PLATING WASTEWATER MANAGEMENT

BY

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RESEARCH REPORT

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ABSTRACT

A study was made of existing methods of management, treatment and disposal of water and wastewater effluents at a large aerospace facility (Martin Marietta Aerospace) in Central Florida. Water consumption and handling were evaluated, with emphasis being placed on the handling of plating wastes, since they are the main contributor of industrial wastewater pollutants at the facility. The flow, storage, and treatment of the plating wastes were studied.

Literature concerning plating wastes was surveyed to determine the latest "state of the art" on handling of plating pollutants. Then, the "state of the art" processes were compared with the existing processes to determine the need for improvements. This comparison resulted in recommendations for improvements to the existing facility.
CHAPTER I
INTRODUCTION

The manufacturing plant of the Orlando Division of Martin Marietta Aerospace is located in the Kissimmee River watershed of Central Florida. One of the creeks feeding the Kissimmee River is Shingle Creek which adjoins the property and is the focal point of water pollution control. Since the Kissimmee River watershed is a major source of water supply for Central Florida, it is very important that adequate control be applied to the industrial wastewater flowing from the plant.

The responsibility for this control and the monitoring function is assigned to the Plant Engineering Department of Martin Marietta that assures compliance with federal, state, and local government laws. This task is accomplished by use of an internal set of operation procedures that provide for:

1. Certification of equipment performance, internal procedures change coordination, and manufacturing process review and approval prior to production use
2. In-process effluent and emissions sampling, patrol inspection, data collection and filing of objective evidence of compliance with laws
3. Offsite testing of stream quality
4. In-house corrective action when required
5. Submittal of a monthly water pollution control report to state and local regulatory agencies.

A. Wastewater Systems

In order to provide efficient segregation of waters to be treated, three separate sewer systems are used: sanitary, storm and industrial wastewater. The sanitary and storm sewers are installed underground, while the flow of industrial wastewater is primarily through an above the ground piping system. All sanitary sewer systems, which include food service facilities, rest rooms, locker rooms, shower rooms, janitorial facilities, and drinking fountains, are connected directly to the Sand Lake Road Orange county sewer plant. All roof drains, outside yard run-off areas and parking lots are drained into ditches that empty into existing ponds on the property. The importance of this feature is highlighted in a study on sources of metals in New York City wastewater which indicates that as much as 10 percent of the contamination was from storm water runoff. (9) The storm system does not collect any water from inside plant buildings. All of the water from the manufacturing facilities is collected separately through the plant water pollution control system.

Data on water usage and treatment was tabulated for the months of August 1974 through January 1975, as shown in Table 1. Since the only data on the effluent are the actual number of gallons processed through the pollution control facility, the difference between the influent and the effluent is that portion of the water supply going directly to the County sewer treatment facility through the sanitary sewer system. However, the Sand Lake Orange County sewer plant
estimates higher flows from the Martin Marietta plant than the total incoming supply. This could possibly be caused by infiltration. The data show that per capita sanitary water usage tends to increase as the employment decreases.

TABLE 1
WATER SUPPLY AND DISPOSAL

<table>
<thead>
<tr>
<th></th>
<th>Waste Consumption (gal/month)</th>
<th>Treated Effluent (gal/month)</th>
<th>Sanitary Effluent (gal/month)</th>
<th>No. of Employees</th>
<th>Work Days</th>
<th>Sanitary (gal/employee/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1974</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aug</td>
<td>42,543,000</td>
<td>6,238,200</td>
<td>36,304,800</td>
<td>6100</td>
<td>22</td>
<td>270.52</td>
</tr>
<tr>
<td>Sept</td>
<td>37,073,000</td>
<td>4,568,637</td>
<td>32,504,363</td>
<td>5900</td>
<td>20</td>
<td>275.46</td>
</tr>
<tr>
<td>Oct</td>
<td>40,036,000</td>
<td>5,901,201</td>
<td>34,134,799</td>
<td>5800</td>
<td>23</td>
<td>255.88</td>
</tr>
<tr>
<td>Nov</td>
<td>42,543,000</td>
<td>4,943,176</td>
<td>37,599,824</td>
<td>5250</td>
<td>20</td>
<td>358.09</td>
</tr>
<tr>
<td>Dec</td>
<td>37,073,000</td>
<td>4,094,393</td>
<td>32,978,607</td>
<td>4940</td>
<td>15</td>
<td>445.05</td>
</tr>
<tr>
<td>1975</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jan</td>
<td>40,036,000</td>
<td>5,969,556</td>
<td>34,066,444</td>
<td>4730</td>
<td>20</td>
<td>360.11</td>
</tr>
</tbody>
</table>

B. Objectives and Scope

The purpose of the study was to evaluate the treatment of plating wastes at Martin Marietta to determine if procedures are adequate to meet existing and future pollution control requirements. The study was conducted to:

1. Survey existing plating requirements and facilities for handling the plating wastewater.

2. Evaluate the effectiveness of the plating waste facilities.
3. Survey the literature for the latest "state of the art" processes.
4. Determine if recommendations for improvements are necessary.
CHAPTER II

SOURCES, CHEMICAL TREATMENT, HANDLING AND
CONTROL OF METAL FINISHING WASTES

The Orlando Division designs and manufactures a variety of weapons and communications systems. The major source of water pollution is from metal finishing operations. The products are manufactured from a great variety of materials, many of which require supplementary corrosion protection in the form of electro-deposited coatings, conversion chemical coatings, and organic finishes such as paint. Additional sources are the reproduction and printed circuit board facilities which require large amounts of chemical and water baths. Figure 1 shows the location and types of pollution contributed by the facility. Other processes such as the final curing of plastic parts, potting and encapsulation of connector cables, etc., produce minimal volumes of by-products of polymerization of plastics.

Since the primary source of water pollution at Martin Marietta is the metal finishing process, this area received the most emphasis in the study. The following is a description of the plating processes used, the wastes generated, and the treatments used to neutralize the wastes in order to meet the County requirements for effluent quality.

A. Sources

1. Plating Process

Metal plating is the process by which a uniform metallic coating is applied to the surface of a metal part by electrochemical
Figure 1. Sources of Pollution From Various Processes at Martin Marietta
deposition. The metal part is called the work piece and the metallic coating which is deposited on the surface of the work piece is called the plate or finish.

Plating is carried out in a plating bath which is a formulated aqueous solution of various chemical compounds. The formulation is related to the metal to be deposited, the nature of the deposit and the chemical composition of the work piece to be plated. In each case, however, the solution will contain, in addition to various complex ionic species, ions of the metal to be deposited. A suitable metallic conductor is suspended in the bath. In most cases this is a bar of the pure metal to be deposited from the bath. For example, copper, cadmium and nickel bars are used in copper, cadmium and nickel plating baths. In other cases, the bar is of a different composition than the metal to be deposited. For example, a lead bar containing 4 to 7 percent tin is used in a chromium plating bath, a steel bar is used in an arsenic plating bath, and a stainless steel bar is used in a gold plating bath.

In operation, the work pieces are immersed in the plating bath, and depending upon their size and shape, they are either suspended from a movable rack or are placed within a rotating basket or perforated barrel. Using a suitable source of dc current, the work piece is made the cathode or negative terminal, and the metal bar is made the anode or positive terminal. As current flows, the positively charged metal ions migrate to the negatively charged surface of the work piece where they are converted to metal atoms and simultaneously deposited. At the same time other ions are formed at the surface of the anode at a rate which maintains electrical neutrality within the bath.
When the anode is constructed of the metal to be deposited, the metal atoms of the anode are converted into ions and released to the plating solution. The anode slowly dissolves with the passage of current. In effect, then, the metal is transferred from the surface of the bar in the form of ions to the surface of the work piece being transported through the plating bath. Under ideal operating conditions only the anode need be replaced periodically when plating with this type of bath.

When the anode is not constructed of the metal to be deposited, it does not dissolve with the passage of current. Instead, other ions are formed and released to the bath as a result of certain chemical changes that occur at the anode. Naturally the anode need not be replaced; however, the bath must be reconstituted regularly to replenish the metal ions that are continuously removed during the plating. In addition, sufficient chemicals must be added to replace those removed by "dragout."

2. Wastes Generated

The wastes that originate in metal plating may be divided into two general categories: concentrated wastes and dilute wastes.

In both categories there are five general types of toxic or contaminating materials: acids, alkalies, cyanides, chromates and heavy metals. The sources of these five types are as follows (see Table 2):

1. Acids - Pickling solutions, acids dips, bright dip solutions and their subsequent rinses
<table>
<thead>
<tr>
<th>Type of Waste</th>
<th>Process</th>
<th>Tank Volume</th>
<th>Control Limits (waste concentration)</th>
<th>Test Frequency</th>
<th>Normal Disposal Time Spans</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Sulfuric anodize</td>
<td>410 gal</td>
<td>$H_2SO_4$ 12-18% by wt Al 10g/l max</td>
<td>Weekly</td>
<td>Every 6 months</td>
</tr>
<tr>
<td>Alkalies</td>
<td>Alkaline cleaner</td>
<td>7540 gal</td>
<td>ISO Prep #37 4-6 oz/gal pH 11.0 min</td>
<td>Weekly</td>
<td>Every 2 to 3 months</td>
</tr>
<tr>
<td>Cyanides</td>
<td>Cadmium plating</td>
<td>1555 gal</td>
<td>Cd 2.5-3.5 oz/gal NaCN 14-19 oz/gal</td>
<td>Weekly</td>
<td>Every 12 months</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NaOH 2-3 oz/gal Na$_2$CO$_3$ 12 oz/gal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromates</td>
<td>Cleaning Al alloys</td>
<td>2800 gal</td>
<td>Cr$^{+6}$ 15-20 g/l</td>
<td>Daily</td>
<td>Monthly</td>
</tr>
<tr>
<td></td>
<td>Chromic anodize</td>
<td>2770 gal</td>
<td>$CrO_3$ 150 g/l max pH 0.4-0.7 NaCl 0.2 g/l max H$_2$SO$_4$ 0.5 g/l max</td>
<td>Biweekly</td>
<td>Every 2 years</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3 months</td>
<td>Every 2 years</td>
</tr>
</tbody>
</table>
2 Alkalies - Alkaline degreasing and cleaning and their subsequent rinses

3 Cyanides - Cyanide dips, copper, zinc, cadmium, brass, bronze, silver, and gold plating solutions and their subsequent rinses

4 Chromates - Chrome plating, bright dips, conversion coating and their subsequent rinses

5 Metals - All of the above plus nickel plating and copper and zinc acid plating solutions

3. Concentrated and Diluted Wastes

The plating process consists of a sequence of chemical and electrochemical steps. Each step in the sequence consists of the solution bath into which the work is immersed and spray rinses or running water rinses. The solution baths are the sources of the concentrated wastes, and the rinses are the sources of the diluted wastes.

Over a period of time the acid and alkali solutions lose their usefulness due to the build up of 1) metallic salts, 2) broken down and expended chemical compounds, or 3) organic materials such as oils, greases, etc. These wastes are high in dissolved salts or organic load content.

The composition of the relatively expensive plating bath solutions is carefully controlled by the addition of the proper chemicals as required, and by the removal of impurities or contaminants that find their way into the baths. By proper maintenance of the analysis of the bath and regeneration as necessary, several years can elapse before it may be required to dump the solution to waste. In some cases, however,
it may be more expedient to dump a contaminated plating solution rather than attempt to bring it back to a satisfactory operating condition. This would apply mainly to the less expensive solutions such as zinc, cadmium and copper. Any dumped plating solution is extremely high in toxic content.

B. Chemical Treatments

1. Cyanide Destruction

Cyanides are destroyed in wastes by oxidation with a basic oxidizing agent, chlorine, and alkali or a hypochlorite (an alkaline chlorine solution) at a pH of not less than 8.5. The cyanides are destroyed with chlorine to either the less toxic cyanates or to non-toxic nitrogen gas and carbon dioxide which later unites with the alkali to form bicarbonates.

The reactions showing the oxidation of cyanides with chlorine, \( \text{Cl}_2 \), are given in Table 3. Two reactions are involved in the destruction of cyanides to cyanates: "1.a." and "1.b." In the first reaction "1.a.," the chlorine reacts instantaneously with the cyanide at any pH of 8.5 or above, as noted by the minimum sodium hydroxide, NaOH, requirement, and is completely converted within 10 to 15 minutes to the much less toxic, nonvolatile and relatively stable sodium cyanate, NaCNO.

The destruction of cyanides to cyanates (see Table 3) theoretically requires 2.73 parts or pounds of chlorine for each part or pound of cyanide as CN. Actually, due to the usual presence of other oxidizable material, the chlorine requirement may be 1 percent to 25 percent higher. Theoretically, 1.125 parts or pounds of sodium hydroxide are
<table>
<thead>
<tr>
<th>Destruction of Cyanides to Cyanates</th>
<th>1 a</th>
<th>$2\text{Cl}_2$ + 2NaCN $\rightarrow$ 2CNCl + 2NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 b</td>
<td>$2\text{Cl}_2$ + 2NaOH $\rightarrow$ 2NaCNO + 2NaCl + $2\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chlorine</th>
<th>Sodium Hydroxide</th>
<th>Sodium Cyanide</th>
<th>Sodium Cyanate</th>
<th>Sodium Chloride</th>
<th>Water</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Destruction of Cyanides to Carbon Dioxide (as Bicarbonates) and Nitrogen</th>
<th>2 a</th>
<th>$3\text{Cl}_2$ + 4H$_2$O + 2NaCNO $\rightarrow$ 3Cl$_2$ + (NH$_4$)$_2$CO$_3$ + Na$_2$CO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 b</td>
<td>$3\text{Cl}_2$ + 6NaOH + (NH$_4$)$_2$CO$_3$ + Na$_2$CO$_3$ $\rightarrow$ 2NaHCO$_3$ + N$_2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chlorine</th>
<th>Sodium Hydroxide</th>
<th>Sodium Cyanate</th>
<th>Sodium Cyanate</th>
<th>Sodium Chloride</th>
<th>Nitrogen</th>
<th>Sodium Chloride</th>
<th>Water</th>
</tr>
</thead>
</table>

| Destruction of Cyanides to Carbon Dioxide (as Bicarbonates) and Nitrogen | 3 | $5\text{Cl}_2$ + 10NaOH + 2NaCN $\rightarrow$ 2NaHCO$_3$ + N$_2$ + 10NaCl + $4\text{H}_2\text{O}$ |

<table>
<thead>
<tr>
<th>Chlorine</th>
<th>Sodium Hydroxide</th>
<th>Sodium Cyanide</th>
<th>Sodium Cyanate</th>
<th>Sodium Chloride</th>
<th>Nitrogen</th>
<th>Sodium Chloride</th>
<th>Water</th>
</tr>
</thead>
</table>
also required along with each part or pound of chlorine applied. Actually, most of the cyanide wastes are sufficiently alkaline as to require only 60 - 90 percent of this amount of caustic.

The reactions showing the oxidation of cyanates with chlorine, $\text{CL}_2$, are also given in Table 3. Those involved in the destruction of cyanates to nitrogen gas and carbon dioxide (present as bicarbonates) are two, "2.a." and "2.b." The first, "2.a.," is a reaction in which cyanates are slowly decomposed to ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, and sodium carbonate, $\text{Na}_2\text{CO}_3$, in the presence of chlorine. In this reaction, chlorine does not take part chemically, but does aid in completing the reaction within 1 to 1.5 hours. The second, "2.b.," is a reaction in which the ammonium carbonate at pH of 8.5 to 10.0 as noted by the minimum sodium hydroxide, $\text{NaOH}$, requirement, is rapidly oxidized by the chlorine to nitrogen gas and the carbonates are converted to bicarbonates as the other main constituent. As part of this reaction, but not shown, small amounts of inert nitrous oxide, $\text{N}_2\text{O}$, and volatile nitrogen trichloride, $\text{NCL}_3$, are also formed.

The destruction of cyanates to nitrogen and bicarbonate (see Table 3) theoretically requires 4.09 parts of chlorine for each part of cyanate in terms of cyanide, as CN. Actually, due to the presence of other oxidizable matter and the formation of nitrous oxide and nitrogen trichloride, the chlorine requirements are somewhat higher. Theoretically, 1.125 parts of sodium hydroxide are also required along with each part of chlorine applied. This reaction does not take place when the pH is over 10, (and is slow at pH over 8.0).
The overall reaction (see Table 3) involved in the destruction of cyanides to nitrogen and carbon dioxide (as sodium bicarbonate) shows that the alkaline chlorination process theoretically requires 6.82 parts of chlorine per part of cyanide.

The alkaline chlorination process can be accomplished with the following chlorine compounds: chlorine gas with caustic, chlorine water with caustic, or hypochlorite. The same amount of available chlorine is required regardless of the choice of chlorine compound. This is to be noted from the group of reactions shown in Table 4. In these reactions one active chlorine, $\text{CL}_2$, one active hypochlorous acid, $\text{HOCL}$, with its inactive hydrochloric acid, $\text{HCL}$, (made from one chlorine, as $\text{CL}_2$, and water, $\text{H}_2\text{O}$, in a chlorinator) or one active sodium hypo­chlorite, $\text{NaOCL}$, with its inactive sodium chloride, $\text{NaCL}$ (made from one $\text{CL}_2$, and water, $\text{H}_2\text{O}$, in a chlorinator) or one active sodium hypo­chlorite, $\text{NaOCL}$, with its inactive sodium chloride, $\text{NaCL}$ (made from one $\text{CL}_2$, water and two sodium hydroxides) react with one or the same amount of sodium cyanide to form identical amounts of sodium cyanate and sodium chloride. Likewise, similar amounts of the three chlorine oxidizing agents react with the same amount of sodium cyanide to form identical amounts of nitrogen, sodium bicarbonate and sodium chloride.

2. Reduction of Chromium Wastes

Hexavalent chromium is removed from wastes by reduction with a reducing agent and the subsequent precipitation of the resulting triva­lent chromium with lime or caustic. The chromium is reduced with ferrous iron, (specifically copperas) sulfur dioxide (see Tables 5 and 6).
### TABLE 4

REACTION OF CYANIDES WITH VARIOUS CHLORINE COMPOUNDS (12)

#### A. For Destruction of Cyanides to Cyanates

<table>
<thead>
<tr>
<th>Source of Chlorine Compound</th>
<th>Chlorine compound with caustic</th>
<th>Sodium Cyanide</th>
<th>Sodium Cyanate</th>
<th>Sodium Chloride</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Chlorine Gas $\text{Cl}_2$</td>
<td>$\text{Cl}_2 + 2\text{NaOH}$</td>
<td>$\text{NaCN}$</td>
<td>$\text{NaCNO}$</td>
<td>$2\text{NaCl}$</td>
<td>$\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>2. Chlorine water $\text{Cl}_2 + \text{H}_2\text{O}$</td>
<td>$\text{HOCl} + \text{HCl} + 2\text{NaOH}$</td>
<td>$\text{NaCN}$</td>
<td>$\text{NaCNO}$</td>
<td>$2\text{NaCl}$</td>
<td>$2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>3. Sodium Hypochlorite $\text{Cl}_2 + \text{H}_2\text{O} = \text{HOCl} + \text{HCl}$</td>
<td>$\text{NaOCl} + \text{NaCl}$</td>
<td>$\text{NaCN}$</td>
<td>$\text{NaCNO}$</td>
<td>$2\text{NaCl}$</td>
<td></td>
</tr>
</tbody>
</table>

#### B. For Destruction of Cyanides to carbon dioxide (as bicarbonates) B: Nitrogen

<table>
<thead>
<tr>
<th>Source of Chlorine compound</th>
<th>Chlorine compound with caustic</th>
<th>Sodium Cyanide</th>
<th>Sodium Bicarbonate</th>
<th>Nitrogen</th>
<th>Sodium Chloride</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Chlorine Gas $\text{Cl}_2$</td>
<td>$5\text{Cl}_2 + 10\text{NaOH}$</td>
<td>$2\text{NaCN}$</td>
<td>$2\text{NaHCO}_3$</td>
<td>$\text{N}_2$</td>
<td>$10\text{NaCl}$</td>
<td>$4\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>2. Chlorine Water $\text{Cl}_2 + \text{H}_2\text{O} = \text{HOCl} + \text{HCl}$</td>
<td>$5\text{HOCl} + 5\text{HCl} + 10\text{NaOH}$</td>
<td>$2\text{NaCN}$</td>
<td>$2\text{NaHCO}_3$</td>
<td>$\text{N}_2$</td>
<td>$10\text{NaCl}$</td>
<td>$9\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>3. Sodium Hypochlorite $\text{Cl}_2 + \text{H}_2\text{O} = \text{HOCl} + \text{HCl}$</td>
<td>$5\text{NaOCl} + 5\text{NaCl} + \text{H}_2\text{O}$</td>
<td>$2\text{NaCN}$</td>
<td>$2\text{NaHCO}_3$</td>
<td>$\text{N}_2$</td>
<td>$10\text{NaCl}$</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 5

REACTION SHOWING REDUCTION OF HEXAVALENT CHROMIUM WITH FERROUS IRON SALTS

Reduction in Acid Solution

\[ 6\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + 6\text{H}_2\text{SO}_4 + 2\text{H}_2\text{CrO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + 3\text{Fe}_2(\text{SO}_4)_3 + 50\text{H}_2\text{O} \]

Copperas Sulfuric Acid Chromic Acid Chromic Ferric Water Sulfate Sulfate

TABLE 6

REACTION SHOWING REMOVAL OF TRIVALENT CHROMIUM WITH LIME

Removal in Slightly Alkaline Solution

\[ 12\text{Ca(OH)}_2 + \text{Cr}_2(\text{SO}_4)_3 + 3\text{Fe}_2(\text{SO}_4)_3 \rightarrow 2\text{Cr(OH)}_3 + 6\text{Fe(OH)}_3 + 12\text{CaSO}_4 \]

Hyd Lime Chromic Ferric Chromic Ferric Calcium Sulfate Sulfate Hydroxide Hydroxide Sulfate

3. Treatment of Acids and Alkalies

It is necessary to neutralize any excess acidity or alkalinity in the plant effluent and to remove the resulting insoluble substances from the effluent before it is discharged to the Orange County sewer system.

Acid wastes are treated by the addition of alkaline materials. Waste alkaline cleaners or other waste alkaline materials are used wherever possible. If the available alkaline waste is not sufficient to neutralize the acid, then materials such as hydrated lime, caustic soda or soda ash are used.

Neutralization of the waste solutions is usually carried to a pH value of between 8.0 and 9.0. The precipitate is separated from the solution before discharge into the sewer system.
Any excess alkali waste solutions not used in the neutralization of acids require treatment before disposal. Mineral acids are used for this purpose.

C. Handling

1. Wastewater Distribution

The wastes from 120 process tanks are directed into four major, segregated, drain trench, and piping systems, according to specific chemical properties and degree of compatibility with other wastes, as follows:

1. Alkaline rinses and spent solutions
2. Acid rinses and spent solutions
3. Chromium rinses and spent solutions
4. Cyanide rinses and spent solutions

The drains discharge to retaining sumps, or captive pits, from which the solutions are preferentially pumped to acid/alkali, chromium reduction, or cyanide/cyanate destruction processing tanks. The liquors are neutralized, settled, and after final quantitative tests, are released into the industrial system leading to the county sewage treatment plant. The raw water data used for the design parameters for the treatment system design included information such as chemical composition of the solutions in each tank, rate of rinse water flow from each tank, estimated life of each process solution, etc. The data are still valid and are listed below:
Typical Design Criteria

<table>
<thead>
<tr>
<th>Type Chemical</th>
<th>Gallons per Hour Flow</th>
<th>Metal Concentration Lbs/Day</th>
<th>Metal Concentration Lbs/Gal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalis</td>
<td>10,000 gal</td>
<td>102.0 lb</td>
<td>0.0102 lb</td>
</tr>
<tr>
<td>Acids</td>
<td>6,000 gal</td>
<td>101.0 lb</td>
<td>0.0168 lb</td>
</tr>
<tr>
<td>Chromates</td>
<td>10,000 gal</td>
<td>0.7 lb</td>
<td>0.00007 lb</td>
</tr>
<tr>
<td>Cyanides/cyanates</td>
<td>4,000 gal</td>
<td>2.5 lb</td>
<td>0.00006 lb</td>
</tr>
</tbody>
</table>

Summary:

240,000 gallons of rinse water flow per 8 hr shift
3.2 lbs of various metal ions
203 lbs of all other solids

Figure 2 shows the detailed flow sequence of the system.
Figure 3 is an operations schematic of the water treatment plant.

2. Wastewater Sludge

Since the intent of the pollution laws are that nothing shall be discharged to the ground which could conceivably migrate through the soil and pollute subterranean waters, or lie on the surface to contaminate surface water runoff, or which could become airborne and cause air pollution, Martin Marietta takes all of the sludge produced by the wastewater treatment facilities and buries it, as shown in Figure 4.

When a pit is filled with the dewatered sludge, the pit is backfilled with soil, and compacted. Pits are never located where there is any danger of ground water flooding. There are three such pits. All are identified and located on high ground at least 11 feet above the ground water table so as to comply with state and local laws.
Figure 2. Waste Water Control Flow Diagram
FROM THE PLATING SHOP TRENCHES:
SPENT SOLUTIONS
"A" LINE
CAPTIVE PIT
CAPTIVE PIT
"A" LINE
CHROME LINE
ACID-ALK LINE
CYANIDE
CAPTIVE PIT

SLUDGE PUMP
CAPTIVE PIT
CHROME RINSE
ACID ALKALI
CYANIDE
CAPTIVE PIT

ACID
LIME
SO₂
NEUTRALIZATION TANK
CONTINUOUS SAMPLING STATION
TO SANITARY SEWER

SLUDGE TANK
SAMPLE LINE TO DRAIN
SLUDGE PUMP
SPENT SOLUTION TANK
SPENT SOLUTION TANK
DECANTATION LINE
CLARIFIER
CAUSTIC CHLORINE

SLUDGE LINE
SLUDGE PUMP

Figure 3. Waste Treatment Plant Flow Diagram

SOIL ANALYZED FOR Cd, Cu, Ni, Pb, Sn, Ag, Cr

MIGRATION OF METALS HAS NOT EXCEEDED 1.20 INCHES/YEAR WITH UNLINED BEDS

CLASS 3, McKINLEY POORLY DRAINED, LOW PERCOLATION RATE SOIL

Figure 4. Chemical Sludge Disposal
D. Control

1. Requirements

Florida's pollution control law has evolved from a generalized definition of "water pollutants" (no deleterious substances), through progressively discrete levels of definition until we now have precise water quality standards.

Prior laws were enforced by the Florida State Board of Health, but the recent emphasis on total environmental quality has led to the creation of a new regulatory and enforcement agency known as the Florida Pollution Control Department. This agency is interested in all forms of pollution.

The industrial wastewater standards imposed by Martin Marietta on its output to the Orange County treatment plant is listed below: (also listed are the references to the government requirement).

a. References

1. Rules of the Florida Department of Pollution Control, Chapter 17-3, "Pollution of Waters," section 17-3 "Water Quality Standards," and section 17-3.09 "Class III Waters - Recreation - Propagation and Management of Fish and Wildlife."

2. Rules of the Orange County Pollution Control Board, Chapters 1 - 5, "Water Pollution," section 1-2.05, "Water Quality Standards" and section 1-2.09A, "Criteria, Class IIIB Waters (SHINGLE CREEK CLASSIFICATION)."

Reference 1 above, Chapter 17-3.05(1) states: "Criteria will be applied only after reasonable opportunity for mixture of wastes with
receiving waters has been afforded. Reference 2 above expresses this intent as: "Mix Zone - 24 feet from point of discharge."

b. Standards

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. fluorides</td>
<td>10 ppm</td>
</tr>
<tr>
<td>2. chlorides</td>
<td>250 ppm</td>
</tr>
<tr>
<td>3. turbidity</td>
<td>40 Jackson Units max.</td>
</tr>
<tr>
<td>4. dissolved oxygen (D.O.)</td>
<td>5 ppm minimum</td>
</tr>
<tr>
<td>5. biological oxygen demand (B.O.D.)</td>
<td>Not to affect D.O. level</td>
</tr>
<tr>
<td>6. temperature</td>
<td>+10% of natural background</td>
</tr>
<tr>
<td>7. dissolved solids</td>
<td>100 ppm</td>
</tr>
<tr>
<td>8. specific conductivity</td>
<td>250 micromhos</td>
</tr>
<tr>
<td>9. radioactivity</td>
<td>1,000 microCuries - beta activity</td>
</tr>
<tr>
<td>10. cyanides</td>
<td>0.00 ppm</td>
</tr>
<tr>
<td>11. cyanates</td>
<td>0.00 ppm</td>
</tr>
<tr>
<td>12. copper</td>
<td>0.10 ppm</td>
</tr>
<tr>
<td>13. cadmium</td>
<td>0.50 ppm</td>
</tr>
<tr>
<td>14. nickel</td>
<td>0.50 ppm</td>
</tr>
<tr>
<td>15. zinc</td>
<td>0.10 ppm</td>
</tr>
<tr>
<td>16. chromium</td>
<td>0.50 ppm at source</td>
</tr>
<tr>
<td></td>
<td>0.10 in receiving stream</td>
</tr>
<tr>
<td>17. phenol</td>
<td>0.001 ppm</td>
</tr>
<tr>
<td>18. lead</td>
<td>0.05 ppm</td>
</tr>
<tr>
<td>19. iron</td>
<td>0.30 ppm</td>
</tr>
<tr>
<td>20. arsenic</td>
<td>0.05 ppm</td>
</tr>
<tr>
<td>21. oils/greases</td>
<td>0.03 ppm</td>
</tr>
<tr>
<td>22. crude oil</td>
<td>0.30 ppm</td>
</tr>
<tr>
<td>23. pH</td>
<td>6.0 thru 8.5</td>
</tr>
<tr>
<td>24. detergents</td>
<td>0.05 ppm</td>
</tr>
<tr>
<td>25. ammonia</td>
<td>0.60 ppm - 60 day avge.</td>
</tr>
<tr>
<td>26. sulfates</td>
<td>2.5% above natural background</td>
</tr>
<tr>
<td>27. sulfides</td>
<td>2.5% above natural background</td>
</tr>
<tr>
<td>28. potassium</td>
<td>10.0 ppm</td>
</tr>
<tr>
<td>29. phosphate, nitrogen</td>
<td>Not to unbalance stream biology</td>
</tr>
</tbody>
</table>

2. Wastewater Test Points

Water pollution is controlled by an internal surveillance, sampling, and evaluation program. This program is a continuous 24-hour-day, 7-day-week sampling, testing, and continuous monitoring program, utilizing controlling and recording instrumentation, and automatic visual/audible alarm systems. In addition special internal
procedures are available for shutting down production operations in the event that an out-of-control situation develops. Corrective action procedures provide for establishing the mode, mechanisms, cause, and responsibility/accountability for failure and punitive action as required. Only two things can stop a production operation:

1. Unacceptable product quality level
2. Unacceptable pollution control level

Figure 5 shows the sampling and test control points. After treatment, all of the wastewater pollutants are discharged through closed piping systems, directly to the southwest Orange County treatment plant.

Great emphasis is placed on the sampling program, since an out of control condition could result in discontinuance of county sanitary sewer treatment. One author recommends that out of control facilities not only have their sewer treatment discontinued but, in addition, have their water service discontinued as a means of enforcing control.

Shingle Creek was selected as the sample point. Its water was surveyed, chemically and biologically, prior to the start of operations at the plant. This survey established the Shingle Creek water quality reference against which all future conditions were to be evaluated. In the original survey there were five sample points. Two of these points have been maintained for routine sampling. Point one is at the bridge on Sand Lake Road, over Shingle Creek and just above the outfall from the county sewage treatment plant. Point two is at the bridge on the Taft-Vineland Road, over Shingle Creek. The Shingle Creek water samples are analyzed periodically since this is the receiving stream.
and serves as a final check for stream pollution that could have been caused by Martin Marietta. The exact total of all metal ions released from the plant is known and is correlated against the concentration of metal ions in the stream. Thus, any level of concentration above that possible, if Martin Marietta were the only source, must be presumed to originate from some other source.

There are occasions when the concentration (which is usually reported as "trace only") is "nil." This means that metal ions have been taken up by the organic sewage sludges in the sewage plant digesters.

Figure 6 shows the Shingle Creek sampling points.
Figure 5. Pollution Testing and Control Points
Figure 6. Shingle Creek Sampling Points
Since all industrial plants are potential sources of water pollution, it is important to know which type of pollutants can cause the greatest damage to the environment.

The water Pollution Control Act Amendments of 1972 charge the United States Environmental Protection Agency with the responsibility of establishing effluent limitations to be achieved by point source dischargers. As a first step, the EPA established various categories of industry which could have similar wastewater problems. One such category was for the metal finishing industry. EPA was specifically instructed to develop two sets of standards, with the first representing Best Practicable Control Technology Currently Available and to be fully implemented in all plants in the country by 1977, and the second set to represent Best Available Technology Economically Achievable and to be fully implemented by 1983. One final requirement was development of separate standards for those new sources constructed after the proposed regulations were published in the Federal Register. These new source standards were included in recognition of the fact that important advantages in waste handling can be gained when designing and laying out a new plant. In order to expedite issuance of standards for the more critical polluting operations, the industry categories were further broken down into two parts, with the Phase I group to receive attention
first and, thus have some additional time to be in full compliance by 1977. Standards would be developed for the Phase II group within each category at a somewhat more relaxed pace. (19)

In Phase I, copper, nickel, chromium and zinc plating were singled out as being the largest contributors of pollution; therefore any industry using such plating processes would be among the first to come under EPA control. Based on the above, the Martin Marietta plant would fall into Phase I. The final published regulations for Phase I can be met by industry only with a very carefully designed treatment plant. Very close control over the waste treatment system operation would be required. Fortunately Martin Marietta had the foresight to design such a waste treatment facility when the plant was built in 1959. Of course, current thinking would be a treatment facility and industrial processes that would require "zero discharge."

In approaching pollution abatement, the problem must first be completely defined by identifying all waste sources, including the characteristics, volumes, and contaminant loads associated with each discharge. The next step is to evaluate the implementation of process changes and in-plant control techniques for conserving water and eliminating all unnecessary wastes. The prime goal is to prevent process chemicals from entering the wastewater, which will result in a saving in both the chemicals lost and the cost to remove these contaminants from the waste. Another goal of the process review is to consider internal modifications of the production process that will reduce, or perhaps even eliminate, some of the various waste streams. (4) This is done by evaluating input and output requirements of each segment of the
production process to locate possible areas for recycling, reuse, or flow reduction. Another major objective is to conserve water and reduce the volume of the waste, thereby decreasing intake water requirements as well as the size of the waste treatment equipment.

In considering process changes, a complete reappraisal should be made of all metal finishing operations carried out in the plant that contribute to the pollution problem. Basically, this involves evaluating the technical and economic features of both the processing and waste disposal aspects of the problem.

When the reappraisal of the processing operations is complete, the implementation of in-plant control techniques for reducing contaminant loads and wastewater volumes can be considered. In-plant abatement practice is generally categorized into techniques for reducing dragout from process tanks into rinse waters, effective rinsing, water reuse, and preventing spills, leaks, and other accidental losses.

Various techniques are available for treating metal finishing wastes, but the generally accepted procedure involves separation of grease and oil, oxidative destruction of cyanides, reduction of chromates, neutralization, separation of the precipitated metal hydroxides, and disposal of sludge.

Other techniques that have achieved significant application for treating metal finishing waste are ion exchange to accomplish purification and reuse of strong baths and rinse waters, the use of evaporation to recover chemicals and purify rinse waters, and the integrated or chemical rinse system for treating dragout before water rinsing. There are also a large number of metal finishing waste treatment techniques
that have had only a somewhat limited application or are in various stages of development or demonstration.

Technology presently in use or under development and demonstration for treating metal finishing wastewaters is listed in Table 7.

The treatment of plating wastes can be broadly classified to whether plating chemicals are destroyed or recovered. The destructive processes, as used at Martin Marietta, include chemical or electrolytic treatment and are aimed primarily at reducing contaminant levels in effluents rather than reclaiming chemicals that are lost in both drag-out and subsequent rinsing operations.

Recovery processes offer considerable potential for an economically viable solution to the plating waste problem. Recovery processes treat effluents so that ionic species are recovered in a form suitable either for recycling in the plating operation or for other reuse. Examples of recovery processes are ion exchange, evaporation, reverse osmosis (RO) and, more recently, electrodialysis. Each is described in some detail in the following sections, A through D.

A. Reverse Osmosis

The potential of reverse osmosis for achieving closed-loop control has spurred considerable activity in the development, demonstration and application of this technique for treating metal finishing rinse water. Although these efforts have been under way for a number of years, reverse osmosis is only now beginning to receive commercial recognition throughout the industry.

The technique involves the use of pressure to force pure water through a membrane while the chemicals are rejected and concentrated in
the rinse water. Reverse osmosis equipment is available in plate-and-frame, tubular, spiral wound, and hollow fiber types.

**TABLE 7**

**METAL FINISHING WASTE TREATMENT TECHNOLOGY**

Conventional

- Alkaline chlorination of cyanide
- Chemical reduction of hexavalent chromium to trivalent form
- Precipitation of metals as hydroxides

Ion Exchange

Evaporation

Integrated Chemical Rinsing

Precipitation of Hexavalent Chromium

Electrolytic

Reverse Osmosis

Electrodialysis

Kastone Process (hydrogen peroxide/formaldehyde oxidation of cyanide)

Ozone Destruction of Cyanide

Carbon Absorption

Carbon Bed Catalytic Destruction of Cyanide

Ion Flotation

Waste Plus Waste

Freezing Processes

Sulfide Precipitation of Metals

Reduction of Chromium by Scrap Iron (simultaneous cementation of copper may also be feasible)(2)
Reverse osmosis is used primarily for treating nickel plating rinse waters. The process is also used commercially on several other metal finishing wastes including waters for rinsing parts from acid, copper, acid zinc, and zinc cyanide baths. Several types of reverse osmosis systems are commercially available.\(^{(21)}\)

Figure 7 shows a typical block diagram for closed-loop treatment of electroplating rinse water by reverse osmosis (RO). Any other recovery technique, e.g., evaporation, would be applied in a similar manner. Rinse water from the first rinse tank, which would otherwise be discharged to drain, is first treated to remove impurities, primarily particulates, and then pumped to the RO membrane concentrator. The concentrator separates the feed stream into a "concentrate" stream, containing a relatively high concentration of plating chemicals, and a "permeate" stream, containing purified water. Before returning the concentrate stream to the plating bath it may be necessary to remove additional water by evaporation. The permeate stream is recycled to the final rinsing stage after makeup water is added to compensate for bath evaporation. It is necessary to use deionized makeup water in order to avoid a buildup in the bath of impurities contained in untreated water.

The operation of a closed-loop process such as shown in Figure 7 not only eliminates the problem of rinse water disposal, but also recovers valuable plating chemicals and reduces the amount of purchased water required for rinsing.

Over the past several years reverse osmosis has received increasing attention as an attractive recovery process for electroplating waste streams.\(^{(3)}\)
Figure 7. Generalized Process Flow Schematic
B. Evaporation

Evaporation to recover processing chemicals and purify rinse waters for reuse has become an established method for controlling pollution in the metal finishing industry. This approach, however, has found only limited application. To be economical, it is necessary to apply evaporation to relatively concentrated rinses, such as those produced by still or countercurrent rinsing. The technique is attractive in operations where the amount of dragout is large, but is also significantly influenced by the value of the chemicals to be recovered. The evaporative approach requires segregation of the rinse waters and the use of techniques such as ion exchange, precipitation and activated carbon to remove impurities which build up in the process solution.

In closed-loop operation (Figure 8), the system is designed to recover all of the processing chemicals lost in the dragout for reuse in the metal finishing bath. The only chemicals which must be supplied to the metal finishing bath are those required to replace what is actually deposited on the parts, and any spillage or accidental losses. When a metal finishing layout does not meet conditions for a closed evaporator loop, a partial recovery system referred to as open-loop evaporation may still be attractive. In this operation, the water from a single rinse tank following the bath is recirculated through the evaporator. A second rinse tank is furnished with a separate supply of water which, after washing the dragout from the parts, is discharged to waste. Only a very small fraction of the chemicals dragged out of the bath enters the second rinse tank. The effluent from the second rinse tank may be treated chemically or by some other method before entering the sewer.
Figure 8. Closed-Loop Evaporative Recovery System
Both vacuum and atmospheric evaporators are used for recovery of chemicals from metal finishing wastes. Conventional stream-heated thermosyphon, forced recirculation and flash evaporators have been widely accepted throughout the industry, but, occasionally, vapor recompression units have been applied. Recently, a rising film vacuum evaporator has been installed in several plants and is now undergoing field testing on chromium and nickel plating rinse waters. In addition, preliminary development investigations are being conducted on cyanide and other rinse waters. The important features of this evaporator are its simplicity of operation, relatively low maintenance requirement, and a modular concept of design which permits a wide flexibility of sizes in terms both of scale-up and scale-down.

The commonly used atmospheric evaporators are packed bed units. However, a falling film atmospheric evaporator has been recently introduced and several of these units are in operation at metal finishing plants.

C. Ion Exchange

Ion exchange is an accepted treatment process for certain types of waste and is used to a limited extent for a variety of other effluents in the metal finishing industry. There are two basic applications of ion exchange for treating metal finishing wastes:

1. The removal of heavy metal contamination from spent processing baths and reclaim or still rinses to purify the solution for reuse in the metal finishing operation.
The demineralization of individual or mixed flowing rinses to obtain a high quality water for reuse while concentrating the dragout for chemical treatment or recovery.

The most widespread use of ion exchange in the metal finishing industry has been in the treatment of chromic acid process baths and rinses, as well as mixed rinse waters. (13, 14)

The treatment of chromic acid plating, stripping and aluminum anodizing baths is accomplished by passing the processing solution through a hydrogen cation exchange unit to remove the metallic contaminant buildup and thus overcome the problem of dumping these baths. The chromic acid plating and stripping baths must be diluted before treatment and subsequently concentrated. Highly crosslinked and macroreticular resins are used in the treatment of chromic acid solutions because of their ability to withstand oxidizing conditions.

In addition to chromic acid bath purification, ion exchange is also applied commercially to reconstitute other processing baths including sodium dichromate passivating or chromating solutions, phosphoric acid solutions used to pickle steel or bright finish aluminum, and acetic acid solutions used to pickle magnesium.

The use of ion exchange to demineralize rinse waters provides pollution control by both purifying the waste water for reuse and recovering or concentrating the chemicals. To achieve chemical recovery, the ion exchange treatment must be applied to individual rinse waters. With mixed rinse waters, the contaminants are concentrated to very small volumes in the regenerants, which permits easy and effective chemical treatment.
D. Electrodialysis

Electrodialysis is presently on the verge of commercial application in the metal finishing industry. The feasibility of electrodialysis for recovering chemicals while purifying rinse water for reuse has recently been established in several pilot plant and in-plant demonstrations.

This approach involves the transport of ionic species through every other compartment. The cation exchange membrane permits the passage of cations and rejects anions, while the anion membrane allows the passage of anions and rejects cations, thus purifying the rinse water while a concentrate forms in the adjacent compartments.

In prototype and in-plant demonstrations conducted on nickel plating, brass plating, and copper cyanide plating rinse waters, electrodialysis has been shown to be an effective method for concentrating rinse waters to a high percentage of bath strength. The ability to achieve high concentrations is an important feature of the technique, since relatively little bath evaporation would permit return to the processing tank of essentially all of the chemicals dragged into the rinse water. In many cases, the natural evaporation taking place in the bath will suffice, and electrodialysis will be able to close the loop without the need for an evaporator.

As with other closed-loop methods, the increase of impurities in the system must be considered and steps taken when necessary to keep the level of these contaminants below the limit that can be tolerated by the processing operation. This may involve either a purification technique, or periodic or continuous withdrawal of a small amount of solution from the system.
In a study sponsored by the U.S. Environmental Protection Agency,(20) a prototype electrodialysis system was used to demonstrate the feasibility of treating a simulated copper cyanide rinse water to concentrate the chemicals for return to the bath. The study showed that the chemicals in the rinse water could be concentrated to slightly over 70 percent of the bath strength. For copper cyanide plating, this amount of concentration may be sufficient to permit the direct return of all the chemicals to the processing operation since the bath is operated hot and a significant amount of natural evaporation occurs. The electrodialysis scheme proposed in the study for treating metal finishing rinse waters is shown in Figure 9.

E. Future Developments

In addition to the new processes being developed for control of plating wastes, new processes to reduce pollutants and use less water are being developed for the pretreatment of metals for painting. This operation represents a large segment of the plating business. Particularly harmful substances such as phosphate or chromates have been eliminated.(7) Research is in process on a one-stage patented process using a peroxxygen compound system for destroying cyanide in zinc and cadmium electroplating rinse water.(11)

1. Counter Flow Rinsing

Since rinse water between stages contributes the highest volume of waste to be treated, problems can be minimized by obtaining the maximum usage from each unit volume of fresh water used. With a smaller total volume to be treated, the concentrations of contaminants are increased and they are more easily treated. One way of reducing
Figure 9. Electrodialysis Recovery System
rinse water flow is to use counter flow rinsing techniques. The least contaminated rinse water is used at rinse stages at the end of the conversion coating line and subsequently is reused in rinse stages near the beginning of the line. Greatest benefit occurs if at least two rinse stages are used following each treating step, i.e., cleaning or conversion coating. In this case, fresh rinse water is added to the second rinse only. This rinse is the least contaminated and is maintained at some specified contamination level, e.g., 1-3 percent of the concentration of the operating bath. Rinse water from this time, not fresh water, is used to replenish the level of the first rinse, which is maintained at a higher level of contamination. In this way, rinse flow can be reduced. If only single rinses are used, and if the line cannot be modified to add additional rinse stages, monitoring devices should be used to sense the contamination level of the rinses and that level held below some specified maximum by adding fresh water only when necessary. Strict maintenance can prevent needless contamination of the rinses from overspray from clogged or misaligned nozzles of adjacent cleaning or coating stages.

Another area concerning process change involves the use of water reducible industrial coatings instead of solvent base coatings. This would reduce pollution problems caused by wastewater from the paint shop. In addition to reducing plating rinse water, work is also being done in the use of atmospheric evaporation towers for recycling of plating rinse water.(10)

In the past few years, there has been an accelerated interest in water reducible coatings for industrial applications. The advent of
pollution requirements, high industrial insurance rates and federal OSHA legislation has spurred the development and use of these coatings. The more recent national petrochemical shortage has allowed water reducible coatings to be offered at a more competitive price. These facts, coupled with recent technology polymer development, have resulted in water reducible industrial coatings that are equivalent in application and physical properties to organic solvent types.

2. Water Base Coatings

Water base industrial coatings are not new to the industrial manufacturer. Water reducible latex modified primers based on solubilized maleinized oil and acrylic latices were commercial in large automotive dip tanks in the late 1950's. Water base acrylic maintenance coatings have found broad commercial acceptance as chemical resistant primers and medium gloss finish coats in the petroleum industry since early 1960. Electrodeposited primers and one coat finishes have been broadly used and have found a wide range of acceptance in industrial coatings over the past ten years.

Water base coatings are not new to the coatings industry, but general industrial use has not matched the growth of water base coatings in trade sales finishes. In 1962, 50 percent of all interior trade sales wall paints were latex based. Today water base latex coatings are dominant in the trade sales market. Seventy-eight percent of interior flat wall paint is now water base. In the past five years, 39 percent of the interior semi-gloss and 32 percent of the exterior finish trade sales markets have converted to the water base type coatings.
3. Neutralization

In addition to the processes for removal or reduction of plating wastes, some interest is also being generated in considering the simple process of neutralization as a possible solution. (17) A new controlled neutralization/oxidation process for sulfuric acid pickle liquor has been developed by E.I. duPont de Nemours and Company for recovery of sulfuric acid from the waste pickle solution. (15)

4. Water Reduction

One final area of plating waste control is in the reduction of water use. In all plating processes, a large amount of water is used in the rinse cycle. Quality of the product need not suffer from water conservation measures. (18)

Why Rinse?

1. To prevent chemical carry forward
2. To prevent adverse effects of bath chemicals on work surfaces
3. To prevent adverse effects on coatings, deposits, or chemical films on subsequent coatings

Why Save Water?

1. To reduce basic water bill
2. To reduce sewer use charges
3. To minimize investment recovery surcharges--regarding the EPA regulations
4. To reduce size of industrial waste treatment facilities
5. To reduce cost of treatment equipment
6. To facilitate chemical recovery, where feasible.
Water Conservation Measures:

1. Multiple tank rinsing
2. Counter flow rinsing
3. Fog rinsing
4. Spray rinsing
5. Counterflow spray
6. Chemical rinsing agents
7. Flow-restriction valves
8. Conductivity controllers
9. Elevate rinse water temperature
10. Agitation
   a. Work
   b. Air
   c. Hydraulic
   d. Mechanical mixer or pump
   e. Ultrasonic.

There are few processes in use today which could not be improved to reduce wastewater. In order to consider wastewater reduction, it is required to separate the plating process into three parts as shown in Figure 10.

Cleaning the surface prior to plating is perhaps the most critical step in any finishing process. The state of the parts as received determines the cleaning steps required. If the part has heavy oil or grease, it must be removed using a solvent, detergent or alkaline cleanser. The use of sprays, brushes, or other mechanical means of assisting the cleanser should be considered. (Grease and scum
Figure 10. Plating Process - Cleaning, Plating, and Passivating
traps should be provided.) Rinses for the entire cleaning system should be considered as a unit.

After rough or precleaning (which is not always needed) the parts are fine cleaned. Here light oil and light rust is removed and the surface readied to receive the plating metal. Both alkaline and acid cleaning are usually used. Alkali removes the oil and dirt; acid removes the rust and smut.

A double cleaning cycle should be considered. This uses up some floor space, but it cleans better and reduces waste. It also utilizes the chemicals more completely than does single cleaning. This is done in the following way: (See Figure 11.)

The tanks are designated A, B, C, & D in the order of part flow: tanks A and C alkaline-electro-clean tanks; B and D acid-clean tanks. Tank A would be the strongest tank of A and C. As tank A tends toward becoming spent, it is dumped to waste, tank C is dumped into tank A, and a new solution made for C, keeping a clean alkali near the end of the cleaning cycle. Fresh chemical must be added to tank A to make the solution stronger, but it is allowed to be used much longer since tank C finishes the cleaning.

The same procedure is used with tanks B and D deriving more use from the acid; therefore, the chemicals are more fully used, and the parts made cleaner. If the parts are not clean, there will be a high reject rate, requiring stripping and replating which is wasteful.

The acid and alkali usage can be reduced by one third, a tank charge lasting 600 hours rather than the customary 400 hours. This
Figure 11. Double Cleaning Removes More Oil and Dirt, Rust and Smut; Reduces Waste, and Gets More Work from the Same Amount of Chemicals
would mean using 0.60 pound of acid/10000 ft$^2$ against 0.90 pound, and 0.45 pound of alkali/10000 ft$^2$ plated versus 0.67 pound.

The counter flow rinsing technique that was mentioned earlier can be handled by overflowing in the following manner: starting in fresh water into the rinse tank Rd after tank D, then flowing to tank Rc between C and D, then to Rb (between B and C), once more to Ra between A and B, then to Rb (between the rough clean and A), and finally letting the rinse water go to waste treatment.

This helps in three ways. It reduces the water usage to about one fifth of usage for unit rinsing. It provides a slightly acidic rinse for the part before it enters the acid cleaning tank and an alkaline rinse before the alkali cleaning. It also tends to neutralize each dragout so that the rinse water leaving the plater is already pretreated. (5)
CHAPTER IV

SYSTEM ANALYSIS - EXISTING WASTE-WATER TREATMENT FACILITY

Water flow data shows that the industrial wastes facilities have been operated beyond the total design capacity. The ability to handle any increase in the loading with the present facility is therefore, limited. Several factors limit the productive capabilities of the present facility:

1. Physical limitations - pit, tank piping, pump and drains, either hydraulic load handling (Table 8) or retention capacity

2. Chemical process rate limitations - increasing complexity of wastes necessitating extensive retreatment of wastes to break down chemical complexes formed through synergism of certain elements

3. Work loading beyond present system capacity

4. A general deterioration of the facility's construction materials - tanks liners, pit liners, pipe liners, tank walls, tank supports, pumps, etc.
TABLE 8

SYSTEM HYDRAULIC LOADING

<table>
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<th></th>
<th></th>
<th></th>
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</thead>
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<tr>
<td>Actual Operation (% of Hydraulic Capacity)</td>
<td>65</td>
<td>85</td>
<td>78</td>
<td>100</td>
<td>78</td>
</tr>
<tr>
<td>Total Effluent (Gallons per month)</td>
<td>4,500,000</td>
<td>6,000,000</td>
<td>5,500,000</td>
<td>7,000,000</td>
<td>5,500,000</td>
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</table>

To determine the possible loads that the facility could be required to process because of metal pollutants, data were obtained from production planning of possible production rates using existing production facilities. The possible volumes and concentrations of water pollutants are recorded in Table 9. Based on these possible production rates, plating work would have to be subcontracted when the design loads are reached. An alternative would be to enlarge the in-house treatment facilities or operate the facility on a two shift basis.

An analysis of the type of plating performed at the facility and sampling of the process rinse water show that the metal and non-metal ions normal to the process rinse water are:

Class 1 ions - Critical: occur continuously and in the greatest concentrations -

- cadmium
- cyanide
- copper
- chromium
- chlorine
- fluorine
Class 2 ions - Major: occur frequently, but usually at such low concentrations that normal dilution renders them innocuous -

- borates
- silver
- lead
- tin

Class 3 ions - Minor: occur infrequently and/or are in such chemical forms as to be innocuous -

- aluminum
- gold
- magnesium
- sulphates
- beryllium
- iron
- phosphates
<table>
<thead>
<tr>
<th>Type of Pollutant</th>
<th>Metals</th>
<th>Cyanides</th>
<th>Chromates</th>
<th>Acids</th>
<th>Alkalis</th>
<th>Totals</th>
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<tr>
<td>Design Load</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>116.0</td>
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<td>Actual Load</td>
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<td>0.1</td>
<td>0.4</td>
<td>0.2</td>
<td>284.0</td>
<td>1.3</td>
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<tr>
<td>Pounds Per 8 Hour Pollutants</td>
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<td>116.0</td>
<td>284.0</td>
<td>122.0</td>
<td>314.3</td>
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Summary

<table>
<thead>
<tr>
<th>Type Pollutant</th>
<th>Design Load</th>
<th>Actual Load</th>
<th>Potential % Overloaded</th>
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<tr>
<td>Metals</td>
<td>2.0</td>
<td>5.5</td>
<td>40</td>
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<tr>
<td>Cyanides</td>
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<tr>
<td>Chromates</td>
<td>0.8</td>
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<td>Acids</td>
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<td>284.0</td>
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<tr>
<td>Alkalis</td>
<td>97.0</td>
<td>122.0</td>
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CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

The existing facilities for treatment of water pollution at Martin Marietta were well planned when they were constructed in 1958. Because of this good planning, the facility has been able to meet the current discharge requirements of the State of Florida and Orange County.

An article by D.P. Caplice(1) on industrial pollution control states that, "The ultimate solution to many industrial pollution problems may involve a staged program of waste reduction followed by effluent treatment or pretreatment facilities." This approach is in practice at Martin Marietta. In addition, the sampling system used is also in line with current recommendations.(16)

Because of expanded manufacturing facilities since the construction of the treatment facilities, the design load is not adequate to handle the potential production volume of water pollutants. In addition, requirements on discharge effluents are going to be further restrictive.

Since the design and construction of the facility in 1958, new improved processes for handling of plating wastes have been developed. The existing facilities need to be modified to incorporate the new process changes - mainly rinse water regeneration and metal reclamation.
B. Recommendations

In order to meet the potential production capability from existing production facilities and to meet future state and federal government requirements (zero output), the facilities need to be modified. It is recommended that the changes be done in the following two phases:

Phase I

Enlarge capacity to receive increased loading by:

1. Installing reclaim rinse water tanks at each critical class process tank to allow for holding of wastes until they can be processed.

2. Providing additional chlorination capacity.

Phase II

Design and install a rinse water regeneration and metal reclaim system using some of the new chemical processes available. Figure 12 is a general outline of the recommended system.
Figure 12. Recommended Rinse Water Regeneration and Metal Reclaim System
BIBLIOGRAPHY


