate treatment and painted with Enamel per Specification TT-E-489F Class A. These panels were then exposed to a salt spray (fog) for 96 hours per ASTM Test Method B117.

The Cadvert and Kadizid cadmium solutions were tested in an oblique barrel apparatus located in the production plating facility of RIA. The apparatus is used for plating of parts too small to be rack plated. Assorted sizes of bolts and set screws were glass grit blasted, vapor degreased and activated in dilute hydrochloric acid before being placed in the barrel plater.

A search was made for a noncyanide derusting material that would meet the requirements of Military Specification Mil-C-14460B, Type I, "Corrosion Removing Compound, Sodium Hydroxide Base, for Electrolytic or Immersion Applications." The Type II material ("Sodium Hydroxide-Sodium Cyanide mixture plus a Chelate or Sequestrant Compound") was the derusting compound being used. Oakite Super Rustripper, Oakite Low Heat Cleaner 1, Nuvat LT and Super Maxamp Electrocleaner were tested to determine their cleaning ability as derusting solutions.

3.0 RESULTS AND DISCUSSION

Panels plated in the Kadizid cadmium bath were uniformly bright across the panel. The brightest coating was produced using a current density between 10 and 60 amperes per square foot (ASF) on the Hull Cell Scale. Cadvert cadmium showed its brightest range when using a current density from two to 20 ASF. Some dullness was seen in the high current density area. The Cupure copper system was brightest at a current density of four to 30 ASF and exhibited burnt (heavy and dull) spots in high current density areas.

Cadmium and copper coated panels plated in the plating facility and in the laboratory showed good adhesion when tested by the knife test and the 180° bend test. The deposits could not be scraped or peeled off with a knife or pulled off with adhesive tape.

All cadmium coated panels with chromate treatment and the painted phosphate treated panels passed the 96 hours salt spray fog test with no evidence of corrosion.

With proper control of plating time, amperage, and solution, both cadmium and copper baths produced coating thicknesses specified for present production requirements. Cadmium plated at a rate of 0.0001 inches in 2.5 minutes at 43 ASF, and copper plated at a rate of 0.0001 inches in 4 minutes at 22 ASF. Adequate throwing power of both cadmium and copper baths was confirmed by an acceptable, uniform coating coverage on panels bent to 90° and 130° angles prior to plating.

Barrel plating small set screws and bolts with the Kadizid cadmium process was accomplished with application of a plating current of 40 A which is the amperage used in cyanide based cadmium plating. A bright homogeneous coating was deposited in 20 minutes. Visual examination revealed good coverage in the recessed areas of set screws and on the base and sides of the threads of the screws and bolts. The same procedure was followed using the Cadvert cadmium process but the bath did not work at a plating current of 40 amps. Plating did commence when amperage was increased to 50 amps and a dull grayish coating was deposited after 45 minutes. Dipping in a proprietary brightener solution, Iridite #8P Bluebrite, produced a bright luster. Chromated articles, from both the Kadizid and Cadvert baths, were exposed to 96 hours salt spray fog and showed no corrosion. Extending exposure time to 192 hours, twice that of the specification requirement, failed to produce any evidence of corrosion.

The Kadizid cadmium process was chosen over the Cadvert system because it plated over a broader current density range and produced a brighter deposit in the "as plated" condition. The Cupure copper plating system was the only totally cyanide-free copper bath that was found suitable for production plating.

Both Kadizid cadmium and Cupure copper processes have been implemented into production plating at RIA. These processes are being used in the same plating tanks that were used for cyanide plating. Typical cadmium rack plating of an M198 Yoke is illustrated in Figure 1 and a rack of M85 chain guides being lowered into the Cupure copper bath is shown in Figure 2. No change in the rack design, other than being plastisol coated, was required.

A summary of commercial cleaning materials that were evaluated is presented in Table 3. Oakite Super Rustripper has been found to make up an efficient derusting bath. The bath is maintained at 2.5 pounds of Super Rustripper per gallon of water. Operation at 160°F and 100 ASF shows satisfactory removal of soil, processing lubricants and other debris that is detrimental to the electroplating process.

Oakite Low Heat Cleaner 1 was also evaluated as it was designed for cleaning at temperatures as low as 80°F for energy conservation. However, this material did not clean as well as the Oakite Super Rustripper and it contains phosphate which is undesirable from a waste disposal standpoint. Nuvat LT was tested at temperatures in the range of 120°F to 130°F. This bath also failed to be efficient as a derusting bath but would be useful as a precleaner. Super Maxamp Electrocleaner used at 10 ounces per gallon at 160°F and 80 ASF was effective as a derusting bath but no better than Oakite Super Rustripper. Super Maxamp also has the disadvantage of containing phosphate.

Disposal of Kadizid cadmium and Cupure copper baths require only the removal of the metals by treatment with lime. The Oakite Super Rustripper is biodegradable and contains no phosphates. This alkaline derusting solution can be neutralized and diluted for safe disposal.

Approximately 2,000 gallons of production cyanide base solutions from the plating facility were destroyed batchwise by chlorination. Caustic was added to neutralize hydrochloric acid produced by the destruction process. Chlorination was carried out until the free cyanide was reduced to less than one ppm. The batches were acidified to pH 5-6 and the sludge filtered off and packaged for disposal. The filtrate was combined with other plating shop effluent in RIA's waste treatment facility.

4.0 CONCLUSIONS

Kadizid cadmium and Cupure copper plating solutions produce coatings which meet the requirements of Federal Specification QQ-P-416C(1) and Mil-C-14550A for cadmium and copper plating, respectively, and are appropriate replacements for their cyanide based counterparts.

Kadizid cadmium coatings are receptive to both chromate and phosphate supplementary treatments for added corrosion protection.

The noncyanide Oakite Super Rustripper alkaline derusting bath meets the requirements of Mil-C-14460B and is adequate for the cleaning requirements on a production basis.

Waste treatment of the noncyanide baths is simple and considerably less time consuming since there is no need for cyanide destruction.

5.0 RECOMMENDATIONS

It is recommended that:

a. Kadizid cadmium plating process be used to replace cyanide based cadmium plating processes.

b. Cupure copper plating process be used to replace cyanide based copper plating processes.

c. Oakite Super Rustripper be used to replace cyanide based metal cleaners and/or metal cleaners containing phosphates.

TABLE 1

COMPOSITIONS OF NONCYANIDE CADMIUM PLATING BATHS

Kadizid Bright Acid Cadmium System

Solution Make-Up	100 gallons
Cadmium oxide	37.5 pounds
Sulfuric acid Sp. G. 1.84	96 pounds
Kadizid Starter K	5 gallons
Kadizid Stabilizer	0.75 gallons
Kadizid KR (Brightener)	2 gallons
Kadizid K13 (Wetting Agent)	1 gallon
Water to make	100 gallons

Operating Conditions	Range
Cadmium	4 - 6 oz/gal
Free sulfuric acid	8 - 12 oz/gal
Temperature	60 - 90°F
Current density	10 - 30 ASF

Cadvert Sulfate Cadmium System

Solution Make-Up	100 gallons
Cadmium oxide	14.5 pounds
Sulfuric acid Sp. G. 1.84	3.1 gallons
Cadvert - 374	3.0 gallons
Cadvert - 375	0.3 gallon
Water to make	100 gallons

Operating Conditions	Range
Cadmium	11.25 - 18.75 g/l
Free sulfuric acid	31.2 - 62.4 ml/l
Temperature	65 - 80°F
Current density	5 - 25 ASF

TABLE 2

COMPOSITION OF NONCYANIDE CUPURE COPPER SYSTEM

Cupure Copper Process

Solution Make-Up	100 Gallons
Cupure Make-Up Concentrate	33-1/3% volume
Potassium hydroxide	17 % volume
Cupure H501	1 % volume
Cupure L301	1/4% volume
Cupure Wetting Agent	1/4% volume
Cupure Anti-Foam	.05 % volume
Water to make	100 gallons

Operating Conditions	Range
Copper	1.5 - 2.5 oz/gal
Specific Gravity, R. T.	20.5° Baume
Temperature, °F	140 - 160°F
Current density	5 - 40 ASF

TABLE 3

COMMERCIAL METAL CLEANERS
EVALUATED FOR DERUSTING BATHS

Commercial Cleaner	Supplier	Remarks
Oakite Super Rustripper	Oakite Products, Inc.	Performed efficiently and presents no disposal problem. Meets requirements of Mil-C-14460 B, Type I, sodium hydroxide base.
Oakite Low Heat Cleaner 1	Oakite Products, Inc.	Not an efficient derusting material. Contains phosphate.
Nuvat LT	BASF Wyandotte Corporation	Not a good derusting material but may be useful as a precleaner.
Super Maxamp	BASF Wyandotte Corporation	A good derusting material. Contains phosphate.

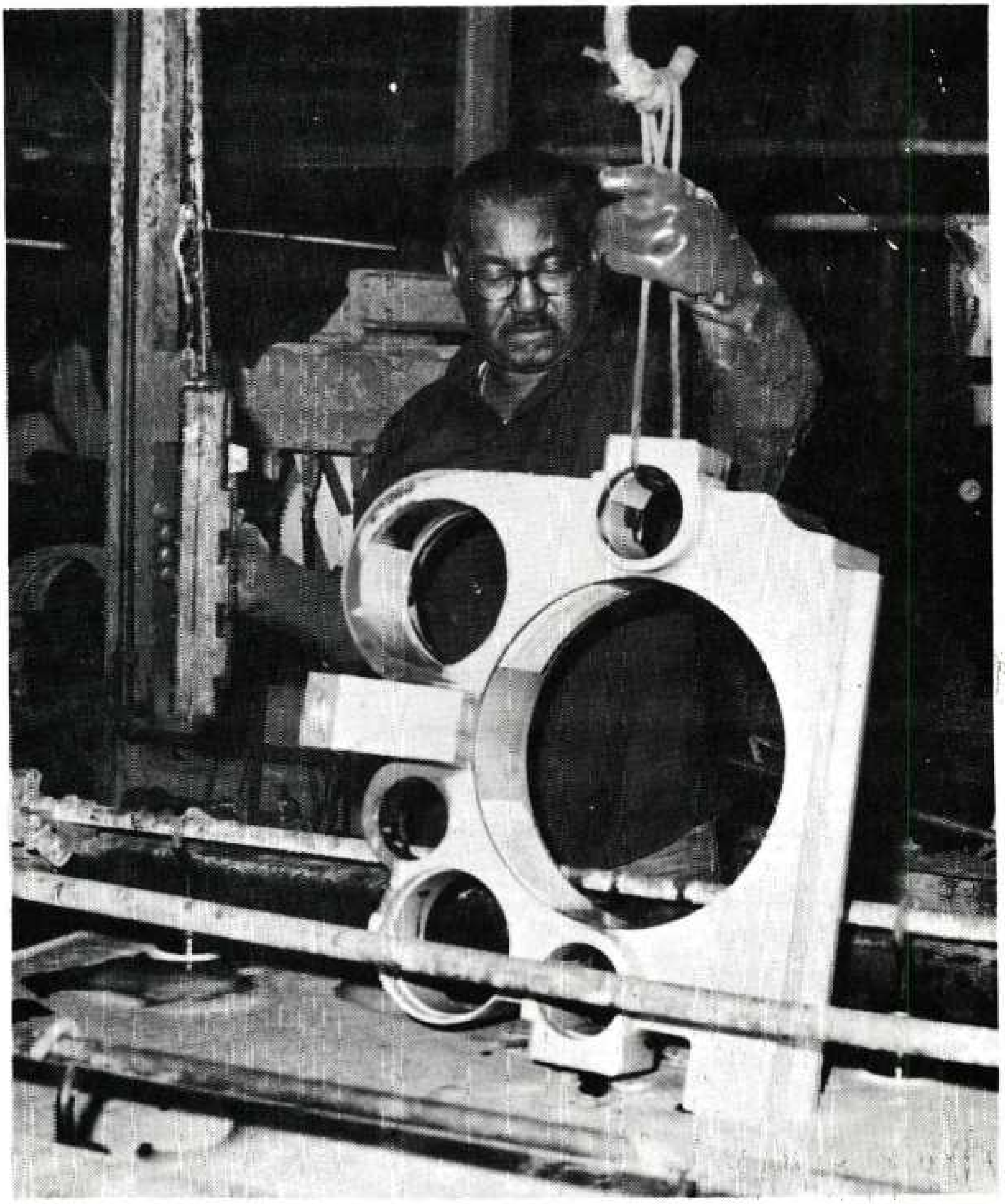

FIGURE 1. RACK PLATING OF M198 YOKE IN THE KADIZID CADMIUM PROCESS.

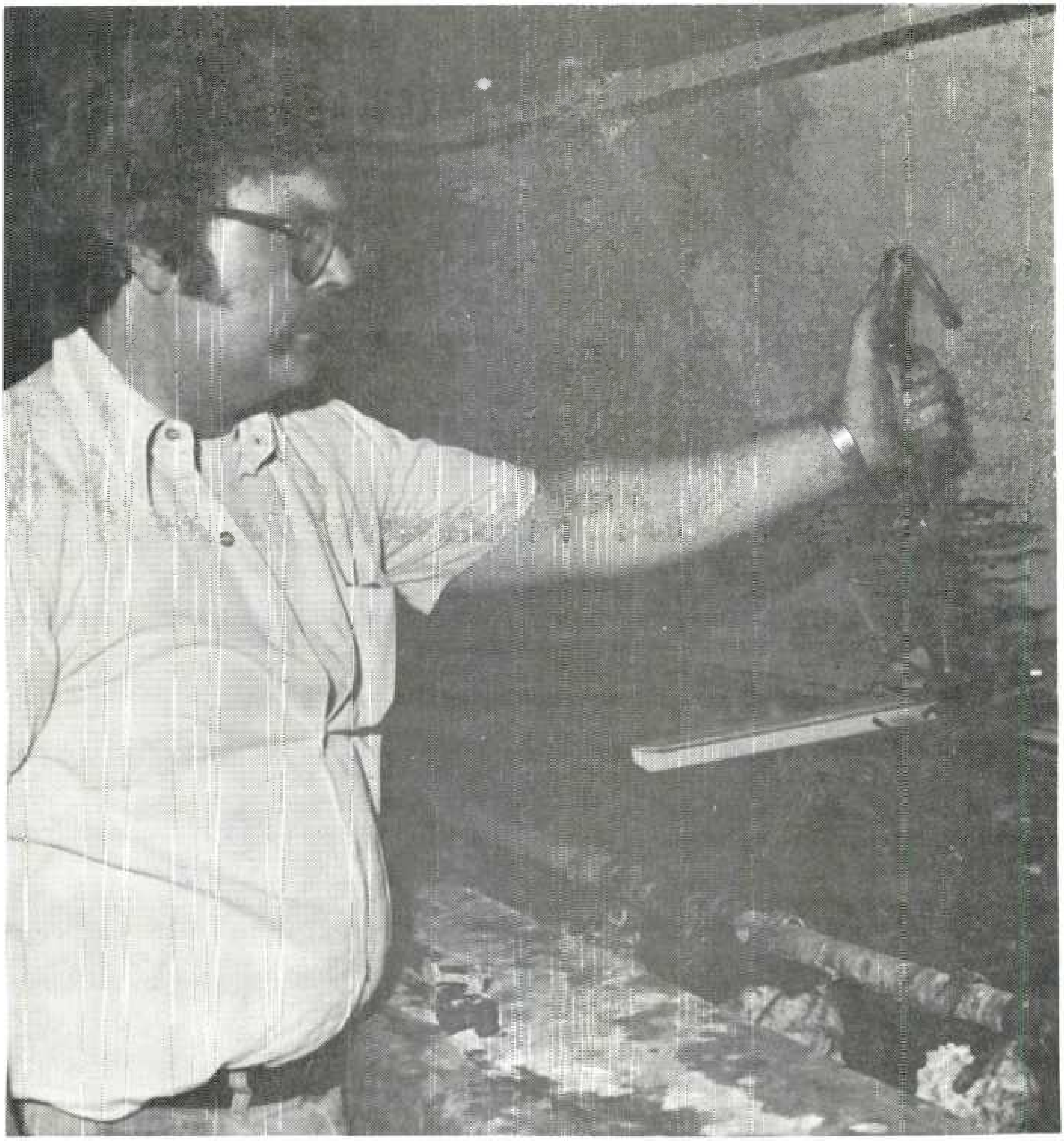

FIGURE 2. RACK PLATING OF M85 CHAIN GUIDES IN THE CUPURE COPPER PROCESS.

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3. Noncyanide Derust
4. Noncyanide Cadmium
5. Noncyanide Copper

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NONCYANIDE PLATING AND DERUSTING PROCESSES FOR POLLUTION ABATEMENT, by Frank Testroet

Report EN-82-07, Jul 82, 17 p. incl. illus, tables, (AMS Code 3297.06.8017) Unclassified Report.

This project was undertaken to eliminate pollution of wastewater effluent caused by electroplating operations using cyanide based plating solutions. Noncyanide derusting and plating baths were investigated to compare their ability to perform as well as the cyanide based counterparts. Suitable materials were found and noncyanide derusting as well as noncyanide cadmium and copper plating were implemented in Rock Island Arsenal's production plating facility. All cyanide based baths were removed from the plating production area and were properly disposed of in compliance with pertinent regulations.

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