Development Document for Interim Final Effuent Limitations Guidelines and

Proposed New Source Performance Standards for the

METAL FINISHING

Segment of the

ELECTROPLATING

Point Source Category

DEVELOPMENT DOCUMENT

for

INTERIM FINAL EFFLUENT LIMITATIONS

and

NEW SOURCE PERFORMANCE STANDARDS

for the

METAL FINISHING SEGMENT OF THE
ELECTROPLATING MANUFACTURING POINT SOURCE CATEGORY

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ABSTRACT

This document presents the findings of an extensive study of major segments of the metal finishing industry by Battelle's Columbus Laboratories for the Environmental Protection Agency for the purpose of developing effluent limitations guidelines, Federal Standards of performance, and pretreatment standards for the industry, to implement Sections 304, 306, and 307 of the Federal Water Pollution Control Act, as amended (33 USC 1251, 1314, and 1316; 86 Stat 816).

Effluent limitations guidelines contained herein set forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best available technology economically achievable which must be achieved by existing point sources by July 1, 1977 and July 1, 1983 respectively. The standards of performance for new sources contained herein set forth the degree of effluent reduction which is achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives.

In developing the data and recommendations in this document the metal finishing processes have been divided into two subcategories that are distinguished from each other by differences in water use and the presence or absence of chelating agents. Subcategory (1) consists of processes anodizing, immersion plating, chemical milling, chemical conversion processes and etching. chemical milling, and etching. Subcategory (2) consists of processes for electroless plating on plastics.

Chemical treatment of waste waters to destroy oxidizable cyanide, reduce hexavalent chromium, and remove all but small amounts of heavy metals represents the best practicable control technology currently available for existing point sources in Subcategories (1) and (2).

Chemical treatment of waste waters to destroy oxidizable cyanide, reduce hexavalent chromium, and remove all but small amounts of metals, augmented by in-process procedures to further reduce the amount of waste water and the total pollutional load is the new source performance standard for point sources in Subcategories (1) and (2).

The Best Available Technology Economically Achievable to be achieved by 1983 is no discharge of pollutants for Subcategories (1) and (2).

Supportive data and rationale for development of the proposed effluent limitation guidelines and standards of performance are contained in this report.

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CONCLUSIONS

For the purpose of establishing effluent limitations guidelines and standards of performance for the metal finishing segment of the electroplating industry, the metal finishing process covered by this study have been divided into two subcategories. The selection of processes for inclusion in each subcategory is based upon a similarity in process configuration, in the method of treating the waste waters and a similarity in the amount of water required for the metal finishing processes. The consideration of the age of the plant, processes employed, geographical locations, and wastes generated support this conclusion. Guidelines for the application of the effluent limitations and standards of performance take into account the plant size in that the allowable amount of pollutant that can be discharged is proportional to the size of the plant.

Subcategories of the metal finishing point source category are:

(1)   Anodizing.

(2)   Coatings.

(3)   Chemical etching and milling.

The best practicable control technology for subcategories (1) and (2) is chemical treatment. It is estimated that a water use of 90 liters per sq m per operation can be achieved for the anodizing subcategory, 80 liters per sq m per operation for the coatings subcategory and 120 liters per sq m per operation in the chemical etching and milling subcategory.

The average cost for waste treatment reported by 30 plants was $1.06/1000 liters of waste water treated. Investment costs ranged from $1.15 to $43.39/1/hr. Estimates made from two modeled waste treatment plants carrying out cyanide destruction, chromate reduction, precipitation, clarification and filtering were $1.09 and $1.41/1000 liters of waste water treated. Investment costs ranged from $22,980 for a 5-man plant plating 75 sq m/hr and treating wastes only by neutralizing it to $378,455 for a 47-man plant plating 815 sq m/hr and treating for cyanide,

chromate, and heavy metals including clarification and filtering. A minimum cost batch waste treatment system was designed for $17,700. This system treats cyanide, chromate, and heavy metals but relies heavily on an operator for proper functioning and many manual operations. Operating costs were estimated to be $10,186/yr exclusive of analytical costs.

The best available technology economically achievable by 1983 is no discharge of pollutants for all subcategories. The technology involved consists of both in-process and end-of-process methods of minimizing and eliminating water use and eliminating effluent.

The new source performance standards are based upon chemical treatment and a water use estimated to be of the order of 90 1/sq m/operation for subcategory (1), 80 1/sq m/operation for subcategory (2) and 120 1/sq m/operation for subcategory (3).

SECTION II

RECOMMENDATIONS

Best Practicable Control Technology Currently Available

Recommended effluent limitations for the metal finishing industry applicable to existing sources discharging to navigable waters are summarized in Table 1 and the specific effluent limitation guidelines and rationale are discussed in greater detail in Section IX of this report. The guidelines have been derived from the product of pollutant concentrations and water uses considered achievable. Chemical treatment of waste waters to destroy oxidizable cyanide, reduce hexavalent chromium, and remove all but small amounts of the heavy metal pollutants represents the best practicable control technology currently available (BPCTCA) for existing point sources. A water use of 90 l/sq m/operation for subcategory 1, 80 l/sq m/operation for subcategory 2 and 120 l/sq m/operation for subcategory 3 have been estimated to be achievable by the industry.

Additional currently available in-process control technology designed to recover and reuse process chemicals and water and/or reduce water consumption may be required to meet the effluent limitations depending upon the kind of parts being finished or the nature of available process facilities.

Best Available Technology Economically Achievable

The effluent limitations attainable through the application of the best available technology economically achievable by existing point sources in the subcategories listed in Section I is no discharge of process waste water pollutants to navigable waters by July 1, 1983. The achievement of no discharge of pollutants is believed to be possible through a combination of technologies that are in existence, that are being developed, and that remain to be developed before 1983. There is considerable information available on how to reduce water use in the plant through proper design of processing lines and correct operating procedures. Minimizing this water use reduces the problem of treating the waste water that is produced. Reverse osmosis, electrodialysis, and special ion-exchange systems are under development to recycle water in process loops and thereby reduce water to be treated and are also being tested for recovery of process water from waste effluent. New techniques for water recovery should come from the broad

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scientific and engineering base in the United States, although it is difficult to pinpoint what specific technologies will emerge before 1983.

New Source Performance Standards

Recommended standards of performance for subcategories (1), (2) and (3) of the metal finishing industry applicable to new sources discharging to navigable waters are summarized in Table 2. The limitations are applicable to sources constructed after publication of proposed regulations prescribing a standard of performance. The standards of performance are lower in value than the corresponding effluent limitation guidelines in Table 1. New sources have the opportunity to design and economically install in-process systems that can be operated with a lower water use than can be achieved in many existing plants.

The single-day maximum is two times the 30-day average given in Table 2. The rationale for establishing the factor of two is given in Section IX.

Table 1 - BPCTCA Limitations
for Anodizing Subcategory

Effluent Characteristic	Effluent Limitations	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)	milligrams per sq m per operation	
Copper	90	45
Nickel	90	45
Cr,Total	90	45
CrVI	9	4.5
Zinc	90	45
CN,Total	90	45
CN,A	9	4.5
Fluoride	3600	1800
Cadmium	54	27
Lead	90	45
Iron	180	90
Tin	180	90
Phosphorus	180	90
TSS	3600	1800
pH	Within the range 6.0 to 9.5.	
(English units)	pounds per million sq ft per operation	
Copper	18.4	9.2
Nickel	18.4	9.2
Cr,Total	18.4	9.2
CrVI	1.8	.92
Zinc	18.4	9.2
CN,Total	18.4	9.2
CN,A	1.8	.92
Fluoride	738	369
Cadmium	8.8	4.4
Lead	18.4	9.2
Iron	36.8	18.4
Tin	36.8	18.4
Phosphorus	36.8	18.4
TSS	738	369
pH	Within the range 6.0 to 9.5.	

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Table 1 – BPCTCA Limitations
for Coatings Subcategory

Effluent Characteristic	Effluent Limitations	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)		milligrams per sq m per operation
Copper	80	40
Nickel	80	40
Cr,Total	80	40
CrVI	8	4
Zinc	80	40
CN,Total	80	40
CN,A	8	4
Fluoride	3600	1800
Cadmium	48	24
Lead	80	40
Iron	160	80
Tin	160	80
Phosphorus	160	80
TSS	3600	1800
pH	Within the range 6.0 to 9.5.	
(English units)		pounds per million sq ft per operation
Copper	16.4	8.2
Nickel	16.4	8.2
Cr,Total	16.4	8.2
CrVI	1.6	.82
Zinc	16.4	8.2
CN,Total	16.4	8.2
CN,A	1.6	.82
Fluoride	646	323
Cadmium	9.8	4.9
Lead	16.4	8.2
Iron	32.8	16.4
Tin	32.8	16.4
Phosphorus	32.8	16.4
TSS	646	323
pH	Within the range 6.0 to 9.5.	

Table 1 - BPCTCA Limitations
for Chemical Milling and Etching
Subcategory

Effluent Characteristic	Effluent Limitations	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)	milligrams per sq m per operation	
Copper	120	60
Nickel	120	60
Cr,Total	120	60
CrVI	12	6
Zinc	120	60
CN,Total	120	60
CN,A	18	9
Fluoride	4800	2400
Cadmium	72	36
Lead	120	60
Iron	240	120
Tin	240	120
Phosphorus	240	120
TSS	4800	2400
pH	Within the range 6.0 to 9.5.	
(English units)	pounds per million sq ft per operation	
Copper	24.6	12.3
Nickel	24.6	12.3
Cr,Total	24.6	12.3
CrVI	2.4	1.2
Zinc	24.6	12.3
CN,Total	24.6	12.3
CN,A	3.8	1.9
Fluoride	984	492
Cadmium	14.8	7.4
Lead	24.6	12.3
Iron	49.2	24.6
Tin	49.2	24.6
Phosphorus	49.2	24.6
TSS	984	492
pH	Within the range 6.0 to 9.5.	

Table 2 - NSPS Limitations
for Anodizing Subcategory

Effluent Characteristic	Effluent Limitations	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)	milligrams per sq m per operation	
Copper	45	23
Nickel	45	23
Cr,Total	45	23
CrVI	4.5	2.3
Zinc	45	23
CN,Total	45	23
CN,A	4.5	2.3
Fluoride	1800	900
Cadmium	27	14
Lead	45	23
Iron	90	45
Tin	90	45
Phosphorus	90	45
TSS	1800	900
pH	Within the range 6.0 to 9.5.	
(English units)	pounds per million sq ft per operation	
Copper	9.2	4.6
Nickel	9.2	4.6
Cr,Total	9.2	4.6
CrVI	.92	.46
Zinc	9.2	4.6
CN,Total	9.2	4.6
CN,A	.92	.46
Fluoride	369	185
Cadmium	4.4	2.2
Lead	9.2	4.6
Iron	18.4	9.2
Tin	18.4	9.2
Phosphorus	18.4	9.2
TSS	369	185
pH	Within the range 6.0 to 9.5.	

Table 2 - NSPS Limitations
for Coatings Subcategory

Effluent Characteristic	Effluent Limitations	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)	milligrams per sq m	per operation
Copper	40	20
Nickel	40	20
Cr,Total	40	20
CrVI	4	2
Zinc	40	20
CN,Total	40	20
CN,A	4	2
Fluoride	1800	900
Cadmium	24	12
Lead	40	20
Iron	80	40
Tin	80	40
Phosphorus	80	40
TSS	1800	900
pH	Within the range 6.0 to 9.5.	
(English units)	pounds per million sq ft	per operation
Copper	8.2	4.1
Nickel	8.2	4.1
Cr,Total	8.2	4.1
CrVI	.82	.41
Zinc	8.2	4.1
CN,Total	8.2	4.1
CN,A	.82	.41
Fluoride	323	161
Cadmium	4.9	2.5
Lead	8.2	4.1
Iron	16.4	8.2
Tin	16.4	8.2
Phosphorus	16.4	8.2
TSS	323	161
pH	Within the range 6.0 to 9.5.	

Table 2 - NSPS Limitations
for Chemical Milling and Etching
Subcategory

Effluent Characteristic	Effluent Limitations	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)	milligrams per sq m per operation	
Copper	60	30
Nickel	60	30
Cr,Total	60	30
CrVI	6	3
Zinc	60	30
CN,Total	60	30
CN,A	9	5
Fluoride	2400	1200
Cadmium	36	18
Lead	60	30
Iron	120	60
Tin	120	60
Phosphorus	120	60
TSS	2400	1200
pH	Within the range 6.0 to 9.5.	
(English units)	pounds per million sq ft per operation	
Copper	12.3	6.2
Nickel	12.3	6.2
Cr,Total	12.3	6.2
CrVI	1.2	0.6
Zinc	12.3	6.2
CN,Total	12.3	6.2
CN,A	1.9	0.9
Fluoride	492	246
Cadmium	7.4	3.7
Lead	12.3	6.2
Iron	24.6	12.3
Tin	24.6	12.3
Phosphorus	24.6	12.3
TSS	492	246
pH	Within the range 6.0 to 9.5.	

FOOTNOTES FOR TABLES 1 AND 2

(a) The effluent limitations and standards of performance are defined as the weight of pollutant in milligrams discharged per sq m per operation (pounds per million sq ft per operation). The definition of operation depends upon the subcategory. For anodizing, the term operation shall mean any step followed by a rinse in which a protective film is deposited on the object which acts as an anode. In coatings, the term operation shall mean any step followed by a rinse in which a protective film is deposited on the basis material. In chemical etching and milling, the term operation shall mean any step followed by a rinse in which some portion of the basis material is removed. The term "sq m" ("sq ft") shall mean the area plated expressed in square meters (square feet).

(b) Single-Day Maximum is the maximum value for any one day, and is 2.0 times the 30-Day Average.

(c) Thirty-Day Average is the maximum average of daily values for any consecutive 30 days.

(d) Total metal (in solution and in suspended solids) in sample.

(e) Chromium (total) is the sum of hexavalent and trivalent chromium, in solution and in suspended solids.

(f) Oxidizable cyanide is defined as all detectable cyanide amenable to oxidation by chlorine as described in 1972 Annual Book of ASTM Standards, 1972, Standard D 2036-72, Method B, p. 553.

(g) Total suspended solids retained by a filter according to standard analytical procedures.

SECTION III

INTRODUCTION

Purpose and Authority

Section 301(b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) to the Act. Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including where practicable, a standard permitting no discharge of pollutants.

Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operation methods and other alternatives. The regulations proposed herein set forth effluent limitations guidelines pursuant to Section 304(c) of the Act for the metal finishing source category.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b)(1)(A) of the Act, to propose regulations establishing Federal standards of

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performance for new sources within such categories. The Administrator published in the Federal Register of January 16, 1973 (38 FR 1624), a list of 27 source categories.

Publication of the list constituted announcement of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources within the metal finishing industry which was included within the list published January 16, 1973.

Summary of Methods Used for Development of the Effluent Limitation Guidelines and Standards of Performance

The effluent limitations guidelines and standards of performance recommended herein were developed in the following manner. Electroplating processes were considered separately from metal finishing processes and the development of effluent limitations guidelines and standards of performance for electroplating processes are covered in two other documents. This document covers the following metal finishing processes: anodizing, coatings (chemical conversion coatings of phosphating and chromating and immersion plating), and chemical etching and milling. Subcategorization of these processes was based upon raw material used, operations employed, and other factors. The raw-waste characteristics were identified by analyses of the source and volume of water used in the process employed and the sources of waste and waste waters in representative plants and the constituents of all waste waters.

Ranges of control and treatment technologies existing within each subcategory were identified, including both in-plant and end-of-process technologies, which are existent or capable of being designed for waste control. The problems, limitations, and reliability of treatment and control technology were also identified.

In addition, the nonwater quality environmental impact, such as the effects of the application of such technologies upon other pollution problems, including air, solid waste, and noise were also identified. The energy requirements of each of the control and treatment technologies were identified as well as the cost of the application of such technologies.

The information, as outlined above, was then evaluated in order to determine what levels of technology constituted the "best practicable control technology currently available", the "best available technology economically achievable", and the "best available demonstrated control technology,

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processes, operating methods, or other alternatives". In identifying such technologies, the factors considered included the total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application, the age of equipment and facilities involved, the process employed, the engineering aspects of the application of various types of control techniques and process changes, nonwater quality environmental impact (including energy requirements), and other factors.

Sources of information utilized for developing the data in this document include the following:

(1) Published literature (References appear in Section XIII)
(2) Trade literature
(3) EPA Technology Transfer Seminar on Upgrading Metal-Finishing Facilities to Reduce Pollution, Braintree, Massachusetts, October 30-31, 1973
(4) Three EPA regional offices and eight state pollution abatement offices
(5) Representatives of approximately 75 companies with facilities for metal finishing who returned mailed questionnaires and who were subsequently contacted by telephone or further correspondence in many cases.
(6) Representatives of 11 companies who were visited by BCL staff for development of detailed data
(7) Analytical verification of effluent data for seven plants engaged in metal finishing processes.

The decision as to which companies to send questionnaires to was a matter of judgement combined with information from the prior sources listed. A plant or company was contacted if there was any evidence that it was engaged in any of the metal finishing processes of interest and that it was treating the wastes from these processes. Plants were identified over a period of approximately 3 months, after which further activity of this sort was minimal and most effort was devoted to summarizing the information that had been obtained. Thus, a number of plants were identified that could be classified as exemplary, but many more may not have been identified.

This effort includes the following metal finishing processes:

Anodizing
Immersion plating
Chemical conversion coating (phosphate, chromate,

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etc.)
Chemical milling and etching

All the above-mentioned operations are point sources for
pollution control.

General Description of the Metal Finishing Industry

The metal finishing industry, as included in Standard
Industrial Classification (SIC) 3471, is defined for the
purpose of this document as that segment of industry
applying (a) coatings on surfaces by electrodeposition,
electroless or immersion plating, anodizing, chemical
conversion techniques, and (b) special contours or finishes
obtained by electrochemical or chemical processes such as
chemical milling, and etching. Pretreatment of the basis
material and post finishing operations are included and are
carried out by both independent (job) platers and captive
operations associated with product by metal finishing
exceeds $2,000,000,000. Approximately 15,000 companies are
engaged in metal finishing. Approximately 1000 of these
plants are engaged in processes which are covered by these
regulations. The annual dollars added value for this
segment of the metal finishing industry exceeds
$300,000,000. About 25 percent of this segment is con-
centrated in the middle western states of Illinois,
Michigan, and Ohio. Another 25 percent is concentrated in
Eastern Pennsylvania and the Atlantic Coastline states of
Connecticut, Rhode Island, New York, and New Jersey. Figure
1 shows the growth of companies in this group.

Metal finishing facilities of the kind in SIC 3471 vary
greatly in size and character from one plant to another. A
single facility for plating individual parts formed by
stamping, casting, machining, etc., may employ plating or
processing solutions (excluding water rinses) ranging in
total volume from less than 380 liters (100 gallons). The
area of the products being finished in these facilities
varies as much as three orders of magnitude from less than
10 to more than 1000 sq meters/day (100 to 10,000 sq
ft/day). The power consumed by a single facility varies
from a few kilowatt-hours/day to as much as 20,000 kilowatt-
hours/day. Products being finished vary in size from less
than 6.5 sq cm (1 sq inch) to more than 1 sq meter (10 sq
ft) and in weight from less than 30 g (1 oz) to more than
9000 kg (10 tons). Continuous strip and wire are plated in
some plants on a 24-hour/day basis.

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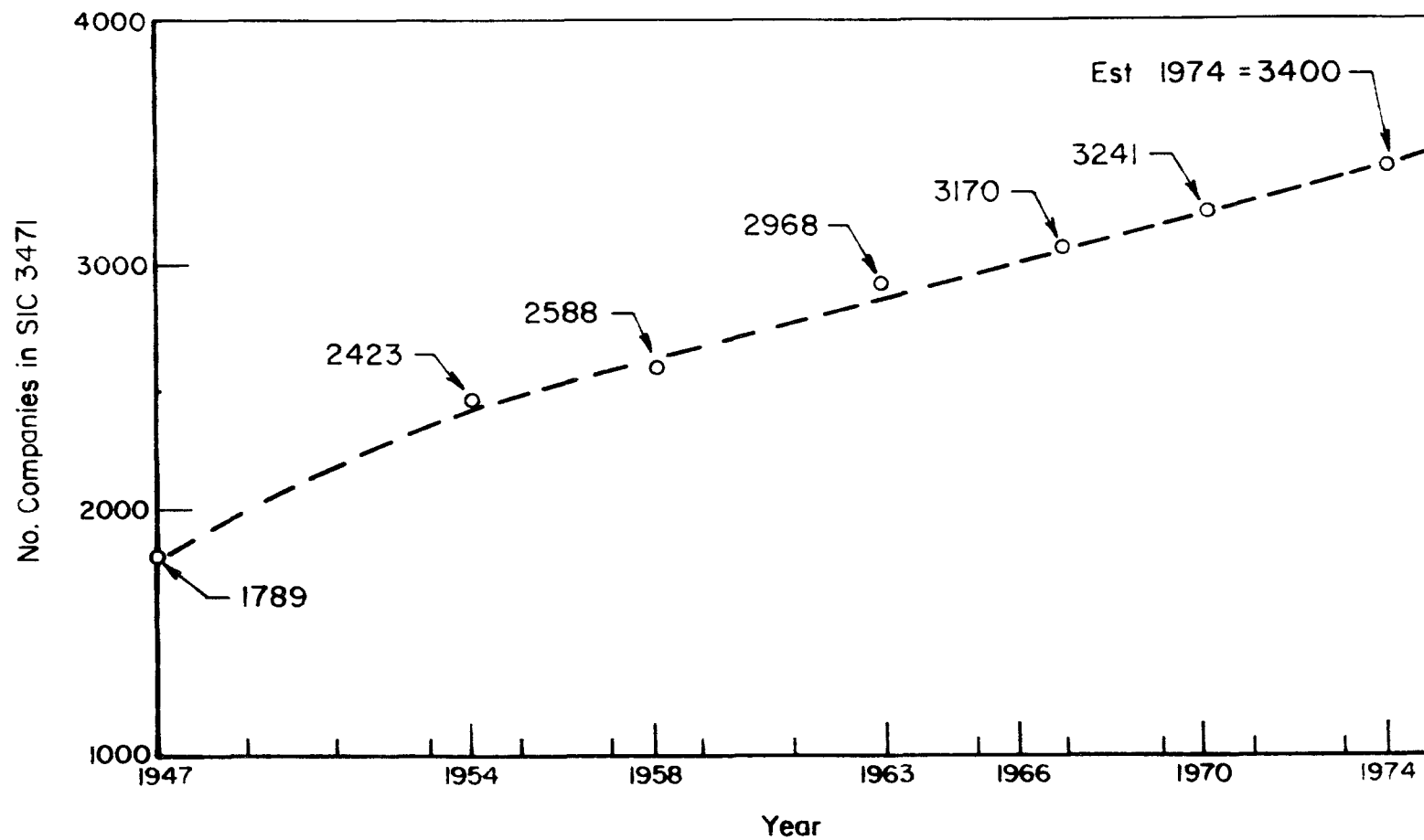
FIGURE 1.   NUMBER OF COMPANIES IN SIC 3471 ACCORDING TO DATA IN TABLE 5,
PAGE 9-30, "1967 CENSUS OF MANUFACTURERS" U.S. BUREAU OF
COMMERCE

Some companies have capabilities for finishing ten or twelve different metals and alloys, but others specialize in just one or two. Because of differences in character, size and processes, few or no similar plants exist at the present time. Construction of facilities have been custom tailored to the specific needs of each individual plant.

In the Phase I report the energy consumed by industry in the electroplating subcategory was estimated to be 1.7 x 10^9 kilowatt hours. It also cites that from 90,718 to 10^8,861 metric tons (100,000 to 120,000 short tons) of metal (principally copper, nickel, zinc, and tin) are converted annually to electroplated coatings. The figures for sheets, strip, and wire include nonelectroplated coatings, applied by hot dipping. All the aluminum is applied by hot dipping, as is about 90 percent of the zinc, as are significant but unidentified percentages of the tin and lead.

These coatings provide corrosion protection, wear or erosion resistance, antifrictional characteristics, lubricity, electrical conductivity, heat and light reflectivity or other special surface characteristics, which enable industry to conserve several millions of tons of critical metals. In the finishing of individual products, electroplated coating thickness usually ranges from 0.0006 to 0.004 cm (0.00025 to 0.0015 inch), but thicker coatings to 0.025 or 0.04 cm (0.010 or 0.015 inch) are sometimes required for special engineering purposes or for salvaging worn or mismachined parts. Tin and chromium coatings from 0.3 to 1 mm (1 x 10-5 to 4 x 10-5 inch) and 0.003 mm (1 x 10-7 inch) thickness respectively are applied to continuous steel strip as a prefinish before coating with an organic material by the container industry.

General Description of Surface Treatment

Surface treatments include anodizing, chemical brightening, electroless plating, and chromate or other conversion coating treatment.

Of 158 companies listed by one source of data on metal finishing, 94 do anodizing. Of these 94, 43 do both anodizing and plating, and 30 do mechanical treatments (polishing, buffing, tumbling, etc.) but no electroplating. Anodizing to customer specification is done manually by 48 percent of the plants, and 25 percent do hard-coat anodizing. A sulfuric acid electrolyte is used for most anodizing operations, but chromic acid anodizing is generally specified for aircraft parts, assemblies of intricate design, or parts subject to stress. Whereas, some

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companies will treat a variety of lengths and widths, others will limit processing of parts to those under 1 to 2 feet long. Continuous coil is anodized in 4.5 percent of these firms. Furthermore, 28.5 percent of the firms do electroless nickel plating. Chemical brightening is done by 46 percent of the companies and 60 percent do conversion coating.

Such a mixture of operations is typical of the metal finishing industry and shows the complexity of determining the best practicable waste treatment for all facilities. The apparent procedure is to view each operation as a unit operation that can and should have an associate best waste treatment practice and control.

Anodizing provides a protective oxide on metals. This benefit is accomplished by making the metals anodic in an electrolytically conducting solution. Protection is achieved against corrosion, tarnish, and wear. Aluminum and its alloys are the most extensively anodized materials. Other materials much less extensively anodized are magnesium, titanium, and zinc.

Electroless plating of copper, nickel, cobalt, and gold are achieved by chemical reduction, catalyzed either by the basis material or by a pretreatment to activate the basis material surface.

Conversion coatings of zinc and iron phosphates are applied to steel as preparation for subsequent organic coatings and for lubrication in forming dies. Other types of conversion coatings impart special color to metals as, for example: colors on copper, bronze, brass, and zinc by chemical oxidation or treatment in sulfide solutions; protective films on zinc, tin, cadmium plate by treatment in chromium containing or other oxidizing solutions.

Some of the operations as shown in Phase I, chromating of zinc plate and coloring of copper are carried out after electroplating. Thus, the waste treatment and control are a part of the systems for handling the electroplating operations.

General Description of Metal Removal

The only process for removal of metal by chemical dissolution pertinent to the objectives of the present report is etching. The printed circuit industry, with a dollar volume of approximately $600,000,000, does a considerable amount of etching. A single plant has

facilities to etch 125,000 boards (printed circuits) per week. Each board has 206 sq cm (32 sq in.) with 610 g/sq m (2 oz/sq ft) of copper. On an annual basis of 3,100,000 boards or 63,358 sq m (682,000 sq ft), produced 27,522 kg (60,550 lb) of copper are dissolved and reclaimed in an electroplating operation and the stripped etchant is recycled. Thus, no dumps of concentrated etchant enter the waste treatment system. Only rinse water is treated.

The yearly average production (by electrodeposition) of copper foil for the printed circuit industry is about 136,363 kg/week (300,000 lb/week). Sometimes production is 159,091 kg/week (350,000 lb/week). About 75 percent of the foil is 610 g/m2 (2 oz/sq ft) plus special small quantities of other weight foil. Relatively, the amount of nickel foil is negligible.

There is no single universal figure for the amount of metal dissolved away in etching printed circuits. The amount is estimated to be 75 to 85 percent. In order to estimate total square feet processed and using an average of 80 percent removal, the above mentioned 27,523 kg (60,550 lb.) of recovered copper corresponds to about 34,318 kg (75,500 lb.) of 610 g/sq m (2 oz/sq ft) foil having 63,357 sq m (682,000 sq ft) of surface area.

Chemical etching of aluminum, brass, copper, steel and stainless steel is used in the production of name plates, information plates, etc. After etching, the aluminum is usually anodized and copper, brass, and steel are electroplated for protection.

Water Usage in the Metal Finishing Industry

In SIC 3471, the total intake of water was cited as 3.27×10^{10} liters (8.7×10^9 gallon) in 1968[7]. Of this amount 2.78×10^{10} liters (7.4×10^9 gallon) was discharged as follows:

2.10×10^{10} liters	(5.6×10^9 gal)	to public sewers
6.02×10^9 "	(1.6×10^9 gal)	to surface water bodies
3.76×10^8 "	(1.0×10^8 gal)	to ground
7.14×10^8 "	(1.9×10^8 gal)	treated before discharge.

This segment of industry, in 1967, had 55,100 employees[7], or an average of about 503,840 liters (134,000 gal) per employee.

Of the firms with captive electroplating facilities, 2191 of them had a few more than 25,709 total employees. However,

the number of employees was not cited where the SIC showed one or two firms. At the same water use rate these firms would discharge over 1.182×10^{10} liters (3.144×10^{9} gal) and assuming the same average rate the remaining 14,500 companies would discharge over 7.802×10^{10} liters (2.075×10^{10} gal).

SECTION IV

INDUSTRY CATEGORIZATION

Introduction

The rationale is developed for subcategorizing metal finishing processes according to processes which have essentially the same water use.

Objectives of Categorization

The primary purpose of industry categorization is to develop quantitative effluent limitations and standards for discharge of pollutants that are uniformly applicable to a specific category or subcategory. This does not preclude further classification within a category for the purpose of monitoring to insure compliance.

Electroplating is one of several processes in the broader category of metal finishing. It is listed under SIC 3471 (Standard Industrial Classification Manual) along with numerous other metal finishing processes. The metal finishing industry was divided into two segments, electroplating and metal finishing, for the purposes of developing effluent limitations guidelines. Phase I covered the electroplating of copper, nickel, chromium and zinc or combination thereof. Phase II covers tin, lead, cadmium, iron, silver, gold, platinum, palladium, rhodium, iridium, ruthenium, titanium, or any combination thereof. It also covers stripping. This addition is justified because all electroplating shops have a stripping line to salvage poorly plated or badly corroded parts. This usually exists as a separate line. Also considered are the pre and posttreatment operations of alkaline cleaning, acid pickling, conversion coatings, coloring, and descaling. Although these processes are not strictly electroplating, they usually form an integral part of an electroplating line and therefore must be considered under the auspices of electroplating. Other metal finishing operations which are an end unto themselves and stand as a separate line are considered in separate documents. These are anodizing, immersion plating, chromating, phosphating, chemical milling and etching.

Profile of Production Processes

The metal finishing industry utilizes chemical and electrochemical operations to effect an improvement in the

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surface and structural properties of metals and other materials. In practice, the operations are put together in sequences that become the processes which effect the improvement. Thus, metal finishing operations may be both process and materials oriented. The processes considered in Phase II may be briefly described as follows:

Pretreatment

Pretreatment steps involve cleaning, pickling, degreasing, descaling, desmutting, vapor blasting, surface activation, etching, abrasion and bright dipping. Plating steps are strikes and electroplates, coatings and metal coloring. Post treatment steps are conversion and drying. Stripping, while performed separately, is an integral part of an electroplating shop. It is employed for the reclamation of badly plated parts.

Cleaning

Cleaning involves the removal of oil, grease and dirt from the surface of the basis material. Cleaning or degreasing may be accomplished in one of several ways. These include alkaline electrolytic (anodic and cathodic), diphase, emulsion, soak, solvent, and ultrasonic cleaning.

Alkaline cleaners are the most widely used in preparing the basis material. A good alkaline or soak cleaner must be soluble in water, wet the surface of the basis material, wet and penetrate soil, saponify or dissolve oil and greases or emulsify or suspend insoluble or nonsaponifiable oils and greases, prevent formation of calcium and magnesium deposits from hard water, prevent tarnish and corrosion of basis material, rinse freely and minimize foaming. For possible compositions of alkaline cleaners, see Chapter V. Ferrous metals and alloys can be cleaned using heavy duty (pH = 12.1 - 13.5) uninhibited alkaline solutions. Usually, though, weaker solutions (pH = 10.5 - 12) are used to avoid etching and pitting. When cleaning nonferrous materials, an inhibitor must be added to stop the corrosive action of the cleaner.

Small volumes of work are usually cleaned by hand. Solutions are applied by brushes, swabs, or cloth. Parts may also be immersed in cleaning tanks which may be agitated or heated to increase efficiency. The fastest method of cleaning is by spraying the cleaning solution in an automatic or semi-automatic washing machine. The mechanical force of the spray combined with the chemical and physical action of the cleaning solution increases efficiency.

Electrolytic cleaning is best employed when plating with brass, cadmium, chromium, copper, gold, lead, nickel, silver, tin, and zinc. The basis metal acts as either the cathode or the anode and a low voltage current for each square foot of metal is passed through the alkaline cleaning solution. The generation of gases (H_2 at the cathode and O_2 at the anode) cause increased agitation and the removal of soil particles.

Diphase cleaning is composed of a two layer system of water soluble and a water insoluble organic solvent. This set up is particularly useful where soil removal requires the action of water and organic compounds and when temperature may not be elevated. Usually, the organic solvent is chlorinated. Because they are non-flammable and are denser than water, trichloroethylene, methylene chloride, and perchloroethylene are in common use. This is also known as solvent cleaning. Emulsion cleaning uses water, organic solvents and emulsifying agent.

Ultrasonic energy is finding increased use in the agitation of cleaning solutions. Although it is more expensive to install, there are substantial savings in labor and time. It is used to remove difficult inorganic and organic soils from intricate parts.

Descaling

Descaling involves the removal of oxide films and the buildup of other contaminants on the surface of the basis material. Such removal may be accomplished through mechanical or chemical means.

Pickling

During the production of metals, oxides build up on their surface during such operations as heat treating and welding. Also rust may have built up if the part is not used immediately. Acid pickling is used to remove these oxide films and involves dissolution of oxide scale in an acid. A generalized reaction may be written.

$$MO_2 + 2HA \quad MA_2 + H_2O$$
$$\text{where} \quad M = \text{metal}$$
$$HA = \text{acid}$$
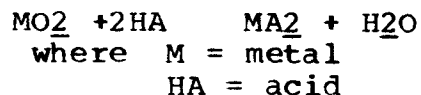
Sulfuric, hydrochloric, phosphoric and chromic acids all find use in this regard. Sulfuric is most often used because it is the least expensive. Rates of reactions are

increased by an increase in acid concentration, temperature and degree of agitation.

Hydrochloric acid is more costly and there is a fuming problem. Nevertheless, many small establishments use it because it works well without the addition of heat. It is also used for light acid dips before plating.

Phosphoric acid is intermediate in cost, but it forms phosphates at the surface of the basis material. This is desirable if rust resistance is needed but not if an electroplate is to follow.

Mechanical

Removal of scale through mechanical means consists of tumbling, (barrel finishing), burnishing, dry rolling, buffing, deburring, polishing, desmutting, and blasting. Such mechanical treatment eliminates or minimizes the pickling to follow.

Activation

Activation involves the elimination of a condition on the surface of the basis material which would preclude the adhesion of an effective electroplate.

Bright Dipping

Bright dipping is used to impart a shiny, clean appearance to the basis material. Solutions are comprised of mixtures of nitric, sulfuric, phosphoric, chromic and hydrochloric acids.

Anodizing

Anodizing involves the basis metals aluminum, zinc, and magnesium and solutions containing sulfuric and chromic acids. Waste Water constituents can be reduced to a low concentration by chemical treatment, water use is similar to that for immersion plating processes, and anodizing is subcategorized with immersion plating processes. Operations involved in anodizing are shown in Table 3.

Chemical Conversion Coatings

Chemical conversion coatings are produced by either chromating or phosphating aluminum, zinc, (die castings, hot-dipped or electroplated), steel, copper, or magnesium. Ions in the waste water are reduced to low concentrations by

TABLE 3   PROCESSES FOR ANODIZING

Operation	Basis Metal			
	Aluminum		Magnesium	Zinc
Alkaline clean/rinse	X	X	X	X
Acid dip/rinse	X	X	X	X
Decorative anodize/rinse	X			
Hard or protective anodize/rinse		X	X	X
Dye/rinse	X			
Seal/rinse	X			

chemical treatment, water use is similar to that for immersion plating and anodizing and chemical conversion is therefore subcategorized with these processes. Operations involved in producing chemical conversion coatings are shown in Table 4.

Immersion Plating

Immersion plating requires similar pretreatment on the same basis metals described previously. Waste water constituents from the plating operation contain ions such as iron, copper, nickel, tin, and aluminum, which can be reduced to a low concentration by chemical treatment. Operations involved in immersion plating are shown in Table 5.

Milling and Etching

Milling and etching can involve the removal of substantial amounts of steel, aluminum, copper, and zinc basis metals by chemical dissolution. Pretreatment procedures are similar to those for anodizing and immersion plating operations and waste water constituents can be reduced to a low level by chemical treatment. Water use is similar to that for anodizing and immersion plating processes. Therefore, milling and etching are subcategorized with these processes. Operations involved in milling and etching are shown in Table 6.

Factors Considered in Categorization

When the nature of the industry and the operations performed were analyzed, consideration was given to the further categorization of metal finishing processes according to one or more of the following:

(1) Type of basis material
(2) Product design
(3) Raw materials used
(4) Size and age of facility
(5) Number of employees
(6) Geographic location
(7) Quantity of work processed
(8) Waste characteristics
(9) Rack finishing vs. barrel finishing
(10) Treatment technology
(11) Water use
(12) Processing differences

A major factor in categorization was water use, based upon evidence collected from plants, upon knowledge of the

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TABLE 4   PROCESSES FOR CHEMICAL CONVERSION COATINGS

Operation	Basis Metal				
	Steel	Zinc	Aluminum	Steel	Tin
Alkaline clean/rinse	X X	X X	X	X	X
Acid dip/rinse	X X	X X	X	X	
Desmut/rinse			X		
Phosphate/rinse	X X	X	X	X	
Chromate/rinse	X	X X	X		X

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TABLE 5   PROCESSES FOR IMMERSION PLATING

Operation	Copper on Steel Basis	Tin on Copper Basis	Tin on Steel Basis	Lead on Steel Basis	Zinc on Aluminum Basis	Tin on Aluminum Basis	Gold on Copper Basis
Alkaline clean/rinse	X X	X	X	X	X	X	X
Acid dip	X X	X	X	X	X	X	X
Neutralizer dip/rinse	X			X		.	
1-Immersion plate/rinse	X X	X	X	X	X	X	X
2-Immersion plate/rinse				X			

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TABLE 6   PROCESSES FOR CHEMICAL MILLING AND ETCHING

Operation	Basis Metal			
	Aluminum	Zinc	Copper	Steels
Alkaline clean/rinse	X X	X	X	X X
Acid dip/rinse	X X	X	X	X X
Etch/rinse	X	X	X	X
Chemical mill/rinse	X		X	

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processes involved, and upon estimates of which processes should use more or less water than others. This factor was primarily responsible for distinguishing between Subcategory (1) and Subcategory (2).

Type of Basis Material

The wastes produced by processing all common basis materials are similar. A single facility can process all basis materials without significant change in the raw materials consumed or the waste-treatment technique adopted for control of end-of-pipe water discharge. Any materials dissolved from the surface of the customary basis metals during processing are removed from waste water discharge by the chemical treatment processes described in Section VII. Furthermore, the basis materials selected for most consumer products frequently are interchanged from one model year to another. Therefore, the type of basis material does not constitute a basis for subcategorization.

Product Design

Product design concepts for minimizing metal finishing costs also reduce wastes created by metal finishing processes. Furthermore, the in-process controls and rinsing techniques described in Section VII for minimizing the wastes generated by metal finishing processes have been adopted for canceling the effect of the shape factor. Therefore, product design variance is not a basis for subcategorization.

Raw Materials Used

Raw materials do not provide a basis for subcategorization, because practical waste-treatement technology identified in Section VII is equally applicable to all of the usual procedures and solutions described previously for metal finishing. In any facility carrying out one or more of the processes shown, the same waste treatment needs arise. Such variations as exist for each operation are not unique and do not affect the waste-treatment technology and control.

Size and Age of Facility

The nature of metal finishing is the same in all facilities regardless of size and age. For example, anodizing is technically the same in 190 liters (50 gallons), as in 19,000 liters (5000 gallons), or larger installations. The age of the facility does not alter this situation. Other metal finishing operations follow the same pattern. Thus, the characteristics of the waste will be the same for plants

of all ages and sizes. Only the quantity of waste per unit time will differ. Yet, this factor is not a basis for subcategorization, because waste discharge after treatment is directly proportional to the size of the facility expressed as surface area processed per unit time. The guidelines recommended in this document provide for variable production volume with no need to differentiate plant capacity as a subcategory.

It is recognized that some small metal finishing installations may have insufficient space for accommodating effective inprocess controls for minimizing water use and/or conventional chemical waste treatment equipment. The capital investment for installing waste control facilities may be greater for small companies relative to their investment in the remaining production facilities than for larger plants. In such cases, heavy metal pollutants can be adsorbed on resins in small ion-exchange units available. At least one vendor of such equipment will replace the resin beds, back wash the used beds in their own facilities and regenerate the resins for reuse. Alternatively, both local and regional organizations equipped with large tank trucks supply a hauling and treating service in several areas. It is also possible that a small electrodialysis system would provide recycling of cyanide. Costs depend on water volume and the concentration of pollutants.

Number of Employees

The number of employees engaged in metal finishing does not directly provide a basis for subcategorization, because metal finishing operations can be carried out manually or in automatic machines which greatly conserve labor. For example, an operation with 3800 liter (1000 gallon) processing tanks may require six people if operated manually, whereas a plant of the same tank size and carrying out the same operations in an automatic machine would need only two people. The same amount of waste would be generated in each case, if the products being plated were equal to total area. Other examples could be cited to show that no basis exists for relating the number of employees to the metal finishing processes carried out and/or to the waste that results from those processes. However, it is believed that one can relate the number of employees to the production capacity of a non-automatic facility.

Geographic Location

Geographic location is not a basis for subcategorization. No condition is known whereby the choice of metal finishing

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processes is affected by the physical location of the facility, except availability of process water. If water is not available, no modification of metal finishing procedures can compensate for this deficiency. No metal finishing facilities would be installed at a water deficient location. The waste treatment procedures described in Section VII can be utilized in any geographical area. In the event of a limitation in the availability of land space for constructing a waste treatment facility, the in-process controls and rinse water conservation techniques described in Section VII can be adopted for minimizing the land space required for the end-of-process treating facility. A compact unit can easily handle end-of-process waste if the best in-process techniques are utilized to conserve raw materials and water.

Quantity of Work Processed

Quantity of work processed is analogous to plant size. Therefore, the discussion about plant size is equally applicable to the quantity of work processed. The application of the guidelines provides for the production volume of a particular facility.

Rack Plating Versus Barrel Plating

The choice of rack or barrel methods for plating is based on the size and quantity of the parts to be processed per unit of time. Neither of these conditions imposes a significant technical change in the operations for electroplating. The selection is always based on economic considerations because hand racking of small parts is usually more costly than barrel processing in bulk. Sometimes plating bath compositions will be modified by altering the concentration of solution constituents. However, the same types of salts, acids, and additives will be used. Thus, the impact on waste characteristics is not changed. The volume of waste water (dragout) is frequently greater in barrel plating operations but the final effluent quality is not a function of influent concentration. Techniques are available to reduce the rinse water volumes in barrel plating to the levels of rack plating. These techniques are detailed in Section VII. Therefore, rack plating and barrel plating are not appropriate subcategories.

Treatment Technology

As no peculiarity exists between raw materials and waste characteristics as a basis to separate facilities into subcategories, none exists for treatability of wastes as a

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FIGURE 2   ANODIZING
l/m² - op

50% = 60
65% = 90
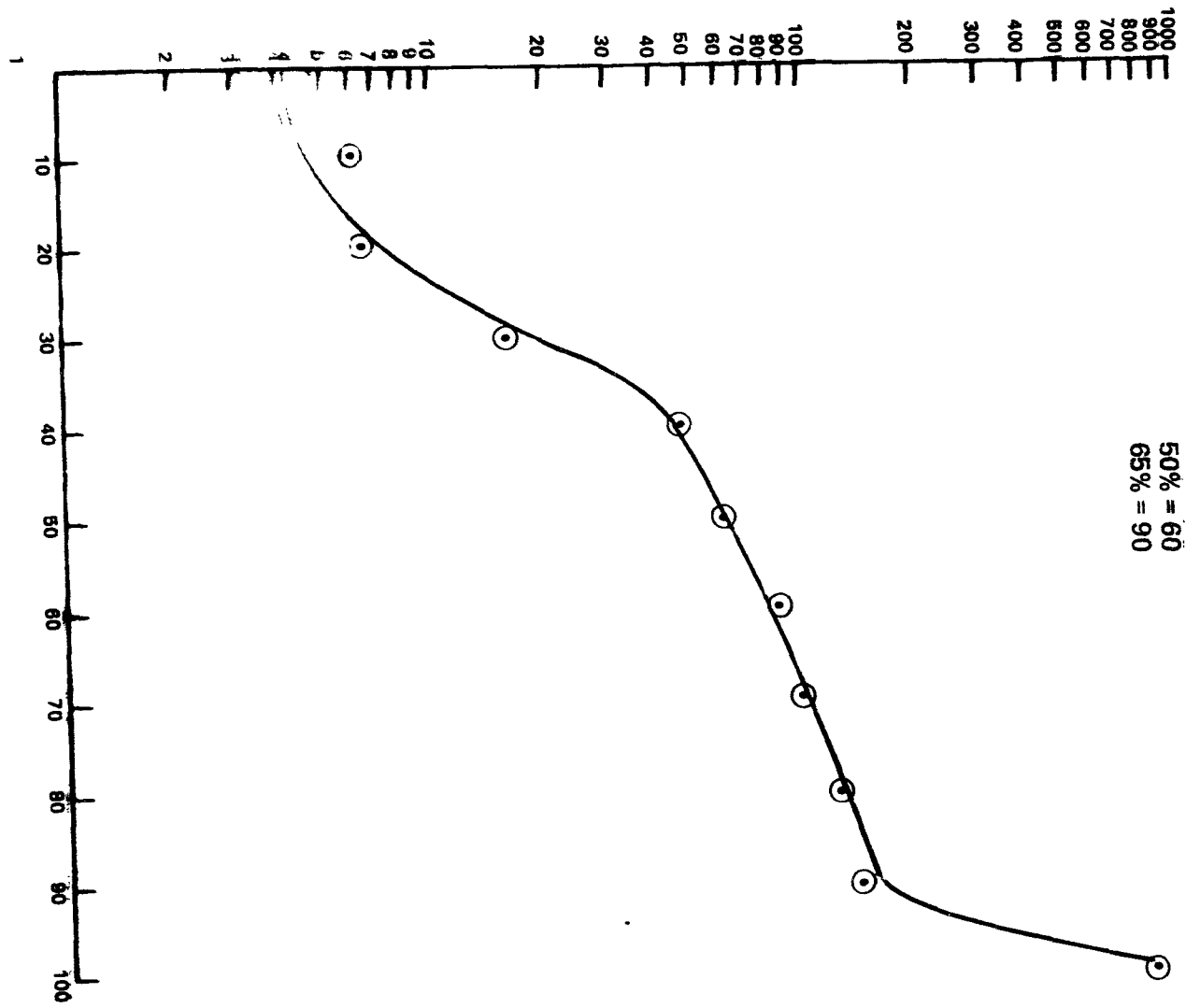
FIGURE 3

COATINGS

$l/m^2 - op$
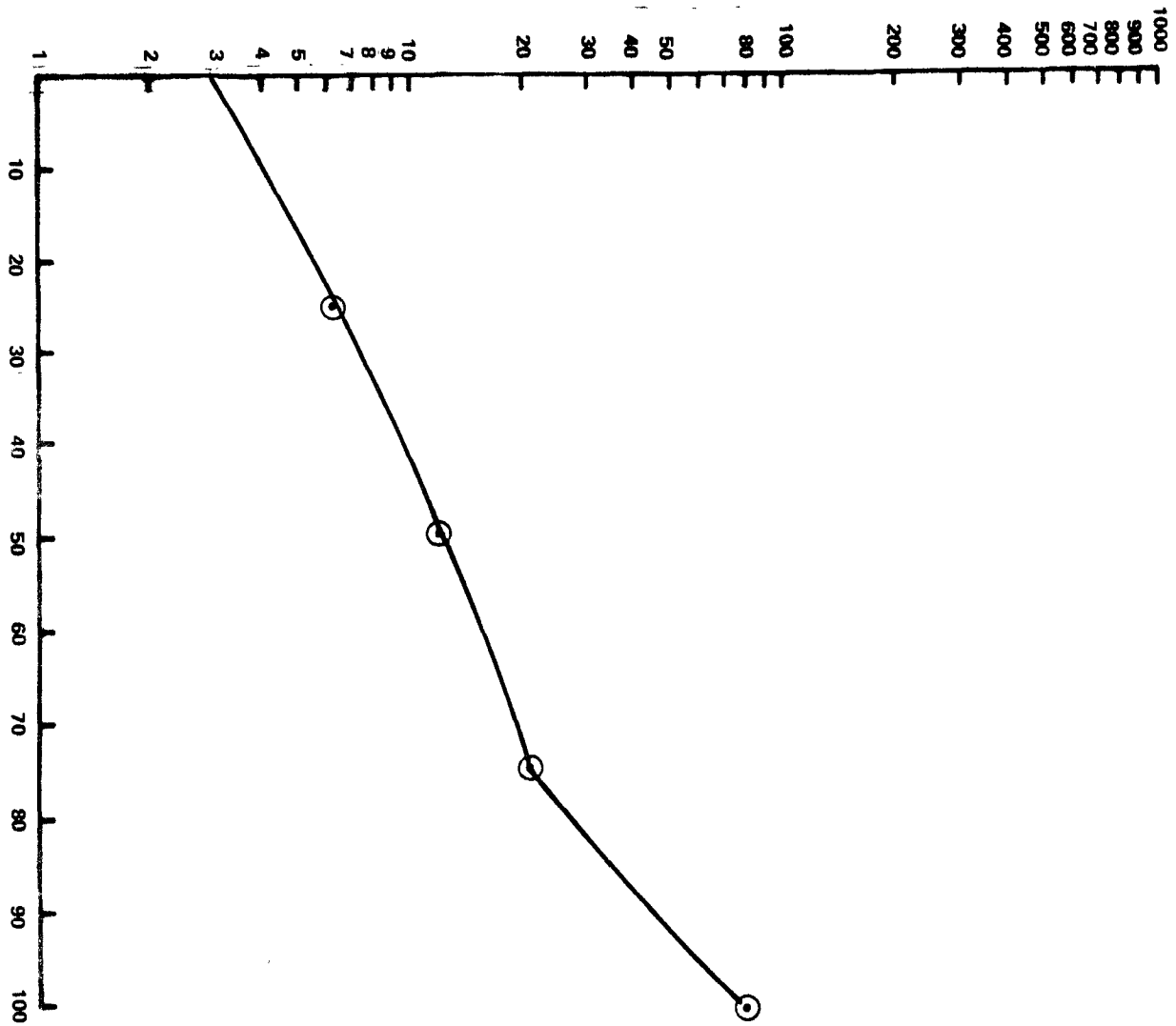
FIGURE 4   ETCHING & MILLING
l/m^2 – op

50% = 90
65% = 120

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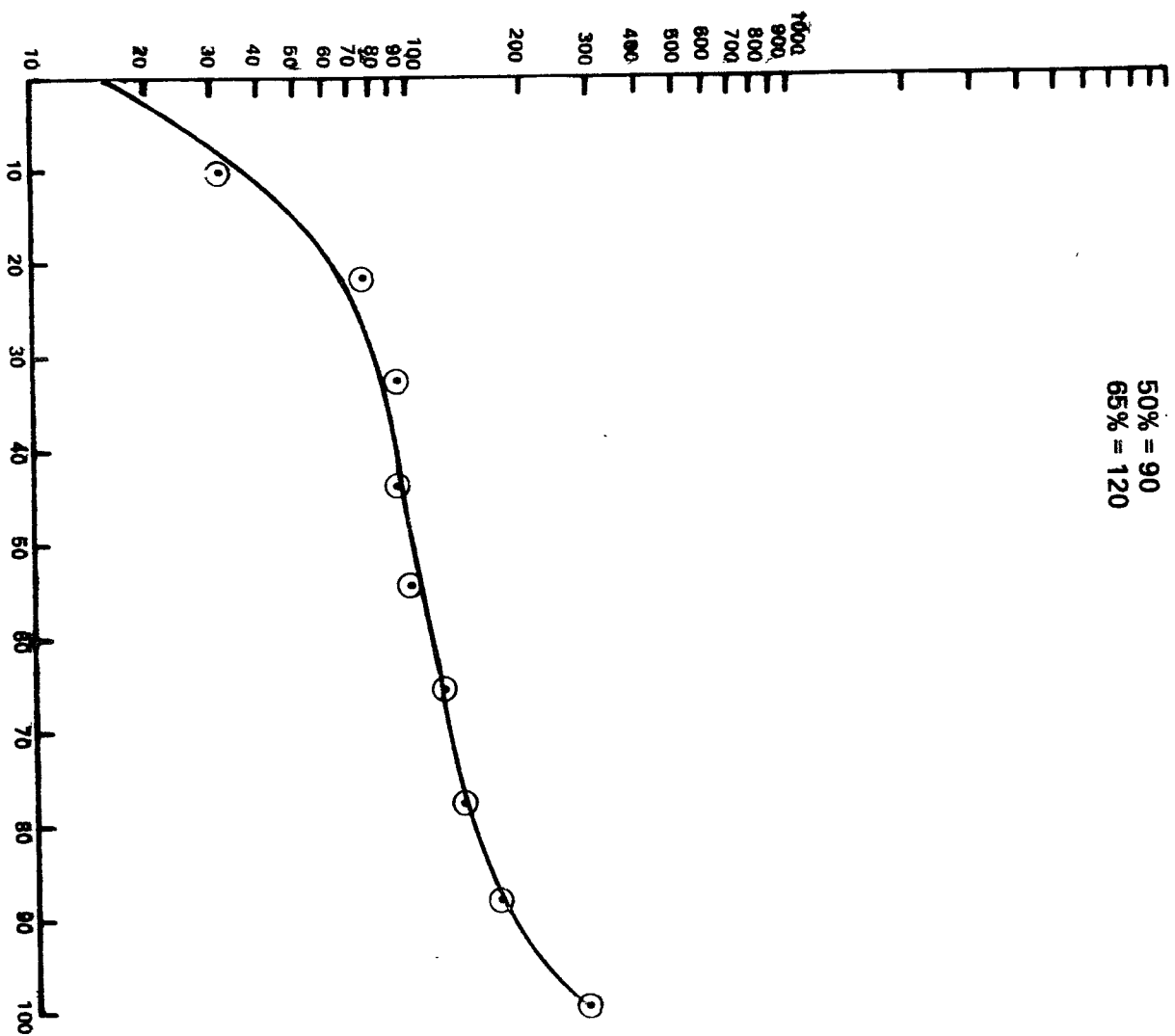
basis for subcategorization. All of the principal treatment procedures and in-process controls are technically applicable by choice for any given waste and all operations generate the same type of raw waste regardless of the facility.

Water Use

Water use formed a major basis for differentiation of the subcategories. The median water use for each of the subcategories is shown in Figures 2, 3 and 4. It is 60 l/sq m/operation for anodizing, 12 l/sq m/operation for coatings, and 90 l/sq m/operation for chemical etching and milling. Since it is not known to what extent rinsing technique and product size and shape contribute to this factor the water has been increased to 90 l/sq m/operation for anodizing and 120 l/sq m/operation for chemical milling and etching. Coatings represent a special case. The water use of 12 l/sq m/operation indicated on Figure 3 cannot be justified. Therefore, the highest figure of 80 l/sq m/operation is chosen as being more representative.

Processing Differences

Basic differences in the type of process performed was another factor in subcategorization. Anodizing involves the deposition of a protective layer on the object which itself acts as the anode. Coatings covering phosphating, chromating and immersion plating involve the deposition of a protective layer. Chemical etching and milling involve the dissolution of the basis material.

Categorization Summary

The metal finishing industry consists of three subcategories for the purpose of establishing effluent limitations guidelines and standards of performance. The selection of processes for inclusion in each subcategory is based upon a similarity in the characteristics of the wastes present and a similarity in the amount of water required for the processes and basic processing differences. Guidelines for the application of the effluent limitations and standards of performance to specific facilities take into account the size of the finishing facility and the mix of different metal finishing processes possible in a single plant.

WASTE CHARACTERIZATION

Introduction

Water flow and the nature and quantity of the wastes dissolved in the water during metal finishing processes are described in this section for each subcategory. Sources of waste are also discussed in this section.

Water is a major material in the metal finishing industry and is associated with every process. Yet, none of the water enters the products so that it does not directly add to the product value.

Characteristics of Waste for Each Subcategory

Waste water from metal finishing processes comes from cleaning, pickling, plating, etching, etc., operations and includes constituents coming from the basis material being finished as well as from the components in the processing solution. Predominant among the waste water constituents are the metal cations (sometimes complexed as anions) such as copper, nickel, chromium, zinc, lead, tin, cadmium, gold, silver, platinum metals, and anions that occur in cleaning, pickling, or processing baths such as phosphates, and chlorides, and various metal complexing agents.

Specific Water Uses

Water is used in the following ways:

(1) Rinsing to remove films of processing solution from the surface of work pieces at the site of each operation

(2) Washing away spills in the areas of the operations

(3) Washing the air that passes through ventilation ducts so as to remove spray from the air before it is exhausted

(4) Rinse water (and dumps) of solutions from auxiliary operations such as rack stripping

(5) Washing of equipment (e.g., pumps, filters, tanks, ion-exchange units)

(6) Cooling water used in heat exchangers to cool solutions in metal finishing processes.

Supplementing the above uses for water which acquires pollutants, process solutions, especially for pre- and

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posttreatment solutions, contribute to the waste water requiring treatment before discharge to navigable waters. Such dumps are required when contaminants reach concentrations that prevent efficient processing.

Rinsing

A large proportion (perhaps 90 percent) of the water usage is in the rinsing operations. That used as cooling water usually does second duty in rinsing steps. The water is used to rinse away the films of processing solutions from the surface of the work pieces. In performing this task, the water acquires the constituents of the operating solutions and is not directly "reusable". Thus, the cost of water is an operating expense to which is added the cost of treating the water to clean it up for reuse or for discard. Dilute water solutions result from the raw waste from each operation. Therefore, the location of rinse steps is important relative to the operations performed in the metal finishing process.

There is no fixed relation between water usage and amount of work processed. Some plants use more water than the minimum required to maintain good quality work.

Spills and Air Scrubbing

The water from washing away spills and that from washing down ventilation exhaust air is added to the chemically corresponding rinse water for treatment.

Dumps

Operating solutions to be dumped are slowly trickled into rinse water following the operation and prior to treatment. Alternatively, the operating solutions, which are much more concentrated than the rinse water, may be processed batchwise in a treating facility. Subsequent discussion of waste treatment of rinse water covers all the water in the facility.

Water from Auxiliary Operations

Cyanide solutions are used for stripping deposits and rack tips to form cyanide compounds that are not decomposed by treatment with chlorine, i.e., nickel cyanide. However, there are suitable alternatives to cyanide stripping solutions with which the formation of stable cyanide compounds can be avoided in many cases.

Washing Equipment

Water used for washing filters, pumps, and tanks picks up residues of concentrated solutions or salts and should be routed to the appropriate rinse water stream for chemical treatment.

Cooling Water

As noted previously, cooling water used in heat exchangers for cooling metal finishing solutions should be used for rinsing purposes in the interest of conserving water. A further advantage of this practice is that if the cooling water is contaminated by the metal finishing bath due to leaks in the heat exchanger, the contaminated water will be subjected to treatment to remove the contaminants before the water is discharged.

Sources of Waste

Alkaline Cleaners. Cleaners are made up with one or more of the following chemicals regardless of the material to be electroplated: sodium hydroxide, sodium carbonate, sodium metasilicate, sodium phosphate (di- or trisodium), sodium silicate, sodium tetraphosphate, and a wetting agent. Compositions for cleaning steel are more alkaline and active than those for cleaning brass, zinc die castings, and aluminum. Therefore, cleaners vary with the type of basis metal being cleaned and also with the type of soil being removed.

Wastes contain not only the chemicals found in the alkaline cleaners but also soaps from the saponifications of greases left on the surface by polishing and buffing operations. Some oils and greases are not saponified, but nevertheless, emulsified. The raw wastes from the basis materials and process solutions for cleaning the work show up in the rinse waters, spills, dumps of concentrated solutions, wash waters from air-exhaust ducts, and leaky heating and cooling coils and heat exchangers.

Acid Dips. Acid solutions are made up from one or more of the following: hydrochloric acid, sulfuric acid, phosphoric acid, fluoboric acid, chromic acid, and nitric acid. The solution compositions vary according to the nature of the basis metals, the type of tarnish or scale. The acid dipping baths for treating metal substrates prior to plating usually have a relatively short life. When these solutions are dumped and replaced large amounts of chemicals must be treated and/or reclaimed. Water used for rinsing following

acid dipping collects impurities, including heavy metal waste from dragout of acid solutions into the rinse water.

Acid solutions used for pickling, acid dipping, or activating accumulate appreciable amounts of heavy metals, as a result of metal dissolution from metallic work pieces and/or uncoated areas of plating racks that are recycled repeatedly through the cleaning, acid treating, and electroplating cycle. The copper (and zinc) accumulate in acid bright dip solutions used to prepare electrical copper and brass contacts for plating.

The amount of waste contributed by preplate preparation steps varies appreciably from one facility to another depending on the substrate material, the formulation of the solution adopted for cleaning or activating the material, the solution temperature, the cycle time, and other factors. The initial condition of the substrate material affects the amount of waste generated during preplate treatment. A dense, scalefree copper alloy article can be easily prepared for plating by using a mild hydrochloric acid solution that dissolves little or no copper, whereas products with a heavy scale require stronger and hotter solutions and longer treating periods for insuring the complete removal of any oxide, prior to plating.

Anodizing

Description of the Process

Anodizing is an electrolytic oxidation process by which the surface of the metal is converted to an insoluble oxide having desirable chemical and physical properties. Considerable aluminum is treated, some magnesium, and limited amounts of zinc and titanium. Anodizing provides corrosion protection, decorative surfaces, a base for painting and other coating operations, and special electrical and engineering properties.

Preparation for Anodizing

Preparative operations for anodizing can be comparatively simple or extensive. Soak cleaning may be carried out in an inhibited alkaline cleaner such as sodium carbonate containing phosphate or silicate. A phosphoric acid solution may also function as a cleaner. In most cases the cleaner is strong enough to etch the aluminum slightly or is followed by an alkaline etching solution containing sodium hydroxide. The etching assures an active surface for anodizing. Alloying elements in the aluminum, particularily

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copper, may not be dissolved by the etchant and give rise to a smut on the surface. A desmutting bath such as nitric acid may then be used to remove the smut. Finally, if a bright appearance is to be maintained, a bright dip made of nitric and phosphoric acids may be used.

Magnesium, zinc, and titanium are prepared for anodizing by cleaning in an inhibited alkaline cleaner. Titanium is further activated by immersion in a nitric acid-hydrofluoric acid solution.

Anodic Treatment

Aluminum is anodized in sulfuric acid to produce a conventional oxide coating for corrosion protection or a hard coat for extra wear resistance. Both composition and operating conditions are listed in Table 7. A chromic acid bath is used where parts have recesses so that complete rinsing of the part may not be achieved. In such a case the sulfuric acid would attack the aluminum. Particular application of the chromic acid process is to aircraft parts. The bath composition and operating conditions are shown in Table 8.

Aluminum may also be anodized in oxalic acid or boric acid. The coating from the latter bath has good dielectric properties.

The characteristics of anodic coatings on magnesium can be varied from thin coatings to give good plant adhesion to heavy coatings for abrasion and corrosion resistance by adjusting the time and operating conditions during anodizing. Both compositions and operating conditions for the two most commonly used processes are given in Table 9.

Zinc parts, i.e., for automatic clothes washers, are anodized to improve corrosion resistance. The Iridizing process uses alternating current to produce a coating made up of a fritted structure of oxides, phosphates, chromates, and fluorides. Anodizing is accomplished with a current of 430 amp/sq m (40 amp/sq ft) for 4.5 to 8 minutes at 155 to 185°F. The bath is replenished with ammonia and the Iridizing powder. Sludge builds up in the tank and is periodically removed.

Table 10 lists the principal constituents in waste water generated during the anodizing operation.

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TABLE 7   TYPICAL OPERATING CONDITIONS FOR SULFURIC-ACID ANODIZING OF ALUMINUM

	Conventional Anodizing	Hard-Coat Anodizing
Electrolyte	15 weight percent sulfuric acid	12 weight percent sulfuric acid ⎫ Alumelite 1 weight percent oxalic acid ⎭ Process or 15 weight percent sulfuric acid ⎫ Martin (Saturated with carbon dioxide) ⎭ Process
Temperature	21 C (70 F)	3.9 to 10 C (25 to 50 F)
Current density	130 A/sq M (12 ASF)	258 to 387 A/sq M (24 to 36 ASF)
Voltage	12 to 22 volts	Up to 70 volts and higher

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TABLE 8   TYPICAL OPERATING CONDITIONS
            FOR CHROMIC-ACID ANODIZING
            OF ALUMINUM ALLOYS

Electrolyte concentration	5-10% CrO_3
Temperature	95F
Voltage	40 v, programmed
Time	5-7 min for 0.40 v 30 min at 40 v
Current density	0.1 - 0.3 amp/dm^2 1.8 amp/dm^2 at start

Film thickness	0.06 mil in 1/2 hour for
	Al 2024 with:
	    10% CrO_3
	    40 v, pH 0.4, 95F.

TABLE 9 OPERATING CONDITION FOR ANODIZING MAGNESIUM

Process	Typical Bath Composition			Type Coating	Voltage, volts	Time, minutes	Coating Appearance	Remarks
Dow No. 17 (Dow Chemical Company	Solution B	For AC Use	For DC Use					
	Ammonium acid fluoride (NH_4HF_2)	32 oz/gal	48 oz/gal	Clear-very thin	40	1-2	Clear	Excellent corrosion and abrasion resistance; good paint base; either AC or DC may be used; available through licensing arrangement
	Sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$)	13.3 oz/gal	13.3 oz/gal	Low voltage-thin (0.2 to 0.3 mil)	60 to 75 (end voltage)	2.5-5	Light gray to pale green	
	Phosphoric acid (35% H_3PO_4)	11.5 fl oz/gal	11.5 fl oz/gal	Regular-full (0.9 to 1.2 mils)	75-95	15-25	Medium green	
	or							
	Solution B							
	Ammonium acid fluoride (NH_4HF_2)	27 oz/gal	36 oz/gal					
	Ammonium acid phosphate ($NH_4H_2PO_4$)	13.3 oz/gal	13.3 oz/gal					
	Sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$)	10.6 oz/gal	10.6 oz/gal					
HAE (Frankford Arsenal)	Potassium hydroxide (KOH)	22 oz/gal		Low voltage (Light coating)	9v AC (40 ASF)	15-20 (140-150 F)	Tan color, smooth	High corrosion and excellent abrasion resistance; use only AC; the high voltage coating is the hardest of anodized coatings on Mg; available with permission
	Aluminum hydroxide Al (OH)$_3$	4.5 oz/gal						
	Potassium fluoride (KF)	4.5 oz/gal						
	Trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	4.5 oz/gal		High voltage (Hard coating)	85 (end voltage) (18-20 ASF)	60-75 (70-80 F)	Brown color rougher than low voltage coating	
	Potassium manganate (K_2MnO_4) or Potassium permanganate ($KMnO_4$)	2.5 oz/gal						

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TABLE 10 PRINCIPAL WASTEWATER CONSTITUENTS IN WASTES GENERATED
DURING THE ANODIZING OF METALS

Constituent	Basic Metals and Alloys						
	Aluminum			Magnesium			
	Sulfuric Acid Processes		Chromic Acid Process	Dow No. 17 Process	HAE Process	Zinc	Titanium
	Conventional	Hard Coat					
Chromate, CrO_4^{-2}			X	X		X	
Sulfate, SO_4^{-2}	X	X					
Oxalate		X					
Borate		X					
Dichromate, Cr_2O_7				X			
Fluoride, F^{-1}				X	X	X	
Phosphate, PO_4^{-3}				X	X	X	X
Ammonium, NH_4^{+1}				X		X	
Manganate, MnO_4^{-2}					X		
Potassium					X		
Aluminum, Al^{+3}	X	X	X				X
Magnesium, Mg^{+2}	X	X	X	X	X		
Zinc, Zn^{+2}						X	
Titanium, Ti^{+3}							X
Chromium, Cr^{+3}			X				

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The corrosion resistance of anodic coatings on aluminum and its alloys is improved by sealing in hot water at a temperature of approximately 99°C (210°F), using deionized water. Sodium dichromate or sodium silicate are sometimes added to the water. Unsealed coatings on aluminum are colored by immersing in a solution containing 0.025 to 1.0 percent of an organic dye at 66°C (150°F). After rinsing, sealing of the dye is accomplished by immersion in a hot solution of nickel or cobalt acetate. Inorganic dyes may also be used. Colloidal iron oxide in the anodic film is produced by immersion in ferric ammonium oxalate followed by rinsing.

Anodic coatings on magnesium may be sealed with a sodium silicate solution heated to 100°C (2.2°F). Sealing may also be accomplished with a solution containing 100 g/l (13.3 oz/gal) of ammonium acid fluoride and 20 g/l (2.7 oz/gal) of sodium dichromate.

Table 11 lists the principal constituents in waste water generated during posttreatment of anodized coatings.

Immersion Plating

Description of Process. The term "Immersion Plating" is used to describe a chemical plating process in which a thin metal deposit is obtained by chemical displacement of the basis metal. The thickness of such deposits is usually of the order of 0.25 um (10 microinches), although a few processes produce deposits as thick as 2.5 to 5.0 um (100 to 200 microinches). In immersion plating a metal will displace from solution any other metal that is below it in the electromotive series of elements. The lower (more noble) metal will be deposited from solution while the more active metal higher in the series will be dissolved. A common example of immersion plating is the deposition of copper on steel from an acid copper solution. The thinness of immersion deposits limits their usefulness to applications other than corrosion protection, such as decoration or as preparation for further processing such as painting or rubber bonding.

The most widely used immersion plating processes are (1) tin on brass, copper, steel, or aluminum, (2) copper on steel, (3) gold on copper or brass, and (4) nickel on steel. These four processes will be discussed below under "treatment".

Preparation for Plating. Preparation for immersion plating on brass, copper, steel, and aluminum requires alkaline cleaning, which can involve electrolysis but usually does

TABLE 11   PRINCIPAL WASTEWATER CONSTITUENTS IN WASTES GENERATED DURING POSTTREATMENT OF ANODIC COATINGS ON METALS

Constituent	Basic Metals and Alloys						
	Aluminum			Magnesium			
	Sulfuric Acid Processes		Chromic	Dow No. 17	HAE		
	Conventional	Hard Coat	Acid Process	Process	Process	Zinc	Titanium
Posttreatment							
Dichromate, $Cr_2O_7^{-2}$	X			X	X		
Silicate, SiO_3^{-2}	X			X	X		
Fluoride, F^{-1}				X	X		
Sodium	X		X	X			
Organic dyes	X		X				
Inorganic pigments	X		X				
Nickel acetate	X		X				
Cobalt acetate	X		X				
Borate			X				
Iron	X						
Ammonium	X			X	X		
Oxalate	X						

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not. Alkaline cleaners contain silicates, carbonates, phosphates, singly or in combinations and are formulated to clean the work without attacking the metal itself. The cleaner becomes contaminated with organic materials from the oil and grease on the work.

Following alkaline cleaning the basis metal is pickled in sulfuric or hydrochloric acid, which dissolves a small amount of the base metal.

The principal waste water constituents generated during preparation of the work prior to immersion plating are listed in Table 12.

Immersion Plating Treatment. Immersion tin plating is used to "whiten" pins, hooks, eyelets, screws, buttons, and other hardware items made of copper, brass, or steel. In addition, aluminum alloy pistons for internal combustion engines are coated with an immersion deposit of tin. All immersion tin plating baths for copper, brass, and steel are based on stannous chloride solutions. Immersion tin solutions contain, in addition to stannous chloride, cream of tartar (potassium bitartrate), ammonium aluminum sulfate, or sodium cyanide and sodium hydroxide.

Copper is immersion deposited on steel wire prior to drawing in order to reduce wear on the dies. Copper is deposited from an acid copper sulfate solution. Copper-tin alloy is obtained on steel wire by adding tin salts to the copper sulfate solutions.

Gold is immersion deposited on copper and brass to gild inexpensive items of jewelry. Typical immersion gold plating solutions contain gold chloride and potassium cyanide or pyrophosphate.

Nickel is immersion deposited on steel prior to ceramic enameling to improve the adhesion of the enamel. Immersion nickel solutions contain nickel sulfate, or nickel chloride and boric acid.

Table 13 lists the principal constituents in waste water generated during immersion plating of tin, copper, gold, and nickel on various basis metals. Gold is not listed.

Chemical Conversion Coatings-Chromating

Description of the Process. Chromate conversion coatings are protective films formed on metal surfaces. A portion of the base metal is converted to one of the components of the

TABLE 12   PRINCIPAL WASTEWATER CONSTITUENTS IN WASTES GENERATED DURING PREPARATION FOR IMMERSION PLATING ON VARIOUS BASIS METALS

Pollutant	Basis Metal			
	Brass	Copper	Steel	Aluminum
Alkaline Cleaning				
Iron, ferrous, Fe^{+2}			X	
Aluminum, Al^{+3}			X	
Silicate, SiO_3^{-2}	X	X	X	X
Carbonate, CO_3^{-2}	X	X	X	X
Phosphate, PO_4^{-3}	X	X	X	X
Organics	X	X	X	X'
Acid Dipping				
Iron, Ferrous, Fe^{+2}			X	
Aluminum, Al^{+3}				X
Copper, Cupric, Cu^{+2}	X	X		
Zinc, Zn^{+2}	X			
Sulfate, SO_4^{-2}	X	X	X	X
Chloride, Cl^-	X	X	X	X

TABLE 13   PRINCIPAL WASTEWATER CONSTITUENTS IN WASTES
GENERATED DURING IMMERSION PLATING OF TIN,
COPPER, GOLD, AND NICKEL

Pollutant	Basis Metal			
	Brass	Copper	Steel	Aluminum
Immersion Tin Plating				
Tin	X	X	X	X
Chloride	X	X	X	X
Tartrate	X	X	X	
Cyanide	X	X	X	
Ammonium	X	X	X	
Aluminum	X	X	X	
Sulfate	X	X	X	
Sodium	X	X	X	
Immersion Copper Plating				
Copper			X	
Sulfate			X	
Immersion Gold Plating				
Chloride	X	X		
Bicarbonate	X	X		
Pyrophosphate	X	X		
Cyanide	X	X		
Potassium	X	X		
Immersion Nickel Plating				
Nickel			X	
Sulfate			X	
Borate			X	
Chloride			X	

film by reaction with aqueous solutions containing hexavalent chromium and other active organic or inorganic compounds. Chromate coatings are most frequently applied to the following metals: zinc, cadmium, aluminum, magnesium, copper, brass, bronze, and silver. Generally the chromating solution is acidic and contains chromic acid or its sodium or potassium salts, plus other organic or inorganic compounds as activators, accelerators, or catalysts. Although chromate conversion coatings can be applied by chemical or electrochemical action, the bulk of the coatings are usually applied by a chemical immersion, spray or brush treatment. Most chromate treatments used in industry employ proprietary solutions. With these processes, a wide variety of decorative and protective films ranging from colorless to iridescent yellow, brass, brown and olive drab can be produced. The coating appearance will depend on the basis metal and the processing procedures employed. Additional coloring of the coatings can be achieved by dipping the parts in organic dye baths to impart red, green, blue and other colors. Besides their use as protective or decorative films, chromate conversion coatings are extensively employed to provide an excellent base for paint and other organic finishes, which do not adhere well to untreated metal surfaces.

Chromate coatings are widely used on aluminum in the aircraft, electronics, and home appliance industries. The process, being lower in cost than anodizing, is generally employed for applications where the abrasion resistance or highly decorative colors of anodized aluminum are not required. The coatings have good adhesion properties for subsequent organic coatings, offer good resistance to corrosion, especially in chloride environments, and range from clear to yellow, depending mostly on immersion time, pH, solution composition, and to some extent on the particular aluminum alloy treated.

Bright chromate treatments have advantages over conventional acid bright dips for copper alloys, in that they produce a passive film and also a surface with a high luster or polish. The chromate film provides good protection against corrosion and sulfide tarnishing on unplated parts. The film also provides a good paint base.

Chromate coatings are applied to silver electroplates to prevent sulfide tarnishing using proprietary formulations. Table 14 lists the principal waste water constituents generated during pretreatment, coating and postreatments steps in chromating zinc, cadmium, aluminum and other metals.

TABLE 14 PRINCIPAL WASTEWATER CONSTITUENTS IN WASTES GENERATED
DURING CHROMATING OPERATIONS ON VARIOUS METALS

Basis/Materials

Constituent	Al	Magnesium		Zinc or Cadmium Electroplates		Zinc Die Castings	Copper, Brass Bronze or Silver
		Chrome-Pickle Process	Dichromate Process	Bright Coatings	Yellow, Bronze or Olive Drab Coatings	Yellow, Bronze or Olive Drab Coatings	
Preparation– Cleaning and Activating							
Aluminum, Al^{+3}	X						
Magnesium, Mg^{+2}		X	X			X	
Zinc, Zn^{+2}				X	X		
Cadmium, Cd^{+2}				X	X		
Copper, Cu^+	X						X
Manganese	X						
Tin, Sn^{+2}							X
Silver, Ag^{+1}							X
Cyanide, CN^{-1}				X	X		
Carbonate, CO_3^{-2}	X	X	X			X	X
Phosphate, PO_4^{-3}	X	X	X			X	X
Silicate SiO_3^{-2}	X	X	X			X	X
Kerylbenzene sulfinate	X						
Glivconates	X						
Citrates	X						
Tartrates	X						
Nitrate, NO_3^{-1}	X			X	X		
Fluoride, F^{-1}	X		X				
Sulfate, SO_4^{-2}	X					X	
Chromate, CrO_4^{-2}	X						
Aluminum, NH_4^{+1}			X				
Sodium	X	X	X			X	
Coating							
Sodium	X			X	X	X	X
Chromate, CrO_4^{-2}	X			X	X	X	X
Iron Cyanide	X						
Fluoride, F^{-1}	X			X	X	X	X
Dichromate, $Cr_2O_7^{-2}$		X	X				
Nitrate, NO_3^{-1}	X	X					
Aluminum, Al^{+3}	X						
Magnesium, Mg^{+2}		X	X				
Zinc, Zn^{+2}			X				
Cadmium, Cd^{+2}				X	X	X	X
Copper, Cu^{+2}							X
Tin, Sn^{+2}							X
Silver, Ag^{+1}							X
Calcium, Ca^{+2}			X				X
Organics	X	X	X	X	X	X	X
Potassium	X			X	X	X	X
Posttreatment							
Phosphate, PO_4^{+3}				X	X	X	
Carbonate CO_3^{-2}				X	X	X	
Organic Dyes	X				X		
Sodium				X	X	X	

TABLE 15   ALKALINE CLEANERS FOR ALUMINUM

Type	Composition	Temp, C	Time
Noninhibited-Etching	Sodium carbonate (Na_2CO_3): 22.5 g/l (3.0 oz/gal) Sodium orthophosphate ($Na_3PO_4 \cdot 12H_2O$: 22.0 g/l (2.9 oz/gal)	71-82	As Required
Inhibited-Nonetching	Sodium carbonate (Na_2CO_3): 22.5 g/l (3.0 oz/gal) Sodium orthophosphate ($Na_3PO_4 \cdot 12H_2O$: 22.5 g/l (3.0 oz/gal) Sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$: 15.0 g/l (2.0 oz/gal) Kerylbenzene sulfonate (40%): 2.5 g/l (0.3 oz/gal)	71-82	As Required

Preparation for Chromating. Chromate conversion coatings are frequently applied to zinc or cadmium-plated parts immediately following electrodeposition. No preparation is necessary. In some cases, a baking operation to eliminate hydrogen from the deposit is carried out following electrodeposition. Alkaline cleaning and an acid dip may then be necessary before chromating.

Alkaline cleaning of zinc die castings is generally carried out in a proprietary solution, or a solution such as given below, under the conditions shown.

Sodium carbonate	7.5 g/l (1 oz/gal)
Sodium hydroxide	7.5 g/l (1 oz/gal)
Temperature	93°C (200 F)
Time	30-60 seconds.

This cleaned work is rinsed thoroughly and then dipped in 1 to 2 percent sulfuric or phosphoric acid for 15-30 seconds at room temperature to assure neutralization of any remaining alkaline films. Following another thorough rinse, it is then chromated.

Conventional cleaning procedures involving solvent cleaners or vapor degreasing are used routinely on aluminum for removal of grease and other organic contaminants. The removal of soil from aluminum is most frequently achieved by using alkaline cleaners, that function by dissolving or dispersing soils, augmented in some instances by etching of the metal. Two representative cleaner formulations for aluminum are shown in Table 15. The silicate in the second formulation works as both a detergent and corrosion inhibitor; the kerylbenzene sulfonate is a wetting agent. An etching-type cleaning treatment may be used prior to other treatments when a mat or nonspecular surface is desired. Inhibited nonetching cleaners are employed when attack or roughening of the aluminum part surface are undesirable. Prolonged operations with aggressive alkaline cleaners such as those containing caustic soda frequently cause the precipitation of a flocculent hydrated aluminum oxide which can interfere with effective rinsing of the work. Several additional agents, which contain gluconates, citrates, or tartrates, have been developed to avoid or minimize such effects. These agents work by sequestering the hydrated aluminum oxide to yield a more granular precipitate which is less likely to cake and responds better to rinsing.

Aluminum alloys containing copper, manganese, or silicon are especially susceptible to smut on their surfaces during

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alkaline cleaning operations. The smut generally consists of loosely adherent, finely divided particles of the aluminum alloy metals or their oxides. Table 16 lists some typical deoxidizing and desmutting treatments for aluminum. Nitric acid (Formulation A) is a general-purpose reagent for removal of smut from aluminum and other metals. Formulation B, containing about 75% nitric acid and 25% hydrofluoric acid is especially effective in the removal of smut formed on high silicon (5% or more) alloys. The chromic acid-phosphoric acid (Formulation D) mixtures are generally used for the selective removal of oxide without significant attack of the metal surface. Proprietary desmutting and deoxidizing solutions are extensively used.

Alkaline cleaning is generally the most satisfactory method for degreasing and cleaning magnesium prior to chromating. Representative alkaline cleaner compositions and operating conditions for processing magnesium are presented in Table 17.

Pretreatment of copper, copper alloys, and silver is similar to the procedures described for zinc, cadmium, and aluminum.

Chromating Treatments. Zinc and cadmium may be chromated to provide:

(1) bright chromates on zinc and cadmium electro-
     deposits,

(2) colored coatings on zinc and cadmium electro-
     deposits, and

(3) colored coatings on zinc die castings.

The bright chromate treatments impart a high luster to zinc or cadmium plates and also provide tarnish and corrosion resistance. The chromate treatment of electrodeposits generally follows immediately after the last rinse in the plating cycle. The chromate bath for coating zinc and cadmium parts is an acid solution containing hexavalent chromium, such as chromic acid, plus other inorganic and organic compounds to promote or catalyze the reaction.

The chromate coating solution for aluminum usually contains hexavalent chromium, a fluoride, and an accelerator, such as ferrocyanide or ferricyanide. The pH range is usually 1.0 to 2.5. Nitric acid frequently is added as an acidifying agent. The fluoride, in the acidified solution, is the active reagent; it dissolves the existing oxide film and

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TABLE 16 REPRESENTATIVE DEOXIDIZING AND DESMUTTING
TREATMENTS FOR ALUMINUM

Formulation	Temp, C	Time	Purpose
(A) Conc. HNO_3 (10 to 50% by vol)	Ambient	30 to 60 sec	Smut removal
(B) 75% vol conc HNO_3 25% vol HF (48 wt%)	Ambient	5 to 10 sec	Smut removal, especially for high silicon Al alloys
(C) 20 g/l (2.66 oz/gal) CrO_3 35 ml/l 85 wt% H_3PO_3	88-93	2 to 10 min	Oxide removal
(D) 100 ml/l 96 wt% H_2SO_4 35 g/l (4.66 oz/gal) CrO_3	64-82	1 to 5 min	Oxide removal

TABLE 17 REPRESENTATIVE ALKALINE CLEANERS FOR MAGNESIUM

Type	Bath	Procedure
Heavy Duty Alkaline[a]	Sodium hydroxide (NaOH): 15-60 g/l (2-8 oz/gal) Trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$) 11 g/l (1-1/2 oz/gal)	Immerse parts 3 to 10 minutes in bath at 88-100C; clean until no water break occurs in rinse; rinse thoroughly
Caustic Soak[a]	Sodium hydroxide (NaOH): 98 g/l (13 oz/gal)	Immerse parts in bath at 88-100C; soak for 10-20 minutes; rinse thoroughly

(a) Add 0.1 oz soap or wetting agent per gallon if heavy mineral oil films are to be removed.

reacts with the aluminum. During the coating process, some of the hexavalent chromium is reduced to the trivalent state, and a gel-like film consisting primarily of aluminum and chromium chromates is formed. As freshly formed, the gel-like coating is dissolved readily in nitric acid. If desired, the yellow chromate can be leached with hot water. With aging, the film becomes insoluble. For many application, rinsing and drying complete the overall chromating operation.

Much of the development work on chromate coatings on magnesium has been carried out by the Dow Chemical Company. Chemical Treatment No. 1, also known as "chrome pickle", is the most commonly used chemical treatment developed for magnesium. It can be used on all magnesium alloys. The coatings have good qualities as a paint base and protect magnesium parts during shipment and storage. A typical chrome-pickel procedure is shown in Table 18. The coating appearance is usually mat gray to yellow red, and about 0.00006 inch of metal is removed from the magnesium.

The dichromate treatment (Dow No. 7) for processing magnesium alloys (except the thorium containing alloy) produces a brassy to dark brown film, which provides a good combination of protective and paint-base qualities. The dichromate procedure is described in Table 19.

Generally, a cold rinse followed by a hot rinse to facilitate drying complete the overall chromating process on magnesium alloys.

Chromating treatments for copper, copper alloys, and silver are similar to those described for zinc and cadmium.

Posttreatment. Posttreatment of chromated parts, when used, can involve bleaching or dying operations to produce or impart special characteristics to the film. Clear bright finishes for zinc and cadmium can be obtained by bleaching or leaching the yellow coloring from the chromate film. Various mildly acidic or alkaline aqueous solutions are employed, such as

    (1)   Sodium hydroxide 23 g/l (3 oz/gal),
           room temperature 5 to 10 seconds,

    (2)   Sodium carbonate 15 to 23 g/l (2 to 3 oz/gal)
           49 to 54°C (120 to 130 F),

    (3)   Phosphoric acid, 1.0 ml/l (.13 fl oz/gal),
           room temperature, 5 to 30 seconds.

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TABLE 13   CHROMATE COATING OF MAGNESIUM BY
THE CHROME PICKLE PROCESS

Step	Bath	Procedure or Comments
Cleaning	Alkaline	Immersion
Rinse	Cold Water	Rinse thoroughly in cold running water
Chrome Pickle	Sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$): 180 g/l (24 oz/gal) Concentrated nitric acid (to Wt% HNO_3): 187 ml/l (24 fl oz/gal)	Immerse parts 1/2 to 2 minutes in room temperature solution. After dip, hold parts above tank for about 5 seconds.
Rinse	Cold Water	Rinse thoroughly in cold running water
Rinse	Hot Water	Hot water rinse used to facilitate drying

TABLE 19   DICHROMATE PROCESS CYCLE FOR
           MAGNESIUM ALLOYS[a]

Step	Bath	Procedure or Comments
Cleaning	Alkaline	Immersion
Rinsing	Cold Water	Rinse thoroughly in cold running water
Acid-fluoride pickling	50 g/l (6 2/3 oz/gal) sodium acid fluoride (NaHF$_2$), potassium acid fluoride (KHF$_2$), or ammonium acid fluoride (NH$_4$HF$_2$)	Immerse parts 5 minutes at room temperature.
Rinsing	Cold Water	Rinse thoroughly in cold running water
Dichromate treating	120 to 180 g/l (16-24 oz/gal) sodium dichromate (Na$_2$Cr$_2$O$_7$ · 2H$_2$O)	Boil parts for 30 minutes - minimum temperature 93C, 200F
Rinsing	Cold Water	Rinse thoroughly in cold running water
Rinsing	Hot Water	Hot water rinse used to facilitate drying

(a)   The dichromate process is frequently referred to as
      Dow Chemical Treatment No. 7.

Dyed coatings can also be applied.

Chemical Conversion Coatings - Phosphating

Description of the Process

Phosphating is the treatment of iron, steel, zinc plated steel, and other metals by immersion in a dilute solution of phosphoric acid plus other reagents to produce an integral conversion coating on the surface. Phosphate coatings are used to: (1) provide a good base for paints and other organic coatings, (2) condition the surfaces for cold forming operations by providing a base for drawing compounds and lubricants, and (3) impart corrosion resistance to the metal surface by the coating itself or by providing a suitable base for rust-preventative oils or waxes.

The amorphous aluminum phosphate films are used extensively as a base for organic coatings. Crystalline aluminum phosphate coatings are used chiefly for paint bonding to aluminum and also to provide lubrication for cold forming.

Commercial phosphating solutions are frequently proprietary and usually consist of metal phosphates dissolved in phosphoric acid solutions containing accelerators and other special reagents to improve bath performance. Commonly used accelerators include nitrites, nitrates, chlorates, and peroxides. Phosphating occurs as follows:

$$3Me(H_2PO_4)_2 + Fe \quad Me_3(PO_4)_2 + FeHPO_4 + 3H_3PO_4 + H_2$$
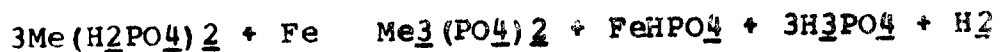
where:

$$Me = Zn, Mn, or Fe.$$

The metal is provided by the basis material or from the phosphating solution.

Pretreatment Procedures

Cleaning of iron or steel parts is generally accomplished by alkaline cleaning or solvent degreasing. Pickling in phosphoric acid or other mineral acid solutions is used for removal of rust or other corrosion products. Rinsing in hot water, or in special activating solutions, generally completes the pretreatment. In some instances, cleaning is carried out simultaneously in the same solution.

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The pretreatment procedures for phosphating aluminum alloys include alkaline cleaning, and sometimes acid or caustic etching, desmutting or deoxidizing dips, along with the attendant rinses. These procedures were described in the earlier sections of the report dealing with anodizing and chromating of aluminum.

Table 20 lists the principal waste water constituents generated during preparation, coating, and posttreatment operations in phosphating iron, steel, and aluminum.

Phosphating Treatments. Zinc and iron phosphate coatings are applied by spray and immersion techniques. Parts are immersed in a 2-1/2% by volume zinc phosphate solution at (90°F) for 30 seconds or sprayed with a 4% by volume zinc phosphate solution at (140 to 180 F) for 3 to 5 minutes. Zinc phosphate may be applied to parts in an automatic barrel line by immersion in a proprietary solution containing zinc phosphate, phosphoric acid, and nitrates. Iron phosphate is applied by immersion in a 5% by volume solution at (125 F to 160 F) and pH 3.5 to 4.5 for 3 to 5 minutes or spraying with a (1/2 to 2 oz/gal) solution at (90 to 160 F) and pH 3.5 to 5.0 for 1 to 2 minutes. Manganese phosphate is applied by immersion in a solution at (200 F) for 10 to 20 minutes.

A typical solution for producing amorphous phosphate coatings on aluminum contains 70 g/l phosphoric acid and a ratio of fluoride ion to chromic acid of 0.25. The fluoride removes the oxide film on the surface and attacks the aluminum base metal to provide the ions needed to form aluminum phosphate. The treatment times for temperatures of 100 to 130°F vary from a few seconds to several minutes. The coating weights can be varied from 0.11 to 4.3 g/sq m (10 to 400 mg/sq ft).

Crystalline phosphate coatings on aluminum are produced using solutions containing zinc or manganese acid phosphates, an oxidizing agent such as nitrate, and a complex fluoride to serve as the activating agent. A typical phosphating solution contains: 0.7% zinc ion, 1.0% phosphate ion $(PO4)3-$, 2.0% nitrate ion $(NO3)1-$, and fluoborate ion $(BF4)1-$. A satisfactory film can be produced by spraying solution for 1 to 2 minutes at 54 to 57°C (130 to 135 F), or by immersing for 5 minutes in a solution at 54 to 57°C (130 to 135 F).

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TABLE 20   PRINCIPAL WASTEWATER CONSTITUENTS IN WASTES
GENERATED DURING PHOSPHATING OPERATIONS ON
VARIOUS METALS AND ALLOYS

| | Basis Metals and Alloys | |
Constituent	Iron, Steel, and Zinc-Plated Steel	Aluminum
Preparation-Cleaning		
and Activating		
Sodium, Na^+	X	X
Aluminum Al^{+3}		X
Zinc, Zn^{+2+2}	X	
Iron, Fe^{+2}	X	
Carbonate, CO_3^{-2}	X	X
Phosphate, PO_4^{-3}	X	X
Silicate, SiO_2^{-2}	X	X
Gluconate	X	X
Sulfate	X	X
Chloride	X	X
Nitrate	X	X
Chromate	X	X
Titanium, Ti^{+3}	X	
Antimony, Sb^{+3}	X	
Phosphating		
Sodium, Na^+	X	X
Aluminum, Al^{+3}		X
Zinc, Zn^{+2}	X	X
Iron, Fe^{+2}	X	
Manganese, Mn^{+2}	X	X
Phosphate, PO_4^{-3}	X	X
Chromate, CrO_4^{-2}		X
Fluoride, F^{-1}		X
Fluoborate, BF_4^{-1}		X
Nitrite, NO_2^{-1}	X	
Nitrate, NO_3^{-1}	X	X
Chlorate, ClO_3^{-1}	X	
Posttreatment		
Chromate, CrO_4^{-2}	X	
Phosphate, PO_4^{-2}	X	
Water soluble oils and waxes	X	X

The final rinse after phosphating of iron, steel, and zinc is usually carried out in a dilute chromic acid-phosphoric acid solution (0.1% by volume). This rinse removes unreacted chemicals and improves the corrosion resistance of the phosphated surface. The rinse step is frequently followed by a dip in a suitable oil, wax, or other lubricant before drying in hot air.

Chemical Milling and Etching

Introduction. Chemical milling is the process of shaping, machining, fabricating, or blanking metal parts to specific design configurations and tolerances by controlled dissolution with chemical reagents or etchants. The process is somewhat similar to the etching procedures used for decades by photoengravers, except that the rates and depths of metal removal are usually much greater. Chemical etching is the process of removing relatively small amounts of metal from the surface (e.g., 1-5 mils) to improve the surface condition of the basis metal or to produce a pattern such as for printed circuit boards. Chemical brightening and chemical polishing are specialized examples of processes for improving surfaces by chemical dissolution.

Much of the early chemical milling work was done on aluminum and magnesium parts for the aircraft industry. Chemical milling is especially suited for removing metal from the surface of formed or complex-shaped parts (e.g., forgings, castings, extrusions), from thin sections, and from large areas to shallow depths. The weight saving achieved is especially important in aircraft and space vehicle design. In chemical milling or etching processes, metal can be removed from an entire part or restricted to selective areas by masking. The amount of metal removed or depth of etch is determined by the time of immersion in the etching solutions.

The overall chemical milling or machining process consists of four main operations

        (1)   Cleaning or surface preparation
        (2)   Masking
        (3)   Etching
        (4)   Mask removal and rinsing.

Preparative Operations. Grease and dirt from metal and alloy surfaces are removed by conventional methods such as vapor degreasing and alkaline cleaning. Scale, passive films, or oxidation products, or other foreign materials that are firmly attached are removed by acid pickling or

mechanical cleaning (e.g., vapor blasting). Where scale is heavy, a caustic or other type descaling bath may be used to loosen, modify or remove the scale followed by acid etching. Failure to properly clean the metal surface will cause masking problems and uneven attack by the etchant.

Areas where no metal removal is desired are masked off. Masks are applied by dip, spray, brush, roll or flow-coating and silk-screen techniques. The patterns on masked workpieces are usually applied by means of templates, followed by scribing and then manual peeling of the mask from areas to be etched. Mask patterns can also be applied to metallic workpieces by use of photosensitive resists. This latter technique is generally employed on jobs where fine detail and shallow cuts are desired as in the production of printed circuits, name plates, dials, fine mesh screens, etc. The photographic techniques are used almost exclusively for the blanking of small intricately shaped parts of relatively thin cross section (e.g., thicknesses usually less than 1/16 inch). Parts can be blanked by removal of metal from one or both sides of the sheet workpiece. Upon completion of the overall masking operation, the parts may be given an acid dip to activate the surface for the etching step. Table 21 shows the waste water constituents generated during preparative operations.

Chemical Milling or Etching Operations. A good chemical etchant removes metal at a predetermined and uniform rate to produce a smooth surface, without adversely affecting dimensional tolerances and the mechanical properties of the part. Chemical stability and the ability to operate well over a wide concentration and temperature range are other desirable features of an etchant system.

Table 22 lists representative aqueous etching solutions for chemical milling or etching of various metals and alloys. As can be seen from the table, ferric chloride solutions are suitable for etching the bulk of the metals and alloys, and are frequently employed in spray etching or fine-detailed parts and in blanking operations. Nitric acid by itself, or in combination with other acids, is extensively used for etching many metals and alloys. Etchants for copper on printed circuit boards includes ferric chloride, sodium and ammonium persulfate, chromic acid, and cupric chloride.

TABLE 21 PRINCIPLE WASTEWATER CONSTITUENTS IN EFFLUENTS GENERATED DURING CHEMICAL MILLING OR ETCHING

Constituent	Basic Material						
	Aluminum and Its Alloys	Copper and Its Alloys	Low Alloy Steels and Stainless Steels	Nickel and Its Alloys	Titanium and Its Alloys	Magnesium and Its Alloys	Zinc and Its Alloys
Preparative— Cleaning and Activating							
Aluminum, Al^{+3}	X						
Copper, Cu^{+2}		X					
Zinc, Zn^{+2}		X			X	X	X
Tin, Sn^{+2}		X					
Chromium, Cr^{+3}		X				X	X
Nickel, Ni^{+2}			X	X	X		
Manganese, Mn^{+2}			X	X			
Iron, Fe^{+2}			X				
Cobalt, Co^{+2}			X		X		
Molybdenum, Mo^{+3}				X			
Titanium, Ti^{+3}				X			
Vanadium, V^{+4}			X	X	X		
Magnesium, Mg^{+2}			X		X		
Tungsten, W^{+3}					X		
Carbonate				X		X	
Phosphate	X	X	X	X			
Silicate	X	X	X	X	X	X	X
Nitrate, NO_3^{-1}					X	X	X
Fluoride, F	X	X	X	X	X	X	X
Sulfate, SO_4^{-2}	X		X	X	X	X	
Chromate, CrO_4^{-2}	X	X	X	X	X		
Chloride, Cl^{-1}		X	X	X			
Tartrate	X	X	X	X		X	X
Acetate				X		X	X
Aluminate, AlO_2^{-2}	X		X				
Sodium	X	X	X	X	X	X	
Chemical Metal Removal							
Sodium							
Aluminum, Al^{+3}	X	X					
Copper, Cu^{+1} and Cu^{+2}	X						
Zinc, Zn^{+2}		X			X		X
Tin, Sn^{+2}		X					
Chromium, Cr^{+3}		X					X
Nickel, Ni^{+2}			X	X			
Manganese, Mn^{+2}			X	X			
Iron, Fe^{+2} and Fe^{+3}			X				
Cobalt, Co^{+2}	X	X	X				
Molybdenum, Mo^{+3}				X	X		
Titanium, Ti^{+3}			X	X			
Vanadium, V^{+4}				X	X		
Magnesium, Mg^{+2}					X		
Tungsten, W^{+3}					X		
Ammonium, NH_4^{+1}							
Nitrate, NO_3^{-1}		X		X		X	
Fluoride, F^{-1}			X	X			
Sulfate, SO_4^{-2}					X	X	X
Chromate, CrO_4^{-2}		X			X		
Chloride, Cl^{-1}	X	X			X		
Persulfate, $S_2O_8^{-2}$		X	X	X	X		
Phosphate, PO_4^{-3}	X		X				
Aluminate, AlO_2^{-2}			X				
Posttreatment(a)	--	--	--	--	--	--	--

(a) The posttreatment results in no contaminants if desmutting operations are not required. If required the constituents would be similar to those indicated above under Chemical Metal Removal.

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TABLE 22   REPRESENTATIVE AQUEOUS SOLUTIONS FOR CHEMICAL MILLING OR ETCHING VARIOUS METALS AND ALLOYS[a]

Metals and Alloys	Etching Solutions
Aluminum and its alloys	$FeCl_3$ or HCl or NaOH
Copper and its alloys	$FeCl_3$ or $CuCl_2$ or $CuCl_2$-HCl or $(NH_4)_2S_2O_8$ or $(NH_4)_2S_2O_8$-NaCl-NH_4Cl or CrO_3
Magnesium	HNO_3
Nickel and its alloys	$FeCl_3$ or HNO_3-HCl-$FeCl_3$
Steel (carbon and low alloy)	$FeCl_3$ or HNO_3 or HNO_3-HCl or HNO_3-HCl-H_3PO_4
Stainless steel	$FeCl_3$ or HNO_3-HCl or HNO_3-HCl-H_3PO_4
Titanium and its alloys	HF-HNO_3 or HF-CrO_3 or HF
Zinc	HNO_3

(a)   Data are from references and other sources.

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

Introduction

This section of the report reviews the waste character-
ization detailed in Section V and identifies in terms of
chemical and physical constituents that which constitutes
pollutants as defined in the act. Rationales for the
selection and, more particularly, the rejection of waste-
water constituents as pollutants are presented.

First, consideration was given to the broad range of
chemicals used in the metal finishing industry. Those
considered to be amenable to treatment are identified.

Metal Finishing Waste Water Constituents

A large variety of chemicals that become waste water
constituents are used in the metal finishing. The important
ones were identified in Section V. Not all of these
constituents will be found in the waste waters from every
facility, since the number of processes in a single facility
varies as well as the number of basic materials pretreated
and types of posttreatment operations. When present, metal
ions are usually coprecipitated with copper, nickel,
chromium, and/or zinc. The nonmetallic cations and anions
(hydrogen, ammonium, sulfate, phosphate, chloride, etc.)
from electroplating copper, nickel, chromium, and zinc can
be considered typical of the metal finishing industry.

Waste Water Constituents and Parameters of Pollutional
Significance

The waste water constituents of pollutional significance are
total suspended solids, phosphate, oxidizable cyanide, total
cyanide, fluoride, aluminum, cadmium, hexavalent chromium,
total chromium, copper, iron, nickel, tin, zinc, and pH.
These constituents are the subject of effluent limitations
and standards of performance regardless of the physical form
(soluble or insoluble metal) or chemical form (valence state
of a metal and whether or not it is complexed).

The pH is subject to effluent limitations because it affects
the solubility of metallic compounds such as zinc hydroxide
and the soluble metal content of the treated effluent.

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Thus, the major chemical, physical, and biological waste water constituents and parameters of pollutional significance are as follows

Total suspended solids

Phosphate

Oxidizable cyanide

Total cyanide

Fluoride

Aluminum

Cadmium

Hexavalent Chromium

Total Chromium

Copper

Iron

Nickel

Tin

Zinc

pH.

Other waste water constituents of secondary importance that are not the subject of effluent limitations or standards of performance are as follows

Total dissolved solids

Chemical oxygen demand

Oil and grease

Turbidity

Color

Temperature

Nitrate

Ammonia

Rationale for the Selection of Waste Water Constituents and Parameters.

Total Suspended Solids. Suspended solids was selected as a parameter to further assure that efficient clarification is practiced. Control of total metal discharged, i.e., lead, also assures that clarification will be efficient. However, control of suspended solids also assures that excess solids will not be unnecessarily discharged. Furthermore, in spite of extensive review of both compositions and a listing of waste water constituents there may be waste water constituents in individual plants not covered by the listings and not selected as pollutant parameters. If such constituents are also precipitated by the chemical treatment methods employed to remove pollutants that have been selected as pollutant parameters, they will be removed providing there is a limitation on suspended solids. Metals such as arsenic, beyllium, columbium, gallium, germanium, hafnium, manganese, molybdenum, titanium, tungsten, uranium, vanadium, and zirconium would be removed to some extent by neutralization and clarification.

Phosphorous. Phosphate is present in significant amounts in cleaners, acid dips, and processing baths in Subcategory (1) processes and can be removed by reaction with lime to form insoluble calcium phosphate. Lime is a suitable neutralizing agent and the phosphate may therefore be coprecipitated with the heavy metals.

Cyanide, Amenable to Oxidation by Chlorine. Oxidizable cyanide may be present in significant amounts in the waste water from this segment of the electroplating industry and is amenable to oxidation by chlorine under alkaline conditions.

Cyanide, Total. Some forms of cyanide are not amenable to chlorine oxidation and can appear in the waste water in significant amounts which cannot be removed. Cyanide is present in waste waters as the free cyanide ion (CN^-) or complexed with metals such as copper, zinc, cadmium, and silver. The free cyanide and the cyanide in the metal complexes mentioned are destroyed by chlorine. However, more stable cyanide complexes such as those with nickel, cobalt, and iron are not effectively oxidized by chlorine, although may be by ozone (see Section VII). Since iron, cobalt, and nickel are not plated from cyanide solutions

their source, if present, is not from electroplating baths. However, some cleaners and stripping solutions contain cyanide and the dumps and rinses from these are normally combined with rinses from nickel, cobalt, and iron baths to constitute the acid-alkali waste water stream. There are alternatives to use of cyanide in stripping solutions and it is believed that the cyanide in cleaners can be minimized or eliminated. Thus, it is practicable to limit the amount of cyanide that is not amenable to oxidation and this may be considered a pollutant parameter. Total cyanide is more easily determined than difficult-to-oxidize cyanide. Since it is made up of oxidizable cyanide which is a pollutant parameter and difficult-to-oxidize cyanide, which could be regarded as a pollutant parameter, the total cyanide is also a pollutant parameter.

Fluorides

As the most reactive non-metal, fluorine is never found free in nature but as a constituent of fluorite or fluorspar, calcium fluoride, in sedimentary rocks and also of cryolite, sodium aluminum fluoride, in igneous rocks. Owing to their origin only in certain types of rocks and only in a few regions, fluorides in high concentrations are not a common constituent of natural surface waters, but they may occur in detrimental concentrations in ground waters.

Fluorides are used as insecticides, for disinfecting brewery apparatus, as a flux in the manufacture of steel, for preserving wood and mucilages, for the manufacture of glass and enamels, in chemical industries, for water treatment, and for other uses.

Fluorides in sufficient quantity are toxic to humans, with doses of 250 to 450 mg giving severe symptoms or causing death.

There are numerous articles describing the effects of fluoride-bearing waters on dental enamel of children; these studies lead to the generalization that water containing less than 0.9 to 1.0 mg/l of fluoride will seldom cause mottled enamel in children, and for adults, concentrations less than 3 or 4 mg/l are not likely to cause endemic cumulative fluorosis and skeletal effects. Abundant literature is also available describing the advantages of maintaining 0.8 to 1.5 mg/l of fluoride ion in drinking water to aid in the reduction of dental decay, especially among children.

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Chronic fluoride poisoning of livestock has been observed in areas where water contained 10 to 15 mg/l fluoride. Concentrations of 30 - 50 mg/l of fluoride in the total ration of dairy cows is considered the upper safe limit. Fluoride from waters apparently does not accumulate in soft tissue to a significant degree and it is transferred to a very small extent into the milk and to a somewhat greater degree into eggs. Data for fresh water indicate that fluorides are toxic to fish at concentrations higher than 1.5 mg/l.

Cadmium

Cadmium in drinking water supplies is extremely hazardous to humans, and conventional treatment, as practiced in the United States, does not remove it. Cadmium is cumulative in the liver, kidney, pancreas, and thyroid of humans and other animals. A severe bone and kidney syndrome in Japan has been associated with the ingestion of as little as 600 ug/day of cadmium.

Cadmium is an extremely dangerous cumulative toxicant, causing insidious progressive chronic poisoning in mammals, fish, and probably other animals because the metal is not excreted. Cadmium could form organic compounds which might lead to mutagenic or teratogenic effects. Cadmium is known to have marked acute and chronic effects on aquatic organisms also.

Cadmium acts synergistically with other metals. Copper and zinc substantially increase its toxicity. Cadmium is concentrated by marine organisms, particularly molluscs, which accumulate cadmium in calcareous tissues and in the viscera. A concentration factor of 1000 for cadmium in fish muscle has been reported, as have concentration factors of 3000 in marine plants, and up to 29,600 in certain marine animals. The eggs and larvae of fish are apparently more sensitive than adult fish to poisoning by cadmium, and crustaceans appear to be more sensitive than fish eggs and larvae.

Chromium

Chromium, in its various valence states, is hazardous to man. It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammation of the kidneys. Levels of chromate ions that have no effect on man appear to be so low as to prohibit determination to date.

The toxicity of chromium salts toward aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially that of hardness. Fish are relatively tolerant of chromium salts, but fish food organisms and other lower forms of aquatic life are extremely sensitive. Chromium also inhibits the growth of algae.

In some agricultural crops, chromium can cause reduced growth or death of the crop. Adverse effects of low concentrations of chromium on corn, tobacco and sugar beets have been documented.

Lead

Lead is a cumulative poison to the human system and concentrates itself primarily in bones. Symptoms of advanced lead poisoning are anemia, abdominal pain, and gradual paralysis. Immunity to lead does not develop but reaction grows more acute. It is not an elemental essential to the metabolism of animals.

Lead poisoning has been reported in humans drinking water with a concentration as small as 0.042 mg/l. However, concentrations of 0.16 mg/l seem to have had no effect over long periods. It is generally felt that 0.1 mg/l can cause poisoning if ingisted regularly.

Chronic lead poisoning among animals has been caused by concentrations less than 0.18 mg/l. Changes have been noted in nervous systems of laboratory rats after ingistion of 0.005 mg/ per kg of body weight.

Lead concentrations of approximately of 0.5 mg/l appear to be the maximum safe limit.

Studies on the effect of lead on fishes indicate that lead reacts with an organic constituent causing a mucus to obstruct the gills and body. The fish ultimately dies of suffocation. Concentrations between 0.1 mg/l and 0.41 mg/l have resulted in a TL 50 within 48 hours to sticklebacks, guppies, minnous, brown trouts and coho salmon.

Iron

Iron in small amounts is an essential constituent to animal diets. The daily nutritional requirement is 1-2 mg and most people intake an average of 16 mg. However, drinking water becomes umpalatable at approximately 1.0 mg/l. Ferrous iron imparts as taste at 0.1 mg/l and ferric iron at 0.2 mg/l.

It also tends to precipitate causing stains and discoloration of water. For these reasons drinking water limitations have been recommended at 0.1 mg/l.

Very high concentrations of iron have been toxic to fish. Iron hydroxides have been known to precipitate on the gills of fish causing obstruction. Also heavy precipitation may smother eggs.

Tin

Tin is not a nutritional requisite but neither does it appear harmufl to human or animal life. The average diet contains 17.14 mg/day. Very large doses of 30-50 mg/kg of body weight caused much loss of weight in cats. Trace amounts of tin appear beneficial to some fish.

pH, Acidity and Alkalinity

Acidity and alkalinity are reciprocal terms. Acidity is produced by substances that yield hydrogen ions upon hydrolysis and alkalinity is produced by substances that yield hydroxyl ions. The terms "total acidity" and "total alkalinity" are often used to express the buffering capacity of a solution. Acidity in natural waters is caused by carbon dioxide, mineral acids, weakly dissociated acids, and the salts of strong acids and weak bases. Alkalinity is caused by strong bases and the salts of strong alkalies and weak acids.

The term pH is a logarithmic expression of the concentration of hydrogen ions. At a pH of 7, the hydrogen and hydroxyl ion concentrations are essentially equal and the water is neutral. Lower pH values indicate acidity while higher values indicate alkalinity. The relationship between pH and acidity or alkalinity is not necessarily linear or direct.

Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures and can thus add such constituents to drinking water as iron, copper, zinc, cadmium and lead. The hydrogen ion concentration can affect the "taste" of the water. At a low pH water tastes "sour". The bactericidal effect of chlorine is weakened as the pH increases, and it is advantageous to keep the pH close to 7. This is very important for providing safe drinking water.

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Dead fish, associated algal blooms, and foul stenches are aesthetic

liabilities of any waterway. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity to aquatic life of many materials is increased by changes in the water pH. Metalocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. The availability of many nutrient substances varies with the alkalinity and acidity. Ammonia is more lethal with a higher pH.

The lacrimal fluid of the human eye has a pH of approximately 7.0 and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Appreciable irritation will cause severe pain.

Rationale for the Selection of Total Metal as a Pollutant Parameter.

Chemical treatment as presently developed is able to reduce the concentration of metals in solution to low values and to remove the precipitated form of the metal (clarification). There is no a priori reason why soluble metal, insoluble metal, complexed metal, etc., should be regarded as separate pollutant parameters in view of the fact that technology is capable of reducing the total metal content to low values.

It is practical, as part of chemical treatment, to remove insoluble metal precipitate from the effluent by sedimentation, clarification, filtering, or centrifuging prior to the discharge of liquid effluent to streams. Large amount of metal hydroxides in the streams are further sources of metal ions if the water later becomes acidic relative to the pH at which the metal hydroxides were originally precipitated. If this happens, the original purpose in precipitating hydroxides is defeated. Therefore, removal of precipitated metal hydroxides by efficient clarification prior to discharge of the effluent to navigable waters is assumed.

With removal of total suspended solids to levels of less than 50 mg/l, significant removal of metal hydroxides occurs. However, some portion of the total suspended solids contains metals either as metal hydroxides or adsorbed metal ions. Regardless of the form, the metal content of suspended solids represents a significant pollutant in the water.

Metals are considered pollutants regardless of form. The standard method of analysis for total metal involves acidification of the sample to analyze for total metal

content (dissolved metal plus any metal in suspended solids left from clarification). For the purpose of establishing effluent limitations and standards of performance it is herein specified, in the absence of any qualifying statement, that the concentration of metals in mg/liter means total metal, as analytically determined by acid digestion prior to filtering.

Rationale for Rejection of Other Waste Water Constituents as Pollutants for Subcategory (1) Processes

Metals. The rationale for rejection of any metal other than those described as a pollutant above is based on one or more of the following reasons:

(1) They are not present in the processing solutions used in the metal finishing industry. It would be redundant to make a long list of materials that can be controlled but that are not present.

(2) Insufficient data exist upon which to base effluent limitations and standards of performance. Waste-water constituents such as sodium, potassium, nitrate and ammonia are present in many processing solutions and waste waters, but there is no practicable method at present of removing them from solution.

Dissolved Solids. Dissolved solids is not a significant pollution parameter in this industry. Although the concentration of total dissolved solids will become higher as efforts are directed to reducing water use and volume of effluent discharged, the total quantity of dissolved solids will remain unchanged.

Chemical Oxygen Demand. The chemical oxygen demand can be significant in some cases because of the oil and grease removed from the work in the cleaning operation, which then constitutes a part of the cleaner when it is dumped. It is possible to minimize chemical oxygen demand in some cases by use of organic vapor degreasers prior to alkaline cleaning. However, if there is a high chemical oxygen demand practicable technology to lower it has not been demonstrated in the electroplating industry.

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Biochemical Oxygen Demand. Biochemical oxygen demand is usually not an important pollution parameter in the Subcategory (1) processes. An electroplating plant in a suburban location not discharging to a publicly owned system must treat its own sanitary sewage in a separate treatment facility. If the plant chooses to mix the treated sanitary effluent with process wastes prior to treatment BOD would be considered a major parameter.

Turbidity. Turbidity is indirectly measured and controlled independently by the limitation on suspended solids.

Temperature. Temperature is not considered a significant pollution parameter in the Subcategory (1) processes. However, cooling water used to cool process tanks and/or evaporative recovery systems that are not subsequently used for rinsing could contain pollutants from leaks in the system.

Aluminum

Aluminum may be present in significant amounts in the waste water stream. Limits are not placed on aluminum at this time due to insufficient data. However, it is believed that significant removal will result when conventional chemical treatment techniques are employed.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

Introduction

The control and treatment technology for reducing the discharge of pollutants from metal finishing operations is discussed in this section.

The control of metal finishing waste waters includes process modifications, material substitutions, good housekeeping practices, and water conservation techniques. The in-plant control techniques discussed are generally considered to be normal practice in these industries.

The treatment of metal finishing waste water includes techniques for the removal of pollutants and techniques for the concentration of pollutants in the waste waters for subsequent removal by treatment or recovery of chemicals. Although all of the treatment technologies discussed have been applied to waste waters from metal finishing operations, some may not be considered normal practice in this industry.

Chemical treatment technology is discussed first in this section because some treatment of this type is required of many waste waters generated by metal finishing operations before discharge into navigable streams. After chemical treatment the amount of pollutants discharged to navigable waters is roughly proportional to the volume of water discharged.

The proper design, operation, and maintenance of all waste water control and treatment systems are considered essential to an effective waste management program. The choice of an optimum waste water control and treatment strategy for a particular metal finishing facility requires an awareness of numerous factors affecting both the quantity of waste water produced and its amenability to treatment.

Chemical Treatment Technology

Applicability

Chemical treatment processes for waste water from metal finishing operations are based upon chemical reactions many of which go back to the beginning of modern chemistry over 200 years ago. These reactions have been used as the basis

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for the design and engineering of systems capable of treating waste water containing a large variety of pollutants and reducing the concentration of metal below 1 mg/l. Control procedures have been devised to assure the effectiveness of the processes.

Processes

Separation of Streams. Waste Waters from different operations in a metal finishing process may be combined in some cases and kept separate in other cases prior to chemical treatment. The nature of the waste waters and the pollutants present will determine where segregation is desirable and where combination is practical. Some pollutants cannot be properly removed in the presence of others, while some are better removed when combined with others. Combination of some streams will result in a reaction to form additional pollutants and ones that can be of immediate danger to personnel involved in the metal finishing operations, e.g., a cyanide containing stream combined with an acid stream may cause evolution of gaseous hydrogen cyanide. In general, waste waters containing cyanide are segregated and treated separately, waste waters containing hexavalent chromium are segregated and treated separately. After treatment the cyanide, chrome, and metal ion streams are combined for further treatment to precipitate metal hydroxides which are settled out, sometimes filtered, and disposed of on land. The treatment facilities may be engineered for batch, continuous, or integrated operations. However, the treatment methods for several pollutants can deviate considerably from this general plan. The design of a suitable procedure and system to treat a specific pollutant mix requires considerable care and experience.

Batch Treatment. The batch method is generally used for small or medium-sized plants. Batch treatment is useful not only for rinse waters but for expendable process solutions containing high concentrations of chemicals or spills, leaks, or other accidental discharge of process solutions. Holding tanks collect the waste water and are large enough to provide ample time to treat, test, and drain a tank while another is being filled. Analytical tests are made before treatment to determine the amount of reagent to add and after treatment to establish that the desired effluent concentrations have been obtained.

Continuous Treatment. The chemical treatment process may be made continuous by (1) sizing and baffling treatment tanks to provide sufficient hold times to complete chemical

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Continuous Treatment. The chemical treatment process may be made continuous by (1) sizing and baffling treatment tanks to provide sufficient hold times to complete chemical

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reactions; (2) providing continuous monitoring of pH and oxidation/reduction potentials and controls for regulating reagent additions by means of these monitors; and (3) providing a continuousoverflow settling tank that allows sludge to be pumped off periodically through the bottom.

A flow diagram for a large continuous-treatment plant is shown in Figure 5. The dilute acid-alkali stream originates from rinses associated with alkaline cleaners, acid dips, and baths containing metal ions, but no cyanide or hexavalent chromium. When concentrated acid and alkali baths are to be discarded they are transferred to a holding tank and added slowly to the dilute stream. In this manner, sudden demands on the reagent additions and upsetting of the treatment conditions are avoided. The dilute acid-alkali stream first enters a surge tank to neutralize the waste water and equalize the composition entering the precipitation tank. The hexavalent chromium is reduced at a pH of 2.0 to 2.5, and the addition of the SO_2 and HCl are controlled by suitable monitors immersed in the well-agitated reduction tank. Cyanide is destroyed in a large tank with compartments to allow a two-stage reduction. Reaction time is about 3 hours.

The treated chrome, cyanide, and neutralized acid-alkali streams are run into a common tank where pH is automatically adjusted to optimize the precipitation of metal hydroxides. The stream then enters a solids contact and settling unit where mixing, coagulation, flocculation, recirculation, solids concentration, sludge collection, and sludge removal are accomplished. Flocculants are usually added to this tank. The overflow from the settling unit constitutes the discharge from the plant. The sludge may be dewatered by filtering and the filtrate returned to the settling unit, if the solid content of this filtrate is higher than the overflow from the clarifier.

Integrated Treatment. The integrated system uses a reservoir tank in conjunction with the rinse tanks for each type of plating bath. A common solution is circulated through the chemical wash tank (which replaces what is normally the first rinse tank) and the reservoir. The solution contains an excess of treatment chemical so that, for example, cyanide destruction takes place in the wash tank and directly on the film of dragout solution on the part itself. Therefore, no cyanide is dragged into the subsequent rinse tank and the effluent requires no further treatment for cyanide.
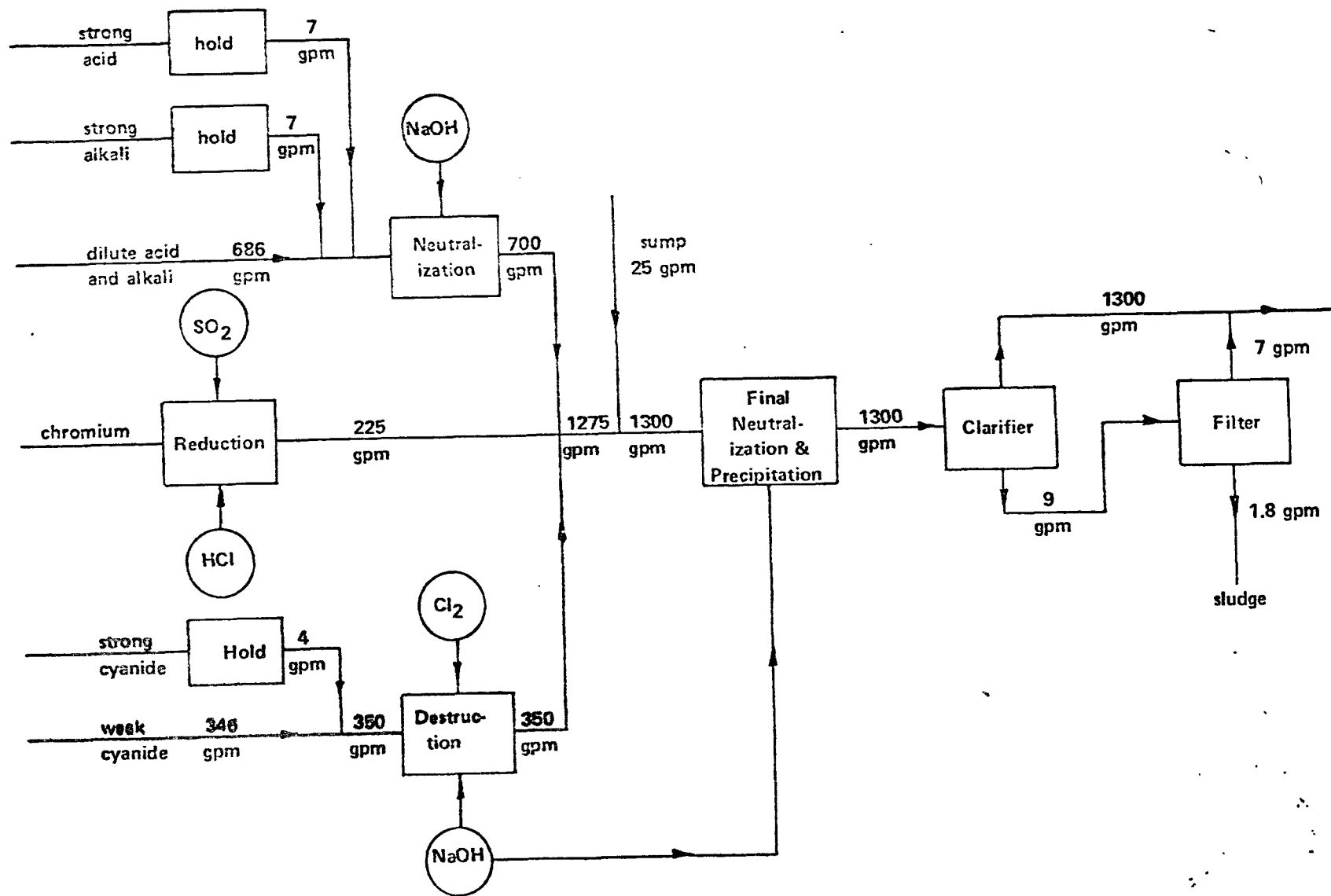
FIGURE 5 DIAGRAM OF A TYPICAL CONTINUOUS-TREATMENT PLANT

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Because metals are precipitated separately at a relatively high concentration, the metal hydroxide settled in the reservoir may be recovered, dissolved, and returned to the plating bath from which it originated. In contrast to batch and continuous treatments, which are generally carried out in a separate facility, the reservoir in the integrated system is in proximity to the plating room because of the necessity for circulation. The layout of an integrated system for treating rinse water waste from a cyanide plating solution and a chromium plating bath is shown in Figure 6.

Unit Operations

Precipitation. The effluent levels of metal attainable by chemical treatment depend upon the insolubility of metal hydrolysis products in the treated water and upon their settling and filtering characteristics which affect the degree to which they can be separated. The solubilities of the hydrolysis products are dependent upon many conditions during precipitations such as pH, presence of other cations and anions, time allowed before separating out the solids, the precipitation agent used, the degree of agitation, etc.

Schlegel and Hartinger have studied precipitation reactions extensively and have been able to obtain low concentrations of metal ions in solution in a reasonable time, i.e., 2 hours.

When metal ions are precipitated separately the pH may have to be adjusted differently for each ion. This immediately raises the question of whether the metals can be efficiently precipitated together at a common pH. This is possible as shown in Table 23 taken from Hartinger.

It is apparent that it is difficult to predict in detail the conditions that will give the best precipitation results in a practical situation. However, just as several parameters can be adjusted in the laboratory to obtain optimum results, suitable conditions may be found in the field. Flocculating agents, added to aid in settling the precipitate, play a significant role in reducing concentration of suspended solids.

When solubilizing complexing agents are present, the equilibrium constant of the complexing reaction has to be taken into account in determining theoretical solubility with the result that the solubility of the metal is generally increased. Cyanide ions must be destroyed not only because they are toxic but also because they prevent effective precipitation of copper and zinc as hydroxides.

Reuse water

Cyanide solutions

Drag out

Cyanide waste treatment

Water rinse

Chromic acid process

Chromic acid waste treatment

Water rinse

To pH control clarifier
Water reuse pump
Water slow down
to sewer

Sodium hypochlorite

Feed pump

Cyanide waste treatment reservoir

Chromium waste treatment reservoir

Feed pump

Sodium carbonate
Sodium hydro-
sulfite

To sludge bed

FIGURE 6 INTEGRATED TREATMENT SYSTEM

TABLE 23   COMPARISON OF PRECIPITATION OF METAL
            HYDROXIDES SEPARATELY AND IN COMPARISON

Initial Ratio of Metal Ions in Solution		Soluble Metal Two Hours after Neutralization, mg/l		
		Cu^{++}	Ni^{++}	Cr^{+++}
Cu:Ni	2:1	0.76	12	---
	1:1	0.6	15	
	1:2	0.32	28	
Cu:Cr	1:1	<0.2	---	0.74
Cu:Ni:Cr	1:1:1	0.25	0.25	0.19

Initial PH 8.5

If cyanide is replaced in a plating bath by a nontoxic complexing agent such as EDTA (ethylenediaminetetraacetic acid), the new complexing agent could have serious consequences as far as the removal of metal ions by precipitation. Ammonium ion, present in many metal finishing baths, will complex copper, zinc, and other heavy metal ions and interfere with their precipitation as hydroxides.

Theory and experimental results confirm that it is not possible to achieve complete removal of metal ions from waste water by precipitation as hydroxides even if separation of precipitate were 100 percent effective. Thus, a finite concentration of pollutant will remain in the effluent. The best indication of what can be achieved in reducing metal concentration is the results of daily operation in exemplary plants rather than theory or laboratory experiments. Clarification efficiency is an important factor in determining the total metal content of the effluent. It is safe to say that the soluble metal content will be no greater than the total content achieved in practice and may be less.

Solids Separation. The first step in separating the precipitated metals is settling, which is very slow for gellike zinc hydroxide, but is accelerated by coprecipitation with the hydroxides of copper and chromium. Coagulation can also be aided by adding metal ions such as ferric iron which forms ferric hydroxide and absorbs some of the other hydroxide, forming a floc that will settle. Ferric iron has been used for this purpose in sewage treatment for many years as has aluminum sulfate. Ferric chloride is frequently added to the clarifier of chemical wastetreatment plants in plating installations. Flocculation and settling are further improved by use of polyelectrolytes, which are high molecular weight polymers containing several ionizable ions. Due to their ionic character they are capable of swelling in water and adsorbing the metal hydroxide which they carry down during settling.

Settling is accomplished in the batch process in a stagnant tank, and after a time the sludge may be emptied through the bottom and the clear effluent drawn off through the side or top. The continuous system uses a baffled tank such that the stream flows first to the bottom but rises with a decreasing vertical velocity until the floc can settle in a practically stagnant fluid.

Although the design of the clarifiers has been improved through many years of experience, no settling techniques or

clarifier will completely remove solids from the effluent which contains typically 5 to 20 mg/l of suspended solids. This floc contains some metal.

Sludge Disposal. Clarifier underflow or "sludge" contains typically 1 to 2 percent solids and can be pumped to a lagoon.

Metal ions in the liquid associated with the sludge can percolate through porous soil and become a potential source of groundwater contamination. Impervious lagoons require evaporation into the atmosphere. However, in many parts of the U.S., the average annual rainfall equals or exceeds the atmospheric evaporation. Additionally, heavy rainfalls can fill and overflow lagoons. Metal ions may be leached from metal hydroxides and the surface run-off to adjacent streams or lakes may be in sufficient quantity to be detrimental.

A case in point is contamination of groundwater by plating wastes held in lagoons in Nassau County, New York. Plating wastes have seeped down from the lagoons into the aquifier intermittently since 1941. This seepage has resulted in a plume of contaminated water some 4,300 feet long, up to 1,000 ft wide, and as much as 70 feet deep, extending downgrade to the headwater of Massapequa Creek. Originally the plating waste water was untreated and the concentration of hexavalent chromium in the groundwater was about 40 mg/l. Since the start of chromium treatment, concentrations have decreased to less than 5 mg/l in most of the plume. Treatment of the plating waste effluent results in discharge of sludge to the lagoons, and the sludge forms a lining on the bottoms and sides which retards infiltration. At another location core-drilled samples were obtained from the shale structure underlying the bed used for disposal of sludge resulting from chemical treatment. The disposal side had been in use for several years. Heavy metal concentrations two feet into the shale structure, were of the order of 50 to 100 ppm.

Lagooning can be avoided by dewatering the sludge to a semidry or dry condition. Several devices are available for dewatering sludge. Rotary vacuum filters will concentrate sludge containing 4 to 8 percent solids to 20 to 25 percent solids. Since the effluent concentration of solids is generally less than 4 percent a thickener tank is often employed between the clarifier and the filter. The filtrate often contains excessive suspended solids and is recirculated to the clarifier.

Centrifuges will also thicken sludges to the above range of consistency and have the advantage of using less floor space. The effluent contains excessive suspended solids and is returned to the clarifier.

Pressure filters may be used. In contrast to rotary filters and centrifuges, pressure filters will produce a filtrate with less than 3 mg/l of suspended solids so that return to the clarifier is not needed. The filter cake contains approximately 20 to 25 percent solids. Pressure filters are usually designed for a filtration rate of 2.04 to 2.44 liters/min/sq m (0.05 to 0.06 gpm/sq ft) of clarifier sludge.

Solids contents from 25 to 35 percent in filter cakes can be achieved with semicontinuous tank filters rated at 10.19 to 13.44 liters/min/sq m (0.25 to 0.33 gpm/sq ft) surface. A solids content of less than 3 mg/l is normally accepted for direct effluent discharge. The units require minimum floor space.

Plate and frame presses produce filter cakes of 40 to 50 percent dry solids and a filtrate with less than 5 mg/l total suspended solids. Because automation of these presses is difficult, labor costs tend to be high. The operating costs are partially offset by low capital equipment costs.

Automated tank type pressure filters are just now finding application. The solids content of the cake can reach as high as 60 percent while the filtrate may have up to 5 mg/l of total suspended solids. The filtration rate is approximately 2.04 liters/min/sq m (0.05 gpm/sq ft) filter surface area. Pressure filters containing from 300 to 500 mg/l suspended solids at design of 4.88 to 6.52 liters/min/sq m (0.12 to 0.16 gpm/sq ft) and still maintain a low solids content in the filtrate.

Filter cakes can easily be collected in solid waste containers and hauled away to landfills. There may be situations, however, where the metal in the filter cake could be redissolved if it came into contact with acidic water. Careful consideration should be given to where such a material is dumped.

A proprietary process is available for solidifying sludge by addition of chemical fixing agents. Relative to filtration, the amount of dried sludge to be hauled away is increased. The fixing process appears to insolubilize the heavy metal ions so that in leaching tests only a fraction of a part per

million is found in solution. A fill is produced that is similar to dried clay.

The possibility of recovering metal values from sludges containing copper, nickel, chromium, and zinc have been considered but such a system appears to be uneconomic under present circumstances. It may be profitable to recover metal values if 900 to 2300 kg (2,000 to 5,000 pounds) of dried sludge solids can be processed per day with a thoroughly developed process. To attain this capacity would almost certainly require that sludge from a large number of plants be brought to a central processing station. The recovery would be simpler if the metallic precipitates were segregated, but segregation would require extensive modification, investment, and increased operating expense for precipitation and clarification. Laboratory experiments showed that zinc could be leached from sludge with caustic after which copper, nickel, and chromium were effectively dissolved with mineral acids. Ammonium carbonate dissolved copper and nickel but not trivalent chromium, thus giving a method of separation. Electrowinning of the nickel and copper appeared to be a feasible method of recovering these metals.

Cyanide Oxidation. Cyanide in waste waters is commonly destroyed by oxidation with chlorine or hypochlorite prior to precipitation of the metal hydroxides. The method is simple, effective, and economically feasible for most waste waters, even for small volume installations. A factor in how rapidly cyanide is destroyed, if at all, is how strongly the cyanide is complexed to metal ions and how rapidly the complex can be broken. Therefore, some waste waters present special problems. A comprehensive study of the method was made by Dodge and Zabban the results of which have been used to work out the practical processes. The following are proposed reactions for chlorine oxidation.

(1) $NaCn + Cl_2 = CNCl + NaCl$

(2) $CNCl + 2NaOH = NaCNO + NaCl + H_2O$

(3) $2NaCNO + 3Cl_2 + 4NaOH = N_2 + 2CO_2 + 6NaCl + 2H_2O.$
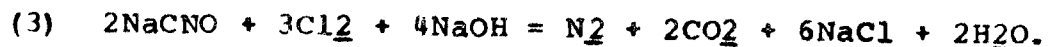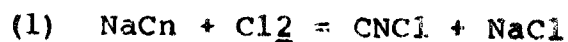
Reaction (2) goes rapidly at pH 11.5, under which conditions build up of the toxic gas CNCl by Reaction (1) is avoided. Treatment of dilute rather than concentrated solutions also minimizes its formulation. Oxidation to cyanate (NaCNO) is completed in 5 minutes or less. Reaction (3) goes more slowly, requiring an hour in the preferred pH range of 7.5 to 9.0, and a longer time at higher pH. After the

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conversion to nitrogen and carbon dioxide, excess chlorine is destroyed with sulfite or thiosulfate.

Sodium hypochlorite may be used in place of chlorine. Recent technical innovations in electrochemical hypochlorite generators for on-site use raise the possibility of controlling the addition of hypochlorite to the cyanide solution by controlling the current to the electrochemical generator, using sodium chloride as the feed material.

Concentrated solutions, such as contaminated or spent baths, cyanide dips, stripping solutions, and highly concentrated rinses, are normally fed at a slow rate into a dilute cyanide stream and treated with chlorine. However, concentrated solutions may also be destroyed by electrolysis with conventional equipment available in the plating shop. In normal industrial practice the process is operated batchwise, whereas the optimum system, from an operating standpoint, would be a cascaded one in which successively larger tanks are operated at successively lower current densities. This is the more efficient system. In addition to the oxidation of cyanide at the anode, valuable metal can be recovered at the cathode. The process becomes very inefficient when the cyanide concentration reaches 10 ppm, but at this point the solution can be fed into the process stream for chemical destruction of cyanide to bring the concentration to the desired level. The addition of chloride ions to the concentrated solutions, followed by electrolysis, produces chlorine or hypochlorite in solution, which can then destroy the cyanide to the same low levels as obtained by direct chlorination. With the provision that chlorine or hypochlorite be formed at a rate equal to the concentration of cyanide passing through the system, the process can be operated continuously:

$$2NaCN + 2NaOCl = 2NaCNO + 2NaCl$$

$$\underline{2NaCNO + 3NaOCl + H_2O = 2CO_2 + N_2 + 2NaOH + 3NaCl}$$

$$2NaCN + 5\ NaOCl + H_2O\ 2CO_2 + N_2 + 2NaOH + 5NaCl.$$
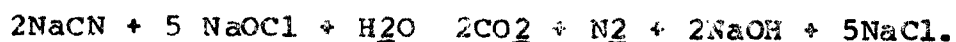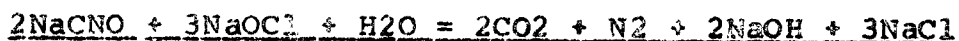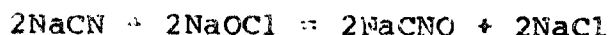
The Cynox process, based on the above principles, produces 1 kg of active chlorine per 5.5 Kwh. Equipment needs are the same with the exception that the tanks must be lined, and graphite or platinized anodes must be used.

Polysulfide-cyanide strip solutions containing copper and nickel do not decompose as readily and as completely as do plating solutions. Although the cyanide content can be reduced from 75,000 to 1000 mg/l during two weeks of

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electrolysis anode scaling prevents further cyanide decomposition unless anodes are replaced or freed from scale. Minimum cyanide concentration attainable is about 10 mg/l after which the solution can be treated chemically.

The electrolysis of dilute cyanide solutions can be improved by increasing the electrode area. Area can be increased by filling the space between flat electrodes with carbonaceous particles. The carbon particles accelerate the destruction process 1000 times, but flow rate through the unit must be carefully adjusted, if used on a continuous basis to achieve complete destruction (Plant 30-1).

Although cyanide can be destroyed by oxygen or air under suitable conditions, cyanide concentrations in the effluent are reported to be 1.3 to 2.2 mg/l, which is high for discharge to sewers or streams. A catalytic oxidation unit using copper cyanide as a catalyst and activated carbon as the reactive surface has been described for oxidizing cyanide with air or oxygen and at least two units were put in operation. Performance data is not available. Catalytic oxidation units must be custom designed for each installation for maximum effectiveness.

Ozone will oxidize cyanide (to cyanate) to below detectable limits independent of the starting concentration or of the complex form of the cyanide. Decomposition can be achieved with cyanides such as those of nickel and iron that are not readily oxidized by chlorine. Systems that will oxidize the cyanides that are usually treated, i.e., copper and zinc compounds have been installed in production units and demonstrated. Development work is continuing to enhance the efficiency and reliability of modern ozone generators and to decompose the more stable cyanides with the help of ultraviolet radiation and heat.

A method employing thermal decomposition for cyanide destruction has been recently announced. Cyanide solutions are heated to 160 to 200 C under pressure for 5 to 10 minutes. Ammonia and formate salts are formed. No information is given on the final cyanide concentration.

One process destroys cyanides of sodium, potassium, zinc, and cadmium and also precipitates zinc and cadmium. The process is discussed later in this section.

Precipitation of cyanide as ferrocyanide is restricted to concentrated wastes. Ferrocyanide is less toxic than cyanide, but is converted back to cyanide in sunlight. Treatment is accomplished by adding an amount in excess of

stoichiometry (2.3 kg of FeSO4 per kg of cyanide). Large amounts of sludge are produced which add to the pollution load. Complex cyanides do not break down readily and the reaction stops when a concentration of 10 mg/l of cyanide is reached. No benefits can be foreseen in terms of reducing waste volume and concentration.

Cyanide is also destroyed by reaction with polysulfides. Reasonable reaction rates are obtained only if the solution is boiled. Since the reaction does not destroy all of the cyanide further treatment is necessary.

Reduction of Hexavalent Chromium. Hexavalent chromium (CrVI) is usually reduced to trivalent chromium at a pH of 2 to 3 with sulfur dioxide (SO2), sodium bisulfite, other sulfite-containing compounds, or ferrous sulfate. The reduction makes possible the removal of chromium as the trivalent hydroxide which precipitates under alkaline conditions. Typical reactions for SO2 reduction are as follows:

$$SO_2 + H_2O = H_2SO_3$$

$$2H_2CrO_4 + 3H_2SO_3 = Cr_2(SO_4)_3 + 5H_2O.$$
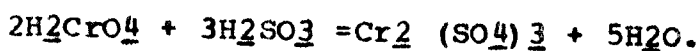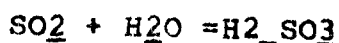
Representative reactions for reduction of hexavalent chromium under acid conditions using sulfite chemicals instead of SO2 are shown below:

(a) Using sodium metabisulfite with sulfuric acid:

$$4H_2CrO_4 + 3Na_2S_2O_5 + 3H_2SO_4 = 3Na_2SO_4 + 2Cr_2(SO_4)_3$$
$$+ 7H_2O$$
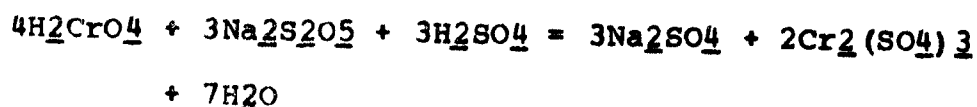
(b) Using sodium bisulfite with sulfuric acid:

$$4H_2CrO_4 + 6NaHSO_3 + 3H_2SO_4 = 3Na_2SO_4 + 2Cr_2(SO_4)_3$$
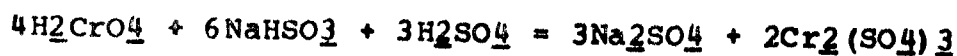
(c) Using sodium sulfite with sulfuric acid:

$$2H_2CrO_4 + 3Na_2SO_3 + 3H_2SO_4 = 3Na_2SO_4 + Cr_2(SO_4)_3$$
$$+ 5H_2O.$$
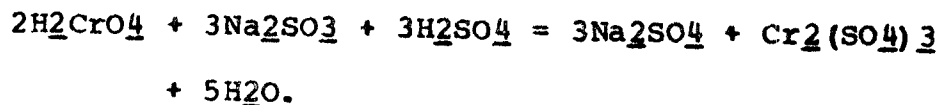
Reduction using sulfur dioxide is the most widely used method, especially with larger installations. The overall reduction is readily controlled by automatic pH and ORP (Oxidation-Reduction Potential) instruments. Treatment can be carried out on either a continuous or batch basis.

Hexavalent chromium can also be reduced to trivalent chromium in an alkaline environment using sodium hydrosulfite as follows:

$$2H_2CrO_4 + 3Na_2S_2O_4 + 6NaOH \quad 6Na_2SO_3 + 2Cr(OH)_3 + 2H_2O.$$
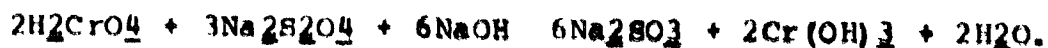
As indicated in the above equation, the chromium is both reduced and precipitated in this one-step operation. Results similar to those obtained with sodium hydrosulfite can be achieved using hydrazine under alkaline conditions.

$$Na_2CO_3$$

$$4H_2CrO_4 + 3N_2H_4 \quad = \quad 4Cr(OH)_3 + 3N_2 + 4H_2O.$$

Sodium hydrosulfite or hydrazine are frequently employed in the precipitation step of the integrated system to insure the complete reduction of any hexavalent chromium that might have been brought over from the prior reduction step employing sulfur dioxide or sodium bisulfite. Where ferrous sulfate is readily available (e.g., from steel pickling operations), it can be used for reduction of hexavalent chromium; the reaction is as follows:

$$2CrO_3 + 6FeSO_4 \cdot 7H_2O + 6H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3$$

$$+ 48H_2O.$$
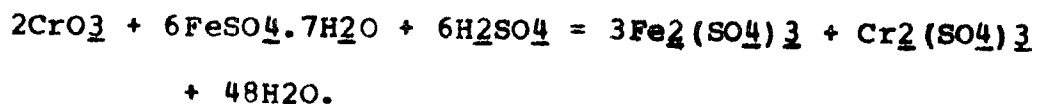
Cr^{+6} may be reduced at a pH as high as 8.5 with a proprietary compound. It is not necessary to segregate chromate-containing waste waters from the acid-alkali stream, and the use of acid to lower pH is eliminated in this case. Precipitation of chromic hydroxide occurs simultaneously in this case with the reduction.

Cr^{+6} ions may be reduced electrochemically. A concentration of 100 mg/l was reduced to less than 1 mg/l with a power consumption of 1.2 kwh/1000 liters. The carbon bed electrolytic process previously described for cyanide may also be used for chromate reduction in acid solution and Plant 30-1 has achieved a Cr^{+6} concentration of .01 mg/l using this method. Electrolysis may also be used to regenerate a reducing agent. A process has been described involving the reduction of Fe (III) to Fe (II) electrochemically and the reduction of Cr (VI) by Fe (II). The method should be capable of achieving low Cr (VI) levels.

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The simulataneous reduction of Cr^{+6} and oxidative destruction of cyanide finds limited application in waste treatment practice. The reaction requires mixing of Cr^{+6} and CN^- in ratios between 2 and 3 using Cu^{+2} as a catalyst in concentrations of 50 to 100 mg/l. The catalyst introduces additional pollutant into the waste stream. Reaction rates are generally slow, requiring from 6 to 24 hours for cyanide concentrations ranging from 2,000 to less than 50 mg/l at a solution pH of 5. The slowness of the reaction and the high initial concentrations of reactants required make the method unsuitable for treating rinse waters. Its use is limited to batch treatment of concentrated solutions. No benefits are obtained in terms of water volume and pollution reduction. Destruction is not as complete as obtained by the more common chemical methods.

Practical Operating Systems

Chemical treatment was used by every plant contacted during the effluent guidelines study with the exception of those that are allowed to discharge plating waste effluents into sewers or streams without treatment.

In Plart 33-2 the discharge of cyanide is eliminated by electrochemical decomposition in a tank held at sufficiently high temperature to evaporate the wastewater as rapidly as it is introduced. Therefore, no liquid stream leaves the tank. Fluorides and fluoborate containing waste waters in Plant 31-16 are collected separately and treated with lime.

Plant 35-8 disposes of sludge in a pit lined with special concrete blocks that filter out solids and allow liquid to permeate into the surroundings. Relatively few finishing plants have installed filters, although the problem of disposing of unfiltered sludge in many cases should provide an impetus for the use of one or more filters in the future. Plants 12-8 and 31-16 use large rotary filters to concentrate sludge form a clarifier. Plant 33-30 is able to filter the solution from the neutralizer directly, without a preceding clarification step. A settling tank centrifuge combination is in use in over 200 waste treatment installations, including those in metal finishing plants. The Chemfix system for solidifying sludge is in use at several plants.

Demonstration Status. The US Bureau of Mines has done some development on a process in which the acid wastes and alkaline cyanide wastes neutralize each other. The acid wastes are slowly added to the alkaline wastes in a closed reactor to form easily filtered metal cyanide precipitates.

The precipitates are heated in air to form stable metal oxides.

Effectiveness of Chemical Treating Techniques

The effectiveness of chemical treatment techniques depends on the nature of the pollutant, the nature and concentration of interfering ions, the procedure of adding the appropriate amount of chemicals (or adjusting pH), the reaction time and temperature and the achievement of effective separation of precipitated solids. Effective removal of heavy metal pollutants is inhibited by some types of chelating ions such as tartrate or ethylene diamine tetracetate ions.

The concentrations of metals and cyanide achievable by the chemical techniques employed for treating waste from copper, nickel, chromium, and zinc electroplating and zinc chromating processes are summarized in Table 24. Concentrations lower than those listed as maximum in Table 24 were reported by companies using all three (continuous, batch, and integrated) treating systems.

Higher-than-normal concentrations of metals, when they occur, are usually caused by: (1) inaccurate pH adjustment (sometimes due to faulty instrument calibration); (2) insufficient reaction time; or (3) excessive concentrations of chelating agents that complex the metal ions and prevent their reaction with hydroxyl ions to form the insoluble metal hydroxides; (4) lack of suitable coprecipitating agents. The causes for higher-than-normal concentrations of cyanide are similar, but another important factor must be added to the list of potential causes for incomplete cyanide destruction. In this case, sodium hydroxide and chlorine must be added continuously during the reaction to maintain the optimum pH and provide sufficient reagent to complete the reaction, which is normally monitored by an Oxidation-Reduction-Potential (ORP) recorder-controller. The maintenance of this system is a critical factor affecting the effectiveness of chemical oxidation.

Suspended Solids. The suspended solids discharged after treatment and clarification sometimes contribute more heavy metal than the dissolved metal. The concentration of total suspended solids in the end-of-pipe discharge from typical chemical treatment operations sampled during this study ranged from 20 to 24 mg/l. Lower values are reported for some facilities. Maintaining conditions so as not to exceed these amounts requires (1) a properly designed settling and/or clarifying facility, (2) effective use of flocculating agents, (3) rate of removal of settled solids,

TABLE 24 CONCENTRATIONS OF HEAVY METALS AND CYANIDE ACHIEVABLE BY
CHEMICAL TREATING OF WASTE CREATED BY COPPER, NICKEL,
CHROMIUM AND ZINC PLATING AND ZINC CHROMATING OPERATIONS

Pollutant	Soluble Concentration After Chemical Treating		Contribution From Suspended Solids [2]	
	Minimum, mg/ℓ	Maximum, mg/ℓ [1]	Minimum, mg/ℓ	Maximum, mg/ℓ
Cyanide, oxidizable [3]	< 0.01	0.03	--	--
Cyanide, total	0.1	0.2	--	--
Phosphorus	0.007	0.6	--	--
Chromium^{6+}	< 0.01	0.05	--	--
Chromium, total	0.05	0.25	0.02	0.30
Copper	< 0.01	0.2	0.02	0.76
Nickel	< 0.01	0.5	0.02	0.15
Zinc	0.05	0.5	0.04	0.80
Total suspended solids [2]	20	24		

(1) Values below these limits have been reported by plants utilizing continuous (Plants 40-6, 8-4,
33-6, and 11-8), batch (Plants 36-1, 21-3, 33-8), and integrated (Plants 36-2 and 20-13) treat-
ment techniques. Others (Plants 3-3 and 33-3) utilize a combination of integrated and batch or
continuous treatments to achieve these or lower limits.

(2) Data for Plants 33-1, 12-8, 36-1 and 11-8.

(3) Oxidizable by chlorine.

and (4) sufficient retention time for settling, and (5) rate of overflow of clarified effluent. Of course, minimum retention time depends on the facility size and design and the rate of solution flow through the facility. In practice, this time ranges from about 2 to 8 hours for plants that are able to reduce suspended solids to about 25 mg/l or less.

Precipitation of Metal Sulfides

Applicability. The sulfides of metals are much less soluble than their corresponding hydroxides. However, direct precipitation of metal ions with hydrogen sulfide or sodium sulfide involves the problem of excess sulfide ion which can then become an additional pollutant parameter. A sulfide precipitation system has recently been developed that avoids the possibility of excess sulfide ion being present in treated effluent. Iron sulfide, which itself has a very small solubility, is used as the reagent to precipitate copper, zinc, and nickel sulfides of even lower solubility. Experimental results are shown in Table 25 indicating that low concentrations can be achieved with sulfide precipitation even when metals are complexed with ammonia.

The disposal of sulfide solid wastes is a serious and unsolved problem. Unlike the metal oxides, metal sulfides, in the presence of air, decompose to sulfates and the metal ions can thereby be solublized. This commonly happens to ferrous sulfide as a result of coal mining operations and contamination of streams with acid and iron is a result. However, there is insufficient information available to determine whether any significant oxidation will occur with mixed metal sulfide sludges disposed of properly on landsites. The lower solubility of metal sulfides should reduce the amount leached directly into rainwater. Therefore, if significant oxidation is found to occur, means will have to be found to contain the sulfide precipitates or insolublize them by some system such as the Chemfix Process.

Practical Operating Systems. Plant 9-2 is precipitating cadmium as the sulfide.

Demonstration Status. The process described is still being developed, and it is anticipated that a demonstration plant will be built and operating in the near future.

Combined Metal Precipitation and Cyanide
Destruction-Proprietary Process A

TABLE 25   COMPARISON OF SOLUBLE POLLUTANT
PARAMETERS AFTER PRECIPITATION
BY IRON SULFIDE OR BY HYDROLYSIS

Waste composition in ppm	Pollutant residues from--	
	Sulfide precipitation in ppm	Hydroxide precipitation in ppm
Unknown	Cu, 0.1	0.8
	Zn, negligible	2.0
Cu, 100	Cu, 1.8	95.8
Ni, 7.7		5.9
NH_3, 475		
NH_3, 475	Cu, 0.4	1.0
	Ni, 2.0	2.0
Cr(VI), 4.8	Cr(VI), negligible	0.05
Zn, 3.5	Zn, 0.03	2.0

Applicability. This process is applicable to zinc and cadmium cyanide solutions. The metal hydroxide is precipitated and cyanide is decomposed. Applicability depends upon deciding whether the products of cyanide decomposition are suitable for discharge or not. The effluent is considered suitable for discharge to sewers in some states. A modified Kastone Process may be applicable to copper cyanide.

Process Principles and Equipment. Cyanide in zinc and cadmium plating baths is destroyed by a mixture of formalin and hydrogen according to the formula:

$$3CN^- + 2H_2O_2 + HCOH + 2H_2O = CNO^- + OH^- + NH_3$$

$$+ H_2C(OH) CONH_2) \text{ (glycolic acid amide)}.$$
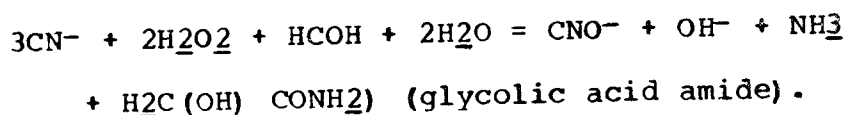
The metal hydroxide is also precipitated. The hydrogen peroxide is contained in the reagent (41%) which contains stabilizers and additives to promote the reactions and help in settling the metal hydroxide precipitate. The process may be carried out on a batch or continuous basis, and is particularly convenient for the small shop. However, the glycolic acid generated is not a desirable constituent for discharge to streams and the use of the Kastone Process should be restricted to plants discharging to sewers.

Figure 7 shows the apparatus for batch treatment. To be economical the rinse water should contain at least 55 ppm of cyanide, and sufficient counter-flow rinses are normally installed to assure a sufficient cyanide concentration. The typical treated effluent contains 0.1 mg/l of cyanide and 1 to 2 mg/l of zinc. Table 26 shows an analysis of the products for decomposing 794 ppm of cyanide.

Practical Operating Systems. This process is well established as a practical means for pollution control and is being used in approximately 30 installations.

Chemical Treatment of Effluents From Specific
Process Operations

Constituents

Iron. Iron baths have relatively simple compositions and neutralization of waste water constituents will reduce the soluble iron concentration well below 1 mg/l. Ferric chloride is a common constituent in such baths and is used as a flocculating agent in clarification systems for Phase I

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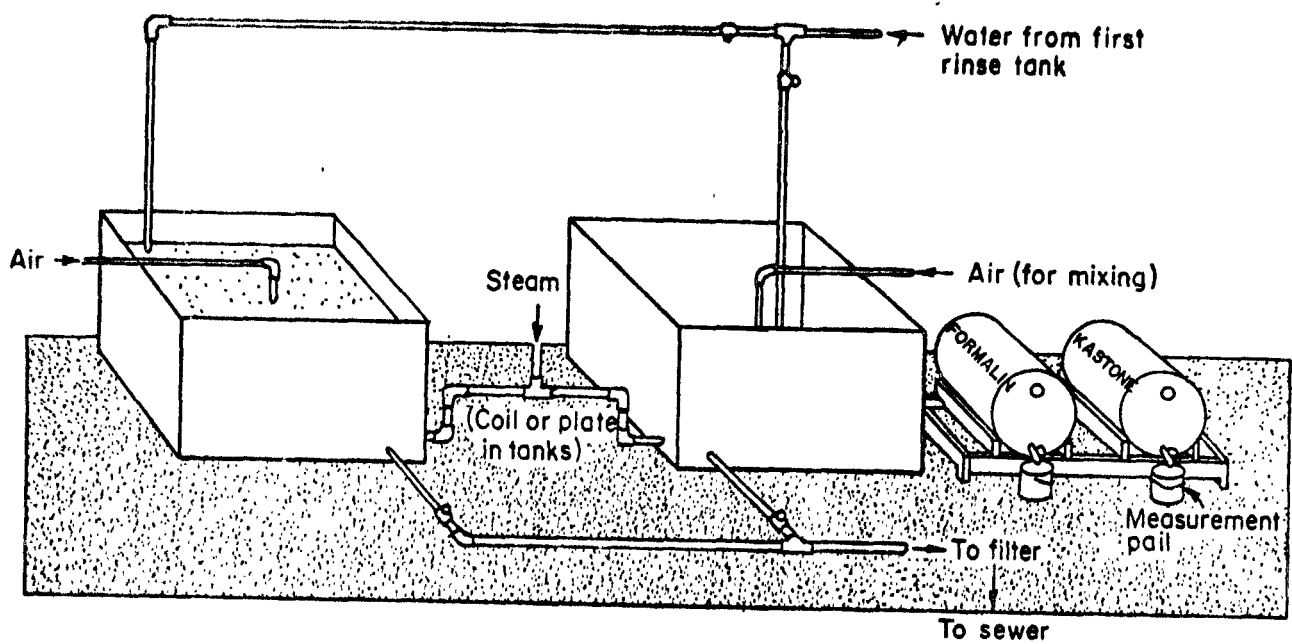
FIGURE 7. BATCH TREATMENT OF CYANIDE RINSE WATERS BY THE KASTONE PROCESS

TABLE 26   DECOMPOSITION PRODUCTS OF CYANIDE IN
RINSE WATER[1] FROM A CYANIDE ZINC
ELECTROPLATING OPERATION AFTER TREATMENT
WITH "KASTONE"[2] PEROXYGEN COMPOUND

Products Formed by Treatment	Amount Formed		
	Actual ppm	Cyanide Equivalent ppm	percent
Cyanate	351	265	33
Ammonia (free			
Dissolved	57	164	21
Volatilized[3]	32	91	11
Combined Ammonia			
Calc'd as NH_3	95		
Calc'd as glycolic		274	35
acid amide	419		
		794	100

(1)   Analysis of water before treatment:
        Cyanide *   794 ppm
        Cyanate * 336 ppm
        Ammonia *   41 ppm

  * Cyanide calculated as NaCN, cyanate as NaOCN, and
ammonia as NH_3.

(2)   Du Pont trademark.

(3)   Not determined; estimated by difference.

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metals following neutralization, to give an effluent suitable for discharge. The waste waters (dilute acid) and the concentrated plating baths (concentrated but weakly acidic) enter the waste treatment system via the "dilute acid-strong acid" streams of Figure 2.

Cadmium. After oxidation of cyanide or in noncyanide waste water, cadmium can be precipitated as the hydroxide by adjustment of pH. The waste water and strong solution discharge streams are shown as "weak cyanide" and "strong cyanide" in Figure 2. Alkalinity has a significant effect on solubility of cadmium. The theoretical solubility values according to Pourbaix are approximately

pH	Solubility mg/l
8	3000
9	30
10	0.03
11	0.003 (minimum)

Therefore, soluble cadmium might not be reduced to a low level by coprecipitation with Cr, Ni, Cr, Zn at pH 8 to 9. Should a pH of 11 be used, there is danger that the zinc concentration in the effluent will be too high. Consideration of the above theoretical data suggests that cadmium might not be reduced to a low level when coprecipitated with Cu, Ni, Cr, Zn at pH 8 to 9. The insolubility of cadmium carbonate suggests that precipitations with soda ash may reduce soluble cadmium to very low levels in effluent. Since many combined waste waters contain some carbonate it is very possible that cadmium carbonate rather than cadmium hydroxide is precipitated when waste waters are neutralized with caustic or lime. Some reported values that seem unrealistically low for hydroxide precipitation may be achieved by this mechanism. Cadmium sulfide is very insoluble (solubility product $K = 10^{-29}$), so that a precipitation system based upon sulfides, combined with efficient removal of dissolved solids, may provide acceptable effluent. A schematic of the treatment scheme is shown in Figure 8. In this figure, the cadmium sulfide sludge is recovered. If segregated treatment of a cadmium stream is required, the best way of holding the sludge may be to ship it to a metal recovery unit, or convert it to a form suitable for return to the plating bath.

Alternative to recovering sulfide precipitate, an evaporator can be installed to recover plating bath and reusable water.
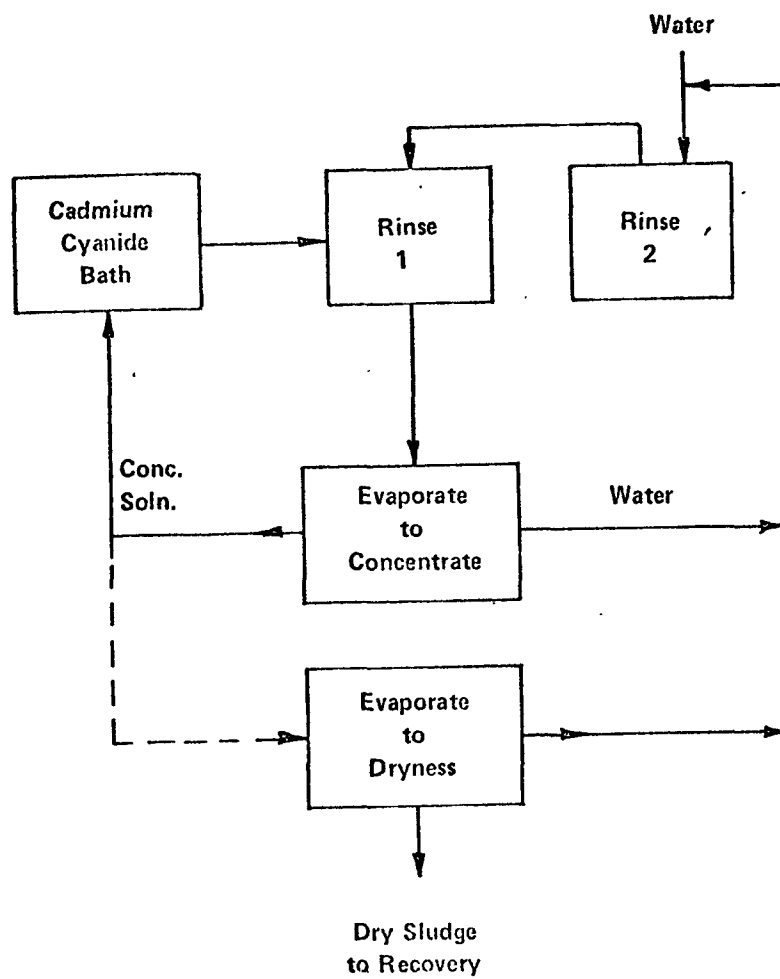
FIGURE 8 SCHEMATIC OF CADMIUM WASTEWATER
TREATMENT WITH MINIMUM SOLID
DISPOSAL

A small bleed-off may be required to decrease contaminants in the plating bath, as shown in Figure 9.

When cadmium plating is done in noncyanide baths, the waste treatment is the same except that the cyanide oxidation step is omitted. Fluoborate containing wastes come from a small amount of cadmium plating. Fluoborate is covered in a separate section.

Lead. There is a theoretical possibility that an adequately low concentration of dissolved lead cannot be achieved by pH adjustment. However, operating data show that low levels are attainable. Pourbaix gives the following solubility data for lead hydroxides.

pH	Solubility mg/l
8	500
9	6
9.4	3 (minimum)

The chloride and sulfate are too soluble to achieve a sufficiently low lead concentration, but sulfide precipitation should reduce the concentration adequately. Lead carbonates and basic carbonates have low solubilities and therefore carbonate present incidentally in the neutralization process or deliberately added may reduce lead to low levels in effluent. The problem of suspended solids remains. Sludge would most appropriately be sent to a metal recovery unit or be converted to a form suitable for return to the plating bath. Waste treatment operations are similar to those shown for cadmium in Figures 8 and 9, omitting the cyanide oxidation. Lead plating wastes contain fluoborate which is covered in a subsequent section.

Tin. The tin concentration can be reduced to low levels by neutralization between pH 8 and 9 whether the tin is present in the divalent form from acid baths or the quadrivalent form from alkaline baths. Therefore, chemical treatment is adequate for this constituent. In principle, the sulfide precipitation method, as discussed for cadmium and lead, is applicable to tin.

Copper Alloys. Copper alloy plating contributes copper, zinc, and tin ions to waste water, all of which are amenable to chemical treatment, as discussed for these metals alone.

Processes
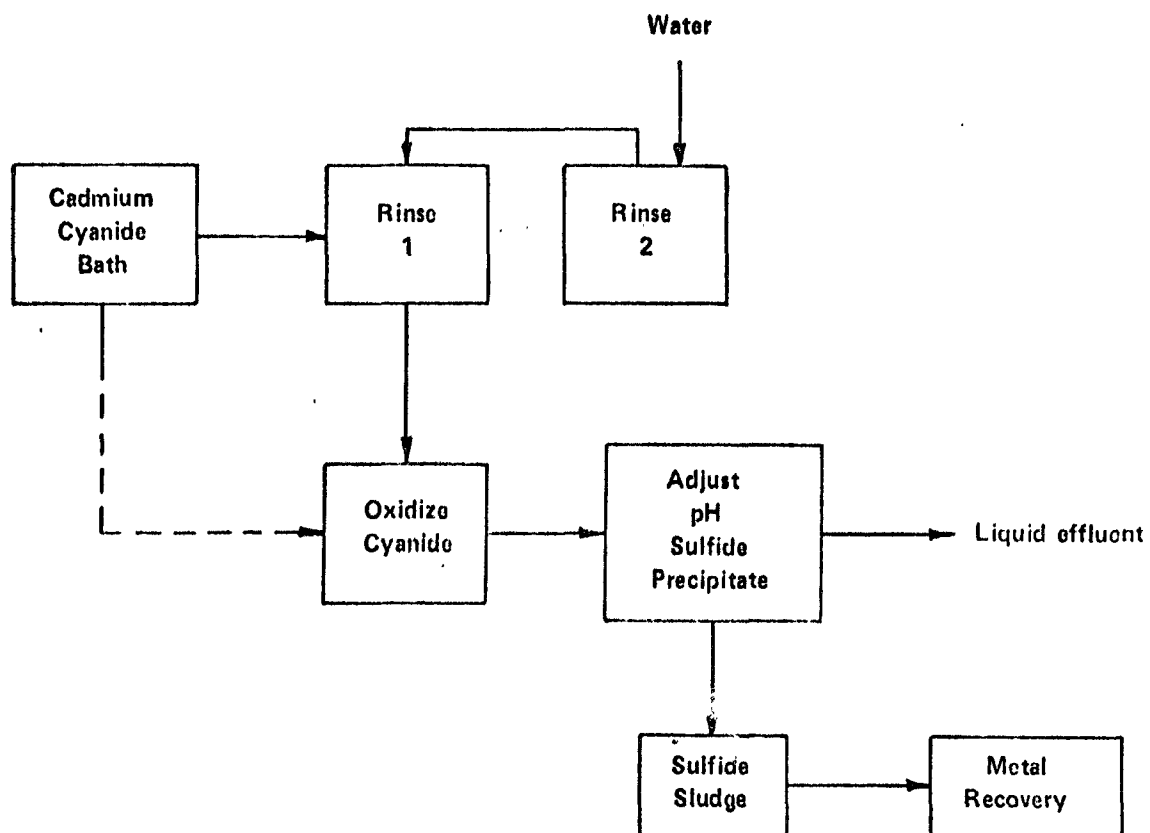
FIGURE 9 SCHEMATIC FOR SULFIDE PRECIPITATION
OF CADMIUM IN WASTEWATERS

Fluoborate. Since several of the plating baths (those for lead, tin, and their alloys) contain the fluoborate ion, the applicability of chemical treatment to remove this ion from liquid effluent is of interest. Upon dilution the fluoborate hydrolyzes:

$$BF_4^- + H_2O = HF + BF_3 + OH^-.$$

The BF_3 is very stable.

Thus, the problem is to reduce the concentration of HF in the waste water. The fluoride may be precipitated with lime, but the concentration can be reduced only to approximately 15 mg/l. This suggests that fluoborate plating baths be operated as closed-loop systems with recovery by evaporation, and that spills and leaks be segregated so that they can be treated separately. In this way, the fluoride discharged in liquid effluent can be held to a very small amount.

Wire and Strip. Effluent constituents from copper, nickel, chromium, zinc, and tin plating of wire and strip are amenable to the same chemical treatment methods as discussed previously.

Activation and Catalyzing. Chemical precipitation is the method generally used for treating wastes from these operations for preparing plastics and nonconductors for plating. Rinse waters contain tin for activating and palladium from catalyzing operations. Waste Waters are segregated and treated separately by neutralization and precipitation. The tin is precipitated at pH 8 and removed by settling or filtration. The palladium is precipitated at pH 8 to 9 and recovered by settling or filtration.

Immersion Plating. The waste water constituents in rinses from immersion plating are essentially the same as the constituents from electroplating wastes for the same metals plated. Waste Water treatment may be either batch or continuous, precipitated solids being removed by settling or filtration. Acids are neutralized to pH 6-9 when heavy metals are precipitated as hydroxides. The sludge is disposed of in the same way as is sludge from treatment of waste water from electroplating the same metal. Cyanide is destroyed by chlorine oxidation in alkaline solutions.

Anodizing. Rinse waters are neutralized with lime to precipitate aluminum, zinc, copper, chromium as Cr^{+3} after Cr^{+6} is reduced, phosphate, and fluoride, as shown in the schematic in Figure 10. A ferric iron salt is added to
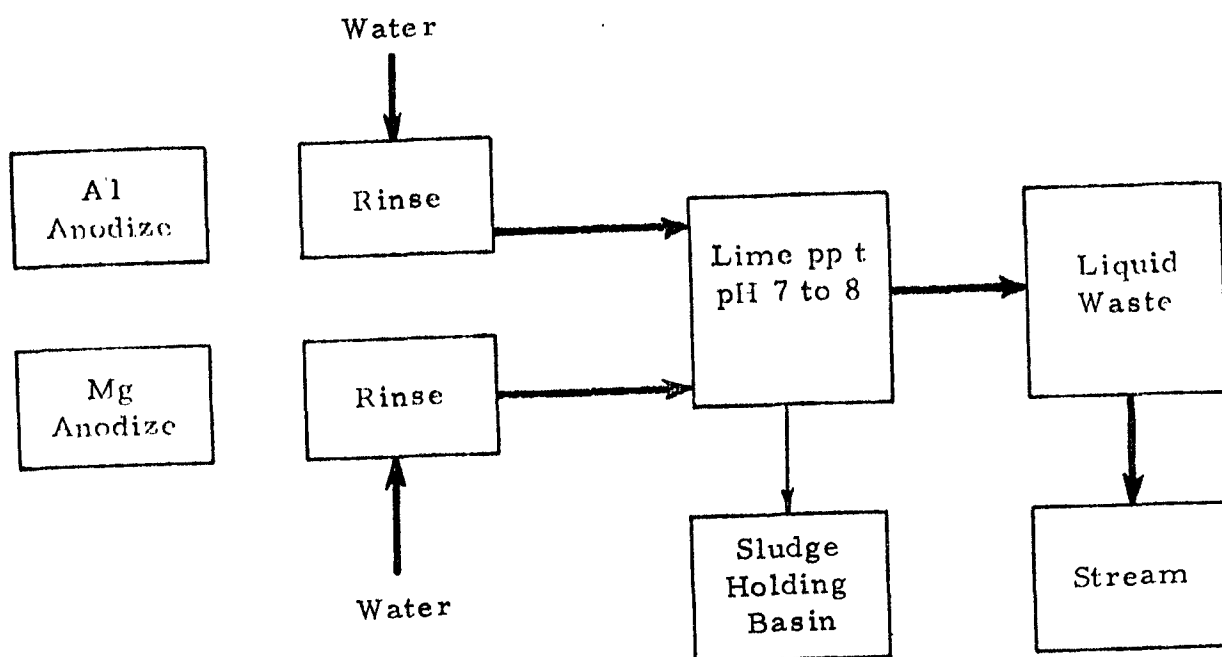
FIGURE 10   SCHEMATIC FOR CHEMICAL TREATMENT OF WASTEWATERS
             FROM ANODIZING OPERATION

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flocculate the precipitated hydroxides of the metals. Aluminum phosphate precipitates when these two ions are in the same neutral solution. Clarification by settling of sludge and liquid overflow is both batch and continuous, depending on effluent water volume. Aluminum concentration is reported to be reduced to 2 mg/l or less by chemical treatment (Edwards and Burrell, p 174) with 0.5 mg/l being reported. Reduction of magnesium concentration to 2 mg/l level would probably require a pH in excess of 10. Orthophosphate is reported as a trace and fluoride as 1.5 to 2.0 mg/l in effluent.

Conversion Coatings. Effluents from chromating operations are amenable to chemical treatment to reduce the hexavalent chromium and precipitate trivalent hydroxide as done in treating waste water from chromium plating. Phosphates from phosphating operations can be reduced to the 1 mg/l level by addition of aluminum ions. Removal of phosphate can occur when aluminum sulfate is added to the clarifier as a flocculating agent. Heavy metals, such as iron and zinc, derived from the basis metals and solution formulations, are removed by neutralization and precipitation.

Chemical Milling. Both alkaline and acid waste waters are involved and contain metals depending on the basis materials being processed. Aluminum is milled in concentrated caustic solution containing proprietary additives that are not disclosed. Water remaining after neutralization of aluminum chemical milling wastes is beneficial to municipal sewage treatments plants that remove phosphates by precipitation. Steel and other alloys (nonaluminum) are milled in acidic solutions. The acidic waste waters are neutralized and heavy metals are precipitated by the same techniques as for analogous waste water in other metal finishing operations.

Etching. Neutralization and chemical precipitation are used to remove metals as for the same metals in other metal finishing operations. If the waste water contains chromium (from etching of stainless steel), reduction is not necessary because the chromium is present in the trivalent form. Because the etching solutions become depleted with use, they are regenerated. Regeneration is most effective in decreasing copper waste from etching or printed circuits. The cupric chloride solutions are electrolyzed in a closed-loop scheme to electrodeposit the excess copper and reoxidize the solutions. Copper etchants containing chromate, NH_4OH to pH 9 to 11, chloride and acetates are used for etching printed circuits. These are now being handled by metal recovery plants. Ammonium persulfate

etchants and peroxide-sulfuric acid etchants are also common and copper can be recovered from them.

Water Conservation Through Control Technology

The volume of effluent is reduced if water is conserved during rinsing operations. The solubility limit of effluent constituents is essentially constant, so that a reduction in the effluent volume accomplishes a reduction in the amount of effluent constituents discharged. Water conservation can be accomplished by in-plant process modifications requiring little capital or new equipment, materials substitutions, and good housekeeping practice. Further water conservation is obtained by installing counterflow rinse tanks and ion-exchange, evaporative recovery, or reverse osmosis systems. Other systems that may accomplish water conservation are freezing, electrodialysis, electrolytic stripping, carbon adsorption, and liquid-liquid extraction.

Process Modifications

Substitution of low-concentration metal finishing solutions for high-concentration baths has been adopted in recent years, principally for reducing the cost of chemicals used for cyanide destruction. The dilute solutions require less water for rinsing when electroplating parts are transferred to rinse tanks. Assuming a 50 percent reduction in total dissolved solids in the plating solution and two rinse tanks in series, a 30 percent reduction in rinse water requirements is achieved. Since Water constituents requiring treatment are reduced by the same amount. Adverse effects in terms of lower efficiency and reduced productivity per unit facility may be encountered when dilution is adopted to conserve rinse water and reduce waste water constituents requiring treatment, unless other factors affecting plating rate are modified to adjust for the effects of dilution. Thus, dilution should not be adopted before a complete analysis is made of all pertinent factors.

The advent of effluent limitations is expected to encourage research and development on other processes that will eliminate or reduce water waste. A dry process for applying chromate coatings, which is currently being developed, may prove useful for such a purpose, for example. Chemical vapor deposition processes partially developed a few years ago may be revived for plating hard chromium.

Material Substitutions

Noncyanide solutions, which have been developed for metal finishing operations in place of cyanide solutions, reduce the costs of treatment by eliminating cyanide destruction, but do not eliminate treatment to precipitate and separate the metals. The chelating agents employed in some non-cyanide baths to keep the metal in soluble form are precipitated when rinse water waste is treated with lime to precipitate the metals, but other agents such as ethylene diamine tetraacetic acid inhibit the precipitation of zinc and contribute organic matter to the treated water waste. Thus, the applicability of the noncyanide solutions as replacements for cyanide baths must be considered carefully in the light of the effluent limitation guidelines recommended in this document.

Trivalent chromium baths have recently been introduced to the electroplating industry. They eliminate the need for sulfur dioxide reduction of waste water associated with chromium plating. The trivalent chromium baths appear to have other advantages for decorative plating such as better throwing power, current efficiency and plating rate. The dark color of the deposits is cited as a disadvantage by some purchasers, however. Nevertheless, this process modification may ultimately prove to be significant for reducing waste treatment costs. No details have been released on the treatment required for minimizing the soluble chromium concentration in treated effluent, however.

Good Housekeeping Practices

Good housekeeping practices that reduce the waste generated in metal finishing facilities include the following:

(1) Maintain racks and rack coatings to prevent the transfer of chemicals from one operation to another. (Loose rack coatings are noteworthy as an example of poor practice.)

(2) Avoid overcrowding parts on a rack, which inhibits drainage when parts are removed from a process solutions.

(3) Plug all floor exits to the sewer and contain spills in segregated curbed areas or trenches, which can be drained to direct the spills to rinse water effluent with the same chemicals.

(4) Wash all filters, pumps and other auxiliary equipment in curbed areas or trenches,

which can be drained to direct the wash
water to a compatible holding tank or
rinse water stream.

(5)   Install anti-syphon devices on all inlet
      water lines to process tanks.

(6)   Inspect and maintain heating and cooling coils
      to avoid leaks.

(7)   Inspect and maintain all piping installed for
      waste water flow, including piping from fume
      scrubbers.

Water Conservation by Reducing Dragout

Dragout.   Dragout is defined as solution on the workpiece
carried beyond the edge of the processing tank. The dragout
of concentrated solution from the processing tank can vary
over a wide range depending on the shape factor of the part.
A value of 16.3 liters/1000 sq m (0.4 gal/1000 sq ft) is
considered a minimum for vertical parts that are well
drained.   The practical range for parts of various shapes
that are well drained is about 40 to 400 liters/1000 sq m (1
to 10 gal/1000 sq ft).

Reduction of dragout with the above methods is not without
problems.   By returning chemicals to the processing tank,
impurities tend to build up in the processing solution.
Therefore, purification systems, such as ion exchange,
batch-chemical treatments, and/or electrolytic purification
are required to control impurities.   The purification
systems create some effluents which must be treated prior to
end-of-pipe discharge.

Water Conservation During Rinsing

Water conservation procedures that are used after processed
work is transferred to a rinse tank include (1) adding a
wetting agent to the rinse water, (2) installing air or
ultrasonic agitation and (3) installing counterflow rinses
whereby water exiting the last tank in the rinsing operation
becomes feed water for the preceding rinse. With two
counterflow rinses, water consumption is reduced 96 percent
in comparison with a single rinse, assuming that the dragout
solution mixes immediately with the rinse water.   This
assumption is incorrect.   While a part of the dragout
solution mixes rapidly with the rinse water, particularly if
agitation is used, the remaining film on the work comes off
rather slowly by a diffusion process. A more typical value

for the water reduction might be 85%, corresponding to a rinsing efficiency of approximately 90%. Use of conductivity meters in the final rinse provides automatic control of water use according to need. Rinse water flow is shut off automatically when no work is being processed. Excessive use of water can also be avoided by use of flow restrictors in the water feed lines.

Although multitank, counterflow rinsing imposes capital investment costs for tanks, pumps, and floor space, these costs are compensated for by a savings in water (and sewer) charges. Further incentive is provided when regulatory agencies require pollutional control. When end-of-process chemical treatment is used, design of wastetreatment facilities usually indicates the economic advantage of reducing rinse-water flow by installing two or more counterflow rinses.

Because waste treatment facilities are usually overdesigned to handle future expansion in production, there is a tendency to use the water flow capacity of the treatment facility whether or not it is needed for effective rinsing. Furthermore, rinse water flows set by an orifice are not always turned off when plating production is shut down. It is probably more economical to reduce rinse water usage by use of good rinsing practice than to increase watertreatment facilities in the event of an increase in production.

Rinsing can be carried out beyond the point consistent with good practice, even though there is an economic incentive to save water. The result is unnecessary pollution. Typical concentration levels permitted in the rinses following various process tanks, should not be decreased unless definite quality problems can be associated with the dissolved solids concentrations listed below for representative rinsing systems:

Process	Max Dissolved Solids in Final Rinse, mg/l
Alkaline cleaners	750
Acid cleaners, dips	750
Cyanide plating	37
Copper plating	37
Chromium plating	15
Nickel plating	37
Chromium bright dip	15
Chromate passivating	350-750

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A problem not considered in proposing a maximum dissolved solids in the final rinse, is the dragin of these rinses into a subsequent processing operation. If the dragin attained from the concentration proposed is deleterious to the following processing operation, the dissolved solids in the final rinse would have to be decreased or means for purification provided.

The following is an example, using various rinse combinations, of the reduction in water volume that can be obtained for rinsing assuming that the dragout and the rinse water mix immediately. A Watts-type plating bath typically contains 270,000 mg/l of total dissolved solids. Obtaining 37 mq/l in the final rinse requires 27,600 (7300 gallons) of rinse water if a single rinse tank is used, in order to dilute 3.78 liters (1 gallon) of a Watts-type plating solution containing 270 g/l of dissolved solids. The same degree of dilution in a final rinse tank may be obtained with less water by use of series and counterflow arrangement of two or more rinse tanks. If the tanks are arranged in series and fresh water is fed in parallel to each tank in equal volume, the ratio, r of rinse water to dragout is:

$$ r = n \ \frac{Co}{CF}^{\frac{1}{n}}, $$

where Co = concentration in the process solution
       CF = concentration in last rinse tank and
       n = number of rinse tanks.

If the tanks are arranged in the same way, but flow proceeds from the last rinse tank to the first rinse tank (counterflow),

$$ r = \frac{Co}{CF}^{\frac{1}{n}} . $$

By feeding water to counterflow tanks instead of in series, the reduction in water varies n-fold. Values of n calculated for several rinsing combinations, using the Co and CF values given above for a nickel bath are as follows:

Rinse Combination	Rinse Ratio, r
Single rinse	7300

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Two rinses, parallel feed   171

Three rinses, parallel feed   58.3

Two rinses, counterflow feed   85.5

Three rinses, counterflow feed   19.5

There is a significant reduction in water use by addition of a second rinse tank, and at least two rinse tanks can be considered normal practice. These should best be fed in counterflow. Counterflow rinse tanks increase the concentration of a metal or other constituent in the first rinse tank following the plating or process bath. The water in the first rinse tank can be used to supply makeup water for the plating bath. As the concentration in the first rinse tank increases, more of the dragout from the plating bath can be returned to the bath in the makeup water, and less will require treatment and/or disposal. Therefore, the addition of countercurrent rinse tanks can decrease both the volume of water to be treated and the amount of dissolved metal that must be removed, at least in some cases. A problem not considered in using counterflow rinses is that the concentration in the first rinse tank can become so high that the diffusion of the dragout from the film on the workpiece can be slowed considerably and, therefore, the rinsing efficiency decreased substantially. Therefore, the more countercurrent rinse tanks that are used, the less accurate is the calculation assuming that the dragout and rinse water mix immediately.

The rate of evaporation from the plating bath is a factor in determining how much makeup water must be added. Operating a bath at a higher temperature will allow more of the dragout to be returned to the bath because of the higher rate of evaporation. However, the temperature at which a bath may be operated is sometimes limited because of the decomposition of bath components. Progress has been made in developing bath components that allow higher bath temperatures to be used. For example, brighteners for zinc cyanide baths have been developed which allow bath operation at 50 C (120 F) as compared to 32 C (90 F). The new brighteners permit the return of more of the dragout to the plating bath and a lessened load on the waste treatment system, in addition to what other processing advantages they may offer.

Advanced Treatment Technologies

Ion Exchange

Applicability. Ion exchange is currently a practical commercially accepted method for the in-process treatment of (1) raw water, (2) processing baths, (3) rinse waters. Raw water is treated to provide deionized water for both makeup and critical final rinsing operations. Plating baths are treated to remove impurities, i.e., removal of nickel ions from a chromic acid bath with a cation exchange resin. Rinse waters are treated to provide water that can be returned to the process solution. The concentrated regenerant can be chemically treated more easily than the original volume of rinse water and in some cases the chemicals can be recovered and returned to the bath. The in-process treatment of chromium and nickel plating effluents by ion-exchange techniques are the more economically attractive treatment operations currently being carried out. Ion exchange also is beginning to find increased use in combination with evaporative and reverse osmosis systems for the processing of metal finishing rinse waters.

Advantages and Limitations. Some advantages of ion exchange for treatment of plating effluents are as follows:

(1) Ion exchange is an economically attractive method for the removal of small amounts of metallic impurities from rinse waters and/or the concentration for recovery of expensive processing chemicals.

(2) Ion exchange permits the recirculation of a high-quality water for reuse in the rinsing operations, thus saving on water consumption.

(3) Ion exchange concentrates processing bath chemicals for easier handling, treatment, subsequent recovery, or disposal operations.

Some limitations or disadvantages of ion exchange for treatment of process effluents follow:

(1) The limited capacity of parallel bed ion exchange systems means that relatively large installations are necessary to provide the exchange capability needed between regeneration cycles. Continuous ion exchange units reduce the size compared to dual-bed units.

(2)   Parallel-bed ion exchange systems require
        periodic regeneration with expenditures
        for regenerant chemicals. Unless regeneration
        is carried out systematically or continuous
        ion exchange units are used, leakage of
        undesirable components through the resin
        bed may occur. In addition, the usual
        treatment methods must be employed to
        dispose of the regenerated materials.

(3)   Cyanide generally tends to adversely affect
        the resin performance because of tightly
        held metal cyanide complexes on strongly
        basic anion resins, so that processing of
        cyanide effluents (except for very dilute
        solutions) does not appear practical at
        the present time.

(4)   Resins, which are not highly cross-linked
        (or macroreticular), slowly deteriorate with
        use under oxidizing conditions.

Process Principles and Equipment. Ion exchange involves a
reversible interchange of ions between a solid phase and a
liquid phase. There is no permanent or substantial change
in the structure of the solid resin particles. The capacity
of an ion exchange material is equal to the number of fixed
ionic sites that can enter into an ion exchange reaction,
and is usually expressed as milliequivalents per gram of
substance. Ion exchange resins can perform several
different operations in the processing of waste water,
including:

(1)   Transformation of ionic species
(2)   Removal of ions
(3)   Concentration of ions.

The performance of some of these functions is illustrated in
Figure 11, which is a generalized schematic presentation of
the application of ion exchange to treatment of electro-
plating effluents. In practice, the solutions to be treated
by ion exchange are generally filtered to remove solids such
as precipitated metals, soaps, etc., which could
mechanically clog the resin bed. Oils, organic wetting
agents, brighteners, etc., which might foul the resins, are
removed by passage through carbon filters.

During processing, the granular ion exchange resin in the
column exchanges one of its ions for one of those in the
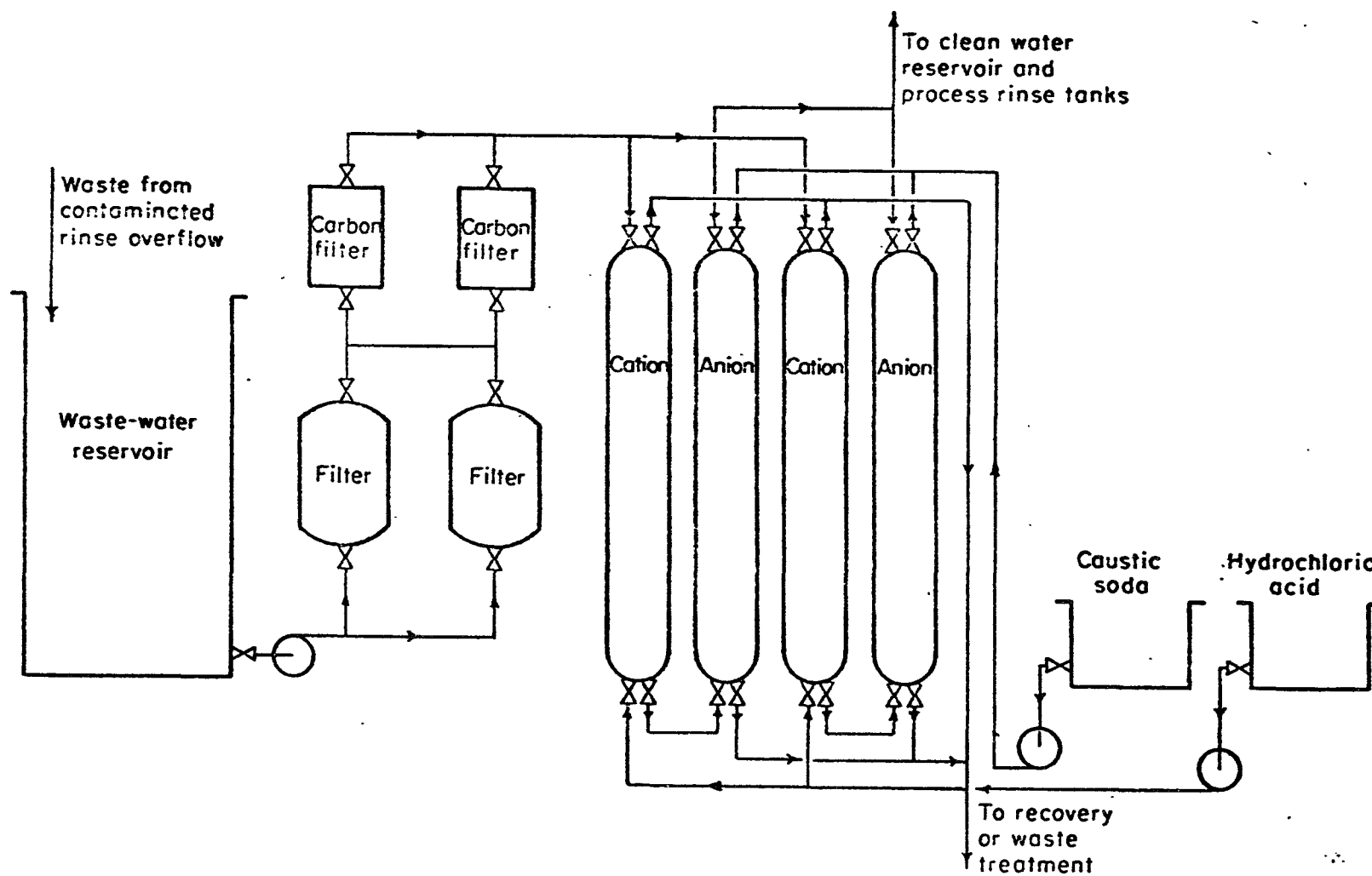
FIGURE 11 SCHEMATIC PRESENTATION OF ION-EXCHANGE APPLICATION FOR PLATING-EFFLUENT TREATMENT (7,25)

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rinse water or other solution being treated. This process continues until the solution being treated exhausts the resin. When this happens, solution flow is transferred to another column with fresh resin. Meanwhile, the exhausted resin is regenerated by another chemical which replaces the ions given up in the ion exchange operation, thus converting the resin back to its original composition. With a four-column installation consisting of two parallel dual-bed units, as shown in Figure 11, the ion exchange process can be applied continuously by utilizing the regenerated units while the exhausted units are being regenerated.

Most ion exchange systems depend upon regenerating with acid and base to form the acid and base forms of the resin. These are capable of exchanging with and thereby removing from solution both heavy metals and dissolved salts such as sodium chloride. However, resins can be regenerated with salts, i.e., sodium chloride to form sodium and chloride forms of the resin. These will exchange with heavy metals but not the soluble salts. Since exchange capacity is reserved for heavy metals only, the frequency of regeneration is decreased as is the cost of heavy metal removed.

Practical Operating Systems. The Phase I report described systems in use to remove nickel ions and trivalent chromium ion from chromium plating baths. The more dilute baths for producing chromium conversion coating are treated in a similar manner to remove, zinc ions. Aluminum is removed from chromic acid anodizing baths, and from phosphoric acid baths used for bright dipping. Cyanides may also be removed, in a 3-bed system, consisting of strongly acidic, weakly basic, and strongly basic ion exchangers. The system provides ease of regeneration and little chance of cyanide leaking through. The three-bed system has been in commercial operation in Europe and only recently introduced in the US. Several of the systems are being installed one of which will be supported to a limited extent under an EPA grant to obtain performance and economic information.

Demonstration Status. An ion exchange system using a short 30-minute cycle, including a 3 to 4-minute back wash to recover chromic acid from rinse waters has been in operation for over a year. The resin undergoes very little performance deterioration since the chromic acid is not deeply absorbed into the resin during such a short cycle.

Another system under development uses an ion exchange column to achieve separation of components in much the same manner that chromatographic columns are used. For example, a

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solution for bright dip.... of aluminum, containing phosphoric acid and aluminum ions... is fed through a strongly basic ion exchange column. The phosphate ions interact with the ion exchange sites and flow of the phosphoric acid is retarded in comparison to that of the aluminum ions, which flow unimpeded through the column. Water, which may be considered a very weak base, is adequate for regenerating the ion exchange resin and eluting the phosphoric acid with much of the aluminum removed. The phosphoric acid is returned to the brightening bath.

Evaporative Recovery

Applicability. When rinse water from one type of bath is distilled in an evaporative unit, the concentrate may be returned to the plating bath and the distillate to the corresponding rinse tank, which is useful for closing the loop on a single plating operation. The economics of distillation, from the standpoint of either investment or operating costs imposes a constraint on the size range of distillation equipment. Units with a capacity of the order of 300 gph are used in practice. Such a low rate of flow of rinse water is achieved in many plating operations only by the use of at least three countercurrent rinses, which by itself reduces the waste water. Evaporative recovery units for all of the rinse cycles would reduce the effluent to zero. So far, recovery units have been installed on rinse tanks following plating baths in order to recover plating chemicals and return them to the bath and thereby reduce plating costs. The units have not been installed on cleaner or acid dip lines because the cost of chemicals is not sufficient to make recovery worthwhile, and the build up of contaminants, i.e. oil and grease makes use of a closed system difficult.

Evaporation is a firmly established industrial procedure for recovering plating chemicals and water from plating waste effluents. Commercial units for handling zinc, copper, nickel, chromium, and other metal plating baths have been operating successfully and economically for periods of one to 10 years or longer. Packaged units for evaporative treatment of plating wastes are available from some manufacturers.

At least 100 evaporative units have been installed, which means that their use is indeed limited to a very small percentage of the shops. Nevertheless, announcements of new installations and savings through their use keep recurring and evaporative recovery appears to be a method that will grow in use. However, if such units are to pay off

strictly on the basis of savings in chemicals such factors as value of the chemicals, their concentration in the process bath, and the dragout rate are important in determining whether a savings is possible

Advantages and Limitations. The following are some of the advantages of using evaporation for handling plating waste effluents:

(1) Recovers expensive plating chemicals, which were either lost by discharge to a sewer or effluent which would have to be treated or destroyed prior to disposal; chemicals concentrated to plating strength can be returned to the plating tank.

(2) Recovers distilled water for reuse in the rinse operations, thus lowering water and sewer disposal.

(3) Eliminates or greatly minimizes the amount of sludge formed during chemical treatment and eliminates or reduces the amount requiring disposal by hauling or lagooning.

(4) The use of vacuum allows evaporation to accur at relatively low temperatures (e.g., 110°F) so that destruction of cyanides or other heat-sensitive materials is lessened.

(5) The technology of evaporators (conventional and vapor recompression units) is firmly established, so their capabilities are well known and their performance should be readily predictable and adaptable to plating effluent handling.

Some of the limitations or disadvantages of evaporative recovery systems are given below:

(1) The rinse water saving (e.g., 1100 l/hr (300 gph)) is rather small, and by itself does not significantly lighten the rinse water load on the final chemical treatment plant.

(2) Evaporative units have relatively high capital and operating costs, especially for the vacuum units. Steam and coolant water are required.

(3) The evaporative units are fairly complex and require highly trained personnel to operate

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and maintain them.

(4) Separate units are required for handling the waste effluent from each line, since various solutions, such as zinc, nickel, copper, chromium, cannot be mixed for chemical recovery.

(5) As with all closed-loop systems, evaporation in most cases results in a build-up of impurities which must be taken care of by a bleed stream or directly in the closed-loop system.

The advantages offered by evaporative recovery often outweigh the disadvantages. Evaporative recovery is a promising and economical method currently available for handling plating waste effluents and limiting treatment plant size. Where existing chemical treatment (cyanide destruction, chromate reduction, and chemical precipitation) facilities are operating at less than capacity, the economics and practicality of installing new evaporative equipment must be closely evaluated. The small decrease in the rinse water effluent (e.g., 1100 l/hr (300 gph)) by itself does not warrant the installation of an evaporative system. The savings produced by the recovery of plating chemicals plays the significant role in judging the overall merits of the evaporative system for a specific operation.

Process Principles and Equipment. A representative closed loop system for recovery of chemicals and water from a plating line with a single-effect evaporator is shown in Figure 12. A single-effect evaporator concentrates flow from the rinse water holding tank. The concentrated rinse solution is returned to the final rinse tank. With the closed-loop system, no external rinse water is added except for makeup of atmospheric evaporation losses. The system is designed for recovering 100 percent of the chemicals, normally lost in dragout, for reuse in the plating process.

Single-, double-, and multiple-effect evaporators, and vapor-recompression evaporator units are used for handling plating effluent. Open-loop and combined evaporation (i.e., evaporation combined with ion exchange, reverse osmosis, or other systems) are also employed for handling plating effluent.

A single-effect evaporator is preferred, if relatively untrained operating personnel are involved, or low initial capital outlay is desired. It's the simplest in design and therefore the easiest to operate. However, it is less
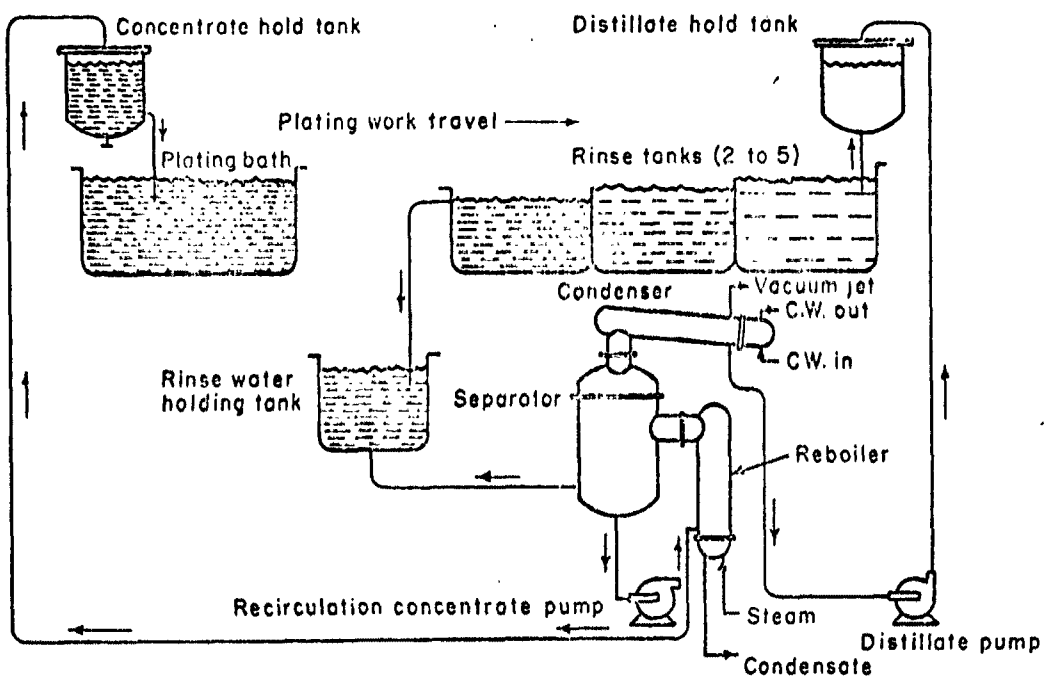
FIGURE 12 REPRESENTATIVE CLOSED-LOOP SYSTEM FOR
RECOVERY OF CHEMICALS AND WATER WITH
A SINGLE-EFFECT EVAPORATOR

economical than a double-effect or vapor recompression unit with regard to utility costs. A double-effect evaporator should be considered when lower operating cost is desired with a modest increase in capital investment.

A vapor-recompression evaporator should be considered if no steam or cooling water is available. Where utilities for a conventional steam evaporator are available, the high initial cost of the vapor recompression unit is not economically justified. Its operating cost is the lowest of the three systems. Its dependence on an expensive and complex mechanical compressor is the main disadvantage.

Some sources report considerable maintenance and down time and have dispensed with use of evaporator units. Other sources report little or no trouble and are very satisfied with the operation. It appears that the units can perform very satisfactorily if the installation is properly engineered, and if preventive maintenance and trouble-shooting are carried out by knowledgeable personnel.

In some instances, evaporation procedures must be used in combination with chemical or other methods in order to handle small amounts of impurity build-up (e.g., brighteners, carbonates, extraneous metal ions, etc., in closed loop operation) or for treatment of minor bleed-off streams (open-loop).

Atmospheric evaporation, which uses air flow through packing media in an evaporator, can concentrate plating solution such as chromic acid up to 480 g/l (4 lb/gal).

The Corning Glass Company has introduced a new concept for evaporative recovery. A glass shell and tube heat exchanger is mounted vertically and the solution is fed through the bottom. The boiling causes liquid surges that produce a "rising film" effect and an improvement in heat transfer. Vapor and liquid overflow the top of the tubes and are separated in a cyclone. Water with less than 0.05 ppm of chromic acid has been produced from chromium plating rinse water.

Practical Operating Systems. Systems operating on copper cyanide, nickel, chromium, and zinc cyanide plating lines were described in the Phase I Report. Systems have also been installed on lines using the following baths: brass cyanide, cadmium cyanide, Pb-Sn-Cu fluoborate, and gold. The practicality of using this system on cadmium and lead plating baths means there is at least one way of eliminating discharge of polluted water from these processes. Small

amounts of spills, leaks, if segregated, are evaporated to dryness, and the solid waste sent to a metal recovery unit. Falling film atmospheric evaporators have been installed in a few plants.

Demonstration Status. The "rising film" units are undergoing pilot and plant test.

Reverse Osmosis

Applicability. Reverse Osmosis uses a pressure differential across a membrane to separate a solution into a concentrate and a more dilute solution that may approach the purity of the solvent. It therefore accomplishes the same type of separation as distillation and has been applied in plating installations in the same manner. Small units under 300 gph have been installed to recover plating baths chemicals and make closed-loop operation of a line possible.

There are limitations on the acidity and alkalinity of solutions suitable for treatment by reverse osmosis that eliminate some alkaline baths and chromic acid baths from consideration unless modifications are made to the solutions prior to treatment. Another use of reverse osmosis is for end-of-process water recovery following chemical treatment. A recently designed system for Plant 11-22 offers promise that large capacity reverse osmosis systems are possible and therefore not subject to the size constraints of evaporative systems. If so, they should play a key role in the design of plants that will have no liquid effluent.

Most of the development work and commercial utilization of the reverse osmosis process, especially for desalination and water treatment and recovery, has occurred during the past 10 years. There is a steadily growing number of commercial installations in plants for concentration and recovery of plating chemicals along with recovery of water under essentially closed-loop conditions. Most of the existing commercial installations are for treatment of nickel plating solutions, since reverse osmosis is especially suited for handling nickel solutions and also because of the favorable economics associated with recovery and reuse of expensive nickel chemicals. Commercial reverse osmosis units for handling acid zinc and acid copper processes also have been installed, however. Laboratory pilot plant and full-scale in-plant studies directed at handling cyanide and chromium-type effluents are under way.

Reverse osmosis is especially useful for treating rinse water containing costly metals and other plating salts or

materials. Generally, the purified water is recycled to the rinse, and the concentrated salts to the plating bath. In instances where the concentrated salts cannot be recycled to the plating tank, considerable savings will be achieved because of the reduced amount of waste-containing water to be treated.

Advantages and Limitations. Some advantages of reverse osmosis for handling process effluents are as follows:

(1) Ability to concentrate dilute solutions for recovery of salts and chemicals

(2) Ability to recovery purified water for reuse

(3) Ability to operate under low power requirements (no latent heat or vaporization or fusion is required for effecting separations; the main energy requirement is for a high-pressure pump).

(4) Operation at ambient temperatures (e.g., about 60 to 90 F)

(5) Relatively small floor space requirement for compact high-capacity units.

Some limitations or disadvantages of the reverse osmosis process for treatment of process effluents are listed below:

(1) Limited temperature range for satisfactory operation. (For cellulose acetate systems the preferred limits are 65 to 85 F; higher temperatures will increase the rate of membrane hydrolysis, while lower temperature will result in decreased fluxes but not damage the membrane).

(2) Inability to handle certain solutions (strong oxidizing agents, solvents and other organic compounds can cause dissolution of the membrane).

(3) Poor rejection of some compounds (some compounds such as borates and organics of low molecular weight exhibit poor rejection).

(4) Fouling of membranes by slightly soluble components in solution.

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(5) Fouling of membranes by feeds high in sus-
pended solids (such feeds must be amenable
to solids separation before treatment by
reverse osmosis).

(6) Inability to treat highly concentrated
solutions (some concentrated solutions may
have initial osmotic pressures which are so
high that they either exceed available
operating pressures or are uneconomical to
treat).

Process Principles and Equipment. Water transport in
reverse osmosis (RO) is opposite to the water transport that
occurs in normal osmosis, where water flows from a less
concentrated solution to a more concentrated solution. In
reverse osmosis, the more concentrated solution is put under
pressure considerably greater than the osmotic pressure to
drive water across the membrane to the dilute stream while
leaving behind most of the dissolved salts. Salts in
plating baths such as nickel sulfate or copper sulfate can
be concentrated to solutions containing up to 15 percent of
the salt, by weight.

Membrane materials for reverse osmosis are fairly limited
and the bulk of the development work has been with specially
prepared cellulose acetate membranes, which can operate in a
pH range of 3 to 8 and are therefore useful for solutions
that are not strongly acid or alkaline, i.e., rinses from
Watts nickel baths. More recently, polyamide membranes have
been developed that will operate up to a pH of 12, and
several of these units are operating in plants for the
treatment of cyanide rinse waters.

Figure 13 is a schematic presentation of the reverse osmosis
process for treating plating-line effluent. The rinse
solution from a countercurrent rinse line is pumped through
a filter, where any suspended solids that could damage or
foul the membrane are removed. The rinse solution is then
raised to the operating pressure by a highpressure pump and
introduced into the reverse osmosis unit. The concentrated
salt stream is returned to the plating tank, while the
dilute permeate stream is returned to the second rinse tank.
Currently, several different configurations of membrane
support systems are in use in commercial reverse osmosis
units. These include plate and frame, tubular, spiral
wound, and hollow fine fiber designs.

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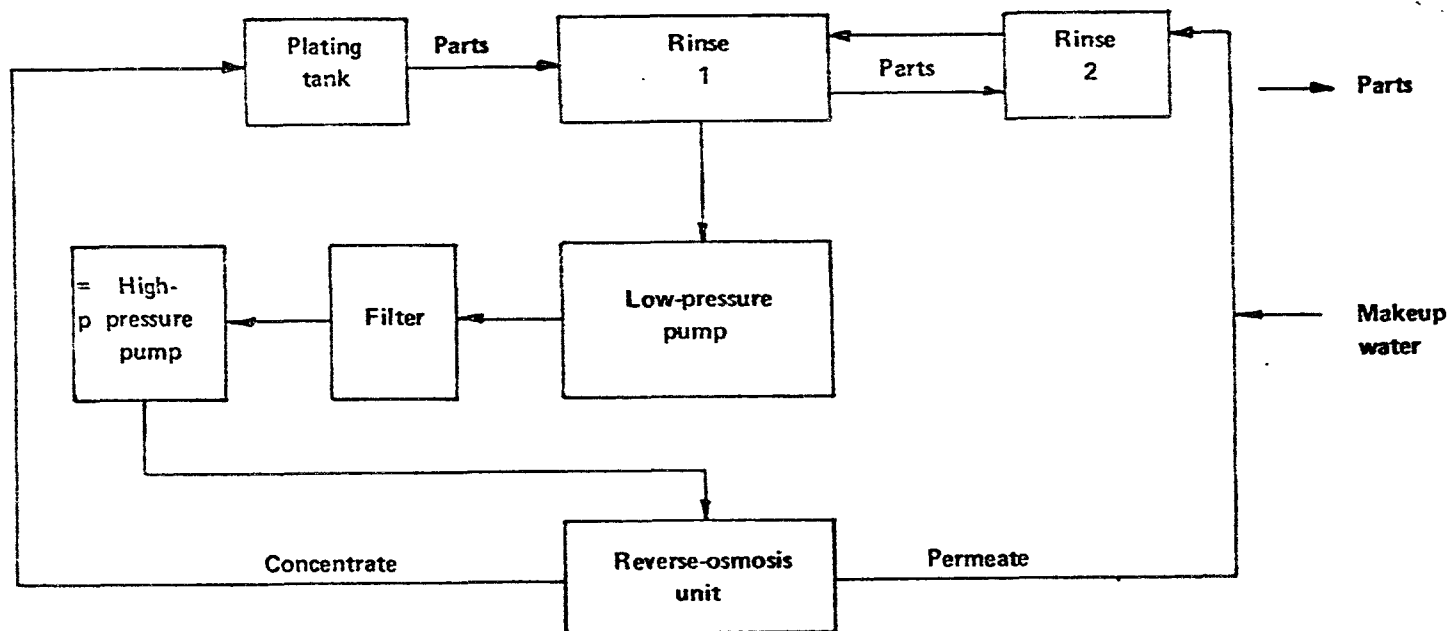
FIGURE 13   SCHEMATIC DIAGRAM OF THE REVERSE-OSMOSIS PROCESS
FOR TREATING PLATING EFFLUENTS

Practical Operating Systems. Reverse osmosis units are in operation for recovering nickel from rinse waters. The concentrate is returned to the plating bath.

Demonstration Status. The reverse osmosis units installed at the Rock Island Arsenal as part of an end-of-process water recovery system, remains to be demonstrated as a part of a total successful system. A project sponsored by the American Electroplating Society has demonstrated that cellulose acetate membranes can operate successfully on nickel and copper sulfate rinse waters and that spiral wound and hollow fiber polyamide membranes can be used to treat copper, zinc, and cadmium cyanide baths. A second phase of this study is a demonstration in a plating shop of a full scale reverse osmosis system on copper cyanide rinse water.

Freezing

Applicability. The freezing process would be capable of recovering metal and water values from plating rinse water to permit essentially closed-loop type operation if fully developed. The feasibility of using freezing for treatment of plating rinse waters was demonstrated on a laboratory scale using a mixed synthetic solution containing about 100 mg/l each of nickel, cadmium, chromium, and zinc, along with 30,000 mg/l of sodium chloride. Greater than 99.5 percent removal of the metallic ions was achieved in the experiments, with the purified water product containing less than 0.5 mg/l each of the individual plating metals. The separation tests were carried out using the 9500 l/hr (2500-gpd) pilot plant unit at Avco Systems Division, Wilmington, Massachusetts.

Process Principles and Equipment. The basic freezing process for concentration and recovery of water from plating effluents is similar to that used for recovery of fresh water from the sea. A schematic diagram of the treatment of plating rinses by the freezing process is shown in Figure 14. The contaminated reuse water is pumped through a heat exchanger (where it is cooled by melted product water) and into a freezer. An immiscible refrigerant (e.g., Freon) is mixed with the reuse water. As the refrigerant evaporates, a slurry of ice and concentrated solution is formed. The refrigerant vapor is pumped out of the freezer with a compressor. The slurry is pumped from the freezer to a counterwasher, where the concentrated solution adhering to the ice crystals is washed off.

The counterwasher is a vertical vessel with a screened outlet located midway between top and bottom. Upon entering

Cooling
water

Pump

Melter/
condenser

Compressor

Refrigerant
vapor

Purified
water

Counter
washer

Concentrate

Refrigerant
(Freon)

Freezer

To plating tank

Slurry

Pump
Pump

To rinse
tank

Contaminated rinse

Heat exchanger

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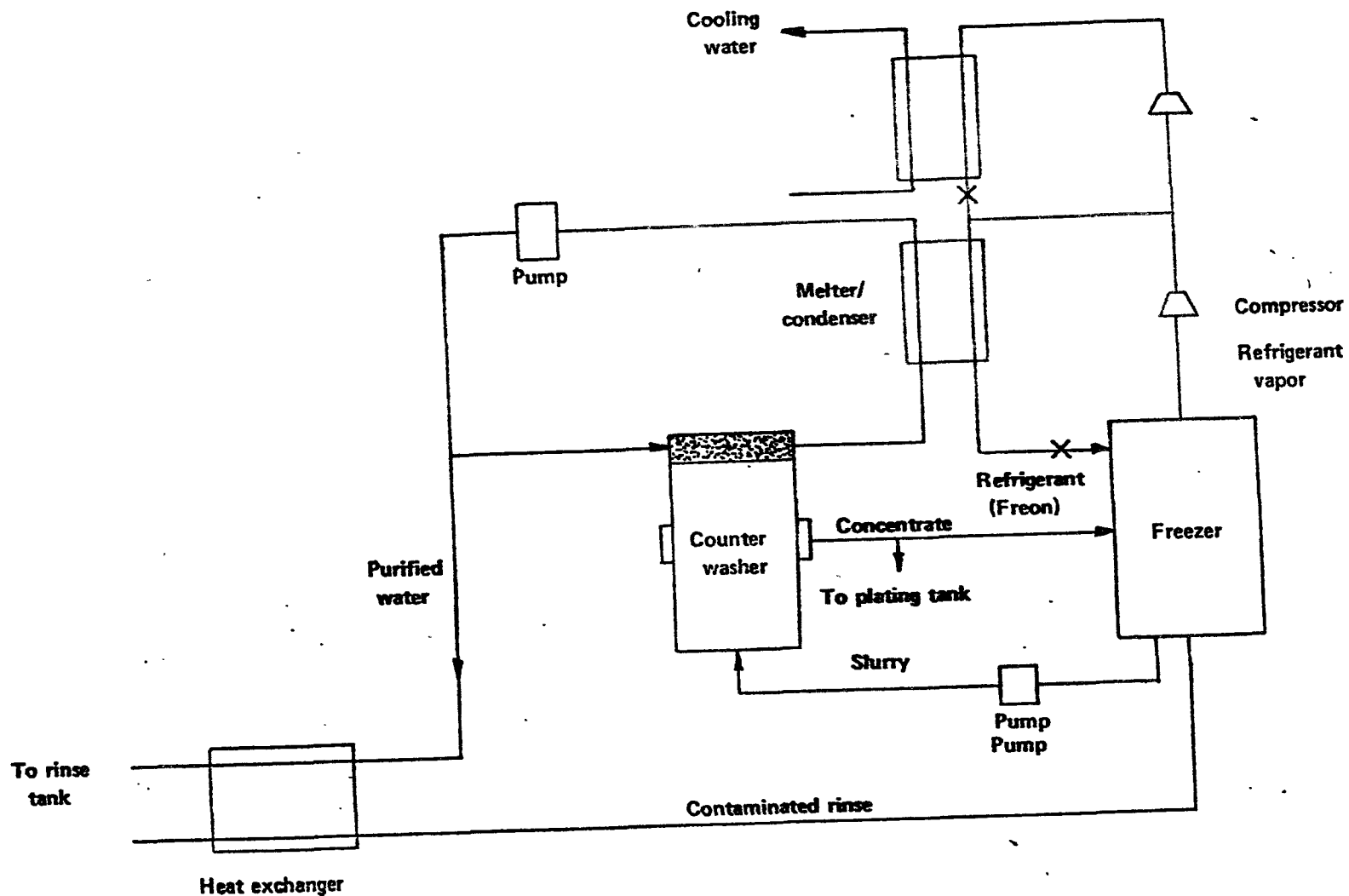
FIGURE 14 SCHEMATIC DIAGRAM OF FREEZING PROCESS FOR RECOVERY
OF WATER AND CHEMICALS FROM PLATING RINSES (37,38)

the bottom, the slurry forms a porous plug. The solution flows upward through the plug and leaves the counterwasher through the screen. A small fraction of the purified product water (less than 5 percent) flows countercurrently to the ice plug to wash off concentrated solution adhering to the ice. The ice is pumped to a condenser and melted by the release of heat from the refrigerant vapor which had been originally evaporated to produce the ice, and which had been heated by compression to a saturation temperature higher then the melting point of the ice.

Because of the pump work, compressor work, and incomplete heat exchange, a greater amount of refrigerant is vaporized than can be condensed by the melting ice. Consequently, a heat removal system is needed to maintain thermal equilibrium. This system consists of a compressor which raises the temperature and pressure of the excess vapor to a point where it will condense on contact with ambient cooling water.

The freezing process offers several advantages over some other techniques. Because concentration takes place by freezing of the water in direct contact with the refrigerant, there is no heat-transfer surface (as in evaporation) or membrane (as in reverse osmosis) to be fouled by the concentrate or other contaminants. Suspended solids do not affect the freezing process and are removed only as required by the end use to be made of the recovered products.

The heat of crystallization is about 1/7 the heat of vaporization, so that considerably less energy is transferred for freezing than for a comparable evaporation operation. Because freezing is a low-temperature process, there will be less of a corrosion problem than with evaporation, and less expensive materials of construction can be employed. The freezing process requires only electrical power, as opposed to the evaporation process which also requires steam generating equipment. The cost of the freezing method may be only 1/3 that for evaporative recovery.

A method of freeze drying metal finishing solutions has been demonstrated in the laboratory. Droplets of the solutions are injected into cold liquid-hexane where they are immediately frozen. The droplets were separated out and the water removed at subfreezing temperature. The method leaves a dry chemical residue, and the pure vaporized water could be recycled to process. The economics of the process on a practical scale are unknown.

Practical Operating Systems. No commercial utilization of freezing for treatment of waste water from metal finishing is known.

Demonstration Status. No demonstrations are in progress in metal finishing plants. However, a 9500 liters/day (2500 gpd) unit is in operation to demonstrate desalination of water.

Electrodialysis

Applicability. Electrodialysis removes both cations and anions from solution and is most effective with multi-valent ions. It is capable of reducing the concentration of heavy metal ions from solutions whether they are complex or not. Chromate and cyanide ions may also be removed.

Process Principles and Equipment. The simplest electrodialysis system consists of an insoluble anode and an insoluble cathode separated by an anion permeable membrane near the anode and a cation permeable membrane near the cathode. An anode chamber, cathode chamber, and middle chamber are thereby formed. Upon electrolysis anions pass from the middle chamber to the anode compartment and cations pass from the middle chamber to the cathode compartment. The concentration of salt in the central compartment is thereby decreased. By employing several anion and cation permeable membranes between the electrodes several chambers are created. A stream may then be run through several of these chambers in which the concentration is successively increased. The net effect is similar to that of a continuous moving bed ion exchange column with electrical energy used for regeneration rather than chemicals.

Practical Operating Systems. No practical operating systems have been reported. However, development has resulted in several demonstrations, discussed below.

Demonstration Status. Several demonstrations have shown that electrodialysis is a promising method. Further development and use of the method may be expected. Copper cyanide rinse water may be concentrated sufficiently to be returned to the bath by using two units on a double counterflow rinse system, i.e., between the first and second rinse tank and between the bath and first rinse tank. Copper may be recovered and chromic acid regenerated in a spent etching solution for printed circuits. The Metal Finishers Foundation has put priority on a future project on cyanide removal by electrodialysis.

Ion-Flotation Techniques

Applicability. Ion-Flotation techniques have not been developed for application to process rinse water effluents. If successfully developed into a practical method for effluent treatment, ion flotation offers possibilities of reducing the amount of water discharged by 60-90 percent for some operations. These savings are based on results of small-scale laboratory studies on solutions containing cyanides or hexavalent chromium.

Process Principles and Equipment. Separation of ions from aqueous solutions by a flotation principle is a concept first recognized about 25 to 30 years ago. In the ion-flotation operation a surface active ion with charge opposite to that of the ion to be concentrated is added to the solution and bubbles of air or other gas are introduced into the solution to form a froth of the surface-active materials. The foam is separated and collapses to form a scum containing an ion concentrate. Ion flotation combines the technologies of mineral flotation and ion exchange. A schematic diagram of an ion-flotation cell is shown in Figure 15.

Experimental results indicate that 90 percent of the hexavalent chromium in a 10 to 100 ppm solution can be removed with primary amine surface-active agents. However, the amine suffered deterioration when regenerated for reuse, since the removal efficiency dropped to 60 percent after two regenerations of the amine.

Grieves, et al., have demonstrated the feasibility of using ion flotation on dichromate solutions with a cationic surfactant (ethylhexadecyldimethylammonium bromide). A continuous operation with a retention time of 150 minutes was devised. The feed stream contained 50 mg/l of dichromate. Approximately 10 percent of the feed stream was foamed off to produce a solution containing 450 mg/l of dichromate, while the stripped solution contained 15 mg/l.

Cyanides have been removed from dilute solutions with mixed results. The extraction efficiency from a cadmium cyanide solution containing 10 ppm of cyanide was 57 percent, using primary, tertiary, and quaternary ammonium compounds as collectors. Extraction efficiencies for nickel and iron cyanide solutions were approximately 90 percent, but these systems are of relatively little interest.

Practical Operating Systems. There are no practical operating systems.

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Air in — Air out

Foam level

Foam concentrate
take-off

Solution level

Purified
solution
removal

Solution sampling
port

Injection port
for collector
agent
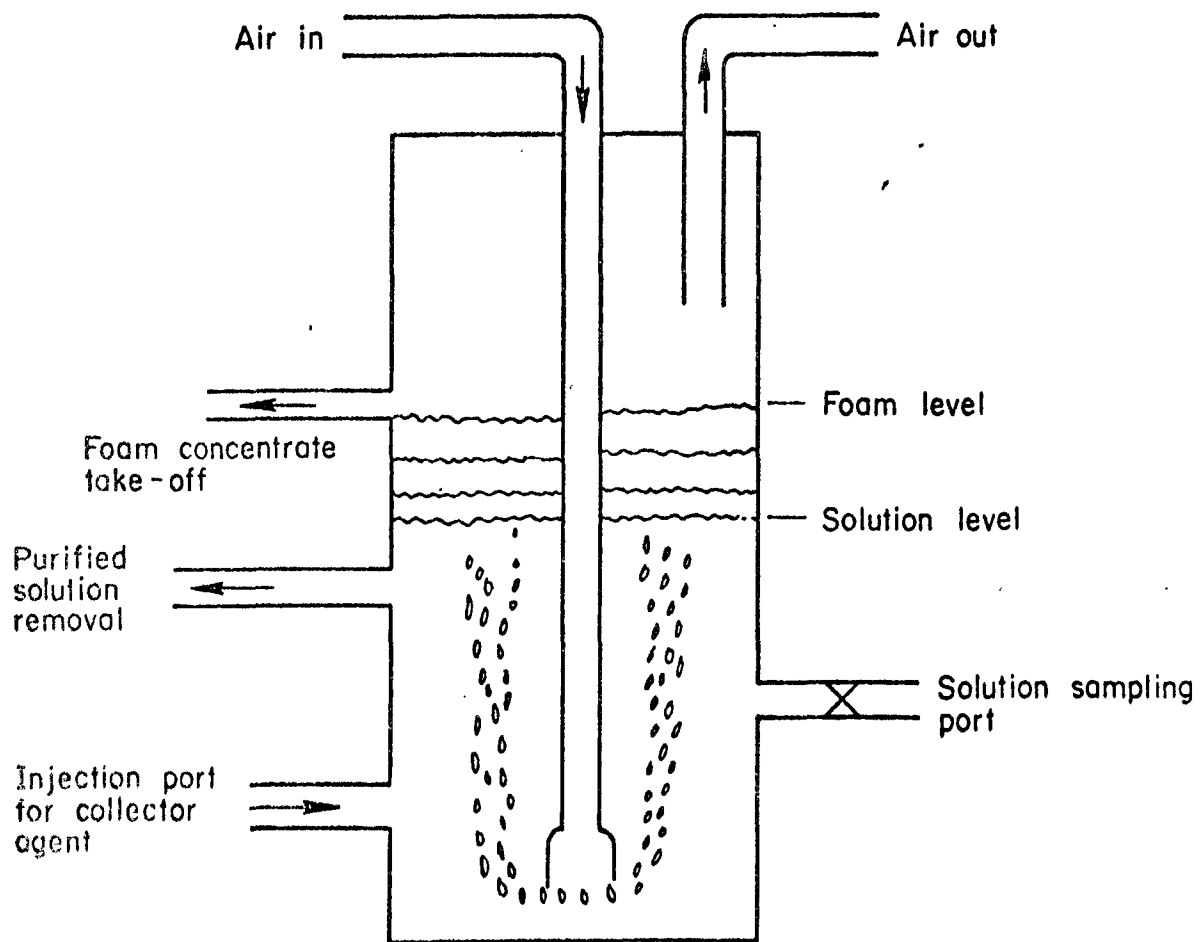
FIGURE 15 SCHEMATIC DIAGRAM OF ION-FLOTATION CELL
FOR TREATMENT OF PLATING EFFLUENT

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Demonstration Status. The process has not been demonstrated in an operating plant.

Electrolytic Stripping

Applicability. Electrolytic stripping is not in general use for removing heavy metals although some procedures have been employed for recovering precious metals.

Process Principles and Equipment. In order to strip a solution by electrodeposition it is necessary that the metallic ions in a dilute solution reach the cathode surface at a sufficient rate so that essentially all of the ions can be deposited in a reasonable time. Surfleet and Crowle have discussed several methods of accomplishing this. One method called the "integrated" system uses baffles in a tank to create a very long path through which the water may be recirculated at a high velocity. The method is suitable only for metals having a relatively high limiting current density for dilute solutions, such as gold, silver, and tin. The fluidized bed electrode is a bed of metal spheres or metal-coated glass spheres that is fluidized by pumping the dilute solution through it and causing an expansion of 5 to 10 percent. With spheres of 100 to 300 microns in diameter, a total geometric area of 75 cm^2/cm^3 is obtained. Thus, the current density is very low and the flow of electrolyte through the bed provides the forced convection to support high currents. Another system employs electrodes made of expanded metal and the turbulence around this structure enhances the rate of deposition of metal when solution is pumped past it. Turbulence and an increase in the rate of deposition at a plane electrode may also be promoted by filling the space between electrodes with a woven plastic screen, glass beads, etc.

In another system the electrode is introduced into a narrow gap between two porous carbon electrodes. The bulk of the solution (99%) is forced through the cathode where copper is deposited out. Predeposited copper on the anodic electrode is dissolved into the 1 percent of the electrolyte that permeates through this electrode and a copper concentrate is produced. The two electrodes are periodically reversed so that copper deposited from a large volume of solution is dissolved into a small volume of electrolyte. Copper in solution has been reduced from 670 mg/l to 0.55 mg/l in the cathode stream and concentrated to 44 g/l in the anode stream. A similar system has been used for depositing metallic impurities from strong caustic solutions.

Practical Operating Systems. There are many systems in operation for the recovery of precious metals.

Demonstration Status. The porous electrode system is still under development at the University of California and has been scaled up to handle 250 gpd of copper sulfate solution. Metal Finishers Foundation has established priority for a future project to remove zinc from effluent by electrodeposition.

Carbon Adsorption

Applicability. Activated carbon has been used for the adsorption of various materials from solution, including metal ions. Experimental data show that up to 98 percent of the chromium can be removed from waste water. The treated water can be recycled to the rinse tanks.

Process Principles and Equipment. The process relies upon the adsorption of metal ions on specific types of activated carbon. In the case of Chromium VI, a partial regeneration of the carbon can be accomplished with caustic solution followed by an acid wash treatment to remove residual caustic and condition and carbon bed for subsequent adsorption cycles. The equipment consists of holding tanks for the raw waste, pumps and piping to circulate the waste through adsorption columns similar to those used for ion exchange.

Practical Operating Systems. Systems based on adsorption and desorption are still under laboratory development and no practical operating systems are known.

Demonstration Status. Pilot plant equipment has been operated successfully in an electroplating plant treating chromium rinses at a flow rate of 19 liters/min (5 gpm) at concentrations from 100 to 820 mg/l hexavalent chromium. Adsorption was continued until the effluent reached concentrations of 10 ppm of Chromium VI.

Water Conservation by Liquid-Liquid Extraction

Applicability. Liquid-liquid extraction has been used on an experimental basis only for the extraction of hexavalent chromium from waste waters. The effect is to concentrate impurities in a smaller volume, which in turn will have to be treated by other means or suitably disposed of. The fully extracted aqueous phase may be recycled to the rinse tanks. Water savings from 50 to 73 percent appear to be possible.

Process Principles and Equipment. The metal-ion pollutant is reacted with an organic phase in acid solution, which separates readily from the aqueous phase. Metal is subsequently stripped from the organic phase with an alkaline solution. Hexavalent chromium, for example, has been extracted from waste water at pH 2 with tertiary and secondary amines dissolved in kerosene. After the reaction of the chromium with the amine and phase separation, the chromium is stripped with alkaline solution from the organic phase restoring the amine to its original composition. For liquid-liquid extraction to be feasible the following conditions would have to be met:

(1) The extraction of chromium should be virtually complete

(2) Reagent recovery by stripping would be efficient

(3) The stripping operation should produce a greatly concentrated solution

(4) The treated effluent solution should be essentially free from organic solvents

(5) Capital and operating costs should be reasonable.

The equipment required consists basically of mechanically agitated mixing and settling tanks, in which the phases are intimately dispersed in one vessel by agitation and then permitted to flow by gravity to a settling vessel for separation. Holding tanks for extractant and stripper and circulating pumps for these solutions, as well as the purified waste water, are necessary. Equipment for liquid-liquid extraction would also include horizontal and vertical columns, pulsed columns and centrifuges.

Practical Operating Systems. Liquid-liquid extraction systems are not known to be operating for treatment of metal finishing wastes.

Demonstration Status. Experimental evidence exists indicating that up to 99 percent of chromium can be successfully extracted from rinse waters containing 10 to 1000 mg/l of Cr^{6+}. With 10 ppm of Cr^{6+} in the rinse water, the treated effluent contained as little as 0.1 mg/l of the ion; with 100 ppm in rinse water concentration was reduced to 0.4 mg/l. Stripping was effective as long as the amines were not allowed in contact with the chromium for a prolonged period of time which would allow oxidation by Cr^{6+} ions.

The effluent, however, contained from 200 to 500 mg/l of kerosene, which is undersirable.

Methods of Achieving No Discharge of Pollutants

Although chemical methods of treating waste waters are achieving the low effluent discharges recorded in this report, they are not improvable to the point of achieving zero discharge of pollutants. Also the problem of recycling sludges or solid wastes remains. It is easy to design systems that will in principle close the process loop and prevent discharge. In practice, however, this can only be done with considerable forethought and experience, since closed systems are in general subject to impurity buildup. Progress in achieving no-discharge systems is likely to take place in a series of steps in which the amount of discharge is consistently reduced until it is negligable.

A major problem with a series of metal finishing processes in a closed cycle is that of dragin. After a closed cycle has been run long enough any stagnant tank, i.e., a plating solution that is normally not discarded, will contain the same concentration of contaminant as the preceding tank in the cycle, the assumption being that the volume of dragin and dragout are equal. Therefore, if the final rinse following nickel plating contains 12 ppm of nickel and chromium plating follows, the chromium bath will ultimately contain 12 ppm of nickel. Nickel is frequently removed from chromium plating baths by ion exchange, but since the ion exchanger requires periodic regeneration, the regenerant must somehow be returned to the system if it is to be considered a closed one. The nickel in the regenerant might be recovered and returned to the nickel bath, but the dissolved solids, i.e., sodium sulfate, and sodium chloride are really excess products that cannot be completely returned to the process. While the main process loop may be closed, the secondary purification loops may be more difficult to close. With some process baths, it may not be possible to find a method for purification that is as adaptable as is ion exchange to the removal of nickel from a chromium bath. Alternatives then are to (1) develop processing baths that can tolerate the impurity buildup or (2) to design rinse systems in which the concentration of impurity in the final rinse tank is reduced to a tolerable level.

Some systems, designed to remove a specific impurity, are found to remove other components as well, which may require further treatment. An example of such a system is that used for removing carbonates from cyanide baths. Whether

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freezing or precipitation with calcium is used, the carbonates occlude and adsorb significant quantities of cyanide that must then be further treated, with the result that cyanide is not maintained in a closed system. Therefore, with present technology, it is likely that there will be some discharge from a process loop in spite of the best efforts that are made to close it. Some waste water effluent will be produced and the next consideration is how well a waste treatment system can be closed.

The effluent will contain heavy metals, cyanide, and chromate all of which can be treated to relatively low levels to give (1) liquid containing small amounts of heavy metals, cyanide and chromate and larger amounts of soluble salts such as sulfate and chlorides, and (2) sludge containing heavy metals, phosphate, carbonates, flocculating agents, etc. The liquid, if large in volume may be concentrated further by evaporation, reverse osmosis, ion exchange, or some other process followed by a further purification to reduce the heavy metal effluent to a negligable value. The liquid may alternatively be passed through a salt loaded ion-exchange column to remove all traces of heavy metals and yield an effluent containing essentially soluble salts that may be discharged to the ocean if not to a stream or sewage facility. Alternatively, solutions of soluble salts may be evaporated to dryness and the solid salt contained or fixed in cement, etc.

Sludge, obtained either directly from waste water or from ion-exchange regenerants, cleaning and pickling baths, etc., would need to be reclaimed for metal values or the metal salts separated out for return to process tanks in order to provide a closed or recycle system.

Thus, to attain the ideal of providing a system where input is energy and materials and output is solely a finished product will require further research and development, considerable ingenuity, and expert engineering and design. However, the capability for progressing towards this goal is available.

COSTS, ENERGY, AND NONWATER QUALITY ASPECTS

Introduction

In this section, costs associated with the degree of effluent reduction that can be achieved by exemplary treatment methods are discussed. The nonwater quality aspects concerning disposal of solid waste and the energy impact of the waste treatment technologies also are discussed.

Treatment and Control Costs

Chemical Treatment to Achieve Low Levels of Pollutants

BPCTCA Limitations (Table 1). Costs associated with control technology consistent with the exemplary practice of chemical treatment in 26 plants averaged $1.06/1000 liters treated with a standard deviation of $1.91/1000 liters (Table 27). Operating costs include a cost of capital equal to 8 percent of the investment and depreciation equal to 10 percent of the investment.

The operating cost of waste treatment as a percent of cost of metal finishing for 13 companies is 7.4 percent with a standard deviation of 5.4 percent. The figures were arrived at from estimates by the plants themselves concerning the relative cost of waste treatment.

The plot in Figure 16 shows the large variation in investment costs for individual plants and reflects the large deviations reported above. Thus, there are no typical plants. Rather, costs are highly dependent upon local conditions. Costs were calculated in terms of volume of waste water treated rather than surface area finished because costs are believed to be more closely related to the volume treated. Water use is highly variable and relating waste treatment costs to area finished would have provided even more variable results. For a nominal water use of 80 liters/sq m (2 g/sq ft) the cost of $1.06/1000 liters is equivalent to $0.085/sq m ($.0079/sq ft).

In addition to the cost data collected from plants with waste treatment facilities, costs were also estimated by modeling metal finishing facilities together with waste treatment facilities providing effluent that would meet

TABLE 27   COSTS FOR WASTE TREATMENT FACILITIES

Plant No.	Processes	Investment (1971)	Operating Cost/Year (1971)	Hours Operated Per Year	Volume to Treatment Plant, l/hr	Volume to Treatment Plant, l/yr	Invest- ment/ l/hr	Operating Cost/ 1000 liters	Treating Cost/ Processing Cost
20-24	Plating Common Metals	34,000	14,195	4,800	26,497	1.271×10^8	$ 1.28	$ 0.30	
33-24	Plating Common Metals	172,000	80,430	4,000	15,897	6.359×10^7	10.82	1.26	14
33-26	Plating Common Metals	27,932	10,694	7,200	4,163	2.997×10^7	6.71	0.36	
36-12	Plating Com.,Prec.Metals	200,000	72,809	7,520	6,813	5.123×10^7	29.36	1.42	
33-2	Plating Prec. Metals	25,000	14,968	1,025	12,615	1.293×10^7	1.98	1.15	3
33-4	Plating Prec. Metals	66,000	18,205	1,800	24,224	4.366×10^7	2.72	0.42	
8-5	Plating Prec. Metals	300,000	115,995	2,400	34,065	8.176×10^7	8.81	1.42	6
6-37	Plating Prec. Metals	400,000	121,905	2,250	113,562	2.555×10^8	3.52	0.48	
19-11	Plating Prec. Metals	110,000	49,985	2,000	45,424	9.08×10^7	2.42	0.55	
15-3	Plating Prec. Metals	66,113	25,552	2,000	57,727	1.154×10^8	1.15	0.22	
9-7	Electropainting, Anodizing	100,000	32,249	4,000	30,851	1.234×10^8	3.24	0.26	
4-9	Electroless Plating	45,325	45,312	4,000	1,741	6.964×10^6	26.03	6.51	5
4-5	Electroless Plating	23,292	9,746	4,000	3,985	1.594×10^7	5.84	0.61	0.65
30-19	Electroless Plating	217,725	168,312	8,400	104,087	8.743×10^8	2.09	0.19	7
8-8	Electroless Plating	51,679	13,430	4,000*	36,794	1.471×10^8	1.40	0.09	
33-22	Anodizing	193,846	51,515	4,000	9,000	3.600×10^7	21.54	1.43	7.5
33-23	Anodizing	167,575	49,658	6,000	18,925	1.136×10^8	8.85	0.44	13
20-22	Anodizing	180,902	113,379	6,000	79,485	4.769×10^8	2.28	0.24	~7
20-20	Anodizing	155,300	64,485	7,200	129,447	9.320×10^8	1.20	0.09	16
33-35	Anodizing	125,000	28,244	7,200	3,028	2.180×10^7	41.28	1.30	3
20-23	Anodizing	123,414	41,855	6,000	22,712	1.362×10^8	5.43	0.31	7.4
4-8	Chemical Milling	17,459	16,675	4,800	7,570	3.634×10^7	2.31	0.46	1.0
5-35	Chemical Milling	300,000	83,758	2,000	7,570	1.514×10^7	39.63	5.53	18
9-2	Chemical Milling	2,008,000	685,847	6,000	189,250	1.136×10^9	15.36	0.60	
23-7	Chemical Milling	582,006	323,216	6,000	159,000	9.540×10^8	3.66	0.35	
36-13	Chemical Milling	29,232	11,313	3,850	6,813	2.623×10^7	4.29	0.43	1.4
33-30	Phosphating	94,500	29,726	3,600	54,509	1.962×10^8	1.73	0.30	4.4
19-24	Etching	295,615	120,211	2,000	6,813	1.362×10^7	43.39	8.83	
6-36	Immersion	58,983	15,702	2,250	11,356	2.555×10^7	5.19	0.62	
31-16	Printed Circuits	1,050,000	237,600	4,000	90,849	3.633×10^8	11.56	0.65	
46-4	Electropolishing	51,925	14,368	4,170	30,659	1.278×10^8	1.37	0.11	
33-29	Electromachining			4,000	22,710	9.084×10^7			

* Assumed 16 hours per day, 5 days per week.

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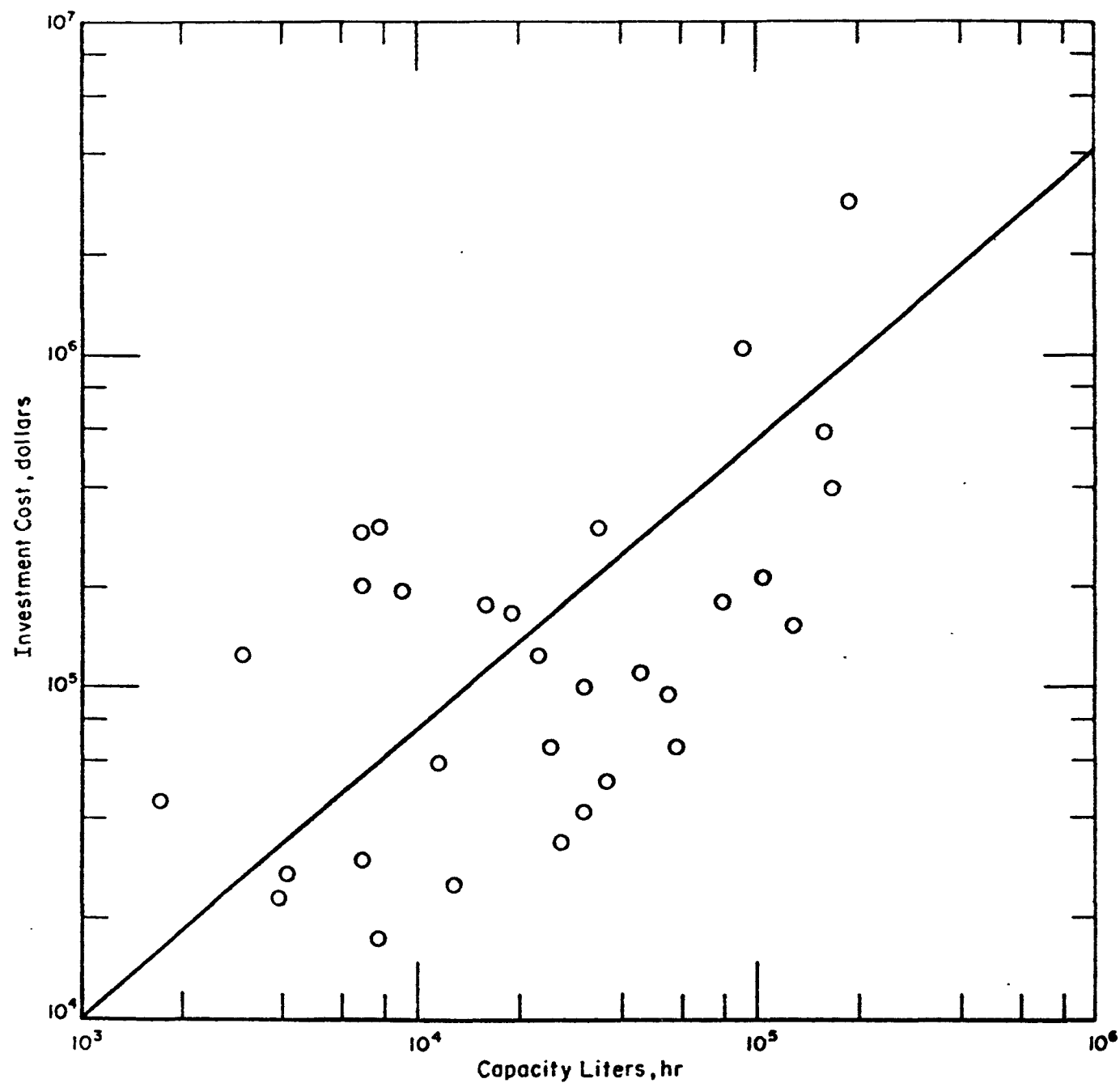
FIGURE 16   INVESTMENT COSTS OF WASTE TREATMENT PLANTS
WITH VARYING VOLUME CAPACITY

BPCTCA standards. By modeling plants it was possible to derive selfconsistent costs for various degrees of treatment and for various plant sizes. Plants were sized according to the number of employees, which is desirable if data are to be used for cost impact studies. Table 28 and 29 summarize the results of one cost estimate.

The lowest investment cost of $22,980 is for a 5-employee urban plant that precipitates heavy metals, does not treat cyanide or hexavalent chromium, and does not clarify. This plant also has the lowest operating cost of $12,294/yr. The highest investment cost of $378,455 is for a plant with 47 employees carrying out complete waste water treatment including clarification and filtering of sludge. This plant also has the highest operating cost of $157,894/yr. The operating cost probably could be reduced somewhat by using a filter press directly on the neutralized waste water. However, this technology is not as well established as that using a clarifier.

Costs per area are $1.02/1000 liters for the 5-man plant neutralizing only and $1.09/1000 liters for the 47-man plant doing complete waste treatment. These figures compare favorably with the $1.06/1000 liters average value for the plants listed in Table 28.

The operating costs as a function of plant size have been plotted in Figure 17 and show that in the size range studied costs are roughly linear with the number of employees. The makeup of the production processes varies somewhat, both with the extent of treatment and with plant size. Processes using cyanide or chromate were not included where treatment for cyanide and/or chromate was omitted. The smaller plants were assumed to be concerned with electroplating only while processes such as anodizing and electroless plating were confined to the largest plant. Even among the smaller plants there are some variations in plating processes. Some of the 5-man plants included cadmium plating as a specialty while the 10-man plant omitted cadmium but concentrated more on tin plating. The product mixes listed are only one of many sets that might have been chosen but reflect in general the amount of finishing that can be accomplished in the various sized plants with diverse operations. The amount of waste water to be treated, and the amount of waste produced are thus typical of the various size plants.

The productivity of a plant, measured in area processed/hour will vary with the process mix even though the number of employees is not changed. Thus, in Table 29 the 5-man plants that require only coprecipitation (A) or cyanide

TABLE 28   TREATMENT EQUIPMENT COSTS, VALUES IN U. S. DOLLARS, 1974

Item	5 Employees				10 Employees				20 Employees				47 Employees			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
A. Concrete Holding Pits	410	420	550	605	950	945	1,335	1,350	1,545	1,525	1,725	1,740	2,490	2,535	2,890	2,965
Valves, Controls, Monitors & Recorders	2,600	4,850	5,080	7,215	2,945	5,080	5,310	7,445	2,945	5,310	5,310	7,445	7,785	10,610	9,690	14,485
Stirrers	1,100	1,100	1,100	1,100	1,100	1,100	1,100	1,100	1,100	1,100	1,100	1,100	2,200	2,200	2,200	2,200
Pumps	3,740	4,770	4,845	6,300	4,940	6,390	6,800	7,890	5,650	7,110	7,880	12,340	9,300	11,610	11,880	12,740
Tanks	2,945	3,550	4,930	5,300	2,780	3,700	4,605	5,105	3,895	3,440	5,715	7,200	8,355	13,955	12,230	11,730
Clarifiers	12,550	12,550	14,900	14,900	19,100	19,000	22,400	22,400	25,400	25,400	28,000	28,000	47,100	47,100	49,600	50,600
Lagoons (Soil)	100	130	230	230	100	130	230	230	160	160	230	230	470	470	600	710
Polishing Filters	2,600	2,700	2,700	3,300	3,150	3,200	5,100	5,100	5,600	6,500	6,500	6,500	14,000	14,000	15,600	15,600
Evaporator	--	--	--	--	--	--	--	--	--	--	--	--	146,000	146,000	146,000	146,000
Ion-exchanger	--	--	--	--	--	--	--	--	--	--	--	--	550	550	--	--
Sulfonator	--	--	3,550	3,550	--	--	3,550	3,550	--	--	3,550	3,550	--	--	3,550	3,550
Chlorinator	--	3,550	--	3,550	--	3,550	--	3,550	--	3,550	--	3,550	--	3,550	--	3,550
Subtotal A	26,045	33,620	37,585	46,050	35,065	43,095	50,430	57,720	46,295	54,095	60,010	71,665	243,200	252,580	254,240	264,130
B. Treatment Building	3,990	5,910	8,160	9,960	9,660	11,760	15,060	16,710	13,020	18,540	19,050	21,180	29,520	33,150	44,370	45,360
Land Cost, Urban	245	365	500	610	595	720	925	1,025	795	1,135	1,170	1,300	1,810	2,030	2,720	2,780
Rural	50	75	100	125	120	145	185	205	160	230	235	260	365	410	545	560
Land Cost, Pits & Lagoons, Urban	40	30	30	45	225	185	285	275	240	370	300	310	475	520	765	805
Rural	10	10	10	10	45	40	60	55	45	75	60	65	95	105	155	160
Subtotal B																
Urban	4,275	6,305	8,690	10,615	10,480	12,665	16,270	18,010	14,025	20,045	20,520	22,790	31,805	35,700	47,855	48,945
Rural	4,050	5,995	8,270	10,095	9,825	11,945	15,305	16,970	13,225	18,845	19,345	21,505	29,980	33,665	45,070	46,080
C. Total A&B																
Urban	30,320	39,925	46,375	56,665	45,545	55,760	66,700	75,730	60,320	74,140	80,530	94,455	275,005	288,280	302,095	313,075
Rural	30,095	39,615	46,155	56,145	44,890	55,040	65,735	74,690	59,520	72,940	79,355	93,170	273,180	286,245	299,310	320,210
D. Equipment Installation	5,210	6,725	7,580	9,210	7,015	8,620	10,090	11,545	9,260	10,820	12,005	14,335	48,640	50,520	50,850	52,830
E. Total C&D Urban	35,530	46,650	54,155	65,875	52,560	64,380	76,790	87,275	69,580	84,960	92,535	108,790	323,645	338,800	352,945	365,905
Rural	35,305	46,340	53,735	65,355	51,905	63,660	75,825	86,235	68,780	83,760	91,360	107,505	321,820	336,765	350,160	363,040
C&D, Less Clarifier, Urban	22,980	34,100	39,255	50,975	33,460	45,380	54,390	64,875	44,180	59,560	64,535	80,790	276,545	291,700	303,335	315,305
F. Sludge Filter (Option)																
Urban	3,860	4,590	4,850	4,300	7,750	7,720	7,745	7,745	11,380	11,360	12,380	12,380	12,930	12,930	12,550	12,550
Rural	3,850	4,620	4,880	4,330	7,880	7,850	7,880	7,880	11,510	11,490	12,580	12,580	13,220	13,220	13,050	13,050
G. Total E&F																
Urban	39,390	51,240	59,005	70,175	60,310	72,100	84,535	95,020	80,960	96,300	104,915	121,170	336,575	351,730	365,495	378,455
Rural	39,195	50,960	58,615	69,685	59,785	71,510	83,705	94,115	80,290	95,250	103,940	120,085	335,040	349,985	363,210	376,090

A- Neutralization.

B - Cyanide oxidation plus neutralization.

C - Chromate reduction plus neutralization.

D - Cyanide oxidation chromate reduction, neutralization.

TABLE 29 ANNUAL OPERATING COSTS, WASTE TREATMENT, U. S. DOLLARS, 1974

No. of Employees	Process Rate m³/hr	Water Use l/hr	Treatment Type	Cost of Capital(1)	Depreciation(2)	Chemical Use	Labor(3)	Maintenance(4)	Electric Power(5)	Water & Sewer(6)	Sludge Removal(7)	Ion Exchange(8)	Evaporator Treatment(9)	Evaporator Save(10)	Credit Balance	Total(11) Urban	Total(11) Rural	No. Clarifier Urban	Total(12) Urban	Total(12) Rural
5	75	6,000	A	2,843	3,553	481	4,000	711	1,440	240	1,536	--	--	--	--	14,804	14,684	12,094	13,368	13,148
	75	6,000	B	3,772	4,665	3,366	4,000	933	1,440	240	864	--	--	--	--	19,340	19,120	16,730	18,376	18,236
	130	8,000	C	4,333	5,416	2,741	4,000	1,084	1,826	306	3,072	--	--	--	--	22,178	22,625	19,798	19,706	19,553
	130	8,000	D	5,270	6,588	4,589	4,000	1,318	1,826	306	2,016	--	--	--	--	25,913	25,760	22,933	23,847	23,744
10	170	13,000	A	4,205	5,256	1,582	12,000	1,052	2,277	380	2,208	--	--	--	--	28,959	28,769	25,139	26,751	26,561
	170	13,000	B	5,151	6,438	8,979	12,000	1,288	2,277	380	2,592	--	--	--	--	39,105	38,915	35,305	36,513	36,323
	230	18,400	C	6,144	7,679	4,655	12,000	1,536	2,409	402	5,184	--	--	--	--	40,009	39,808	35,610	34,825	34,624
	230	18,400	D	6,982	8,728	10,789	12,000	1,746	2,409	402	5,184	--	--	--	--	48,241	48,040	43,761	43,057	42,857
20	230	23,200	A	5,567	6,958	1,793	24,000	1,392	3,036	506	3,456	--	--	--	--	46,708	46,455	41,628	43,352	43,099
	230	23,200	B	6,737	8,496	11,831	24,000	1,700	3,036	506	3,456	--	--	--	--	59,822	59,569	54,742	56,366	56,113
	330	30,400	C	7,403	9,254	5,592	24,000	1,851	3,795	634	5,184	--	--	--	--	57,713	57,396	51,513	52,529	52,212
	330	30,400	D	8,704	10,879	15,413	24,000	2,176	3,795	634	5,184	--	--	--	--	70,785	70,468	65,125	65,601	65,284
27	635	54,800	A	25,892	32,365	4,990	32,000	5,500	11,503	1,918	10,464	550	8,080	11,828	3,748	121,434	120,475	112,014	130,970	130,011
	705	55,400	B	27,104	33,880	15,829	32,000	6,776	11,503	1,918	10,464	550	8,080	11,828	3,748	136,276	135,317	126,556	125,812	124,853
	775	61,600	C	28,236	35,295	10,110	32,000	7,059	11,285	2,258	8,679	--	8,080	11,828	3,748	131,174	130,045	121,254	122,495	121,366
	815	65,200	D	23,273	36,591	24,732	32,000	7,319	13,899	2,228	15,600	--	8,080	11,828	3,748	157,894	156,780	147,774	142,234	141,153

(1) 8 percent of investment
(2) 10 percent of investment
(3) $8.00/hr
(4) 2 percent of investment
(5) $0.012/kwh
(6) 0.25 – 0.25 ¢/1000 gallons of water added with treatment chemicals
(7) $0.17/gallon for sludge containing 4 percent solids
(8) Equal to investment costs
(9) Data from Pfaudler for 900 gal/hr evaporator
(10) Based on a dragout rate of 2 gal/1000 sq ft plated and a solution cost of 2.50/gallon
(11) Difference between urban and rural is the cost of sewage charge only
(12) Credited for the costs of sludge removal. Use in conjunction with Equipment Cost Data.

TABLE 30 INVESTMENT AND ANNUAL OPERATING COSTS FOR VARIOUS TYPES OF WASTE TREATMENT FOR REPRESENTATIVE AVERAGE PLANT (38 EMPLOYEES)(a)

Plant Source	Phase No.	Treatment System[a]	Electroplating Areas[b] Actual Production, m²/hr	Electroplating Areas[b] Processing Area, m²/hr	Capital Investment, dollars Building[c]	Capital Investment, dollars Land[d]	Capital Investment, dollars Instrument Equipment[e]	Capital Investment, dollars Total	Annual Depreciation[f], dollars	Annual Interest Charge[f], dollars	Labor[g], dollars	Maintenance Charge[h], dollars	Electric Power[i], dollars	Water and Sewer Charge[j], dollars	Chemicals Used[k], dollars	Sludge Disposal[l], dollars	Reverse Osmosis (R.O.) Operating Cost[m], dollars	Water and Sewer Savings with R.O.[i], dollars	R.O. Conc. Evaporator Operating Cost[n], dollars	Dried Salt Disposal Cost[i], dollars
Urban	I	Combined chemical treatment and precipitation	425	775	72,000	4700	142,500	219,200	21,900	17,540	29,000(a)	6,580	2500	1040	26,300	6460	--	--	--	--
Rural	I	Combined chemical treatment and precipitation	425	775	72,000	600	142,500	215,100	21,500	17,200	28,000(a)	6,450	2500	550	26,300	6460	--	--	--	--
Urban	IA	Combined chemical treatment and precipitation plus R.O. at end of line for zero liquid effluent discharge	425	775	86,000	8650	366,300	461,000	46,100	36,800	32,000	13,830	2800	1040	29,820	4400	15,700	9920	25,440	1670
Rural	IA	Combined chemical treatment and precipitation plus R.O. at end of line for zero liquid effluent discharge	425	775	86,000	1400	366,300	453,700	45,370	36,300	32,000	13,630	2800	520	29,820	4400	15,700	4360	25,440	1670
Urban	II	Segregated metal stream treatment, (chemical treatment and precipitation)	425	775	81,400	4840	276,300	362,570	36,200	29,010	32,000	10,890	2970	1040	28,100	7400	--	--	--	--
Rural	II	Segregated metal stream treatment, (chemical treatment and precipitation)	425	775	81,400	970	276,300	358,670	35,870	28,680	32,000	10,760	2970	520	28,100	7400	--	--	--	--

(a) Schematic representations of the various treatment systems used are shown in the body of the report under Task 2. Equipment and tanks, etc. were sized to 150 percent of normal operating capacity. Costs are based on an 8-hour day, 5 days/week (i.e., 2000 hr/year).

(b) See body of report under Task 2 for details of various plating line arrangements, plating and rinsing sequences, both compositions, etc.

(c) The cost of building was taken as 820 sq ft.

(d) Land cost was taken as $40,000/acre and $3,000/acre for urban and rural locations, respectively.

(e) Costs for piping, plumbing fittings, installation of equipment, engineering, and other items associated with setting up a waste treatment plant were arrived at by using a factor of 1.49 times the purchased cost of the main equipment items (e.g., tanks, reaction vessels, clarifiers, centrifuges, sulfonators, chlorinators, pumps, pH and ORP monitor/controllers, electric mixers, and other items which were sized for the overall plant design). A factor of 1.15 was used on the R.O. unit and the R.O. concentrate evaporator, since these units are largely assembled at the factory when shipped.

(f) A 10-year straight-line depreciation (i.e., 10% was employed, while an annual 8 percent interest charge was applied to the invested capital.

(g) The same treatment labor charge used was $8.00/hr; a 1-3/4 man/day figure was used for Phase I and a 2 man/day figure was used for Phases IA and II.

(h) A maintenance charge of 3 percent of the total investment was employed.

(i) A power cost of 5¢.15 kwhr was used. A value of 120 gal water treated per kwhr was used for Phase I calculations; this basic value was adjusted lower for the increased processing used in Phases IA and II.

(j) The cost of water was taken as $0.25-1000 gal for both urban and rural plants. A sewer charge of $0.25 gal/1000 gal of water used in the WT operations was applied. These same costs were used to determine the savings achieved by the use of the R.O. treatment.

(k) The costs of chemicals used were based for the most part on current vendor or distributor prices, recent prices paid by WT plant personnel, etc. Chemicals costs are for normal operation and not for 150 percent capacity.

(l) The cost used for disposal of 20% sludge and dried salts was $0.15/gal.

(m) The R.O. operating costs were based on a figure of $0.75/1000 gal processed; this figure includes the cost of labor, electricity, and module replacement at a cost of $2.00 each with a 2-year life. Depreciation and interest charges were not included in the $0.75/1000 gal figure. These costs were included in the annual depreciation and interest-charge columns in the left center of the table. Similar comments apply to the operating costs (which include labor, steam, water and electricity) of $1/2/day for the R.O. concentrate evaporator.
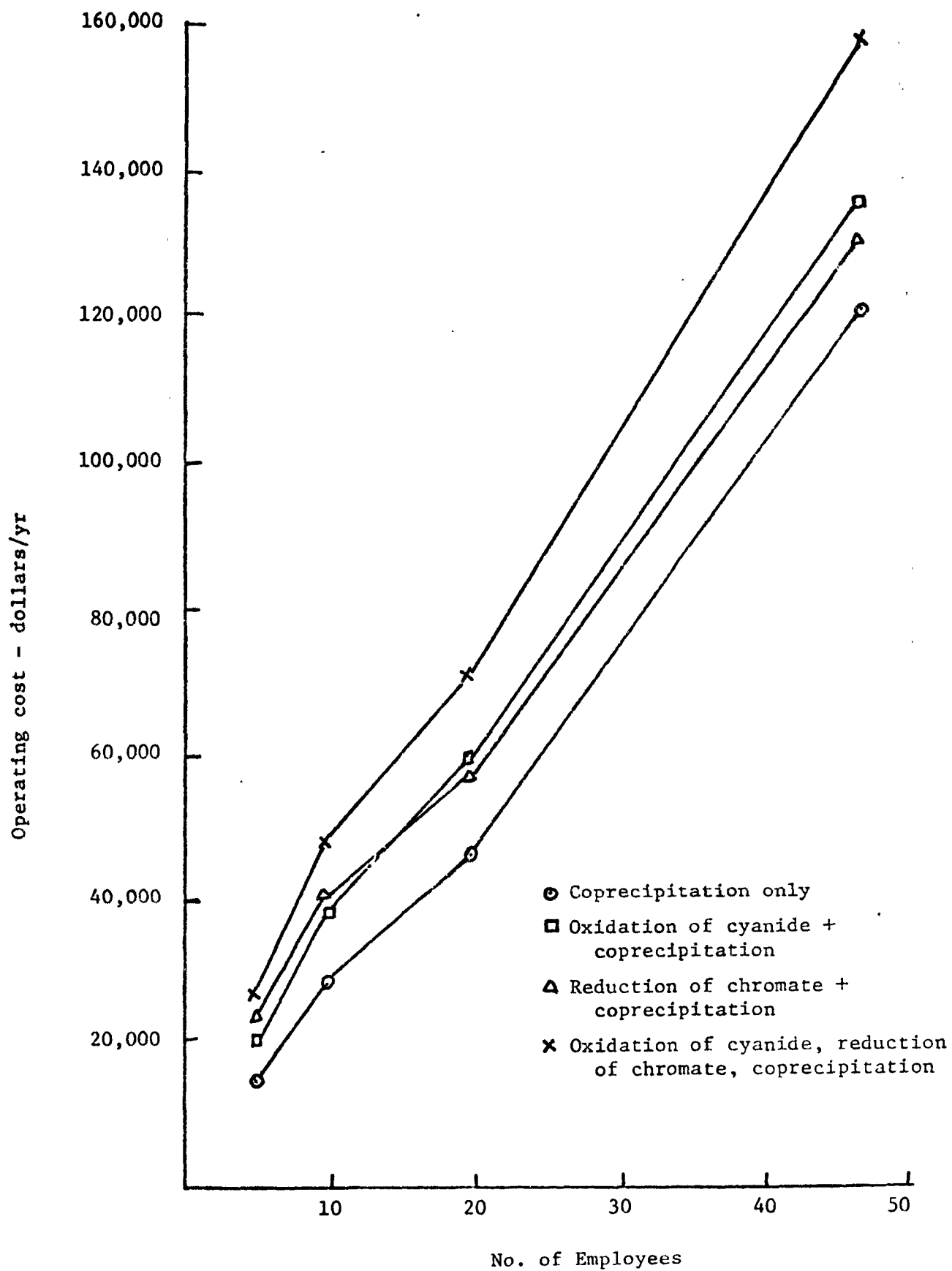
FIGURE 17   OPERATING COSTS RELATED TO PLANT SIZE AND
             EXTENT OF WASTE TREATMENT

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oxidation plus coprecipitation for treatment of wastes can process 75 sq m/hr, while 5-man plants that include chromium plating and chromating (C,D) can process 100 sq m/hr.

It was concluded that costs for a captive or independent shop would be similar if the waste treatment plant was sized for the metal finishing operation only. Captive metal finishing operations may discharge waste waters into large systems that handle other plant wastes, but it would be difficult to estimate what volume percent of waste water typically came from the metal finishing operations and what portion of total waste treatment costs should be allocated to them. Flow sheets of the waste treatment plants that were costed are shown in Figures 18, 19, 20 and 21.

Another plant was modeled to ascertain investment and operating costs of a medium large plant employing (1) segregated chemical treatment of waste waters containing individual metals, and (2) no discharge of pollutants. Costs for waste treatment employing destruction of cyanide, reduction of chromate wastewaters and coprecipitation of all metals were also developed as a basis of comparison. Table 30 summarizes both investment and operating costs of the waste treatment plants. Investment and operating costs increase in the order

(1) Combined chemical treatment and coprecipitation

(2) Segregated chemical treatment and coprecipitation

(3) Combined chemical treatment plus end-of-pipe treatment to eliminate discharge of pollutants.

The operating cost for combined chemical treatment and coprecipitation is equivalent to $1.41/1000 liters, which is approximately 30 percent higher than the $1.09/1000 liter figure for a similar model in the previous discussion. While the two models are slightly different the difference is mainly due to the fact that the two cost values were arrived at by two cost analysts, each of whom assumed what he considered were the most realistic costs. Such a discrepancy is not surprising and indicates the necessity for making analysis self-consistent. Thus, the results in Table 28 and 29 were made by one analyst and are set of cost factors and the cases (1) through (3) above by another analyst with a different set of cost factors. The

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Alkaline cleaners

Acid dips

Plating

High-and low-level control

Acid - alkali holding and mixing

Sump

High-and low-level control

H_2SO_4

Stirrer

pH

Neutralization and precipitation

NaHO

Sump

Pressure pump

Circulating pump

Optional filter

Stirrer

Pump

Flocculant

Sludge

Lagoon

H and L

Settling

Sludge

Lagoon

Haul

Overflow

H and L

High-pressure pump

Filter | Filter

Effluent

Pump

Pump

Backwash

Stream

FIGURE 18. TYPICAL PLANT OPERATION – CHEMICAL TREATMENT (A);
COPRECIPITATION ONLY

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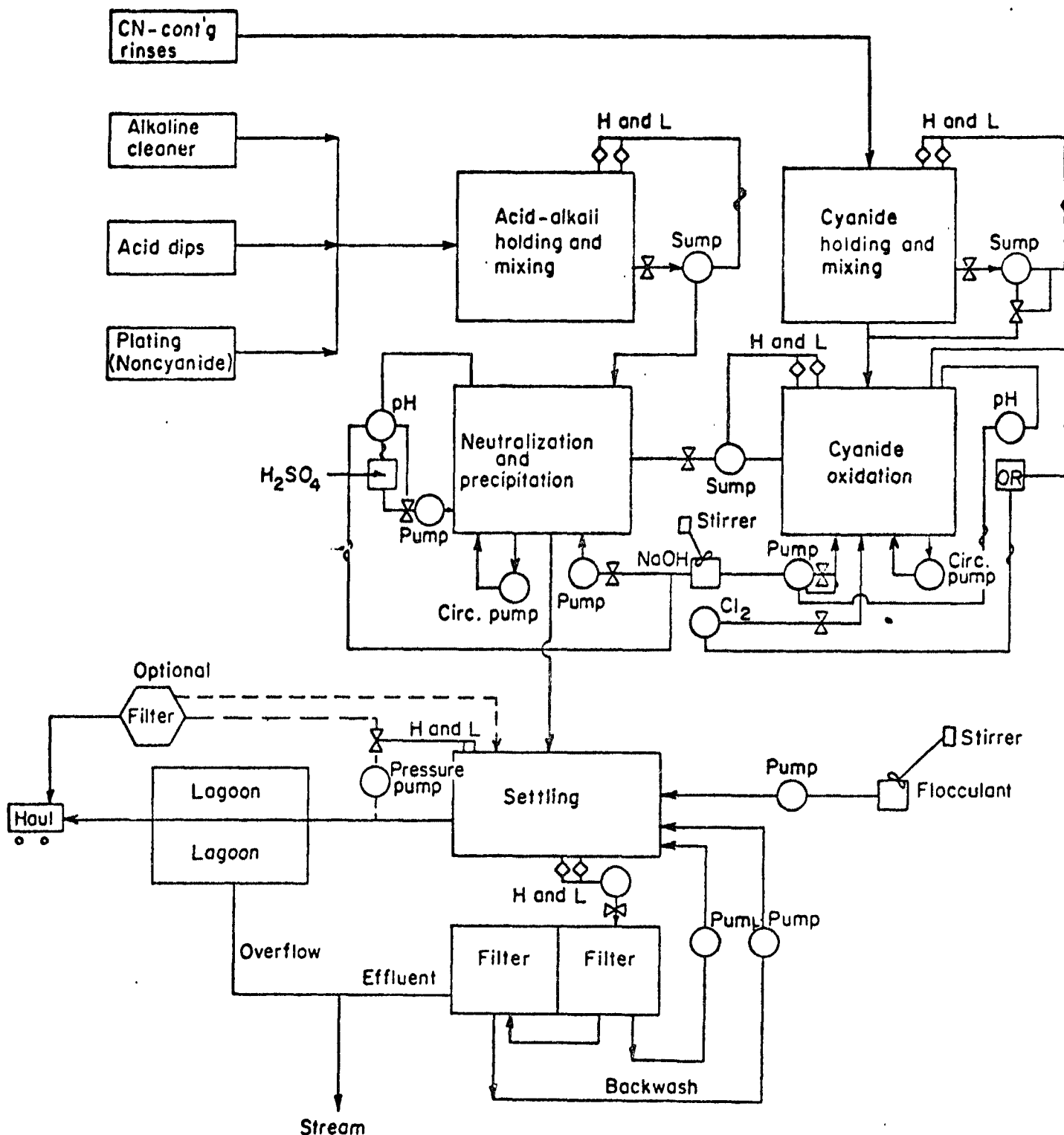
FIGURE 19 . TYPICAL PLANT OPERATION – CHEMICAL TREATMENT (B);
CYANIDE OXIDATION AND COPRECIPITATION

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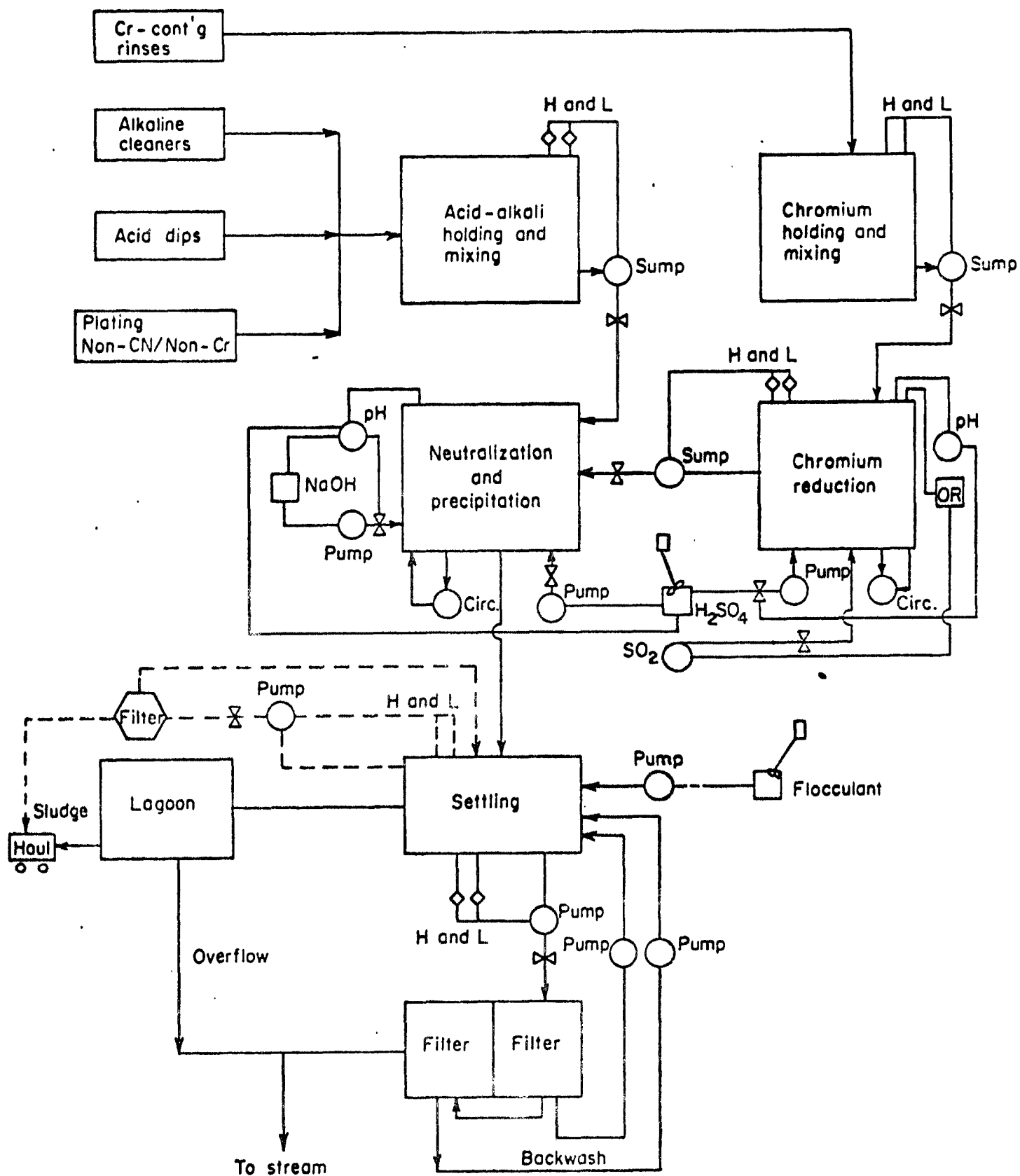
FIGURE 20. TYPICAL PLANT OPERATION – CHEMICAL TREATMENT (C);
CHROMIUM REDUCTION AND COPRECIPITATION

152
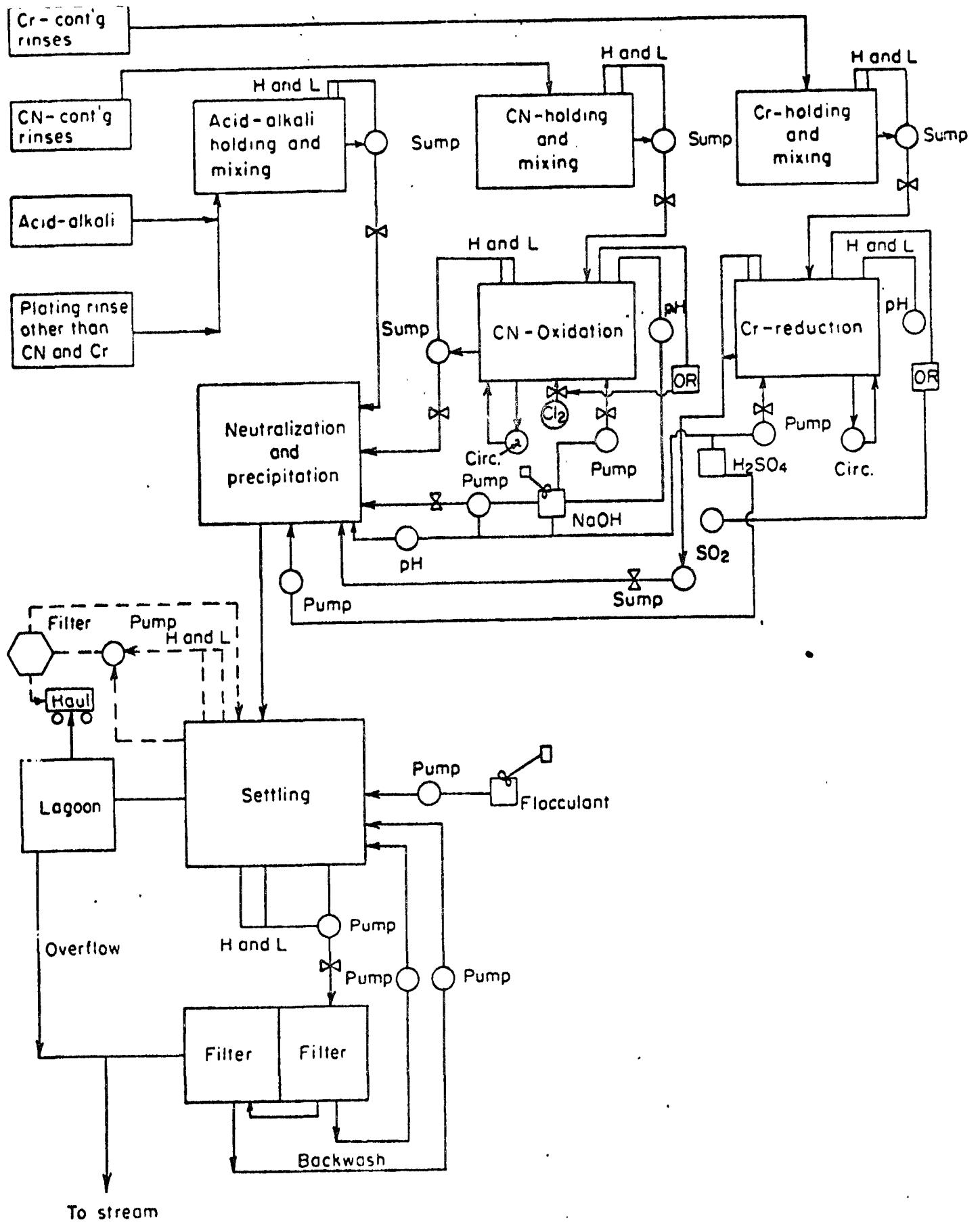
FIGURE 21 .TYPICAL PLANT OPERATION – CHEMICAL TREATMENT (D);
CYANIDE OXIDATION, CHROMIUM REDUCTION, AND
COPRECIPITATION

difference is actually much smaller than that of actual costs reported in Table 27.

The use of a system to eliminate pollutant discharge requires approximately twice the investment and operating cost as a system for combined chemical treatment. The costs can be reduced in some situations by in-process recovery systems where the savings in chemicals more than compensate for the costs of operating the recovery system. Evaporative recovery systems were not economical to use in the plants assumed since the value, bath concentration, and dragout of chemicals were not sufficient to make their in-process recovery worthwhile. The costs of installing more counter-current rinse tanks, evaporative equipment, and steam more than offset the savings in chemicals.

In-process reverse osmosis systems may have lower operating costs than evaporative systems, but are still in a demonstration stage for baths other than nickel. Use of reverse osmosis systems on the nickel lines in the plant model would not be expected to reduce overall in operating costs by more than 5 percent.

Figure 22 shows the operations in the plant and a schematic diagram of a segregated waste treatment system. Figure 23 shows a coprecipitation system and Figure 24 the modifications made at the end of the coprecipitation system with a reverse osmosis unit and salt evaporator to eliminate the discharge of pollutants.

Preliminary calculations indicated that use of evaporators in-process and at the end-of-pipe to eliminate pollution would be more expensive than use of reverse osmosis at end-of-pipe for the particular metal finishing lines considered. With the installation of a reverse osmosis system the neutralizing agent was sodium hydroxide rather than the lime used with the coprecipitation and segregated precipitation systems. Lime was used to precipitate phosphate as well as heavy metals, but precipitation products with lime are likely to foul the reverse osmosis membranes. These membranes remove phosphate directly and lime is not needed.

The cost of a minimum batch treatment system was also estimated. The layout is shown in the schematic diagram of Figure 25. The system was sized to handle 4500 l/hr of waste water, which is less than produced by the 5-man plant discussed above. For calculating operating costs an 8-hour day and 5-day week were assumed.

Small Platers

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Line 1
Cu-Ni-Cr
(Aut. Rack)

CuCN	180 gph
Ni	270 gph
Cr	495 gph
A A	1730 gph

Line 2
Cu-Ni-Cr
Man Rack

CuCN	55 gph
Ni	80 gph
Cr	110
A A	475

Line 3
Aut Rack
Zn(CN)₂
&
Chromate

Zn(CN)₂	355 gph
Zinc & Chromate	110 gph
A A	1050 gph

Line 4
Aut Zn(CN)₂
Barrel
&
Chromate

Zn(CN)₂	355 gph
Zinc & Chromate	110 gph
A A	1050 gph

Line 5
Man. Cadmium
CN Line
&
Chromate

Cd(CN)₂	115 gph
Cd-Chromate	40 gph
A A	400 gph

Line 6
Manual Hard Cr
Line

Cr	75 gph
A A	290 gph

Line 7
Manual Rack
Anod. Line
(Bright Dip)
Ni Acetate

Br. Dip - Al	260 gph
Anod. - Al	130 gph
Ni Acet. - Al	345 gph
A A	980 gph

Line 8
Auto. Barrel
Zn Phosphate

Zn Phosphate	130 gph
A A	700 gph

Line 9
Electroless
Nickel

Elect. Ni	30 gph
A A	375 gph

Combined CuCN
180 + 55 = 235 gph
→ CN Reduction and Cu PPP. → Clarifier → Effluent to Stream / Underflow to Centrifuge #1

Combined Ni
270 + 80 = 350 gph
→ Ni Neut. + PPT → Clarifier → Effluent to Stream / Underflow to Centrifuge #1

Combined Cr Plat.
495 + 140 + 75 = 710 gph
→ Chromium Reduction → Cr Neut + PPT → Clarifier → Centrifuge #2 → Effluent to Stream or Sewer / 20% Sludge to Lagoon Storage

Combined Zn(CN)₂
355 + 355 = 710 gph
→ CN Dest. & Zn PPT → Clarifier → Centrifuge #1 → Effluent to Stream or Sewer / 20% Sludge to Lagoon Storage

Cd(CN)₂
115 gph
→ CN Dest. & Cd PPT → Clarifier → Effluent to Stream / Underflow to Centrifuge #1

Comb. Chromate Streams
110 + 110 + 40 = 260 gph
→ Chrom Reduction → Cr, Zn, & Cd Neut. & PPT → Clarifier → Effluent to Stream or Sewer / Underflow to Centrifug. #2

Acid/Alk Streams 7000 gph
1730 + 995 + 1050 + 1050 + 400 + 290 + 980 + 700 + 375
→ A/A Neutralization and Precipitation → Clarifier → Centrifuge #4 → Effluent to Stream or Sewer / 20% Sludge To Lagoon Storage and Later Haul Away

Combined Al Anod.
260 + 230 + 345 = 835 gph
Zn Phosp. 130 gph
→ Neut & PPT → Clarifier → Centrifuge #3 → Effluent to Stream or Sewer / 20% Sludge To Lagoon Storage

Elect. Ni 30 gph
→ Raise pH to 13.0 to Destroy Complex

FIGURE 22   PHASE I, IA, AND II MASTER FLOW PATTERN

Cl$_2$ NaOH

Conc.
455 mg/l CN
108 mg/l Cu
288 mg/l Zn
54 mg/l Cd

Combined Cyanide Streams

Cu + Zn + Cd

235 + 710 + 115 = 1060 gph

Cyanide
Destruction

H$_2$SO$_4$ SO$_2$

Combined Cr + Chromate Stream

Cr Plating   495 + 140 + 75 = 710 gph

Chromating   113 + 113 + 40 = 266 gph
Total 970 gph

Chromium
Reduction

H$_2$SO$_4$ Lime, Ca(OH)$_2$

Lime

Combined Anodizing & Zn Phosphating

260 + 230 + 345 = 835 gph

Zn Phosp. = 130 gph

Neutralization
·and
Precipitation
of Phosphates

Combined
Neutralization
and
Precipitation

Effluent to Stream
or Sewer

Clarifier

NaOH

Elect. Ni   150 gph

Destruction of
Complex at
pH 13

2% Solids
Underflow

Ni Plating & Acid Alk Streams
350 + 760 gph

Tot = 7410 gph

Centrifuge

20% Sludge
To Lagoon Stora
for Later Haul A

FIGURE   23   COMBINED CHEMICAL TREATMENT AND NEUTRALIZATION-PRECIPITATION

FIGURE 24 COMBINED CHEMICAL TREATMENT AND PRECIPITATION FOLLOWED BY END-OF-LINE
REVERSE OSMOSIS TREATMENT FOR ZERO LIQUID EFFLUENT DISCHARGE

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FIGURE 25. BATCH TREATMENT SYSTEM FOR SMALL PLANT

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Costs have been estimated for the 1-4 man shop and 5-9 man shop and may be found with accompanying assumptions in the following tables:

Sizing Assumptions

- 1-4 employee shop (3 employees)
- 30 sq m plated per hour
- 80 1/sq m per hour
- 1/4 of the flow is cyanide bearing (and can be segregated)
- The cyanide concentration is 20 ppm

The concentrations in the rest of the flow are equivalent to 100 ppm of Fs^{+++}

Engineering Assumptions

- Complete manual operation utilizing minimal equipment
- Store 1 day of cyanide containing waste and treat overnight
- Equalize flow in a tank corresponding to 1/2 of the daily output. Operate in backmix with adjustment every two hours.
- All adjustment from carboys or drums.

Manual Handling Of Chemicals Verification

Cyanide	Total waste flow	2400 1/hr
	Cyanide flow	600 1/hr
	Total cyanide waste	4800 1/day
	Total cyanide in waste	98 gm per day

Chlorine requirement   approximately 700 gm per day or 1.5 lb

Using hypochlorite (1 lb Cl_2 1 gal hypochlorite) 1.5 gallons per day.

Using caustic   1 lb/1 lb of chlorine - say, 1.5 lbs/day

Neutralization   (Assume that the caustic from cyanide treatment is used in the first 1/2 day)

Total caustic required	-	about 2 gm per gm of iron (120/56)
(120/56) 1/2 day flow		9600 l 960 gm of iron
Caustic required	-	2800 gm/or 4.5 lb.
Additional	-	4.5 - 1.5 = 3 lbs.
Rest of day	-	4.5 lbs.
Total per day	-	7.5 lbs

O.K. to add by hand (drum of caustic - approximately
400 lbs)
O.K. to use a small bucket (8 gals. approximately or
80 lbs)

Residence time - 4 hours (nominal or actual) for equalization

Equipment List

Equalization tank - 2500 gals.	$2500
Agitator - 5 HP	1000
Chlorination tanks - 2 x 800 gals.	1500
2 Agitators - 1 HP	800
1 Transfer pump	150
High level alarm - 3	400
Valves - 5	300
Other piping and supplies	150
	$6800
Installation - 25%	1700
	$8500

Instrument

pH meter	400	
colorimeter	200	600
	Total	$9100

Area required - 400-500 square feet (assumed available)

Assume that there is room for equipment, e.g. a 2500 gal.
tank of normal configuration is 6.5' in diameter and
10' in height (without legs).

Sizing Assumptions

- 5-9 employee shop (7 employees)
- 70 sq m plated per hour
- 80 l/sq m   5600 l/hr of flow
- 1/4 flow is cyanide bearing (and can be segregated)
- Cyanide concentration = 20 ppm
- The concentrations in rest of waste flow are equivalent
  to 100 ppm Fs+++

Engineering Assumptions

- Cyanide flow - 1400 l/hr - say, 350 gals/hr.
- Assume that a hand operation once a day is used for
  cyanide (Automatic continuous unit would cost about
  $18,000-22,000).
- Equalize daily flow in a 1/2 day tank.
- Check for hand addition - or cheapest equivalent.

Handling Of Chemicals

Cyanide . Cyanide total - 11,200 l/day   2800
                                        gals. (3000)
        . Total cyanide in wash - 224 gm/day
        . Chlorine required - 1500 gm/day say 3.5 lbs.
        . Hypochlorite - 1 gal/lb of chlorine   3.5
          gallons (can be added out of a plastic lined
          55 gallon drum with a hand pump)
        . Caustic -   3.5 lbs.
          Out of a 55 gallon drum (500 lb) with a
          scoop. (a big scoop is about 5 lb)

pH Adjust   2 gm per gm of iron
            1/2 day flow (total)   22,400 l. (say 6000 gals)
                  Iron   2,240 gm
                  Caustic   4,500 gm   10 lbs.
            2 to 3 scoops.

Manual addition from a drum appears feasible.

Material handling equipment - 1 chlorine resistant
hand pump - say $200

Equipment List

1 Equalization tank - carbon steel   6000 gals. $ 4,100
2 Cyanide treat tanks - carbon steel, epoxy lined*   7,200
  (3000 gal)
3 Agitators (1) 10 HP, (2) 5 HP (3500) (2 x 1000)   5,500
Transfer pump   300
High level alarms   400
Valves (5)   500
Other piping and supplies   300
                                                       _____
                                                        18,300
Installation - 25%   4,600
                                          Total $22,900
Instruments
      Hand pump   200
      pH meter   400
      Colorimeter   200
                                                       _____
                                                       $23,700

*Add 20% for epoxy lining.

If a 2 hour equalization is required
   use a 3000 gal tank + 5 HP agitator (3000 + 1000)   4,000
   instead of 4100 + 3500 (7600)
   thus, 18300 - 3600   14,700
                                                        3,700

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The total capital investment and operating and maintenance costs for both size plants are as follows:

No. of employees	Capital Investment ($1000)				Annual O&M Costs ($1000)			
	80 1/sq m		160 1/sq m		80 1/sq m		160 1/sq m	
	min	max	min	max	min	max	min	max
1-4	9.1	13.7	13.7	20.5	3.9	6.5	3.9	6.5
5-9	23.7	35.6	35.6	53.3	4.3	7.1	4.3	7.1

New Source Performance Standards (NSPS). New sources that are required to meet the recommended standards of performance have the opportunity of designing and building plants that reduce water flow. Such systems as counterflow, spray, and fog rinses, interlocks to provide water flow only during processing sequences, drip tanks, etc., can be provided. The capital investment for installing an extra 3' x 3' tank in each rinsing sequence of a plating line to reduce further the water use in counterflow rinsing is of the order of $3,000. The plant modeled in Figure 22 has 27 rinses so adding one more tank for each rinse would increase capital investment $81,000 for a total of $300,200 for combined chemical treatment and precipitation in an urban plant. It is probable that water use can be reduced 100 percent by installing only half this number of tanks at a cost of $40,000 or an increase in capital investment of 18 percent over a plant meeting BPCTCA standards. Operating costs would increase $7200/yr minus a credit of $520 for water and sewer charges or $6680/yr. The increase in operating cost is 6 percent as compared to those for a plant meeting BPCTCA standards.

No Discharge of Pollutants

The elimination of liquid discharge from metal finishing processes has not been demonstrated with present technology. Anticipating that future development will make this elimination possible, it is desirable to have a rough estimate of the cost impact of doing this. Technically, evaporative recovery, reverse osmosis, and ion exchange can concentrate wastes after which the concentrate can be evaporated essentially to dryness. Purified water can be returned to process. Approximate cost analysis have been made for a medium large plant 240 sq m (2600 sq ft) per hour assuming use of 80 liters/sq m of water. The effects of closing the liquid loop without a purge on the buildup of impurities are not known and the cost of solving problems

connected with impurity buildup will depend greatly upon how much impurity must be removed, the development of efficient systems for their removal, and how many of the components that are recovered can be recycled rather than discarded.

To determine the cost effectiveness of various control and treatment alternatives much of the data developed for Plant 33-1 in Phase I was used. For those examples involving evaporative recovery, an additional investment of $150,000 was allowed for a unit to evaporate concentrate to dryness. Results of the calculations are shown in Table 31. A finishing cost of $2.70/sq m ($0.25/sq ft) is equivalent to $644/hr, and all of the projected costs for waste treatment are less than 10 percent of this figure. Of course, the $2.70/sq m figure is too high for some processes, but provides a basis for at least a rough estimate of the cost impact of waste treatment.

Nonwater Quality Aspects

Energy Requirements

Introduction. Energy requirements will be discussed for chemical treatment, evaporative recovery, ion-exchange, and reverse osmosis.

Chemical Treatment. Energy requirements for chemical treatment are low, the main item being electrical energy for pumps, mixers, and control instruments. Electrical costs have been tabulated for several plants in Table 32. Data for Plants 33-1 through 33-6 were obtained from the Phase I study. Results indicate that approximately 5 percent of the waste treatment cost is for electric power.

It is estimated in the Phase I study that electrical energy for treating 2.271×10^4 liters per hour by a reverse osmosis unit for 4000 hours per year would cost $6,400. The electrical energy cost is therefore 7.045×10^{-5}. The liters per year processed by all plants listed in Table 32 add up to 3.964×10^9 liters and the cost of electricity for processing this water by reverse osmosis is $279,200. The total electrical cost for chemical treatment for the plants listed in Table 32 is $75,330. These figures can be used to roughly estimate the increases in electrical power requirements in going to a system with no liquid effluent. For best practical control technology currently available the electrical cost would be essentially that of current estimates or $75,330. For the best available technology economically achievable the combination of chemical treatment and reverse osmosis plus evaporation of the

TABLE 31 COST EFFECTIVENESS OF
CONTROL ALTERNATIVES
(247 Sq M/Hr)

Type of Control	Investment Cost	Operating Cost/Year	Water Treated 1/Hr	Operating Cost per 100 Sq M
Plant 33-1				
Rinse System – Chemical treatment	$264,274	$112,361	25,210	$17.30
Three countercurrent rinses – chemical treatment	330,000	121,387	9,766	18.68
Single stage evaporators (21 units) Dry evaporator	890,000	327,895	0	50.47
Five single stage evaporative units and one vapor compression unit – dry evaporator	400,000	109,913	0	16.92
Chemical treatment plus reverse osmosis Sludge drier and dry evaporator for concentrate	560,000	161,328	0	24.83

TABLE 32 COST OF POWER RELATIVE TO TOTAL OPERATING
COST FOR CHEMICAL TREATMENT

Plant No.	Processes	Electric Cost/Year	Waste Treatment Operating Cost/Year	Electric Cost x 100/Waste Treatment Cost
33-1	Plating Cu, Ni, Cr, Zn	$ 4,100	$112,361	$ 3.65
11-8	Plating Cu, Ni, Cr, Zn	668	391,406	0.17
36-1	Plating Cu, Ni, Cr, Zn	5,220	221,009	2.36
20-14	Plating Cu, Ni, Cr, Zn	6,000	93,240	6.44
20-17	Plating Cu, Ni, Cr, Zn	8,940	798,840	1.12
3-4	Plating Cu, Ni, Cr, Zn	600	4,064	14.76
33-3	Plating Cu, Ni, Cr, Zn	240	18,019	1.33
33-6	Plating Cu, Ni, Cr, Zn	1,460	77,460	1.88
33-22	Anodizing	1,948	51,515	3.78
20-20	Anodizing	4,763	83,481	5.71
20-22	Anodizing	12,623	113,370	11.13
33-24	Plating Common Metals	1,212	80,430	1.51
36-12	Plating Precious Metals	1,894	72,809	2.60
33-2	Plating Precious Metals	1,082	14,968	7.23
33-4	Plating Precious Metals	120	18,205	0.66
8-5	Plating Precious Metals	16,239	115,995	14.00
6-35	Chemical Milling	3,897	83,758	4.65
30-19	Chemical Milling	4,330	168,312	2.57
		$\bar{x} = 4,185$	$\bar{x} = 139,957$	$\bar{x} = 4.75$
		$\sigma = 4,454$	$\sigma = 187,688$	$\sigma = 4.44$

concentrate (that would require little electrical energy) the electrical cost would be $75,330 plus $279,200 or $354,530. The ratio of $354,530/75,330 is 4.70. On this basis going to a system without discharge of liquid effluent will increase the use and cost of electrical energy 5-fold.

Evaporative Recovery. From the Phase I report the cost of steam for operating a 300 gph single-stage evaporator is approximately $2100/yr corresponding to approximately 1,900,000 lb of steam. The single-effect evaporators require considerable energy. This requirement can be diminished by use of multiple stage or vapor-compression evaporators.

Ion Exchange. The few pumps required for ion-exchange systems should consume very little power.

Reverse Osmosis. The energy requirement for reverse osmosis systems is the electricity for operating the high pressure across the membrane and for operating low pressure transfer pumps. The estimate is $6400/yr for a 6000 gph facility operating 4000 hours/yr.

Impact of Power Requirements for Waste

Treatment. Domestic production of electrical energy in 1971 was 1.717×10^{12} kwh. For the plating industry the electrical energy requirement is estimated to be 9.75×10^{8} kwh. The metal finishing industry as a whole is estimated to consume no more than twice this value, which would be 1.950×10^{9} kwh. The percentage of annual power that is used for metal finishing operations should be no more than:

$1.950 \times 10^{11}/1.717 \times 10^{12} = 0.114$ percent.

Power for pumps, lights, fans, etc., and waste treatment should not more than double this figure to 0.228 percent.

Cost of Recovery of Metal Values from Sludge

Tribler et. al. is a report on the feasibility of recovering metal values from sludge b digesting the sludge with acid to dissolve it followed by electrolysis and neutralization procedures to recover metal values. The case considered was a sludge containing primarily copper, nickel, chromium, and zinc values. A cost estimate was included for a small plant that would treat 45 kg of dry sludge during a 12 hour day to yield 2.27 kg of copper, 0.09 kg of nickel, and 4.54 kg of chromium. However, the chromium was obtained as an oxide mixed with some iron. The investment for a small plant was

estimated to be $15,130. Operating cost per day was estimated to be $85.30. This did not include a cost of capital, which if assumed to be eight percent of the investment per year, would raise the daily operating cost to $91.35. The total weight of metal recovered per day is 6.90 kg so that the cost is estimated to be $13.23 kg. The cost is obviously very high compared to market prices so that the small operation would be far from economic. Undoubtedly, the cost of processing would be less with a larger installation, but if more than one metal finishing installation were served there would be an additional cost for transporting sludge to the recovery operation.

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE, GUIDELINES, AND LIMITATIONS

Introduction

The effluent limitations which must be achieved by July 1, 1977, are to specify the degree of effluent reduction attainable through the application of the best practicable control technology currently available. Best practicable control technology currently available is generally based upon the average of the best existing performance by plants of various sizes, ages, and unit processes within the industrial category and/ or subcategory.

Consideration must also be given to:

(a) the total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application

(b) the size and age of equipment and facilities involved

(c) the processes employed

(d) the engineering aspects of the application of various types of control techniques

(e) process changes

(f) nonwater quality environmental impact (including energy requirements).

The best practicable control technology currently available emphasizes treatment facilities at the end of a manufacturing process but includes the control technologies within the process itself when the latter are considered to be normal practice within an industry.

A further consideration is the degree of economic and engineering reliability which must be established for the technology to be "currently available". As a result of demonstration projects, pilot plants and general use, there must exist a high degree of confidence in the engineering and economic practicability of the technology at the time of commencement of construction or installation of the control facilities.

Industry Category and Subcategory Covered

The effluent limitations recommended herein cover the following metal finishing processes: anodizing, chemical milling and etching, immersion plating, chemical conversion coating. These processes have been divided into three categories: Subcategory (1) consists of anodizing, Subcategory (2) consists of coatings, and Subcategory (3) consists of chemical etching and milling.

Identification of Best Practicable Control Technology Currently Available

Best practicable control technology currently available for Subcategories (1), (2) and (3) is the use of chemical methods of treatment of waste water at the end of the process combined with the best practical in-process control technology to conserve rinse water and reduce the amount of treated waste water discharged.

Chemical treatment methods are exemplified by destruction of cyanide by oxidation, reduction of hexavalent chromium to the trivalent form, neutralization and coprecipitation of heavy metals as hydroxides or hydrated oxides with settling and clarification to remove suspended solids prior to discharge or prior to dilution with other nonelectroplating process water before discharge. The above technology has been widely practiced by many plants for over 25 years. However the above technology cannot achieve zero discharge of heavy metals because of finite solubility of the metals. In addition, it is not practicable to achieve 100 percent clarification and some small amount of metal is contained in the suspended solids. By optimum choice of pH and efficient clarification it is possible to achieve a significant reduction in the heavy metal pollutional load.

Zero discharge of heavy metals in effluent may be achieved only by eliminating the effluent itself by such techniques as reverse osmosis and evaporation, which offer the possibility of purifying all waste water to a sufficient degree to be recycled to process or by evaporating to dryness so that waste water constituents are disposed of as solid waste.

No generalization regarding the degree of metal pollution reduction is possible because of the mix of finishing processes possible in a single plant and the variety of metals in the raw waste of most plants. Because of this fact and the high cost of inplant segregation of all waste

streams according to metal, coprecipitation of metals is the general practice. There is an optimum pH for precipitating each metal that results in the greatest removal by clarification. The optimum pH for removing all metals cannot be utilized for coprecipitation so the pH selected for a mixture of metals is a compromise. However, coprecipitation can result in lower discharge of metals than if each is precipitated separately at its optimum pH value if synergistic effects of the type shown in Table 26 are operating. For coprecipitation to provide lower discharge than segregated precipitation in-process dilution must be minimal.

There are several advanced recovery methods available for closing up the rinse water cycle on individual metal finishing operations. These methods (evaporation, ion exchange, reverse osmosis, countercurrent rinsing) have not yet been applied to rinse waters from pretreatment and posttreatment operations. The corresponding rinse waters plus concentrated solution dumps and floor spills may contain one or all of the pertinent metals (copper, nickel, chromium, and zinc) in significant amounts requiring chemical treatment. Thus, chemical treatment of at least the typical acid/ alkali stream from pretreatment and posttreatment operations represents the best practicable control technology currently available to achieve the effluent limitations recommended.

Having identified the technology for end-of-process treatment and recognizing the technical and practical limitations on removal of heavy metals by this technology (metal solubility and clarification efficiency), further reduction in the quantity of metal pollutants discharged must be achieved by reduction in the volume of treated water discharged. There are many in-process controls designed to reduce the volume of waste water which is principally that resulting from rinsing. Some of these controls, designed to minimize dragout of concentrated solutions or to reclaim as much dragout as practical can be considered normal practice within the industry. It can be assumed according to good practice that reclaim tanks and/or still rinses are being used and that all evaporation losses are made up with the reclaimed solution. Dragout reclaimed does not contribute to the raw waste load normally discharged from remaining rinses. There is economic incentive to reduce the chemicals purchased for bath makeup and the added economic incentive to reduce the cost of treatment chemicals required for end-of-process treatment. Reduction of dragout leads to reduction in water requirements for rinsing.

Further reduction in rinse water use can be achieved by use of a stagnant rinse for recovery or by multiple-tank countercurrent rinsing. Counteracting the cost of installing multiple rinse tanks are the savings in treatment chemicals, water costs, and sewer charges. Further, the use of advanced recovery techniques (evaporation, ion exchange, and reverse osmosis) which concentrate the rinse water sufficiently to allow reclaim of the valuable metal finishing solution can often provide the economic incentive to use this technology and justify the cost of recovery equipment plus the cost of installing multitank countercurrent rinsing. However, it should be recognized that the major water reduction occurs because of the installation and use of multitank countercurrent rinsing.

In the past there has been little economic incentive to reduce water use for rinsing after preparatory and posttreatment operations. The cost of the chemicals has not made their recovery from rinse waters worthwhile. High dragout from preparatory cleaning solutions has not been considered an unfavorable factor since the dragout of impurities along with bath chemicals has prolonged the life of the bath in some cases. The disadvantage of high dragout is that more water must be used for rinsing to prevent significant concentrations of impurities, i.e., grease, from contaminating the processing solutions.

Best practicable control technology currently available also includes water conservation through rinsing. A water use of 160 l/sq m/operation (4 gal/sq m/operation) has been estimated as that achievable by the industry. This figure precludes the use of countercurrent or series rinses. Exclusive use of single stage rinsing will not meet this water use. It has been calculated that for 186 sq m/hr (2000 sq ft/hr) proudction the rinse water need for various rinsing techniques are:

```
1 - single rinse l/hr 499,620 (132,000 gal/hr)
2 - tank countercurrent 2800 l/hr (140 gal/hr)
3 - tank countercurrent 477 l/hr (126 gal/hr)
4 - tank countercurrent 201 l/hr (53 gal/hr)
5 - tank countercurrent 121 l/hr (32 gal/hr)
```

This corresponds to a water use of:

```
1 - single rinse 2686 l/sq m (66 gal/sq ft)
2 - tank countercurrent 15 l/sq m (.37 gal/sq ft)
3 - tank countercurrent 2.56 l/sq m (.06 gal/sq ft)
4 - tank countercurrent 1.2 l/sq m (.026 ga/sq ft)
5 - tank countercurrent .65 l/sq m (.016 gal/sq ft)
```

A 3 - stage series rinse consumes approximately the same quantity of water as a 2 - stage countercurrent.

The 160 l/sq m (4 gal/sq ft) takes into account the contributions made by the pretreatment steps of alkaline cleaning and acid pickling and allows some use of single rinses.

An alternative mode of operation to the above is to dump cleaning baths frequently so that dragout of impurities is minimized. Then the amount of rinse water can be reduced and can be even further reduced by use of multiple countercurrent rinsing techniques. The increased cost of chemicals from more frequent dumping and the cost of multiple rinse tanks is counteracted by savings in water and sewer charges. Water use can therefore be greatly minimized since preparatory solutions, i.e., alkaline cleaners and acid dips contain chemicals that can be tolerated in fairly high concentrations in subsequent processing solutions, i.e., plating baths. In general, the amount of rinse water required should be substantially less for rinsing following alkaline cleaning and pickling than for rinsing following typical metal finishing operations such as electroplating.

While sufficient economic incentive may not be present to achieve reduction in the volume of the rinse water from pre- and posttreatment operations, there is an opportunity for significant reduction in pollution. The above factors are taken into account in recommending the effluent limitations. Even in plants currently achieving good waste treatment results, there are further opportunities for reduction in volume of effluent discharge.

Rationale for Selecting the Best Practicable Control Technology Currently Available

General Approach

In determining what constitutes the best practicable control technology currently available, it was necessary to establish the waste management techniques that can be considered normal practice within the metal finishing industry. Then, waste-management techniques based on advanced technology currently available for in-process control and end-of-process treatment were evaluated to determine what further reduction in pollution might be achieved considering all the important factors that would

influence the determination of best practicable control technology currently available.

Waste Management Techniques Considered Normal Practice in the Metal Finishing Industry

For that portion of the metal finishing industry that discharges to navigable waters, many are currently using chemical treatment for end-of-process pollution reduction. Some of these waste-treatment facilities have been in operation for over 25 years with a continual upgrading of performance to achieve greater pollution abatement. Because of the potentially toxic nature of the chemicals used in the metal finishing industry, there is a relatively high degree of sophistication in its water pollution abatement practices. For example, the accidental release of concentrated solutions without treatment to navigable waters is believed to be a rare occurrence today. This is because adequate safety features are incorporated in the design of end-of-process waste treatment facilities in conjunction with good housekeeping within the electroplating facility. This example and other waste management techniques were considered as examples of normal practice within the metal finishing industry in determining the best practicable control technology currently available. Other examples of normal practice include:

(1) Manufacturing process controls to minimize dragout from concentrated solutions such as

    (a) proper racking of parts for easy drainage

    (b) slow withdrawal of parts from the solution

    (c) adequate drip time or dwell time over the tank

    (d) use of drip collection devices.

(2) Effective use of water to reduce the volume of effluents such as

    (a) use of rinse water for makeup of evaporation losses from solutions

    (b) use of cooling water for noncritical rinses after cleaning

(c) use of treated waste water for
preparing solutions for waste-
treatment chemicals.

(3) Recovery and/or reuse of waste water
constituents such as

(a) use of reclaim tanks after metal
finishing operations to recover
concentrated solutions for return
to the plating tank to make up
evaporation losses

(b) reduction in waste water volume by the
use of at least two series flow rinse
tanks after each finishing operation
with return of as much rinse water as
possible to the finishing tank.

Other waste-management techniques not considered normal
practice, but currently in use in one or more plants, were
evaluated on the basis of reduction in the quantity of
pollutants in the effluent discharged.

Degree of Pollution Reduction Based on
Existing Performance by Plants of Various
Sizes, Ages, and Processes Using
Various Control and Treatment Technology

Identification of Best Waste Treatment Facilities

The initial effort was directed toward identifying those
companies that had well engineered and operated metal
finishing process and waste treatment methods. Such
companies were identified on the basis of personal
knowledge, and referrals by people well acquainted with the
industry (EPA regional representatives, state pollution
control authorities, trade associations, equipment
suppliers, consultants). Representatives of approximately
75 companies returned questionnaires mailed to them and
these representatives were further contacted by telephone or
further correspondence in many cases to clarify the
information in the questionnaires and obtain further data.
Furthermore, visits were made to 11 plants for development
of detailed data on several of the processes. Effluent
samples were collected at five plants and analyzed at
Battelle-Columbus Laboratories. The above constitutes the
data based for the Phase II study.

Volume Capacity of Treatment Plant Studied. Figure 26 shows the volume capacity of the waste treatment plants for which data were received, as measured by the amount of waste water treated per hour. The range of capacities covers approximately two orders of magnitude.

The plot is a cummulative one indicating how many plants have a water use less than the volume corresponding to the cummulative number. Thus, 15 plants have a volume of 100,000 liters/hour or less and 4 plants have a greater volume.

Concentration of Constituents. The concentration of constituents in the treated effluent and the pH are shown in Table 33. The concentrations are for soluble plus suspended constituents in the effluent, unless otherwise noted. These results appear to have little relation to the type of process from which waste waters are derived with the possible exception of electroless plating. The complexing agents, such as ammonia, that are dragged into waste waters from electroless plating baths are capable of inhibiting the precipitation of metals such as copper and nickel.

Water Use. To discuss water use it is first necessary to carefully define several terms.

"Process": A process is the accumulation of steps
required to bring about a metal finishing
result. An electroplating process
includes cleaning and pickling of the
basis metal, a strike if necessary,
the plating step, and all rinses needed
to carry out the process.

"Rinse": A rinse is a step in a process used
to remove components of a bath from
the work following an operation.
A rinse may consist of several
sequences such as successive
countercurrent rinsing or hot
rinsing followed by a cold
rinsing with deionized water.
Nevertheless, there is only one
rinse after an operation.

Table 34 shows the water use for the various processes studied. The water use has been expressed in two ways.
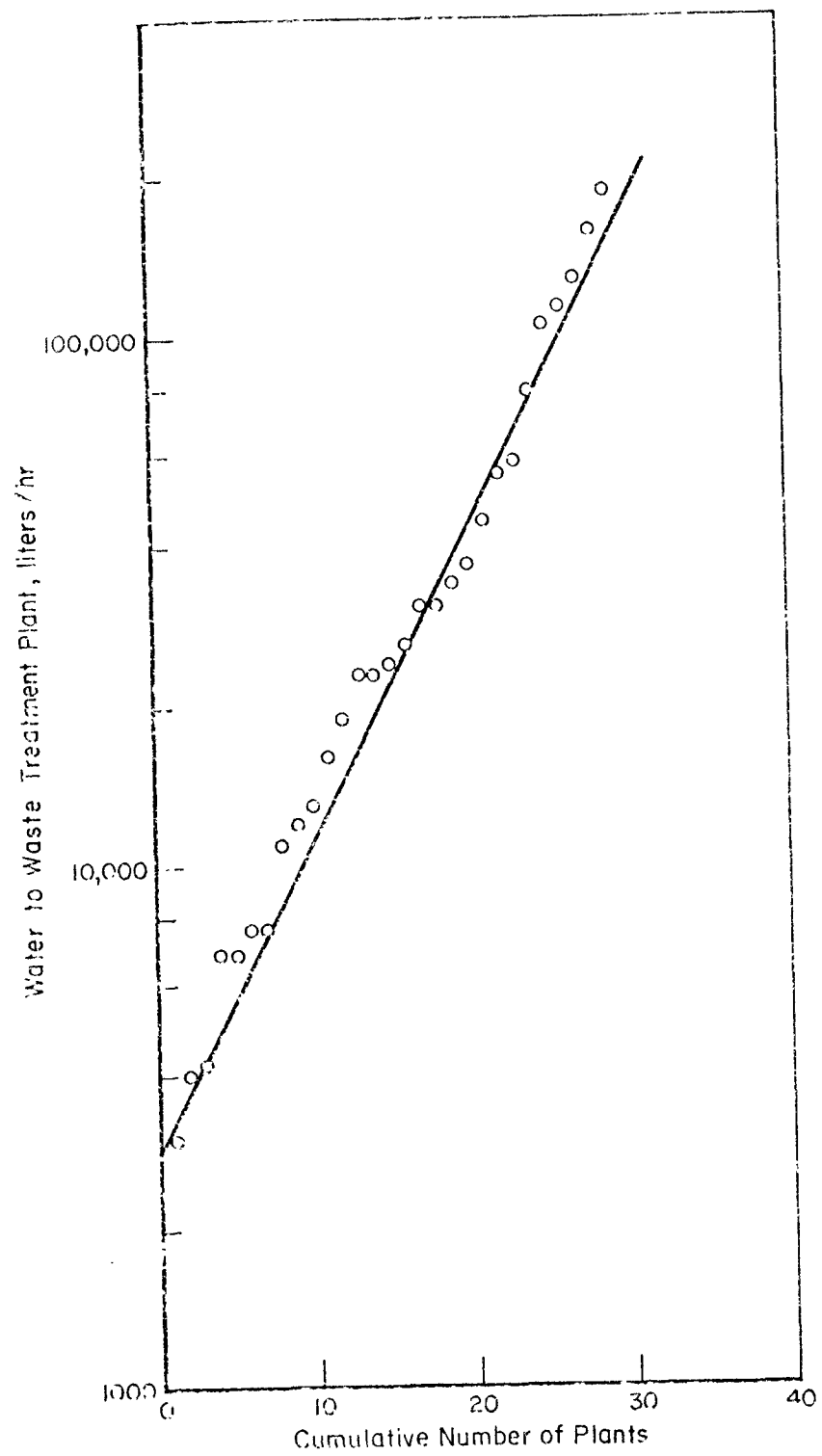
FIGURE 26. DISTRIBUTION OF WASTEWATER VOLUME TREATED

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TABLE 33 CONCENTRATION OF EFFLUENT CONSTITUENTS

Plant No.	Processes	Concentration, mg/l										
		Ag	Al	Au	Cd	CN⁻	Total CR	Cr⁺⁶	Cu	F⁻	Fe	Ni
20-24	Plating Common Metals					0.02	0.54		0.17	11		1.9
33-24	Plating Common Metals					<0.025	<1	<0.05	<1		<1	
33-26	Plating Common Metals								0.05		0.3	7
31-1	Plating Common Metals								1.1S			
36-12	Plating Com.,Prec.Metals	<0.01				<0.1						
33-2	Plating Precious Metals	traces		traces		0.1						
33-4	Plating Precious Metals											
8-5	Plating Precious Metals					(0)						
6-37	Plating Precious Metals	<5				<1			<5			<5
19-11	Plating Precious Metals	(0)		(0)		(0)			<0.5S			<1S
15-3	Plating Precious Metals				0.02	0.04	0.08	0.06	0.03			0.03
9-7	Electropainting, Anodizing		6.5									(·)
9-6	Electropainting											
33-34	Electropainting											
4-5	Electroless Plating											7.7
8-8	Electroless Plating											<0.02
30-19	Electroless Plating					<0.03	0.2	<0.05	20			1.0
33-22	Anodizing		<0.05									
33-23	Anodizing		0.91				0.40	0.37				0.24
20-22	Anodizing		1.0									
29-20	Anodizing		3.7									
33-35	Anodizing		1.0S				0.13	0.05				
20-23	Anodizing		8.1S									<0.18
47-9	Anodizing											
6-35	Chemical Milling		<1		0.1	(0)	1.0	(0)				
9-2	Chemical Milling		0.25				0.05	trace			1.75	
23-7	Chemical Milling		0.5E		.05E		5	5	0.01E		0.05E	
33-30	Phosphating					.9	1.3	0.33	0.32		0.2	
19-24	Etching	0.5				.02	< .05	< .03	0.15	2.2		
31-16	Printed Circuits								0.37		0.1	
6-36	Immersion Plating								1.1		0.1	
46-4	Electropolishing					0.01	0.3-0.7	0.003	0.4-8.4		0.70-0.78	4-15

E - estimated

S - soluble

TABLE 33 CONCENTRATION OF EFFLUENT CONSTITUENTS (Continued)

Plant No.	Processes	Concentration, mg/l								Other
		Pb	PO_4^{-3}	Pt Metal	Sn	Zn	Susp. Solids	Dis. Solids	PH	
20-24	Plating Common Metals	0.6			<2	0.25	4	676	8.5-9.5	
33-24	Plating Common Metals					<1.0	<25	1400	7-9	
33-26	Plating Common Metals	0.3	<1.0		Nil		78	1250	8.0	BF⁻ - 75 mg/l
31-1	Plating Common Metals				0.2S			1642	7.0-8.0	
36-12	Plating Com.,Prec.Metals				0.5S		<10	200	8.0	
33-2	Plating Precious Metals			traces			6		5-10	
33-4	Plating Precious Metals						6.9	640	7.5-8.5	
8-5	Plating Precious Metals								7.5-8.0	
6-37	Plating Precious Metals							2760	7-10.5	
19-11	Plating Precious Metals			(0)			<20		7-8	
15-3	Plating Precious Metals					0.5				COD = 34 mg/l
9-7	Electropainting		<0.4				10	250	7.0	Cobalt - <0.03 mg/l
9-6	Electropainting						40		6.2	COD = 320 mg/l
33-34	Electropainting		8.1				130	400	8.4	Barium - 1.0 mg/l
4-5	Electroless Plating								7	COD = 624 mg/l
8-8	Electroless Plating					<0.02	22.7	204	7	Ammonia - 6.8 mg/l
30-19	Electroless Plating	0.5	50				100	500	6.5-10	Ammonia - 10 mg/l
33-22	Anodizing		13				<10	>10	6.5-9.0	
33-23	Anodizing		180				25-60	3600	6.5-9.0	
20-22	Anodizing		0.3				10	1500	7.5	Nitrate - 50 mg/l
20-20	Anodizing		0.8				5	993	6.8-9.2	
33-35	Anodizing						16			
20-23	Anodizing		0.17				29		6.5-9.5	Nitrate - 18 mg/l
47-9	Anodizing					<0.1	<5		8	
6-35	Chemical Milling						(0)	708	8.0	
9-2	Chemical Milling		trace							
23-7	Chemical Milling							300		
33-30	Phosphating		2			0.1	5	1690	8.6	
19-24	Etching		0.15			2.2	11	927	8.0	
31-16	Printed Circuits	<0.2			<0.1		<10	506		
6-36	Immersion Plating				0.1			220	8.7	
46-4	Electropolishing		70-85				1-34	1200	2.6-5.8	

TABLE 34 WATER USE IN METAL-FINISHING PROCESSES

Plant	Line	Production, sq m/hr	Water Use, l/hr	Number of Operations	Liters/ Sq m/ Operation
36-12	Sn	42.8	454	1	10.61
	Cu-Sn	122.8	908	2	7.39
30-2	Rack Cd-Zn	171.5	5,995	2	17.49
33-30	Rack Cd	123.4	18,160	1	147.2
	Barrel Cd	45.8	11,355	1	247
20-3	Rack alkaline Sn	46.5	9,463	1	203.7
	Rack acid Sn	46.5	3,936	1	84.7
	Rack Ni, CuPbSn, Sn	9.3	6,188	3	222
	Rack zincate dip, Cu, CuPbSn, Sn	9.3	12,737	4	343
33-24	Rack Cu-Sn	92.90	7,040	2	37.9
33-5	Basket Sn	21.1	3,407	1	161.5
	Rack Ni, CuPbSn, PbSn	25.1	2,725	3	36.2
15-3	Rack Cd, manual	1.86	2,161	1	1,162
	Barrel Cd, manual	11.15	220	1	19.7
	Barrel Sn, manual	18.58	1,553	1	83.6
	Ditto	1.39	2,120	1	1,525
9-7	Electropaint	139.4	8,395	1	60.22
33-34	"	529.5	4,315	1	8.15
6-36	Immersion	48.8	1,022	1	20.94
31-16	Electroless Cu	23.23	12,491	5	107.5
	Ditto	25.08	5,678	3	75.5
30-19	"	23.23	5,678	3	81.48
	Electroless Sn	13.94	76	1	5.45
33-27	Electroless Ni	1.39	1,590	7	163
	Ditto	10.03	1,590	5	31.7
	"	11.71	2,271	10	19.4
33-23	Anodizing Al	297.4	18,927	4	15.9
33-22	Ditto	148.7	27,254	3	61.09
9-2	"	83.6	44,895	4	134.3
	Anodizing Mg	4.65	7,382	1	1,558.9
20-20	Anodizing Al	269.5	79,494	3	98.3
33-35	Ditto	55.8	2,082	6	6.2
20-22	"	3,253	87,064	4	6.7
20-23	"	102.2	18,927	4	46.3
41-2	"	16.73	5,678	4	84.9
6-35	"	9.29	2,271	2	122.2
47-9	"	13.94	1,930	1	138.5
4-8	Chemical Milling	37.17	3,785	2	50.9
	Ditto	9.29	1,893	2	101.9
	"	9.29	1,893	2	101.9

TABLE 34 (Continued)

Plant	Line	Production, sq m/hr	Water Use, l/hr	Number of Operations	Liters/ Sq m/ Operation
30-9	Chemical Milling	92.9	6,814	2	36.7
	Ditto	9.29	2,725	2	146.7
9-2	"	59.5	3,785	2	31.8
6-36	"	13.4	3,028	3	75.3
33-20	"	24.6	6,613	2	134.4
23-7	"	27.9	15,141	2	271.3
6-37	Auto rack silver	74.33	13,967	4	46.98
	Ditto	293	20,363	4	17.40
	Man rack silver	59.5	9,084	3	50.92
30-21	Ditto	11.61	8,365	4	180.1
	Auto rack silver	35.3	8,270	4	58.57
	Ditto	11.61	5,602	4	120.6
	"	22.22	9,311	4	100.2
	"	4.65	8,316	4	447.6
	Man rack silver	6.50	908	3	46.54
	"	6.50	908	2	65.32
	Cont strip silver	4.65	5,942	4	319.8
	Auto rack silver	0.84	(0)	1	(0)
	Stripping silver	1.12	757	1	658
	Man rack gold	1.39	8,138	4	1,460
31-16	Ditto	0.74	1,817	3	815
	Auto rack gold	8.55	1,590	2	93
8-5	Man rack silver	0.093	3,028	2	16,280
	Man rack gold	0.093	379	1	4,080
15-3	Man rack silver	0.047	460	2	4,952
	Ditto	1.86	462	2	124
	Man barrel silver	5.57	462	2	41.43
33-4	Auto rack gold	1.21	4,637	3	1,281
33-2	Man rack gold-silver	2.79	5,678	3	679
	Man rack silver-rhodium	2.79	1,703	3	204
36-12	Cont strip silver	31.6	454	2	7.18
30-19	Chemical etching	92.9	13,248	2	71.3
	Ditto	8.36	2,271	2	135.7
31-16	"	16.73	2,725	2	81.5
	"	18.6	3,785	2	101.9
	"	18.6	6,624	2	178.3
	"	11.15	7,570	2	340.2

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TABLE 3 4 (Continued)

Plant	Line	Production, sq m/hr	Water Use, 1/hr	Number of Operations	Liters/ Sq m/ Operation
4-9	Chemical etching	18.6	4,088	2	110.0
	Ditto	13.94	1,362	2	48.9
	"	13.94	1,362	2	48.9
	"	4.65	1,362	2	146.7
36-16	Chemical Machining	6.51	5,299	2	407
	Ditto	3.72	1,514	2	203.5
33-30	Zn phosphating steel	66.91	11,356	2	84.9
20-25	Ditto	464.7	11,356	2	12.2
23-8	Fe phosphating steel	153.4	946	1	6.17
46-1	Electropolishing	10.59	1,817	2	185.8
33-29	Electrochemical machining (Neutral Salt Electrolyte)	0.53	7.6	1	14.3
33-29	Electrochemical machining (Acid Electrolyte)	0.37	22,700	1	61,400
4-4	Electrochemical machining (Neutral Salt Electrolyte)	0.19	7.6	1	40.0

The first method of expressing water use requires choosing what operations in the overall process will be included in calculating water use and what operations will not be included. This method was followed in the Phase I guidelines, where all operations involving electrodeposition and posttreatment were included but cleaning and pickling were omitted. The water use has been calculated in terms of liters/sq m/operation where the square meters refer to the finished work and the operations exclude cleaning and pickling.

This method of expressing water use allows one to consider its variation in terms of those operations that are different from process to process. On the other hand, those operations that are common to most processes, i.e., cleaning and pickling, and involve about the same water use regardless of the process in which they occur, can be eliminated from consideration as a cause of variations in water use. Calculations for Phase II processes have been made using the above formula, omitting the initial cleaning and pickling operations, but counting all subsequent operations in a process.

As mentioned previously, less water is required for rinsing following alkaline cleaning and pickling than for rinsing following most other operations.

Data provided by the companies on area processed and water use is given in Table 34. From this data, frequency distributions for water use (l/sq m operation) for processes in subcategories (1), (2) and (3) were derived. These are given in Figures 2, 3 and 4. The median water use for each subcategory was used as a basis for the guidelines. It was felt that the plants identified by the contractor were well designed and well-operated and therefore the median value was a good approximation of the "average of the best "criteria specified for BPCTCA treatment.

Determination of Effluent Limitations

Effluent limitations were established from three parameters: (1) constituent concentration in the effluent, (2) water use, and (3) area processed or plated. Some dependence among these parameters is known, i.e., coagulation of precipitates out of dilute solution is more difficult than out of more concentrated solutions and area processed in a given line increases with complex shapes that give higher dragout and require more water for rinsing. The plant data obtained show no evident correlation between the three

factors probably because variations in water use and concentration due to other factors mask out the relationship between the three factors mentioned. Within the accuracy of the information available the three factors will be considered independent, that is, the concentration achievable in the effluent by exemplary chemical treatment is not related to the amount of water used for processing. The best water use is not necessarily found in a plant operating an exemplary waste treatment facility and vice versa. However, once exemplary values for both water use and concentrations have been established the product of the two represents an overall figure of merit that takes into account both parameters. Therefore, the guidelines can be expressed in terms of the product of the two parameters: (mg/l) x (l/sq m) = mg/sq m. More water may be used if lower concentrations are achieved and vice versa.

Concentrations of Effluent Constituents and pH. Table 35 lists the concentration basis for each constituent, The values given are for the total amount of constituent, dissolved and suspended. Therefore, both proper precipitation and efficient clarification and/or filtration are required to meet the concentrations considered achievable.

Water Use. The values of water use for each type of process cover a wide range. Variations in dragout, the concentration of dragout, and the degree of rinsing required vary and are in part responsible for the range of values. However, inefficiencies in reducing dragout to a minimum, rinsing beyond requirements, and poor design of rinsing facilities and waste of water are also responsible for making in making a wide range of water use . It is necessary, then, to estimate the minimum water use that can be achieved by essentially all of the lines of a given type of process.

Subcategory (1)

The process covered in this subcategory is anodizing.

Data on water use for anodizing operations from ten plants on eleven different lines are given in Table 34. Supplemental information and configuration data was obtained from two of these plants by plant visits.

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TABLE 35. CONCENTRATION VALUES FOR WASTEWATER
CONSTITUENTS FOR BPCTCA

Constituent	Present Phase II Proposal, mg/l
TSS	20
Cyanide (oxidizable)	.05
Cyanide (total)	0.5
Fluoride	20.0
Cd	0.3
Cr^{+6}	0.05
Cr (total)	0.5
Cu	0.5
Fe	1.0
Pb	0.5
Ni	0.5
Sn	1.0
Zn	0.5
Phosphorus	1.0
pH	6-9

Plant 33-23 is an aluminum anodizing plant which has a large automatic rack line for anodizing aluminum alloy parts. Figure 27 is a schematic of this facility. The waste treatment plant for treating the spent processing solutions and the rinse water effluents from this operation is shown in Figure 28. Data taken during the plant visit for treated effluent pollutant concentration are shown in Table 36.

Plant 6-35 is a large chemical anodizing and milling facility. Although the anodizing line was not operating during the time of the plant visit. Information on the sequence of operating steps and analyses of the waste treatment plant effluent was obtained and is given in Figure 29. Additonal data on rinse water flows and production rates were provided by the plant at a later date. The 65th percentile water use was found to be 90 1/sq m-operation (2.2 gal/sq ft-operation).

Subcategory (2)

Subcategory (2) covers coatings - phosphating, chromating and immersion plating.

One immersion plating plant was visited in this study. Plant 6-36 has an immersion tin plating facility consisting of one barrel plating line. Treatment of the wastes from this plant is done in an integrated waste treatment plant which was installed in 1972. The sludge from the treatment reservoirs is collected in storage tanks and hauled away by truck to a landfill several times a year.

Three chemical conversion coating plants were covered in this study. Two were zinc phosphating on steel and the other was iron phosphating on steel. The data on water use for these operations is listed in Table 34. The 65th percentile was found to be 17 1/sq m-operation (.42 gal/sq ft-operation). Since there was no apparent reason for this much smaller water compared to other subcategories, the largest value reported of 80 1/sq m-operation (2 gal/sq ft-operation) was chosen as the water use factor.

Subcategory (3)

Subcategory 3 covers chemical milling and etching.

Data on nine chemical milling lines in six plants are given in Tables 33 and 34. Supplemental data on two of these plants was obtained on visits to these plants.

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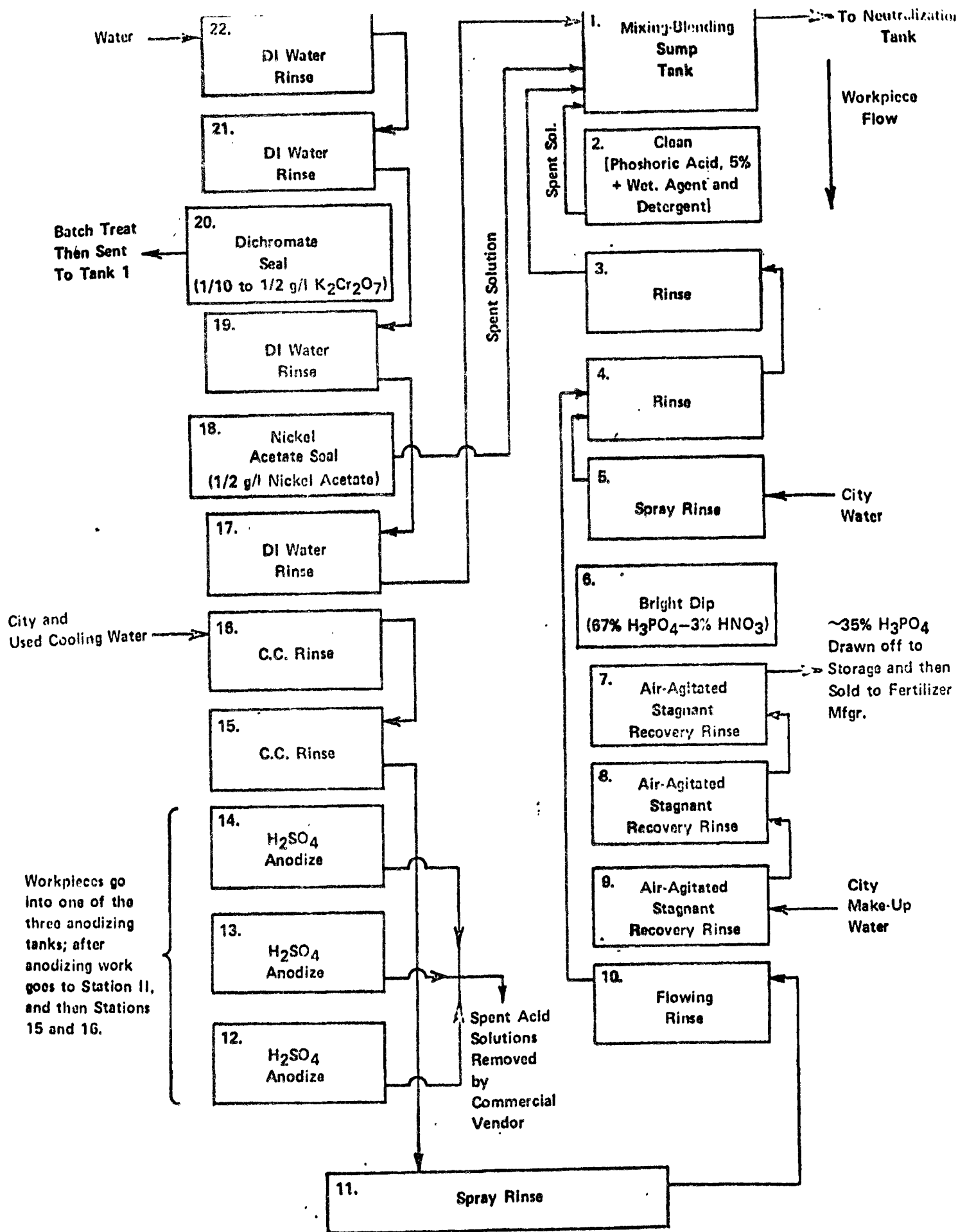
FIGURE 27 . SCHEMATIC REPRESENTATION OF PROGRAMMED AUTOMATIC HOIST RACK
LINE FOR ANODIZING ALUMINUM AT PLANT 33-23.

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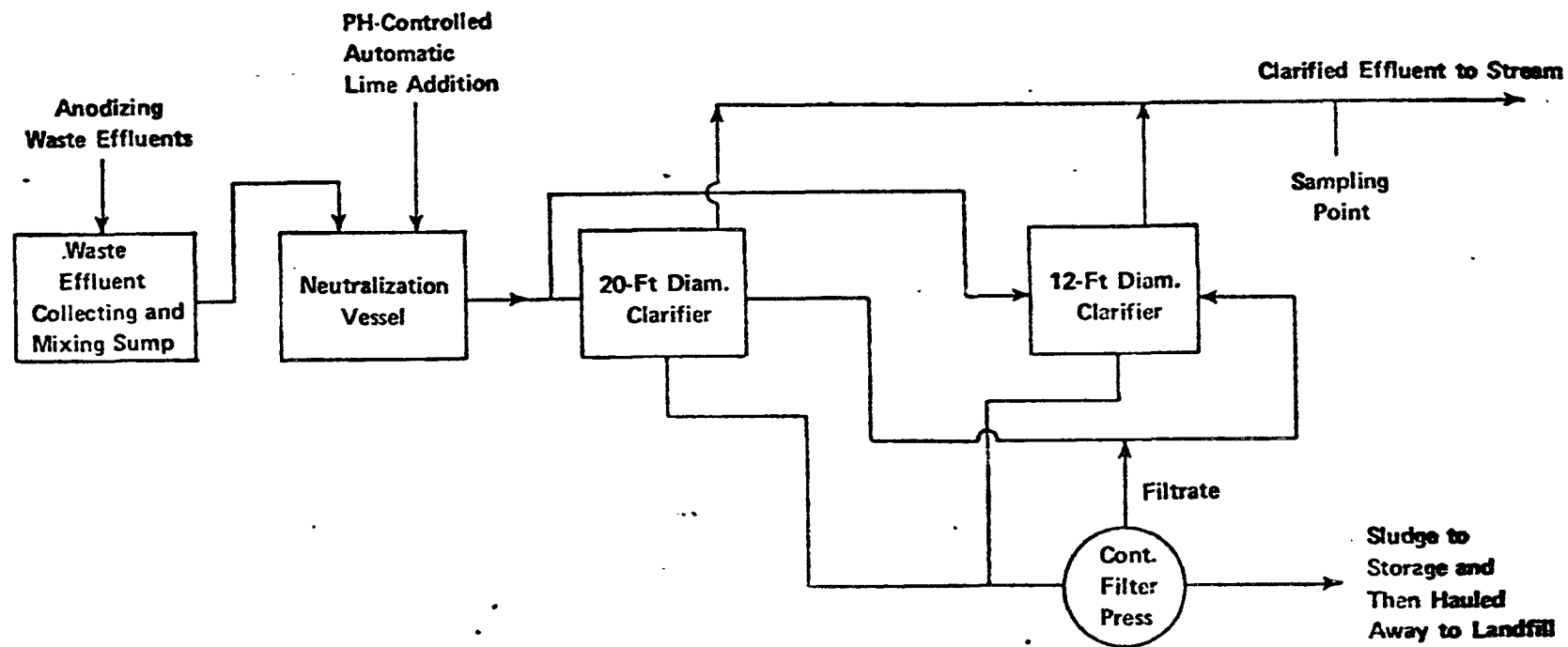
FIGURE 28 SCHEMATIC REPRESENTATION OF WASTE TREATMENT SYSTEM
FOR HANDLING ANODIZING EFFLUENTS AT PLANT 33-23

LEGEND

S SULFONATOR
○ PUMP
⊙ ALARM
Ⅰ VALVE
□ pH & ORP RECORDER - CONTROL
——— WASTE FLOW
········· CHEMICAL FEED
—— —— CONTROL SIGNAL

H₂SO₄

LIME

NON-CHROMATE
WASTES

PUMP

HOLDING
TANK 5

ORB

pH
2S

ORB

pH
2S

S

S

A

pH
(8S)

(LACIFIED)
EFFLUENT
TO RIVER

CHROMATE
WASTES

pH
(6S)

SAMPLING
POINT

SUMP

EQUALIZATION
TANK 1

REACTION
TANK 2A

REACTION
TANK 2B

NEUTRALIZATION
TANK 3

CLARIFIER
TANK 4

SLUDGE TO
DRYING LAGOON

FIGURE 29 SCHEMATIC REPRESENTATION OF THE WASTE TREATMENT FACILITY
FOR HANDLING CHEMICAL MILLING AND OTHER METAL FINISHING
EFFLUENT TO IT PLANT 6-35

TABLE 36   COMPARISON OF BCL ANALYTICAL RESULTS WITH TYPICAL ANALYTICAL
RESULTS REPORTED BY PLANT 33-23 FOR TREATED EFFLUENT

Total Concentration, mg/l

Constituent	Typical Plant 33-23 Effluent Analysis	Contractor Sampled Effluent
Al	0.1	0.2
Cr^{+6}	0.30	0.10
Cr^{tot}	0.32	0.28
PO_4	9.1	10.5
SS	23	22
TDS	3600	3500
pH	7.0	8.0

Plant 30-9 is a large aluminum and titanium chemical milling installation. Chemical milling of the two metals is carried out in the same area and some of the tanks are used interchangably, since some of the operating steps are similar.

The spent chemcial milling etchants a d other processing solution frcm this plant are hauled away by a licensed scavenger, and the rinse waters are nt to large settl'r j roads on company property.

Data on ten etching lines is given in Tables 33 and 34. Plant 31-16 was visited during this study and data tr ken during the plant visit is covered under subcategory (4) processes.

The 65th percentile water use for this subcategory is 120 l/sq m-operation (3.0 gal/sq ft-operation).

Thirty Day Average Vs One Dry Maximum

Five months of daily data were obtained from plant 15-1. This data appears in Table 35. In this time period the 30-day average value of 80 mg/sq m-operation for Zn was exceeded on two occasions, December 4, 1974 and December 10, 1974. The thirty day average of 80 mg/sq m-operation for CNT was never exceeded. The one-day maximum of 160 mg/sq m-operation was never exceeded by Zn or CN.

One month's effluent data was chosen at random from plant 12-6. It appears in Table 36. Ni, TSS, Cu, Zn, CNT are not out of compliance with the thirty day average or one-day maximum. Cr^{+6} is not out of compliance with the 30-day average but is out on the one-day maximum three times during the month.

Five months of twice weekly sampling TSS, for plant 33-15 is shown in Table 39. CrT, Ni, Cu never exceed the 30-day average or one-day maximum. Cr^{+6} is not in compliance for 30-day average or one-day maximum.

Plants Meeting the Guidelines

The effluent concentrations and water use factors have been collected for 21 plants in Table 40. Except as indicated on the table, all values are in total solids. Plants 36-1, 36-12, 15-3, 15-1, 12-6, 33-15 and 12-8 meet the 1977 standards. Plants 36-1 and 36-12 meet the new source performance standards. Plants 11-8 and 33-7 were out of compliance on only one or two parameters.

TABLE 37
PLANT 15 - 1

DATE	pH Hi	pH Lo	CN	Cr+6	CrT	Zn	Cu	Ni	TSS
6-01-74	9.3	7.5	5.7	.52	5.2	5.2	5.2	15.6	1508
6-02-74	8.6	6.9	7.4	5.4	6.8	12.6	20.4	13.6	408
6-03-74	8.4	6.9	5.3	.48	4.8	19.2	48	38.4	696
6-04-74	8.6	6.3	6.2	2.2	5.6	11.2	44.8	56.0	476
6-05-74	8.1	6.6	6.6	1.8	6.0	12.0	48.0	60.0	930
6-06-74	8.1	6.8	7.2	1.3	6.5	19.5	58.5	84.5	813
6-07-74	8.7	7.8	10.6	4.8	9.6	28.8	67.2	96.0	3984
6-08-74	9.5	8.0	16.6	.52	5.2	5.2	31.2	20.8	2392
6-09-74	8.2	6.8	35.3	4.2	6.0	12.0	42.0	42.0	690
6-10-74	9.0	7.1	22.3	.62	.72	7.2	50.4	21.6	806
6-11-74	7.9	6.6	19.2	.60	6.0	12.0	48.0	36.0	360
6-12-74	8.0	6.4	7.0	1.3	6.4	19.2	57.6	57.6	536
6-13-74	8.6	7.4	6.6	.60	6.0	24.0	60	66.0	1560
6-14-74	8.9	6.4	10.1	.92	9.2	36.8	73.0	110.4	3588
6-15-74	9.0	7.5	6.2	.56	5.6	16.8	39.2	56.0	1736
6-16-74	8.6	7.2	7.0	1.3	6.4	12.8	38.0	25.6	832
6-17-74	8.1	6.9	5.7	1.0	5.2	5.2	41.0	46.8	416
6-18-74	8.2	6.6	5.7	1.0	5.2	10.4	36.4	36.4	806
6-19-74	8.5	7.3	6.2	2.8	5.6	11.2	44.8	67.2	308
6-20-74	9.1	7.3	5.7	8.3	10.4	20.8	41.6	31.2	1196
6-21-74	8.3	7.5	6.6	8.4	30.0	12.0	42.0	66.0	810
6-22-74	9.5	8.3	8.4	40.3	15.2	15.0	22.8	30.4	2546
6-23-74	7.9	6.6	7.4	46.2	170.	20.4	61.2	61.2	1156
6-24-74	8.9	7.3	5.7	.52	10.4	10.4	52.	41.6	1378
6-25-74	8.8	7.2	6.2	5.6	16.8	5.6	50.4	56.0	1316
6-26-74	8.9	7.6	6.2	2.2	5.6	16.8	50.4	44.8	980
6-27-74	9.6	7.8	6.2	1.7	5.6	11.2	33.6	39.2	644
6-28-74	9.8	8.0	5.7	7.6	6.8	15.6	52.0	31.2	1040
6-29-74	9.5	8.3	5.7	78.0	130.	15.6	57.2	20.8	1950
6-20-74	8.1	7.0	3.1	.28	22.4	11.2	19.6	8.4	794
Average	8.7	7.2	8.6	8.0	22.4	16.2	44.6	46.0	1170

TABLE 38
PLANT 12 - 6

| DATE | pH | mg/m2-Operation | |
		Zn	CNT
11-13-74	8	1.3	27.7
11-14-74	7	11.9	14.5
11-18-74	6	15.8	18.5
11-19-74	7	13.2	22.4
11-20-74	7	48.8	14.5
11-25-74	8	15.8	29.0
11-26-74	10	6.6	31.7
Average	7.6	17.4	23.3
12-02-74	8	10.6	30.4
12-03-74	7	14.5	46.2
12-04-74	7	12.1	29.0
12-05-74	6	55.4	17.2
12-06-74	6	17.2	21.1
12-09-74	9	15.8	31.7
12-10-74	9	92.4	23.8
12-11-74	7	29.0	21.1
12-12-74	10	5.3	23.8
12-13-74	8	37.0	37.0
12-16-74	8	67.7	22.4
12-18-74	7	9.2	19.8
12-19-74	7	25.1	17.2
Average	7.6	38.4	26.2
1-03-75	6	10.6	23.8
1-06-75	9	11.9	15.8
1-07-75	7	6.6	19.8
1-08-75	7	7.9	13.5
1-09-75	7	33.0	15.3
1-10-75	8	66.0	18.5
1-13-75	8	13.2	29.0
1-14-75	10	11.9	52.8
1-15-75	8	15.8	27.7
1-16-75	7	13.2	14.5
1-17-75	7	48.8	13.2
1-20-75	6	15.8	18.5
1-22-75	8	6.6	15.8
1-23-75	7	5.6	15.8
1-24-75	8	36.3	22.4
1-27-75	8	9.2	17.2
1-28-75	6	7.9	18.5
1-29-75	7	1.3	14.5
1-30-75	7	26.4	29.0
1-31-75	7	21.1	26.
Average	7.4	18.6	20.9

TABLE 38
PLANT 12 - 6 -

| DATE | pH | mg/m2-Operation | |
		Zn	CNT
9-02-74	6	10.6	31.7
9-03-74	8	17.2	23.8
9-04-74	8	15.8	21.1
9-05-74	8	9.2	33.7
9-06-74	8	29.0	37.0
9-09-74	10	5.3	23.4
9-10-74	7	40.6	19.8
9-11-74	7	37.7	23.8
9-12-74	5	15.6	15.8
9-13-74	9	25.1	15.8
9-16-74	6	10.6	18.5
9-17-74	7	11.9	17.2
9-18-74	7	6.6	22.4
9-19-74	8	7.9	15.8
9-20-74	10	33.0	18.5
9-23-74	8	6.6	29.0
9-24-74	7	13.2	5.3
9-25-74	7	11.9	27.7
9-26-74	7	15.8	14.5
9-27-74	6	48.8	9.2
9-30-74	8	6.6	18.5
Average	7.5	16.8	20.5
10-01-74	7	79.2	15.8
10-02-74	6	38.3	22.4
10-03-74	8	48.8	17.2
10-04-74	6	9.2	21.1
10-07-74	7	37.0	18.5
10-08-74	9	13.2	29.0
10-09-74	8	26.4	42.2
10-10-74	8	10.6	31.7
10-11-74	60	11.9	39.6
10-14-74	10	9.2	46.2
10-15-74	9	68.6	26.4
10-16-74	7	10.6	22.4
10-17-74	6	14.5	21.1
10-18-74	6	9.2	31.7
10-21-74	8	55.4	23.8
10-22-74	8	17.2	26.4
10-23-74	8	15.8	21.1
10-24-74	8	9.2	22.4
10-25-74	7	29.0	23.8
10-28-74	7	5.3	37.0
10-29-74	10	37.0	22.4
10-30-74	7	27.7	19.8
Average	7.3	30.8	26.3
11-01-74	7	9.2	22.4
11-02-74	7	11.9	15.8
11-04-74	8	15.6	19.8
11-05-74	8	11.9	18.5
11-06-74	9	6.6	22.4
11-07-74	8	7.9	15.8
11-08-74	7	33.0	18.5
11-11-74	6	66.0	29.0
11-12-74	8	7.9	52.8

TABLE 39
PLANT 33 - 15

DATE	pH	Cu	Ni	Cr+6	CrT	CNT	TSS
							mg/m2-Operation
7-03-74	7.5	18.5	95	69.8	95	10.6	945
7-09-74	8.6	29.3	34.3	39.6	44.9	2.9	1637
7-11-74	8.8	16.2	37.1	46.4	48.7	3.2	858
7-15-74	8.6	11.6	44.1	23.2	27.8	2.8	766
7-17-74	8.3	31.7	95	52.8	55.4	2.6	1109
7-23-74	8.4	17.5	35	61.3	63.5	8.7	1226
7-26-74	8.4	16.3	36.7	53.0	61.2	4.9	734
7-30-74	8.5	30.6	49.0	65.3	71.4	4.1	877
Average	8.4	21.5	53.3	53.9	58.5	5.0	1006
8-02-74	8.7	16.3	42.8	75.5	77.5	6.7	653
8-06-74	8.5	10.2	49.0	65.3	73.4	2.2	714
8-09-74	8.8	14.3	40.8	55.1	61.2	5.3	898
8-12-74	8.9	11.0	44.2	25.8	27.6	1.8	2594
8-14-74	8.7	16.3	57.1	61.2	63.2	2.0	1102
8-19-74	8.5	19.7	39.4	46.0	70.1	2.0	1489
8-23-74	8.8	16.2	51.0	71.8	81.2	3.0	974
8-26-74	8.6	48.2	122.6	74.5	48.2	2.6	1862
8-28-74	8.5	23.2	74.2	69.6	83.5	2.1	766
Average	8.7	21.9	65.1	68.1	73.2	3.5	1382
9-04-74	8.8	18.3	89.7	75.5	77.5	8.2	836
9-06-74	8.8	28.6	65.3	36.7	63.2	4.1	714
9-10-74	8.6	21.9	21.9	32.9	54.8	8.1	701
9-12-74	8.7	19.7	55.7	50.8	55.7	13.2	1067
9-16-74	8.7	15.3	78.8	61.3	63.5	8.1	460
9-19-74	8.8	13.9	46.4	69.6	83.5	4.9	742
9-24-74	8.9	15.3	37.2	37.4	59.1	3.7	548
9-27-74	9.1	30.2	74.2	60.3	65.0	6.5	928
Average	8.8	20.4	58.6	53.1	65.3	7.1	750
10-02-74	8.9	24.1	43.8	50.4	65.7	7.9	1621
10-04-74	8.9	18.6	37.1	32.5	39.4	7.9	742
10-07-74	8.7	30.6	96.4	21.9	21.9	7.7	1051
10-10-74	9.0	16.2	44.1	32.5	32.5	4.9	557
10-15-74	8.6	18.5	89.8	23.7	23.7	3.4	818
10-18-74	8.6	17.5	87.6	24.1	26.3	8.3	635
10-21-74	8.9	36.7	73.4	20.4	24.5	8.8	612
10-23-74	8.9	21.9	65.7	15.3	19.7	13.8	701
10-29-74	8.9	26.3	61.3	6.6	11.0	8.5	876
10-31-74	9.0	32.8	48.2	11.0	30.7	8.1	1007
Average	8.8	30.4	80.9	29.8	36.9	9.9	883
11-04-74	8.7	18.4	40.8	18.4	24.5	5.1	449
11-06-74	8.3	24.5	81.6	30.6	34.7	4.3	1204
11-12-74	8.3	26.5	73.4	4.1	14.3	1.2	1775
11-15-74	8.7	22.4	57.1	53.0	75.5	6.9	1408
11-19-74	8.5	20.2	71.8	7.4	117.8	2.4	1398
11-21-74	8.6	34.9	33.1	25.8	42.3	8.8	626
11-25-74	8.3	35.0	81.0	9.2	31.3	2.4	3864
11-27-74	8.7	17.2	55.0	24.1	46.4	3.5	877
Average	8.5	24.9	61.7	21.6	48.4	.3	1450

TABLE 40   mg/l

PLANT	l/m²-op	(gal/ft²-op)	Cu	Ni	CrT	Cr+6	Zn	Pb	Sn	Fe	Cd	Au	Ag	Rh.	Al	Hg	CNT	CNA	PO₄	F⁻	TSS	pH
*11-9	120	(3.0)	.12	.60	.045	.03	.535	–	–	–	.21	–	–	–	–	–	.42	.41*	.07	–	<10	6.0 - 9.5
20-19	.70	(4.4)	1.5*	.09	.20	.10	.43*	–	.20	.18	.03	–	–	–	–	–	.01	.04	.13	–	10	8.2
4-36-1	29	(.733)	.14	.08	.06	.06	.34	–	–	.16	.03	–	–	–	13	–	.025	.014	.02	–	<10	6.0 - 9.5
3-36-12	13	(.329)	.73	–	–	–	.52	–	0.5	–	–	–	<.01	–	–	–	<.01	–	–	–	<10	8.0
33-5	232	(5.8)	.355	5.7	–	–	–	5.12	.718	.62	–	–	–	–	–	–	–	–	–	59	–	7.18
#15-3	184	(4.6)	.26	.14	.07	.023	.12	–	–	–	.009	–	–	–	–	–	.06	.06	–	–	–	4.55
20-2*	232	(5.8)	.17	1.9	.54	–	.25	–	–	1.0	.01	–	–	–	–	–	<.02	–	.02	11	4	6.5 - 9.5
32-21	128	(3-2)	<1.0	–	<1.0	–	<1.0	<.05°	–	1.0	–	–	–	–	–	–	.025°	–	–	–	<25	–
33-2	4440	(111)	–	–	–	–	–	–	–	–	–	Tr	Tr	Tr	–	–	.1	–	–	–	6	5 - 10
#15-1	132	(3.3)	–	–	–	–	.15	–	–	–	–	–	–	–	–	–	.16	–	–	–	–	6 - 10
#12-6	60	(1.5)	.8	.8	.4	.13	.3	–	–	–	–	–	–	–	–	–	.14	–	–	–	20.5	7.9 - 8.7
#23-15	211	(5.3)	.09	.27	.30	.28	–	–	–	–	–	–	–	–	–	–	.01	–	–	–	5.1	8.67
#12-8	80	(2.0)	.50	–	.72	–	.58	–	–	.26	–	–	–	–	–	–	.11	–	–	–	–	8 - 9
6-37	52	(1.3)	<5	<5	–	–	–	–	–	–	–	5	–	–	–	–	–	<1	–	–	–	7 - 10
43-1	–	–	.2	.5	.05	–	–	–	–	–	.3	–	–	–	.1	.001	.01	–	–	–	–	6.5 - 8.0
10-11	–	–	–	<.5	–	–	–	–	–	–	–	0	0	0	–	–	0	–	–	–	20	7 - 8
5-7	–	–	–	–	–	–	–	–	–	–	–	–	.20	–	–	–	.1	–	.01	–	25	6.8 - 8.7
19-24	–	–	.15	–	.05	.03	2.2	–	–	–	.02	–	.05	–	–	–	–	–	–	2.2	–	–
20-17	–	–	.02	.31	–	–	.17	.05	–	.85	.01	–	0	–	–	–	.06	–	–	–	20	7.18
23-7	–	–	.01	–	5.0	5.0	–	–	–	.5	.05	–	–	–	–	–	–	–	–	–	–	–
30-21	–	–	–	–	–	–	–	–	–	–	–	.003	.03	–	–	–	.07°	–	.3°	–	30	–

\# = in compliance w/ 1977 standards

\+ = in compliance w/ new source performance standards

* = out of compliance on parameters starred

° = dissolved solids

The plated area is the primary unit of production on which the effluent limitations in Table 1 are based. Plated area is defined with reference to Faraday's Law of electrolysis by the following equation:

$$S = \frac{EIT}{100 \, kt}$$

Equation 2

where s = area, sq m (sq ft)
E = cathode current efficiency, percent
I = current used, amperes
T = time, hours
t = average thickness of deposit, mm (mil)
k = a constant for each metal plated based on the electro-chemical equivalent for metal deposition, amp-hr/mm-sq m (amp-hr/mil-sq ft).

The numerical product of current and time (IT) is the value that would be measured by an ampere-hour meter. Values of the constant k based on equivalent weight and the valance of the metal deposited are shown in Table 41.

Average thickness can be approximated by averaging thickness measurements at several points on a single plated part, to establish the ratio of average to minimum thickness. Minimum thickness is customarily monitored to meet the specifications of purchasers of electroplated parts, based on service requirements.

This equation was used in this study to determine the plated areas per unit time in each plating operation when the only available information was the current used and the average thickness of deposit. This equation was also used as a check on estimates of surface area plated provided by the plants contacted.

To calculate the total plated area on which the effluent limitations are based for a specific plant, it was necessary to sum up the area for each electroplating process line using Equation (2). For process lines containing two or more electroplating operations (such as in copper-nickel-chromium decorative plating) the plated area is calculated by Equation (2) for each plating operation in the process. The results should be the same, since the same parts are processed through each operation. However, if the calculated plated area differed for each plating operation in a single process line, the average of the calculated plated areas for the operations was used. The sum of the plated area for each process line is the total plated area for the plant.

Process changes are not currently available for the metal finishing industry that would lead to greater pollution reduction than can be achieved by the recommended effluent limitations. Some possible process changes such as use of noncyanide plating baths may eliminate one pollution parameter, but do not eliminate all and may cause other problems. They may be useful in some facilities for reducing the cost of meeting the effluent limitations recommended in this document.

Nonwater Quality Environmental Impact

As discussed in Section VIII of this report, the principal nonwater quality aspect of metal finishing waste treatment is in the area of solid waste disposal. Disposal of sludges resulting from metal removal by chemical treatment is a current problem in many states that have a high concentration of facilities. The problem might be partially alleviated by disposal of drier sludge. Such added costs for removal of water from sludge would be imposed by the requirements for solid waste disposal and does not directly result from the requirement for water pollution reduction.

The use of advanced technology to recover metal plating chemicals from rinse water rather than chemical treatment which adds to the sludge is being applied in areas where the sludge-disposal problem is greatest. Further impetus in the direction of recovery rather than disposal is expected to be provided by authorities responsible for solid waste disposal. This will have an overall beneficial effect on water pollution because of the concurrent requirements for water conservation for economic application of recovery techniques.

It is estimated that many of the existing sources discharging to navigable waters are already using chemical treatment methods with a high percentage removal of metals. This is particularly true in geographic areas where water pollution reduction has been emphasized and the sludge-disposal problem is most evident.

There will be no direct effect on air quality as a result of the application of recommended technology for water pollution reduction. Indirect effects related to increased energy use are estimated to be modest.

Plated Area Unit of Production

Small discrepencies in the above calculation for two or more plating operations in the same process line might be related to a difference in the actual current efficiencies from those in Table 37 which are to be used for the calculation. However, experience with data from several plants indicated that the more likely cause of the discrepancy is the accuracy of the reported values of average plate thickness.

The use of ampere-hour on rectifiers might have value for monitoring or record keeping for some plants in lieu of measuring the area of the parts plated provided the average thickness plated is known or determined.

Records of plating voltage and ampere-hours on each rectifier (or watt-hours) plus thickness deposited might be correlated with watt-hours of electricity consumed per day or month with allowance for other electricity uses (lighting, pumps, etc) to estimate total plated area per day or month. The total effluent could be approximated by the plant water purchases if mainly for electroplating. Thus, the information on electric power consumption and water consumption from monthly bills for these services might be used in an approximation of daily plated area for a cross check against plated area determined by more direct means.

In practice, it should be possible for electroplaters to readily adapt to keeping records of plated area for reporting purposes. The fact that many platers do not presently know their production rate in terms of surface area plated is not a valid consideration since there has been no prior requirement to keep such records. Determining plated area should not be difficult for platers whose process operation is dependent on use of the correct current density for optimum plating results.

"Process";   A process is the accumulation of steps
              required to bring about an electroplating
              result.

"Operation"; The concept of an operation is a crucial
              one in the formation of limitations
              for each individual installation plant.
              For this purpose, an operation shall

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Element	Atomic weight	Valence	mg/cou-lomb	g/amp hr	oz/amp hr	lb/1,000 amp hr	sp gr	oz/sq ft for 0.001 in.	amp hr to deposit 0.001 in./sq ft	Symbol of element	amp hr to ...	% eff
Aluminum	26.97	3	0.0932	0.3354	0.0118	0.7394	2.7	0.225	19.05	Al		
Antimony	121.76	5	0.2523	0.9085	0.032	2.0028	6.68	0.557	17.4	Sb		
		3	0.4206	1.5141	0.0535	3.3380	6.68	0.557	10.4			
Arsenic	74.91	5	0.1525	0.5589	0.0197	1.2322	5.73	0.475	24.1	As		
		3	0.2587	0.9315	0.0328	2.0536	5.73	0.475	14.5			
Bismuth	209.0	5	0.4332	1.5594	0.055	3.4378	9.8	0.816	14.8	Bi		
		3	0.7219	2.5990	0.0915	5.7297	9.8	0.816	8.93			
Cadmium	112.4	2	0.5824	2.097	0.074	4.6226	8.64	0.72	9.73	Cd	4.12	50-100
Chromium	52.01	6	0.0898	0.323	0.0114	0.7129	7.1	0.591	51.8	Cr	21.9	13
		3	0.1796	0.646	0.0228	1.4258	7.1	0.591	25.9			
Cobalt	58.94	2	0.3054	1.099	0.0388	2.4236	8.9	0.74	19.0	Co	6.05	100
Copper	63.57	2	0.3294	1.186	0.0418	2.6142	8.92	0.74	17.7	Cu	7.50	100
		1	0.6588	2.372	0.0837	5.2283	8.92	0.74	8.84		3.74	50-100
Gallium	69.72	3	0.2408	0.8670	0.0306	1.9114	5.9	0.491	16.0	Ga		
Germanium	72.60	4	0.1881	0.6771	0.02388	1.4928	5.35	0.445	18.6	Ge		
		2	0.3762	1.3542	0.04776	2.9855	5.35	0.445	9.31			
Gold	197.2	3	0.6812	2.4522	0.0865	5.406	19.3	1.61	18.6	Au		
		2	1.0218	3.6783	0.1297	8.1094	19.3	1.61	12.4			
		1	2.0435	7.3567	0.2595	16.2187	19.3	1.61	6.2		2.63	100
Indium	114.76	3	0.3964	1.4271	0.05033	3.1461	7.31	0.608	12.1	In	5.13	20-40
Iridium	193.1	4	0.5003	1.8001	0.06349	3.9704	22.42	1.869	29.4	Ir		
		3	0.6670	2.4012	0.08469	5.2938	22.42	1.869	22.1			
Iron	55.84	2	0.2893	1.042	0.0368	2.2963	7.9	0.66	17.9	Fe	7.38	100
Lead	207.2	2	1.074	3.865	0.1362	8.5210	11.3	0.94	6.91	Pb	2.93	100
Manganese	54.93	2	0.2846	1.0246	0.0362	2.2588	7.2	0.598	16.5	Mn		
Mercury	200.61	2	1.0394	3.7420	0.1320	8.2496	13.55	1.129	8.55	Hg		
		1	2.0788	7.4839	0.2640	16.4992	13.55	1.129	4.27			
Nickel	58.69	2	0.3041	1.095	0.0386	2.4135	8.9	0.742	19.0	Ni	8.05	100
Palladium	106.7	4	0.2764	0.9951	0.035	2.1939	12.0	0.998	28.6	Pd	12.12	
		3	0.3686	1.3268	0.0467	2.9252	12.0	0.998	21.4		9.07	
		2	0.5528	1.9903	0.0703	4.3878	12.0	0.998	14.2		6.02	
Platinum	195.23	4	0.5058	1.8208	0.0645	4.0142	21.4	1.78	27.6	Pt	11.89	60
		2	1.0115	3.6416	0.1284	8.0283	21.4	1.78	13.85		5.85	60
Polonium	210	4	0.5440	1.958	0.0691	4.318	----	----	----	Po		
Rhodium	102.9	4	0.2666	0.9598	0.0338	2.1160	12.5	1.04	30.8	Rh	15.05	
		3	0.3555	1.2797	0.0451	2.8213	12.5	1.04	23.1		9.79	60
		2	0.5332	1.9196	0.0677	4.2319	12.5	1.04	15.37		6.57	
Rhenium	186.31	7	0.2758	0.9929	0.0350	2.1890	20.53	1.710	48.6	Re		
Selenium	78.9	4	0.2046	0.7364	0.0260	1.6235	4.81	0.400	15.4	Se		
Silver	107.88	1	1.1179	4.0245	0.142	8.8726	10.5	0.875	6.16	Ag	2.62	100
Tellurium	127.61	4	0.3306	1.1901	0.0420	2.6238	6.25	0.520	12.4	Te		
		2	0.6612	2.3803	0.0840	5.2476	6.25	0.520	6.19			
Thallium	204.39	1	2.1180	7.6249	0.2583	16.8000	11.85	0.986	3.82	Tl		
Tin	118.7	4	0.3075	1.1070	0.039	2.4406	7.3	0.61	15.63	Sn	6.62	90
		2	0.6150	2.2141	0.078	4.8812	7.3	0.61	7.82		3.31	100
Zinc	65.38	2	0.3387	1.2195	0.043	2.6886	7.1	0.59	13.7	Zn	5.80	100 (ACID) 90 (CN)

* From Electroplating Engineering Handbook

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be defined as any step followed by
a rinse in the electroplating process
in which a metal is electrodeposited
on a basis material. Electroless
plating on non-metallic materials
for the purpose of providing a
conductive surface on the basis
material and preceding the actual
electroplating step, and the past
treatment steps of chromating,
phosphating and coloring where an
integral part of the plating line
and stripping where conducted in
conjunction with electroplating for
the purpose of salvaging improperly
plated parts may be included under
the term operation for the purpose
of calculating effluent discharge.

"Rinse";   A rinse is a step in a process used
to remove components of a bath from
the work following an operation.
A rinse may consist of several
sequences such as successive
countercurrent rinsing or hot
rinsing followed by a cold
rinsing with deionized water.
Nevertheless, there is only one
rinse after an operation.

Applying Effluent Limitation Guidelines

The application of the effluent limitation guidelines
will be illustrated by examples. In all cases, certain
basic information is needed from a plant:

(1)   The number of operations in each process line
        including initial cleaning and pickling
        operations and all rinses

(2)   The sq m/hr through each process line (average
        for 30 sequential days)

(3)   The volume of effluent from the plant
        due to electroplating processes (average
        for 30 sequential days)

(4)   The concentrations of waste water constituents
        in the effluent that are limited by the
        guidelines. These are the concentrations

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in the effluent due to electroplating processes before dilution by effluent from other processes (average for 30 sequential days).

Determination of Finished Area/Hr/Operation

The area for each line will be determined from information on the (1) average amperes used, (2) the sequence of plating operations, and (3) the average thickness in mil of each type of plate. If complete data on thickness is lacking, the following value will be used:

Copper	0.3 mil
Nickel	0.3 mil
Zinc	0.3 mil
Chromium	0.015 mil

Where chromating follows plating, the area will be the same as that of the primary plating operation. The equation:

$$S = EIT/100 \ kt$$

is then used to calculate plated area/hr/operation. In a line with several sequential operations, it is likely that the calculated plated areas for each plating operation will vary from each other although the actual area plated should be the same. The difference in calculated areas may vary by a factor of two or three. When applying the guidelines, the figure used for area plated should be the arithmetic average of the calculated plated areas.

Where actual amperes are not known, a value equal to 2/3 of the installed capacity for the line should be used. Where information on amperes is completely lacking for a line but water use is available, the sq m/hr may be determined by:

$$Sq \ m/hr = \frac{l/hr \ used \ in \ the \ line}{(200 \ l/sq \ m)(no. \ of \ operations)}$$

$$Sq \ ft/hr = \frac{gal/hr \ used \ on \ the \ line}{(5 \ gal/hr)(no. \ of \ operations)}$$

Once the plated area has been measured the guidelines can be used to determine the total allowable discharge of waste water constituents from the plant. Every time the surface is rinsed, following some operation in the process line, it is assumed that more waste water is produced, and a greater quantity of waste water constituents may be discharged under the guidelines. The cleaning and pickling rinses are

therefore incorporated into the rinse following the first plating operation for purposes of calculating the allowable amount of waste water constituents discharged. The total allowable discharge in g/day will be:

(10³) (sq m plated/hr) (effluent limitation in mg/sq m)
(No. of oper.) (hr/day)

The total allowable discharge in lb/day is:

(10⁻⁶) (sq ft plated/hr) (effluent limitation
in lb/million sq ft (No. of oper.) (hr/day)

These relations hold for each effluent limitations guideline value listed in Table 1. The relations apply to each process line or part of a process line if the area plated/hr changes in the line.

The actual discharge from the plant is the product of the volume of effluent/hr and the concentration of waste water constituent in the effluent.

Thus,

q/day = (liters/hr) (mg/l) (10⁻³) (hr/day)
lb/day = (8.33 x 10⁻⁶) (gal/hr) (mg/l) (hr/day)

Figure 30 represents such a situation. The line processes 15 sq m/hr. The volume of effluent is 3,000 l/hr. The plant operates 10 hr/day. There are three operations in this line, chromium electroplating, etching, and anodizing.

The discharger is allowed: (10⁻⁶) (sq m/hr) (effluent limitation in mg/sq m-operation) (number of operation) (hr/day) = kg/day pollutant

The actual discharge is the product of the volume of effluent/hr and the concentration of waste water constituent.

kg/day = (liters/hr) (mg/l) (10⁻⁶) (hr/day)

Thus, in this example the discharger is allowed to discharge the following amount of chromium for chromium electroplate

(10⁻⁶) (15 sq m/hr) (80 mg/sq m-operation) (1 operation)
(10 hr/day) = 1.2 x 10⁻² kg/day

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for anodizing

$(10^{-6})(15)(45)(1)(10) = 6.75 \times 10^{-3}$ kg/day

for etching

$(10^{-6})(15)(60)(1)(10) = 9.0 \times 10^{-3}$ kg/day

In total he may discharge the sum of the three:
2.78×10^{-2} kg/day of chromium total.

He may discharge one-tenth of that or
2.78×10^{-1} kg/day of Cr^{+6}

If the final effluent concentration is equal to 0.56 mg/l
for CrT and 0.06 mg/l for Cr^{+6}, the actual discharge will be
$$\frac{(3000 \text{ l/hr})(.56 \text{ mg/l})(10^{-6})}{(10 \text{ hr/day})} = 1.68 \times 10^{-2}) \text{ kg/day of CrT}$$
and
$$\frac{(3000 \text{ l/hr})(.06 \text{ mg/l})(10^{-6})}{(10 \text{ hr/day})} = 1.8 \times 10^{-1} \text{ kg/day of } Cr^{+6}$$

Thus, the plant is meeting the guidelines.

```
        ┌──────────────┐
        │  Alkaline    │
        │   Clean      │
        └──────┬───────┘
               │
        ┌──────▼───────┐
        │    Rinse     │
        └──────┬───────┘
               │
        ┌──────┴───────┐
        │    Acid      │
        │  Pickling    │
        └──────┬───────┘
               │
        ┌──────┴───────┐
        │    Rinse     │
        └──────┬───────┘
               │
        ┌──────▼───────┐
        │  Chromium    │
        │   Plate      │
        └──────┬───────┘
               │
        ┌──────┴───────┐
        │    Rinse     │
        └──────┬───────┘
               │
        ┌──────┴───────┐
        │    Etch      │
        └──────┬───────┘
               │
        ┌──────┴───────┐
        │    Rinse     │
        └──────┬───────┘
               │
        ┌──────▼───────┐
        │   Anodize    │
        └──────┬───────┘
               │
        ┌──────┴───────┐
        │    Rinse     │
        └──────┬───────┘
               │
        ┌──────┴───────┐
        │     Dry      │
        └──────────────┘
```
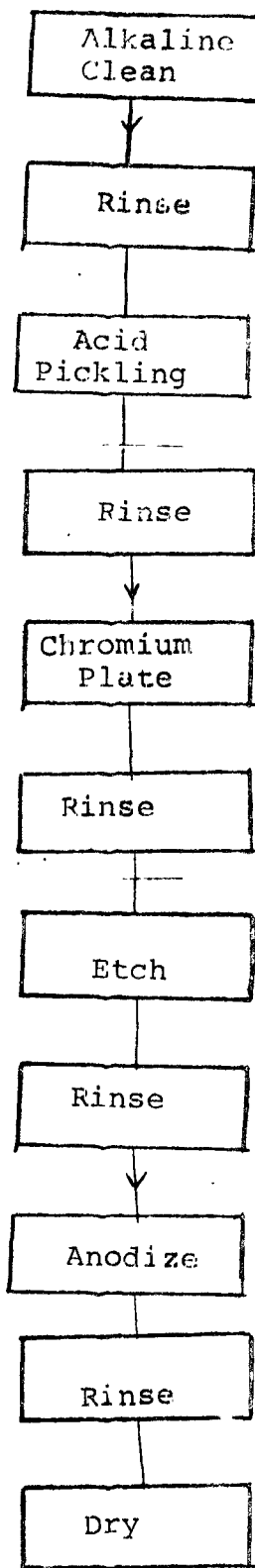
Figure 30

BEST AVAILABLE TECHNOLOGY ECONOMICALLY
ACHIEVABLE, GUIDELINES AND LIMITATIONS

Introduction

The effluent limitations which must be achieved July 1, 1983, are to specify the degree of effluent reduction attainable through the application of the best available technology economically achievable. This technology can be based on the very best control and treatment technology employed by a specific point source within the industry category and/or subcategory of technology that is readily transferable from one industry process to another. A specific finding must be made as to the availability of control measures and practices to eliminate the discharge of pollutants, taking into account the cost of such elimination.

Consideration must also be given to

(a)   the age of the equipment and facilities
        involved

(b)   the process employed

(c)   the engineering aspects of the application
        of various types of control technologies

(d)   process changes

(e)   cost of achieving the effluent reduction
        resulting from the technology

(f)   nonwater quality environmental impact
        (including energy requirements).

The best available technology economically achievable also assesses the availability in all cases of in-process controls as well as the control or additional treatment techniques employed at the end of a production process.

A further consideration is the availability of processes and control technology at the pilot plant, semiworks, or other levels, which have demonstrated both technological performances and economic viability at a level sufficient to reasonably justify investing in such facilities. Best

available technology economically achievable is the highest degree of control technology that has been achieved or has been demonstrated to be capable of being designed for plant scale operation up to and including no discharge of pollutants. Although economic factors are considered, the costs for this level of control are intended to be top-of-the-line of current technology subject to limitations imposed by economic and engineering feasibility. However, best available technology economically achievable may be characterized by some technical risk with respect to performance and with respect to certainty of costs and thus may necessitate some industrially sponsored work prior to its application.

Industry Category and Subcategory Covered

The pertinent industry category is the metal finishing segment of the electroplating industry divided into Subcategories (1) and (2) as previously discussed in Section IV.

Identification of Best Available Economically Achievable

Subcategory (1)

The best available technology economically achievable is the use of in-process and end-of-process control and treatment to achieve no discharge of pollutants. By the use of in-process controls to reduce the volume of waste water, it becomes economical to use end-of-process treatment designed to recover water and reuse the water within the plant thus avoiding any discharge of effluent to navigable waters. Solid constituents in the wastewater are disposed of to landfill or otherwise. A line in Plant 50-21 plating silver has eliminated liquid effluent discharge for several months, and continued demonstration of this operation will support the fact that technology is available to achieve this. Plant 11-22, a chromium electroplater studied in Phase I, is using a system designed to eliminate liquid effluent by subjecting effluent from the clarifier of the chemical treatment plant to reverse osmosis and recycling water to process. The concentrate from the reverse osmosis unit is evaporated to dryness. It is expected that other methods will be developed during the next five years to avoid discharge of effluent to navigable waters and thus achieve no discharge of pollutants in an economical manner. While the above examples of zero discharge are being achieved in conjunction with electroplating operations, the similarity of operations in processes in Subcategory (1) to those in the electroplating processes, and the similarity of the

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waste waters, suggests that techniques of obtaining zero discharge for electroplating processes are equally applicable to the other processes in Subcategory (1).

Subcategory (2) and (3)

The best available technology economically achievable is the use of in-process and end-of-process control and treatment to achieve no discharge of pollutants. Processes in Subcategory (2) are distinguished from those in Subcategory (1) only by water use. The operations in the two subcategories are very similar, the types of waste waters obtained are essentially the same, and the types of waste treatments that are applicable are the same. The evidence that zero discharge is being and will be attained for processes in Subcategory (1) is equally applicable to processes in Subcategory (2).

Rationale for Selection of Best Available
Technology Economically Achievable

Age of Equipment and Facilities

Replacement of older equipment and facilities will permit the installation of modern multitank countercurrent rinsing systems after each operation in each process line with conservation of water use for rinsing. The use of reclaim and recovery systems after each finishing operation should be possible. Use of inprocess controls to the maximum extent will reduce the volume of effluent to the point that recovery and reuse of water is economically feasible.

Process Employed

The application of the technology for end-of-process recovery and reuse of water to the maximum extent possible is not dependent on any significant change in the processes now used. Most water recovery technology can produce a higher quality of water than normally available from public or private water supplies. High purity water for the final rinse after metal finishing operations is desirable to improve the quality of the product.

Engineering Aspects of the Application of Various Types of Control Techniques

Many plants are successfully using evaporative recovery systems after one or more plating operations with a net savings compared to chemical treatment. Evaporative systems are in current use after copper, nickel, chromium, zinc,

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brass, tin, lead, and gold plating operations. Some plants have succeeded in using recovery systems after all plating operations in their facility. The engineering feasibility of in-process controls for recovery of chemicals and reuse of water are sufficiently well established. Sufficient operational use has been accumulated to reduce the technical risk with regard to performance and any uncertainty with respect to costs.

The technical feasibility of end-of-process water recovery systems has been established by extensive development of the recovery of pure water in many related industrial processes. Although some uncertainty may remain concerning the overall costs when applied to metal finishing waste waters, such uncertainty primarily relates to the volume of water that must be processed for recycling and reuse. The fact that the technology as applied to the electroplating industry has progressed beyond the pilot plant stage and has been designed and is being built for fullscale operational use indicates that the technology is available and probably economical. These systems are equally applicable to processes other than electroplating due to the similarity in the waste water produced.

Process Changes

Application of the technology is not dependent on any process changes. However, process changes and improvements are anticipated to be a natural consequence of meeting the effluent limitations in the most economic manner.

Nonwater Quality Environmental Impact

Application of technology to achieve no discharge of pollutants to navigable waters by July 1, 1983, will have little impact on the solid waste disposal problem with regard to metal removal as sludge beyond that envisioned to meet effluent limitations recommended for July 1, 1977. The volume of soluble salts will be substantially increased.

In general, it is anticipated that the technology will be applied in a manner such that no discharge of effluent to surface waters occurs. Thus, metal oxide sludges would be disposed of on land with suitable precautions. The soluble salts which are largely innocuous should be suitable for disposal in salt water. Because these salts are not large in amount and can be dewatered to dry solids (by incineration if necessary) very little additional impact on the solid waste disposal problem is anticipated.

No impact on air pollution is expected as the result of achieving no discharge of pollutants to surface water. The available technology creates no air pollutants.

Effluent Limitations Based on the Application of Best Available Technology Economically Achievable

The recommended effluent limitations to be achieved by July 1, 1983, for existing sources based on the application of Best Available Technology Economically Achievable is no discharge of pollutants to navigable waters for Subcategories (1), (2) and (3).

Guidelines for the Application of Effluent Limitations

Achieving the effluent limitations of no discharge of pollutants by achieving no discharge of effluent to surface waters is the most direct method that eliminates the need for sampling and analysis. If there is other effluent discharge to surface waters from the plant not associated with metal finishing, a determination is required that no waste waters originating from metal finishing processes are admixed with this other plant effluent.

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS

Introduction

The standards of performance which must be achieved by new sources are to correspond to the degree of effluent reduction attainable through the application of higher levels of pollution control than those identified as best available technology economically achievable for existing sources. The added consideration for new sources is the degree of effluent reduction attainable through the use of improved production processes and/or treatment techniques. The term "new sources" is defined by the Act to mean "any source, the construction of which is commenced after publication of proposed regulations prescribing a standard of performance."

New source performance standards are based on the best in-plant and end-of-process technology identified as best available technology economically achievable for existing sources. Additional considerations applicable to new source performance standards take into account techniques for reducing the level of effluent by changing the production process itself or adopting alternative processes, operating methods, or other alternatives. The end result will be the identification of effluent standards which reflect levels of control achievable through the use of improved production processes (as well as control technology), rather than prescribing a particular type of process or technology which must be employed. A further determination must be made as to whether a standard permitting no discharge of pollutants is practicable.

Consideration must also be given to:

(a) The type of process employed and process changes

(b) operating methods

(c) batch as opposed to continuous operations

(d) use of alternative raw materials and mixes of raw materials

(e) use of dry rather than wet processes (including substitution of recoverable solvents for water)

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(f)   r covery of pollutants as by-products.

Standards of performance for new sources are based on applicable technology and related effluent limitations covering discharges directly into waterways.

Consideration must also be given to the fact that Standards of Performance for New Sources could require compliance about three years sooner than the effluent limitations to be achieved by existing sources by July 1, 1977. However, new sources should achieve the same effluent limitations as existing sources by July 1, 1983.

Industry Category and Subcategory Covered

The pertinent industry category is the metal finishing industry divided into Subcategories (1) and (2), as previously discussed in Section IV.

Identification of Control and Treatment Technology Applicable to Performance Standards and Pretreatment Standards of New Sources

Subcategory (1)

The technology previously identified in Section IX under Subcategory (1) as best practicable control technology currently available is also applicable to new source performance standards. In addition, a new source can utilize the best practice in multitank rinsing after each operation in the process as required to meet the effluent limitations at the time of construction. Thus, with no practical restrictions on rinse water conservation after each operation by multitank rinsing, there are fewer restrictions on the use of advanced techniques for recovery of bath chemicals and reduction of wastewater from rinsing after pretreatment and posttreatment. Maximum use of combinations of evaporative, reverse osmosis, and ion exchange systems for in-process control currently available should be investigated. A small end-of-pipe chemical treatment system can be used to treat spills, concentrated solution dumps, and any other water flows not economically amenable to in-process water and chemical recovery.

The net resu of the improvements cited should be a reduction in water use as compared to that considered achievable for best practicable control technology currently available. This reduction should result in a lowe'

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discharge of waste water constituents. Although methods are being developed that may make possible a further reduction in the concentration of constituents and a reduction in the discharge of waste water constituents in chemically treated effluents, present technology is capable only of achieving the concentrations listed in Table 39 by exemplary chemical treatment. It would be anticipated that some plants now operating, due to having been designed recently to minimize water use or because of other favorable circumstances such as adequate space to make modifications, are attaining a water use well below 120 l/sq m/operation. Table 37 shows 12 lines involving processes in Subcategory (1) that achieve a water use of less than 45 l/sq m/operation. These are found in Plants 33-23, 33-35, 20-22, 20-23. It is estimated that a new source can achieve a water use of 45 l/sq m/operation for processes in Subcategory (1) by use of the technology described above for reducing water use.

Subcategory (2)

The technology previously identified in Section IX as best practicable control technology currently available for processes in Subcategory (2) is also applicable to new sources. In addition, a new source can use best rinsing practice and advanced techniques for recovery of bath chemicals and reduction of rinse water as described under Subcategory (1) above. The similarity of operations in processes of Subcategory (2) to the operations of processes in Subcategory (1), and the similarity in waste water compositions and treatment methods can be cited to indicate that the same methods of reducing water use are applicable to Subcategory (2) as are applicable to Subcategory (1). The application of the same techniques to the two Subcategories should reduce the water proportionately so that if a reduction of 90 l/sq m/operation to 45 l/sq m/operation can be achieved by a new source with a Subcategory (1) process, a reduction from 80 l/sq m/operation for a Subcategory (2) process in a present source to 40 l/sq m/operation for the same process in a new source should be achievable. Therefore, it is estimated that new sources can achieve a water use of 40 l/sq m/operation for Subcategory (2) processes. Two lines in Table 34 involving Subcategory (2) processes have a water use of less than 40 l/sq m/operation. These lines are in Plants 6-36, 20-25, 23-8.

Subcategory (3)

The technology previously identified in Section IX as best practicable control technology currently available for

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processes in Subcategory (2) is also applicable to new sources. In addition, a new source can use best rinsing practice and advanced techniques for recovery of bath chemicals and reduction of rinse water as described under Subcategory (1) above. The similarity of operations in processes of Subcategory (2) to the operations of processes in Subcategory (1), and the similarity in waste water compositions and treatment methods can be cited to indicate that the same methods of reducing water use are applicable to Subcategory (2) as are applicable to Subcategory (1). The application of the same techniques to the two Subcategories should reduce the water proportionately so that if a reduction of 90 1/sq m/operation to 45 1/sq m/operation can be achieved by a new source with a Subcategory (1) process, a reduction from 120 1/sq m/operation for a Subcategory (2) process in a present source to 60 1/sq m/operation for the same process in a new source should be achievable. Therefore, it is estimated that new sources can achieve a water use of 60 1/sq m/operation for Subcategory (2) processes. Two lines in Table 34 involving Subcategory (2) processes have a water use of less than 60 1/sq m/operation. These lines are in Plants 4-8, 30-9, 9-2, 4-9.

Rationale for Selection of Control and Treatment Technology Applicable to New Source Performance Standards

The rationale for the selection of the above technology is applicable to new sources discharging to navigable waters is as follows:

(1) In contrast to an existing source, a new source has complete freedom to choose the most advantageous equipment and facility design to maximize water conservation by use of as many multitank rinsing operations as necessary. This, in turn, allows for economic use of in-process controls for chemical and water recovery and reuse.

(2) In contrast to an existing source which may have at present a large capital investment in waste treatment facilities to meet effluent limitations by July 1, 1977, a new source has complete freedom in the selection the design of new waste treatment facilities.

(3) In contrast to an existing source, a new

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source has freedom of choice with regard to geographic location.

Standards of Performance Applicable to New Sources

The recommended Standards of Performance to be achieved by new sources discharging to navigable waters was shown previously in Table 2 of Section II.

The quantitative values for the 30-day average standard for each parameter in mg/sq m (lbs/sq ft) is based on a nominal water use one-half as large as those used to develop 1977 guidelines combined with the concentrations achievable by chemical treatment as previously shown in Table 39 of Section IX. For example, 0.5 mg/l for copper, nickel, total chromium, zinc, and total cyanide, 0.05 mg/l for hexavalent chromium and .075 mg/l for oxidizable cyanide, 20 mg/l for suspended solids, when combined with an effluent factor of 45 l/sq m are the basis for the 30-day average standards of performance for Subcategory (? processes in Table 2.

In effect, standards of performance for new sources as shown in Table 2, are 1/2 of the values of the effluent limitations for existing sources to be achieved by July 1, 1977, as shown in Table 1. The rationale for selection of standards of performance is based on the technical feasibility of achieving greater reduction in water use by multitank rinsing at the time of construction of new facilities in contrast to the present limitations for some existing sources For example, if an existing source can achieve water use of 120 l/sq m, a new source should be able to design a new facility to achieve a water use of 60 l/sq m. As discussed previously in Section IX, the standard of performance in mg/sq m is the product of the water use in l/sq m and the concentration of the parameter in the treated effluent in mg/l. The choice of whether to reduce concentration by emphasis on optimum chemical treatment and clarification or whether to reduce effluent volume by water conservation or a combination of both approaches is left to the discretion of the new source.

The rationale for establishing the daily maximum value of standards of performance at 2.0 times the 30-day average is based on the arguments given in Section IX for BPCTCA.

It is recommended that new sources meet the same effluent limitations as required for existing sources by July 1, 1983, based on the effluent reduction believed to be attainable by the application of the best available technology economically achievable.

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Guidelines for the Application of
New Source Performance Standards

The recommended guidelines for the application of standards of performance for new sources discharging to navigable waters are the same as those in Section IX relating to existing sources based on use of the best practicable control technology currently available and those in Section X based on use of best available technology economically achievable.

SECTION XII

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National Association of Metal Finishers, Upper
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Osmonics, Incorporated, Minneapolis, Minnesota
Oxy Electroplating Corporation, Warren, Michigan
The Permutit Company, Paramus, New Jersey
Pfaudler Sybron Corporation, Rochester, New York

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GLOSSARY

Acid Dip

An acidic solution for activating the workpiece surface prior to electroplating in an acidic solution, especially after the workpiece has been processed in an alkaline solution.

Alkaline Cleaning

Removal of grease or other foreign material from a surface by means of alkaline solutions.

Anodizing

The production of a protective oxide film on aluminum or other light metals by passing a high voltage electric current through a bath in which the metal is suspended. The metal serves as the anode. The bath usually contains sulfuric, chromic, or oxalic acid.

Automatic Plating

(1) full - plating in which the cathodes are automatically conveyed through successive cleaning and plating tanks. (2) semi - plating in which the cathodes are conveyed automatically through only one plating tank.

Barrel Plating

Electroplating of workpieces in barrels (bulk).

Basis Metal or Material

That substance of which the workpieces are made and that receives the electroplate and the treatments in preparation for plating.

Batch Treatment

Treatment of electroplating rinse waters collected in adjacent tanks. Water is not allowed to leave the tank till treatment is completed.

Best Available Technology Economically Achievable

Level of technology applicable to effluent limitations to be achieved by July 1, 1983, for industrial discharges to surface waters as defined by Section 301(b) (2) (A) of the Act.

Level of technology applicable to effluent limitations to be achieved by July 1, 1977, for industrial discharges to surface waters as defined by Section 301(b) (1) (A) of the Act.

Bright Dip

A solution used to produce a bright surface on a metal.

Captive Operation

Electroplating facility owned and operated by the same organization that manufacturers the workpieces.

Chemical Brightening

Process utilizing an addition agent that leads to the formation of a bright plate, or that improves the brightness of the deposit.

Chemical Etching

To dissolve a part of the surface of a metal or all of the metal laminated to a base.

Chemical Metal Coloring

The production of desired colors on metal surfaces by appropriate chemical or electrochemical action.

Chemical Polishing

The improvement in surface smoothness of a metal by simple immersion in a suitable solution.

Chromatizing

To treat or impregnate with a chromate or dichromate especially with potassium dichromate.

Chrome-Pickle Process

Forming a corrosion-resistant oxide film on the surface of magnesium-base metals by immersion in a bath of an alkali bichromate.

Closed-Loop Evaporation System

A system used for the recovery of chemicals and water from a plating line. An evaporator concentrates flow from the rinse water holding tank. The concentrated rinse solution is returned to the plating bath, and distilled water is returned to the final rinse tank. The system is designed for recovering 100 percent of the chemicals, normally lost in dragout, for reuse in the plating process.

Continuous Treatment

Chemical waste treatment operating uninterruptedly as opposed to bath treatment; sometimes referred to as flow through treatment.

Conversion Coating

A coating produced by chemical or electrochemical treatment of a metallic surface that gives a superficial layer containing a compound of the metal, for example, chromate coatings on zinc and cadmium, oxide coatings on steel.

Deoxidizing

The removal of an oxide film from an alloy such as aluminum oxide.

Descaling

The process of removing scale or metallic oxide from metallic surfaces.

Desmutting

The removal of smut, generally by chemical action.

Dragin

The water or solution that adheres to the objects removed from a bath.

Dragout

The solution that adheres to the objects removed from a bath, more preciously defined as that solution which is carried past the edge of the tank.

EDTA

Abbreviation for ethylenediamine-tetraacetic acid.

Effluent

The waste water discharged from a point source to navigable waters.

Electrobrightening

Electrolytic brightening (electropolishing) produces smooth and bright surfaces by electrochemical action similar to those that result from chemical brightening.

Electrochemical Machining (ECM)

A machining process whereby the part to be machined is made the anode and a shaped cathode is maintained in close proximity to the work. Electrolyte is pumped between the electrodes and a potential applied with the result that metal is rapidly dissolved from the work in a selective manner and the shape produced on the work complements that of the cathode.

Electrodialysis

Membrane dialysis under the influence of direct current electricity.

Electroless Plating

Deposition of a metallic coating by a controlled chemical reduction that is catalyzed by the metal or alloy being deposited.

Electropainting

A coating process in which the coating is formed on the workpiece by making it anodic or cathodic in a bath that is generally an aqueous emulsion of the coating material.

Electroplating

The electrodeposition of an adherent metallic coating upon the basis metal or material for the purpose of securing a surface with properties or dimensions different from those of the basis metal or material.

Electroplating Process

An electroplating process includes a succession of operations starting with cleaning in alkaline solutions, acid dipping to neutralize or acidify the wet surface of the parts, followed by electroplating, rinsing to remove the processing solution from the workpiece, and drying.

Electropolishing

Electrolytic corrosion process that increases the percentage of specular reflectance from a metallic surface.

Electrostatic Precipitation

Use of an electrostatic field for precipitating or rapidly removing solid or liquid particles from a gas in which the particles are carried in suspension.

Heavy Metals

Metals which can be precipitated by hydrogen sulfide in acid solution, e.g., lead, silver, gold, mercury, bismuth, copper, nickel, iron, chromium, zinc, cadmium, and tin.

Hot Dipping

A method of coating one metal with another to provide a protective film.

Hydrogen Embrittlement

Embrittlement of a metal or alloy caused by absorption of hydrogen during a pickling, cleaning, or plating process.

Immersion Plate

A metallic deposit produced by a displacement reaction in which one metal displaces another from solution, for example:

$$Fe + Cu^{++} \quad Cu + Fe^{++}$$

Independent Operation

Job shop or contract shop in which electroplating is done on workpieces owned by the customer.

Integrated Chemical Treatment

A waste treatment method in which a chemical rinse tank is inserted in the plating line between the process tank and the water rinse tank. The chemical rinse solution is continuously circulated through the tank and removes the dragout while reacting chemicals with it.

Ion-Flotation Technique

Treatment for electroplating rinse waters (containing chromium and cyanide) in which ions are separated from solutions by flotation.

Iridite Dip Process

Dipping process for zinc or zinc coated objects that deposits an adherent protective film that is a chrome gel, chrome oxide or hydrated chrome oxide compound.

Phosphatizing

Process of forming rust-resistant coating on iron or steel by immersing in a hot solution of acid manganese, iron, or zinc phosphate.

Pickle

An acid solution used to remove oxides or other compounds related to the basis metal from its surface of a metal by chemical or electrochemical action.

Pickling

The removal of oxides or other compounds related to the basis metal from its surface by immersion in a pickle.

Point Source

A single source of water discharge such as an individual plant.

Precious Metals

Gold, Silver, Platinum, etc.

Rack Plating

Electroplating of workpieces on racks.

Reverse Osmosis

A recovery process in which the more concentrated solution is put under a pressure greater than the osmotic pressure to drive water across the membrane to the dilute stream while leaving behind the dissolved salts.

Rochell Salt

Sodium potassium tartrate: KNaC4H4O6 . 4H2O.

Shot Peening

Dry abrasive cleaning of metal surfaces by impacting the surfaces with high velocity steel shot.

Sludge

Residue in the clarifier of a chemical waste treatment process.

Strike

(1) noun - a thin coating of metal (usually less than 0.0001 inch in thickness) to be followed by other coatings. (2) noun - a solution used to deposit a strike. (3) verb - a plate for a short time, usually at a high initial current density.

Stripping

Removal of an electrodeposit by a chemical agent or reversed electrodeposition.

Workpiece

The item to be electroplated.

Conversion Table

MULTIPLY (ENGLISH UNITS)		by		TO OBTAIN (METRIC UNITS)
English Unit	Abbreviation	Conversion	Abbreviation	Metric Unit
acre	ac	0.405	ha	hectares
acre - feet	ac ft	1233.5	cu m	cubic meters
British Thermal Unit	BTU	0.252	kg cal	kilogram - calories
British Thermal Unit/pound	BTU/lb	0.555	kg cal/kg	kilogram calories/kilogram
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute
cubic feet	cu ft	0.028	cu m	cubic meters
cubic feet	cu ft	28.32	l	liters
cubic inches	cu in	16.39	cu cm	cubic centimeters
degree Fahrenheit	°F	0.555(°F-32)*	°C	degree Centigrade
feet	ft	0.3048	m	meters
gallon	gal	3.785	l	liters
gallon/minute	gpm	0.0631	l/sec	liters/second
horsepower	hp	0.7457	kw	kilowatts
inches	in	2.54	cm	centimeters
inches of mercury	in Hg	0.03342	atm	atmospheres
pounds	lb	0.454	kg	kilograms
million gallons/day	mgd	3785	cu m/day	cubic meters/day
mile	mi	1.609	km	kilometer
pound/square inch (gauge)	psig	(0.06805 psig+1)*	atm	atmospheres (absolute)
square feet	sq ft	0.0929	sq m	square meters
square inches	sq in	6.452	sq cm	square centimeters
tons (short)	ton	0.907	kkg	metric tons (1000 kilograms)
yard	yd	0.9144	m	meters

* Actual conversion, not a multiplier