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Session R - Decorative and Functional Finishes

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DECORATIVE AND FUNCTIONAL FINISHES

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Decorative and Functional Finishes Session R

Cyanide and Noncyanide Silver Electroplating

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CYANIDE AND NONCYANIDE SILVER ELECTROPLATING

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The Silver plating is one of the oldest procedures used for beautification of a jewelry, holloware and flatware products. As far back as the 16th century Silver was deposited on a brass substrate by immersion plating. We have written description of the immersion plating process from Parta in his book "Instant Magic" dated as far back as 1558. Approximately 200 years later the first electrodepositon of Silver was successfully accomplished by electrolyzing a solution of Silver nitrate. At that time the source of the electric energy were electrostatic discharges.

The actual electroplating of Silver was invented by Elkington in 1840 by utilizing the then recent discovery of Potassium Silver Cyanide by John Wright.

A fear of infringing on Elkington's patent prevented the cyanide based electrolyte from finding wide acceptance. At that time most of the Silver plating electrolytes were based on Thiosulphate and Ammonium complexes of Silver. After the invention of the Potassium Silver Cyanide small amounts of Potassium or Sodium cyanide were added to the electrolytes to improve the quality of the Silver deposit.

It is interesting to discover that in the history of the electroplating that non cyanide formulations were utilized on the industrial scale. At the same time in the modern era of the electroplating we are struggling to replace present highly effective but poisonous cyanide electrolytes.Before we start to discuss Silver electroplating let's briefly describe the physical properties of the Silver.

Silver has the highest thermal and electric conductivity and optical reflectivity of all other metals. Gold is the only metal more ductile and malleable than Silver. Silver is also recognized to be the whitest in color among all the other metals.

Density	10.49 g per cm^3
Melting point	960.8^oC
Boiling point	2259 ^oC
Vapor pressure	0.1 mm Hg at 1190^oC
Vapor pressure	1.0 mm Hg at 1360^oC

Linear thermal expansion	19.1×10^{-6} per $1^{o}C$
Heat of fusion	25 cal per gram
Heat of sublimation	65,000 cal per gram-atom
Thermal conductivity	1.006 Cal x cm^{-2} x ^{o}C
Electric resistivity	1.59×10^{-6} per cm^{3}
Reflectivity in visible region	95 %
Reflectivity in 3200 A	10 %
Magnetic susceptibility	-0.181×10^{-6} cgs

As we can see the Silver has outstanding physical properties. Only one but very serious flaw is hindering the wide spread use of Silver in the electronic industry. It very vigorously reacts with sulphur containing compounds to form Silver sulfide, which is black in color and increases the electric contact resistivity.

SILVER PLATING FROM CYANIDE ELECTROLYTES

Today Silver is almost exclusively deposited from cyanide electrolytes. Silver deposits are ranging from matt white to mirror bright with electric conductivity approaching solid Silver.

In the old electrolyte formulations the Silver concentration was very high and was approaching 10 to 15 Tr.oz. per gallon. In the absence of any additives the high concentration of the Silver was necessary to achieve a relatively high current densities to maintain a high deposition rate.

This would not be extraordinary if the Silver prices are in the vicinity of 1 to 3 Dollars per Troy ounce. When today prices are approaching on the average $ 10 per Tr.oz. such high concentrations of Silver are not realistic. For this reason additives improving current density range are a must in all modern electrolytes. Already in the year 1936 Birger Egeberg and Nathan Promisel from International Silver Company of Merriden Conn. applied for a Patent describing a Silver plating bath with low concentration of Silver. This electrolyte was able to plate at unheard off 6 ASF bright Silver deposit. The brighteners involved were based on Thiourea derivatives, thiocarbamates and thiocyanates. What is amazing is that this bath was used in the International Silver Company until a few years ago when the International Silver Company closed down its operations.

As time progressed more formulations were discovered and most of them were utilizing condensation products of Carbon disulfide with ketones, amines, imines, alcohols and so on.

A typical cyanide bath formulation consisted of

Silver as Silver cyanide	4 Tr.oz. per gal.
Free Potassium cyanide	25 av.oz. per gal.
Condensation product of CS_2	0.6 gram per gal.
Wetting agent	2 mls. per gal.

Plating baths were very sensitive to temperature. Any temperature above $70^{o}F$ impaired the brightness of the deposit especially at low current densities.

The modern electrolytes operate with relatively low Silver and Potassium cyanide concentrations. The brighteners are a combination of metallic and organic compounds operating synergesticaly. The addition of Potassium carbonate into the a new electrolyte is not necessary.

The typical formulation of a modern electrolyte is

Silver	3.5 Tr.oz. per gal.
Potassium cyanide	10-15 av.oz. per gal.
Metallic brightener	2 grams per gal.
Organic brightener	2 grams per gal.

In many instances the organic brighteners are assuming a role as a wetting agent. Two kind of the metallic brighteners are incorporated in the Silver electrolyte.

1. A metallic brightener which is codeposited with the Silver and
2. A Metallic brightener which is not codeposited with the Silver

In the mirror bright plating electrolytes used in decorative applications the deposit must have higher hardness to achieve high abrasion resistance. For this reason a small codeposition of the brightening metal is very beneficial.

In electronic applications the appearance of the deposit is secondary. The prime objective is the highest electric conductivity. For this reason any codeposition of a foreign metal is not desirable.

Beside high electric conductivity the deposit must survive $450^{o}F$ temperature for 5 minutes without discoloration. Under these conditions purity of the deposited Silver is essential.

Operating characteristics :

Rack plating	20 to 60 ASF
Barrel plating	10 to 15 ASF

Agitation - combination of a cathode rod movement and a dispersion line agitation is required.

Temperature 70 to 100°F

Current efficiency - rack 100 %

Current efficiency - barrel 50 %

The hardness of decorative Silver is 120 Knoobs and it will not change with the time or heat. The hardness of a very pure Silver deposit is in the vicinity of 60 to 90 Knoobs.

The electric specific conductivity approaching that of pure solid Silver.

The next table illustrates a typical plating procedure.

PLATING STEPS	STERLING SILVER	BRASS	ZINC DIECAST	STEEL
Electrocleaning	1-2 min.	1-2 min.	1-2 min.	1-2 min.
Cascade Rinse	15 sec.	15 sec.	15 sec.	15 sec.
Hydrochloric Acid 1:1		20 sec.	20 sec.	20 sec.
Rinse		15 sec.	15 sec.	15 sec.
Fluoroboric Acid 10%			10 sec.	
Cascade Rinse			15 sec.	15 sec.
Copper Plate		yes	yes	yes
Drag-out Rinse		5 sec.	5 sec.	5 sec.
Cascade Rinse		15 sec.	15 sec.	15 sec.
Sulphuric Acid 20%	*	10 sec.	10 sec.	10 sec.
Cascade Rinse	*	15 sec.	15 sec.	15 sec.
Nickel Strike	*	60 sec.	60 sec.	60 sec.
Rinse	*	5 sec.	5 sec.	5 sec.
Nickel Plate	*	yes	yes	yes
Drag-out Rinse	*	5 sec.	5 sec.	5 sec.
Cascade Rinse	*	15 sec.	15 sec.	15 sec.
Hot Rinse	*	5 sec.	5 sec.	5 sec.
Sensitizer	*	20 sec.	20 sec.	20 sec.
Cascade Rinse	*	15 sec.	15 sec.	15 sec.
Silver Strike	10 sec.	10 sec.	10 sec.	10 sec.
Drag-out Rinse	5 sec.	5 sec.	5 sec.	5 sec.
Silver Plate	yes	yes	yes	yes
Drag-out Rinse	5 sec.	5 sec.	5 sec.	5 sec.
Cascade Rinse	15 sec.	15 sec.	15 sec.	15 sec.
Hot DI. Rinse	5 sec.	5 sec.	5 sec.	5 sec.
Drying				

*** Only if Nickel deposit is required.**

The main disadvantages of cyanide electrolytes is the formation of carbonates during the electroplating process and the polymerization of cyanide ions.

When polymerization takes place the Silver electrolyte start to change color from slightly yellow to orange and in some extremes to pitch black. The color change is not detri

mental to the plating process, however, the electrolyte is emitting considerable amount of ammonium hydroxide and HCN gas. The reduced visibility in the electrolyte makes it difficult to retrieve lost plated articles from the tank. Simultaneously with the color change the carbonate concentration in the electrolyte increases as well. To explain this phenomena we must examine some of the chemical and electrochemical reactions taking place in the electrolyte during the electroplating process.

The Potassium Cyanide dissociates in the aqueous solution into a Potassium and cyanide ions :

1. $KCN = K^+ + CN^-$

In the vicinity of the anode cyanide ions are forming Dicyan (ethanedinitrile, oxalonitrile).

2. $2\ CN^- = NC\text{-}CN + 2\ e^-$

The Dicyan is hydrolyzed by Hydronium ions into Hydrogen cyanic acid and Hydrogen cyanate.

3. $NC\text{-}CN + H_3O^+ + OH^- = 2\ HCN + 2\ HCNO$

The Cyanate acid is hydrolyzed into Ammonium Hydroxide and Carbonic Acid

4. $HCNO + 3\ H_2O = NH_4OH + H_2CO_3$

The formation of cyanates during electrolyses was experimentally proved by W.R. Meyer, R.F. Muraca and E.J. Serfass (2).

Potassium Cyanide reacts with the Carbonic Acid to form Potassium Carbonate and two moles of Hydrogen cyanic acid.

5. $KCN + H_2CO_3 = K_2CO_3 + 2\ HCN$

The reactions 3, 4 and 5 can be summarized into one equation

6. $(CN)_2 + 4\ H_2O + 2\ KCN = 3\ HCN + NH_4OH + K_2CO_3$

At very high anodic current densities we can safely assume that in the diffusion anolytic layer the pH is shifted to the slightly acid side. At this point hydrolyzation of Dicyan could take a distinctively different path.

7. $(CN)_2 + 4\ H_2O = C_2O_4N_2H_8$

The Ammonium Oxalate migrates through the electrolyte into the more alkaline region. Potassium cyanide reacts with

Ammonium Oxalate and additional 2 molecules of Hydrogen Cyanide, Potassium oxalate and Ammonium hydroxide are formed.

8. $C_2O_4N_2H_8 + 2\ KCN + H_2 = C_2O_4K_2 + 2\ HCN + 2\ NH_4OH$

Carbon dioxide from the air will react with Potassium cyanide to form more Potassium carbonate ions.

9. $2\ KCN + CO_2 + H_2O = K_2CO_3 + 2\ HCN$

As we can see from equations No.6, 8 and 9 considerable amounts of Hydrogen Cyanide, Ammonium Hydroxide and Potassium Carbonate are generated. During electroplating electrochemical and hydrolyzation reactions are taking place to a variable degree. If the current density on the Silver anodes does not exceed 20 to 30 ASF then the presence of the Dicyan, Ammonium hydroxide, Hydrogen cyanic acid and Potassium oxalate is negligible and can be controlled by a drag-out. However, if anodic current densities are very high or Silver anodes are replaced by Stainless steel, platinized titanium or carbon then generation of byproducts during the electrolytic process is considerable. To prevent polymerization of cyanide ions and formation of carbonate in the Silver electrolyte the following rules should be observed :

1. Do not use in the Silver electrolyte insoluble anodes.

2. The cathode to anode ratio should be 2 : 1 or at least 1 : 1 .

3. Do not return dragged out solution back into the plating bath. Reasonable drag-out coupled with an electrolytic recovery unit to salvage Silver is very beneficial to the plating bath.

4. If it is not necessary, do not use Stainless steel anode bars and hooks immersed in the plating solution.

The only remedy to remove polymerized cyanide from the electrolyte is very intensive long term carbon treatment. If a new Silver plating solution is set up, agitate or airate the electrolyte for at least 24 hours to expel Hydrogen cyanic acid from the solution.

Accumulated Potassium carbonate can be precipitated as insoluble Calcium carbonate with Calcium cyanide. It is not recommended to use Calcium nitrate or Calcium hydroxide.

NON CYANIDE SILVER ELECTROLYTES

As it was mentioned before non-cyanide Silver plating is dated back to the 16 and 17 century. Before we start to discuss non-cyanide electrolytes we must distinguished between

non-cyanide and no free cyanide formulations.

Under the term non-cyanide we mean a plating formulation without any presence of cyanide ions in any form.

The no free cyanide formulation could contain cyanide ions in some limited amount.

We have to admit that inspite intensive research cyanide plating formulations could not be fully replaced by non-cyanide one.

Most non-cyanide Silver plating solutions are based on ammonium, halide, amino or thio complexes with Silver in a combination with variety of conductivity salts and brightening additives.

Silver has very high normal potential (+ 0.8 V) hence is very easily reduced from its salts to the metallic form by even a very weak reducing agents. It may be displaced from its solutions by any metal with lower normal potential. To prevent reduction of Silver or to suppress diplacement by other metals Silver must be present in a rather strong complexes.

For illustration we will examine some of the non-cyanide complexes and compare them with a typical cyanide ones.

Silver is forming with the cyanide solution of a number of a very strong complexes.

$K[Ag(CN)_2]$ = pK 21.8

$K_2[Ag(CN)_3]$ = pK 21.1

$K_3[Ag(CN)_4]$ = pK 20.7

pK is a designation for the stability constant of the complex. The stability constants of Silver cyanide complexes are not changing considerably with the type of complex. For this reason Silver electrolyte is able to operate in a relatively wide range of cyanide ions conce
ntration.

To the contrary stability constants of Silver thiosulphate complexes will considerably vary from each other.

$K[Ag(S_2O_3)]$ = pK 8.9

$K_3[Ag(S_2O_3)_2]$ = pK 13.5

The stability constant indicates that thiosulphate electrolyte of Silver will be sensitive to concentration change of thiosulphate ions.

Very similar situation is encountered with ammonium and sulphite complexes.

$[Ag(NH_3)]^+$ = pK 3.2

$[Ag(NH_3)_2]^{2+}$ = pK 7.03

$K[Ag(SO_3)]$ = pK 5.3

$K_3[Ag(SO_3)_2]$ = pK 7.3

Iodide complex of Silver is the closest to cyanide complexes as to the absolute value of the stability constant.

The stability constant vary only slightly form one type of the complex to another.

$[Ag_3I]^{2+}$ = pK 14.15

$[AgI_3]^{-2}$ = pK 13.95

$[AgI_4]^{-3}$ = pK 13.75

Hence it is not surprising that in 1936 Dr. Max Schllotter from Germany applied for patent protection of a non-cyanide Silver plating electrolyte based on iodide complex. In 1977 RCA Corporation obtained a patent for Silver iodide plating bath which is almost identical to the Schllotter's patent except for Calcium ions additives to the improve the crystalization of the Silver deposit.

The typical formulation of iodide electrolyte is as follow

Silver iodide	5 av.oz./ gal
Potassium iodide	53 av.oz./ gal
Wetting agent	1 ml. / gal
Brightener	optional

The useful current density range is 0.5 to 5 ASF. The electrolyte is operating at room temperature. The deposit is white to semi-bright in appearance, however, it is light sensitive. The light sensitivity is caused by Iodine codeposition with Silver. The concentration of Iodine in the Silver deposit is dependent of the current density and vary from 1 to 5 % .

The light sensitivity and initial cost of the electrolyte render this Silver plating bath not suitable for electronic or decorative applications. Otherwise the electrolyte is very stable and very easy to operate.

Another non-cyanide type of the Silver electrolyte is based on Silver ammonium complexes. For instance in 1968 the IBM Corporation obtained a patent for the following electrolyte :

Silver nitrate	20 grams / liter
Sodium phosphate	100 grams / liter
Ammonium phosphate	20 grams / liter
pH	> 8.5

The electrolyte is depositing a matt and white Silver, however, pH must be maintained by periodic additions of the Ammonium hydroxide. We found that the most useful Silver deposit was obtained in the pH range of 11 to 12.5 . At this pH range Ammonium hydroxide is expelled from the solution and the working environment became unbearable. Hence the stability constant is strongly influence by the concentration of the free Ammonium ions the useful current density is then fluctuating in not predictable manner.

Silver thisulphate complex is well known in the photography industry as so called fixing solution. The thiosulphate ions are dissolving Silver halides in exposed negative films. The stability constant of Silver thiusulphate complex is close to Silver iodide complex. In 1976 Schering AG obtained a patent for non-cyanide Silver plating electrolyte based on the thiosulphate complex.

The following electrolyte composition will illustrate the invention :

Silver	40 grams / litre
Sodium thiosulphate	370 grams / litre
Conductivity salts	40 grams / litre
Brighteners	
pH	7 to 11
Temperature	20 to 30°C

The bath operates with anodic and cathodic current densities around 15 ASF. At one time the Schering AG advertized this electrolyte very intensively. To my knowledge at the present time Schering withdraw this bath from the market. The Silver deposit is of matt to mirror bright appearance, however, at lower current densities the deposit could be discolored.

The most serious problem with thiosulphate ions in electrolyte is its readiness to be oxidized.

In the anodic diffusion layer thiosuplphate ions could loose two electrons and form tetrathionate ions.

$$2\ S_2O_3^{2-} = S_4O_6^{2-} + 2\ e^-$$

If the anodic current density is too high or an insoluble anode is employed then the following reaction could take place :

$$2\ S_2O_3^{2-} + 3\ O_2 + 8\ OH^- = 4\ SO_4^{2-} + 4\ H_2O$$

The sulphate ions are probably not harmful to the electrolyte but tetrathionate ions could seriously impair the brighteness of the deposit.

In conclusion, we can say that at the present time it is very difficult to replace a modern Silver cyanide electrolyte with a non-cyanide formulation without sacrificing the quality of the deposit, current densities or the stability of the electrolyte.

R-2

Decorative and Functional Finishes
Session R

Directing the Implementation of an Automatic Plating System

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DIRECTING THE IMPLEMENTATION OF AN AUTOMATIC PLATING SYSTEM

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Introduction

The decision to introduce automatic plating capability is a major undertaking for any company doing its own finishing and involves a great deal of evaluation and planning both prior to and after the decision to automate.

Many people are involved in such a project. However, details for the most part become the responsibility of the project director. While some of these details seem to be basic, proper decisionmaking and smooth implementation into production of an automatic plating system can be assured if "effective management" procedures are adhered to.

In short, this is really a two-part project, the first part being justifying automation and selecting a supplier, and the second part being design and engineering requirements, manufacture, installation and start-up.

The sequence of events that are listed during the project referred to in this paper are intended to serve as a guide only and are not, by any means, the only way to do it. It should be noted, however, that this project was successfully completed with a minimum of problems.

Evaluation and Goals Committee

Serious consideration by a company concerning the merits of automatic plating should initiate the naming of an Evaluation and Goals Committee. The function of this committee should be to discuss and evaluate the pros and cons of automatic plating (as they apply to the company) and to establish guidelines to be used in making recommendations to top management relative to go/no go decisions. Representation on this committee should come from the manufacturing, engineering and technical services/research functions of the company, with the members being selected from manager and director levels. While titles may vary from company to company, a typical committee would look like this:

Chart 1

Evaluation and Goals Committee

Director of Manufacturing Systems
Director of Manufacturing
Industrial Engineering Manager
Plant Engineering Manager
Director of Research
Controller

The most important duties of this committee are to:

Chart 2

Duties of Evaluation and Goals Committee

1. Select a project director from within the company (from the committee, if possible) or hire one from the outside with automatic plating project experience.
2. Evaluate data generated from a "Production Needs Assessment" (including projected growth plans) and a "Plating Systems Evaluation".
3. Hire engineering consultant (if necessary) with knowledge of environmental laws (wastewater, air) and building construction.
4. Select supplier.
5. Prepare final recommendation to management.

Because the major part of this project is of a technical nature, a good candidate for project director is the Director of Research. In most decorative finishing companies, the technical services and process engineering staffs report to the Director of Research which is important for maintaining continuity in developing data for design engineering concepts and finishing technology.

The project director is now responsible for coordinating and directing the entire project beginning with the "Production Needs Assessment" and "Plating System Evaluation".

Production Needs Assessment

Every company has different needs, as well as different growth plans. Any needs assessment must begin with an assessment of the status quo. An analysis of one's current production plating capability is a fact-finding study of the type of system(s) being used, i.e. any system of hand operations, any limited automatic system, or a combination of each, for comparison with other systems relative to projected growth plans.

Criteria for the study being addressed were a plating system employing 23 alleys (hand operations) housed in three different plants and a projected growth plan of doubling production within five years. Every alley was capable of performing all plating operations (including final color) from start to finish. Each item listed on the following page must be evaluated for comparison with other plating systems:

Chart 3

Production Needs Assessment

To be studied for comparison with other systems:

A Space requirements (area)
B Costs (including expansion costs)
C Productivity (capability and requirements)
D Labor requirements (personnel)
E Efficiency
F Advantages and disadvantages (limitations)
G Utilization
H Equipment
I Flexability (downtime, etc.)
J Quality of plate and plate thickness distribution
K Bath control
L Wastewater treatment
M Precious metal recovery

Once the study is completed, the data is available to be used versus other plating systems. A thorough job on this part of the project can dramatically reduce the options, and therefore, the work in the next step (systems evaluation).

Plating Systems Evaluation

Most companies have plating capabilities that can be classified into one or more of the following categories:

Chart 4

Plating Systems Evaluation

A. Hand operations
B. Automatic with hoist movement
    1. For some operations (cleaning, copper, nickel)
    2. For all operations
    3. Controls (electromechanical, tapes, PC's)
C. Automatic with elevator movement
    1. For some operations
    2. For all operations
    3. Controls (electromechanical, tapes, PC's)
D. Combination of automatic and hand operations

Obviously, it is virtually impossible to make a full evaluation of all categorized items (needs assessment) for all available systems. However, as mentioned before, the desired available options should now be narrowed. Once the Goals Committee decides on automatic plating, the next step

(selecting the supplier) becomes the most important part of the entire project.

Selecting the Supplier

No attempt will be made to suggest that any supplier of automatic plating equipment is the best. There are at least 15 reputable manufacturers in the United States now supplying reliable systems with applications in the finishing industry.

But it cannot be underscored enough, the importance of exploring proposals from several different suppliers before making a final decision. The time spent with suppliers in studying concepts and technology can mean the difference in getting what you really want in an automatic system. Each supplier should be asked to present their best available technology and every effort should be made to make the final product the state-of-the-art. By all means, be sure that the entire Goals Committee, and any key staff members, are part of the screening exercise, since each department represented has a role to play in carrying out the project.

While there are many considerations that can be used, the following can serve as a guide in rating the performance capabilities of one supplier versus another:

Chart 5

Selecting the Supplier

A. Reputation
B. Initial presentation
C. Availability of current technology and concepts
D. Plant tour of their facilities
E. Personnel (especially the assigned project engineer)
F. Cooperation
G. Tour of operating system built by supplier
H. Tour of proposed automatic area with supplier
I. Cost estimates based on several work sessions
J. Timetable for completion
K. Auxiliary systems knowledge
L. Service availability

With the selection of the supplier, the second part of the project is ready to begin, namely, finalizing design engineering and finishing concepts, site review and layout, manufacture, installation of all systems (including auxiliary systems) and start-up.

Finalizing Design Engineering and Finishing Concepts

By this stage in the project, both the committee and the supplier have reached basic agreement on the major design characteristics needed to support both the technical and production requirements of the company. By this,

I mean such things as hoist or elevator, size, bath sequence and desirability of finishing techniques, capacity (racks/hour) and auxiliary systems.

But this is also the same stage where intensive work sessions are needed to consider all the technological options available to enable a final proposal. Future modifications to previously agreed upon design decisions can be minimized with good coordination by the project director.

Design concepts to be considered are:

Chart 6

Design Concepts for Consideration

A. Automatic load/unload
B. Laser scanning for cycle input into programmable controller
C. Cycle flexibility and independence from arm-arm
D. Self-adjusting rectifiers for plating by constant current density (CCD)
E. Flexibility for both precious metal thickness deposition and color capability
F. Automatic replenishment feeders

Pertinent to any final design must be a decision concerning the percentage of production (by type) to be automatic plated relative to those types to be plated by hand operations. In the jewelry industry, the choices are many, i.e. chains, earrings, bracelets, pins, pendants, etc. Not all types, of course, depending upon their design and method of assembly, can be plated automatically. Troublesome styles, requiring "special care", must be plated manually, thus, there is always a need for some manual finishing capability.

In some cases, process engineering experiments become a necessity and must be conducted simultaneously with the week-to-week work sessions. This classic example was encountered during our design engineering sessions. Data indicated that approximately 40 percent of all production required a bright nickel finish prior to final color which was achieved manually (in addition to polishing) by a "double pass" nickel plate. For the automatic, this was undesirable for many reasons (cost, cycles, tank size, tank length), so experimentation was initiated with a bright acid copper plate (prior to nickel) which ultimately not only solved the design problem, but actually produced a superior finish.

Not to be overlooked during this design period are the auxiliary systems required listed on the following page:

Chart 7

Auxiliary Systems

A. Deionized water
B. Exhausts/Push Air
C. Conveyors
D. Dryer
E. Wastewater treatment
F. Precious metal recovery
G. Ultrasonics
H. Holding tanks

Site Review and Layout

Preliminary layout plans having been previously addressed, of course, during the needs assessment and work sessions with supplier, the time has now arrived for a total site layout review by the plant engineering and industrial engineering managers. While the supplier is working on final specifications and a final total cost proposal which usually takes four to six weeks, attention must now be focused on the area needs to support all systems.

Automatic plating lines are usually installed with new buildings, building additions, or at minimum, building modifications. In any event, the task of preparing the layout and supplying supporting mechanical and electrical needs, is the main contribution to be made by the industrial engineering and plant engineering managers in the project. Their expertise in these areas is critical to the successful completion of the project. Likewise, the role of the engineering consultant becomes quite evident, especially if a new building or building addition is required, and his guidance is crucial.

The final layout to be proposed should provide not only for an efficient product flow including storage area but should also include provisions for effective auxiliary operations already mentioned.

The PERT System of Control

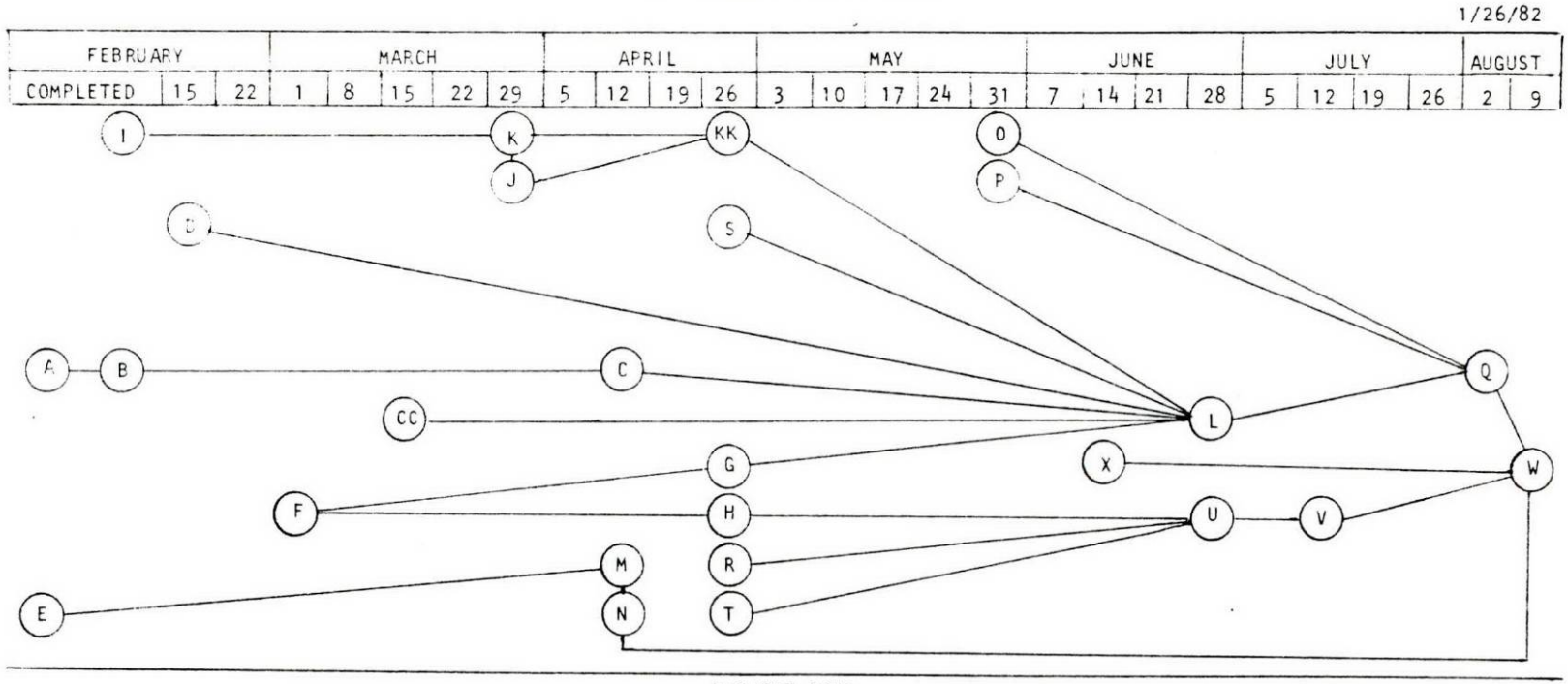
Timely control of all activities now becomes urgent for the project director. The supplier is working on a final proposal for acceptance in order to start manufacture, major site decisions must be made, and many considerations, both short-term and long-term must be addressed.

One system of control that can be used is the PERT system (Program Evaluation Research Task). The introduction of PERT into management planning and control for major projects has added a new dimension to other conventional planning techniques.

Figure 1 on page 7 shows the actual PERT matrix constructed to control activities for the final seven to eight months of the project being addressed. Space does not permit a discussion of each item, however,

FIGURE 1

AUTOMATIC PLATING PROJECT



PROJECT CODE

A. Supplier submit final proposal for line modifications, exhaust system & installation

B. Accept final proposal

C. Complete auto-line modifications (supplier)

CC. Submit schedule for installation (supplier)

D. Complete building addition

E. Develop production planning schedule

F. Develop total site layout

G. Prepare site for auto-line installation

H. Prepare site for auxiliary equipment installation

I. Develop cycles for programmable controller

J. Provide laser ID tickets

K. Finalize acceptance test

KK. Perform acceptance test at supplier

L. Install automatic line

M. Racks

N. Rack carriers

O. Chemicals and electroplating solutions

P. Anodes

Q. Prepare baths and complete trouble shooting

R. Drying system

S. Ultrasonics

T. Nickel treatment tanks

U. Install auxiliary systems

V. Trouble shoot auxiliary systems

W. Start production

X. Develop material identification system

the project codes are self-explanatory and must be completed according to the timetable in the matrix.

Manufacture

Good communications between the project engineer (supplier) and project director are essential during manufacture. Weekly visits to the manufacturing site with staff people are common, not only to check on progress, but to discuss the technical aspects of any project code with appropriate engineering personnel. Among other things, this is the time to initiate plans for developing a material identification system and product flow. Likewise, because developing cycles for the programmable controller is such a tedious task, it can be helpful to learn as much as possible about the programmable controller during manufacture. Another example is to explore the working of the filtration system(s) during manufacture.

Regardless of whether new racks will be made or existing racks are to be modified, much time must be spent on rack design during system manufacture to ensure proper rack dimensions. No less than six plant visits (including two by rack suppliers) were made to ensure a rack design consistent with all operations. Over $30,000 was saved by modifying existing racks used for manual alleys, the final design being such that the racks could be used interchangeably between the automatic and hand lines. This becomes important if the automatic breaks down for any length of time, since the racks can be shifted to hand operations without removing work.

It is imperative that the plant engineer and maintenance engineer make frequent on-site visits during manufacture in order to really learn as much about the system, and system maintenance, as possible prior to installation.

System performance is tested according to predetermined acceptance criteria prior to disassembly and installation. This is merely a dry run of the system through all cycles but it does pinpoint problems that must be corrected.

Installation

Three important figures emerge as the scene is prepared for installation. One is the installation engineer assigned by the supplier, another is the permanently assigned maintenance engineer (plant engineering department) and the third is the "start-up" engineer selected from the process engineering staff (technical services).

Each engineer has clearly defined functions. The installation engineer directs the installation of all systems per approved specifications and within the timetable submitted (six to eight weeks). The maintenace engineer must become familiar with the operation of the entire system as installation proceeds and the "start-up" engineer, who has been involved from the early stages of the project, must not only become familiar with every technical aspect of the operation but must also supervise the preparation of all tanks and the installation of all plating baths.

Figure 2 on page 10 shows part of the worksheet used by the "start-up" engineer for bath preparation. It is referred to here merely because it became so handy in simplifying the start-up operation.

It cannot be overemphasized the importance of these three people working together during installation. Problems of any kind must be reported to the project director for action and follow-up.

With all systems being installed, all baths prepared and all cycles programmed, the last step (start-up) has finally arrived.

Start-Up

The first few days of start-up are spent running the machine without work in order to check all cycles, as well as to analyze all baths for any necessary adjustments. Figure 3 on page 11 shows a typical bath analysis report form on which all results can be tabulated for easy scanning and remedial action by the process engineer.

Having adjusted any baths, the biggest tasks remaining are to adjust all rectifiers for each plating operation, check quality of deposits including final color, and determine individual bath plate thickness distribution. These things take time. Two to four weeks should be allowed before phasing in production.

Chart 8 shows the sequence of events for a typical start-up:

Chart 8

Start-up Events

1. Check all cycles and make any corrections
2. Analyze all baths and make bath adjustments
3. Adjust all rectifiers for each plating operation
4. Check quality of deposits including final color
5. Determine individual bath plate thickness distribution
6. Make adjustments to secure color and desired plate thickness range

The best method for adjusting rectifiers to desired current density is the "known area" method especially if deposition is accomplished by constant current density (CCD). Here, use can be made of Hull cells whereby the area can be exactly calculated.

Plate thickness distribution of copper and nickel can be determined either by cross-section or the "weigh-plate-weigh" method, again making use of Hull cells, while the thickness of the final color (precious metal) can be done either by x-ray fluorescence or "weigh-plate-weigh".

FIGURE 2

CHEMICALS & MATERIALS NEEDED FOR AUTOMATIC PLATING LINE

Treatment No.	Process Name	Total Gal.	Chemical Name	Concentration	Needed	Supplier	Anodes	Comments
T- 2	Soak Cleaner	531	Peptizoid 750-L	4 fl. oz./gal.	16.6 gal.			
T- 5	Ultrasonic Cleaner	176	Peptizoid 750-L	2 fl. oz./gal.	2.75 gal.			
T-10	Electrocleaner	275	Clepo 122	3 oz./gal.	51 lbs.			
T-14	Acid Activate	150	Hydrocloric Acid	20%	30 gal.			
T-18	Copper Strike	308	Pot. Copper Cyanide (double salt)	8 oz./gal. x .22 1.76 oz./gal. Copper	154 lbs.			Adjust Free KCN to 1.5 oz./gal.
T-21	Acid Activate	150	Sulfuric Acid	5%	7.5 gal.			
T-25	Copper Plate	1600	Copper Sulfate Pentahydrate Sulfuric Acid Hydrochloric Acid UBAC Brightener #1	26 oz./gal. 4.1 fl. oz./gal. 50 cc/100 gal. .2% by volume	2600 lbs. 51 gal. 800 cc 3.2 gal.			
T-29	Acid Activate	150	Sulfuric Acid	5%	7.5 gal.			

FIGURE 3

CHEMICAL ANALYSIS REPORT - AUTOMATIC LINE

DATE: _____
NO.: _____

Tank #	Process Name	Total Gal.	Chemical Name	Optimum Concentration	Concentration by Analysis	Recommendations
18	Copper Strike	308	Pot. Copper Cyanide (double salt)	8 oz./gal.		
			KCN (Free)	1-2 oz./gal.		
25	Copper Plate	1600	Copper Sulfate ($CuSO_4 \cdot 5H_2O$)	26 oz./gal.		
			H_2SO_4	9 oz./gal. (4.1 fl. oz./gal.)		
			Chloride	50 ppm		
			UBAC Brightener #1	.2% by volume		
32	Nickel Plate	2700	Nickel Sulfate	40 oz./gal.		
			Nickel Chloride	12 oz./gal.		
			Boric Acid	7 oz./gal.		
			JB 100	6% by volume		
			JB 242	6 qts./1000 gal.		
			BNA Adjuster	1% by volume		
			Non-Pitter (NP-N)	.5% by volume		
46	Rhodium Plate	388	Rhodium	2 gms./liter		
			H_2SO_4	20 cc/liter		
55	Gold Strike	150	Gold	5 dwt./gal. (.25 oz./gal.)		
			Nickel as metal	.5 g/liter Ni (2.2 g/L $NiSO_4 \cdot 6H_2O$)		
			KCN (Free)	.5 oz./gal.		
65	Acid Gold Plate	466	Gold	.85 oz./gal. (8 g/liter)		
			Nickel as metal	1.2 g/liter		
			as metal	g/liter		
			as metal	g/liter		
70	Gold Flash	308	Gold	.85 oz./gal. (8 g/liter)		
			Nickel as metal	1.2 g/liter		
			as metal	g/liter		
			as metal	g/liter		

Summary

The success of any engineering or research project is clearly dependent on the commitment of operations people to make it work. Toward this final success, you must work diligently to involve production personnel in the different stages of development and start-up to instill the confidence to take over future accountability for its operation.

R-3

Decorative and Functional Finishes
Session R

Mechanical Plating & Galvanizing - The Process & Advantages

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MECHANICAL PLATING & GALVANIZING - THE PROCESS & ADVANTAGES

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The readers of this paper might be surprised to learn that they are all very familiar with the basic principles of mechanical plating and have known all about them since their school days. Almost everyone knows that an automobile at a fair speed which suddenly loses all its oil will seize or weld and the piston may plate itself to the cylinder walls. This is mechanical plating. We know that if lubricating oil is cut off from the tool of a lathe making a heavy cut on a piece of steel that the tool will start to chatter or "stick slip" its way along - again mechanical plating at work. One could go on with familiar everyday examples.

Mechanical Plating is the cold welding of a ductile metal onto a metal substrate by the use of mechanical energy. The process is based on the fact that if an oxide free metal is placed in contact with another oxide free metal, metallic bonding can take place because of the free exchange of electrons. Mechanical Plating has also been referred to as peen plating and impact plating. Another process, known as mechanical galvanizing, is similar to mechanical plating and was developed to meet the fastener coating requirements of the construction industry. The process of mechanical plating has been used by automakers, appliance manufacturers, etc. and their suppliers as a low-cost, efficient way to plate fasteners, stampings, extrusions, springs and many other small, exposed parts. These manufacturers have found mechanical plating highly satisfactory with many advantages over other finishes.

This paper will describe mechanical plating and galvanizing and point out those advantages.

How Does Mechanical Plating & Galvanizing Work?

Both mechanical plating and galvanizing are room temperature processes in which metal coatings are applied to parts without electricity as in electroplating and without high heat as in hot-dip galvanizing. The parts to be coated are tumbled in a lined barrel with water, metal powder, special promoters* and glass impact beads. The mechanical energy generated from the barrel's rotation is transmitted through the glass impact beads and causes the spherical metal particles to be peened out flat into a metallurgical bond, first to the substrate and subsequently to previously plated particles, to build up the desired plate thickness.

*Promoter chemicals and surface conditioners are proprietary materials of MacDermid Incorporated, Waterbury, Connecticut.

What Metal Powders Can Be Plated By The Process?

Typically, metals that are Mechanically Plated are ductile - the most common are Cadium, Tin and Zinc as well as various combinations of these powders. Other metals that have been Mechanically Plated are Lead, Indium, Silver, Copper, Brass and Tin/Lead Solder. However, the demand for plating the last group of metal powders has not been large.

What Metals Can Be Protected By Mechanical Plating & Galvanizing?

1. Low carbon steel
2. Cold rolled steel
3. High carbon heat-treated steel
4. Various tool steels
5. High strength alloys
6. Some stainless steels
7. Free machining steels (including leaded steels)
8. Nitrided steels
9. Sintered iron (powder metallurgy)
10. Some Malleable iron and nodular iron
11. Cast iron
12. Copper
13. Brass
14. Bronze
15. Lead
16. Zinc Diecastings

Mechanical Plating & Galvanizing are processes for parts that are normally and typically batch handled, having no greater dimension than 6-8 inches in length and weighing less than 1-2 lbs. each. Significant strides have been made toward coating larger and heavier part types. Parts such as threaded rods in excess of 40 inches in length have been mechanically coated, however, economics typically do no lend themselves to parts of this nature.

Process Description:

The process sequence for mechanical plating and galvanizing is a straight forward sequence of soil and/or scale removal, surface preparation, addition of promoters and metal powder. The descaling and/or soil removal can be accomplished in either the plating barrel or in an off line cleaning system. Once cleaned, parts, glass beads, tempered water and surface conditioners are added to the rotating barrel. Surface conditioners are added to remove residual traces of metal scale, oxides and produce a lightly coppered part. The slurry of glass beads exerts a scrubbing action which facilitates oxide removal during surface damage to edges and sharp conrners. Furthermore, it separates and allows movement between parts preventing flat surfaces from clinging together by surface tension. Finally, the slurry carries the plating materials and mechanical engery into holes and recesses. The addition of a promoter chemical provides the proper chemical environment for the mechanical plating and galvanizing process to

take place. Into this environment the metal powder is added and the metal particles are cold-welded onto the parts by the many impingements of small glass beads under pressure of the overlying parts and media.

Advantages and Benefits:

Mechanical Plating Provides:

1. Assured product reliability through elimination of hydrogen embrittlement. Studies of coating methods for hardened steel parts have shown that embrittlement caused by exposure to acid or other environments in which the steel is randomly anodic and cathodic is of a transient nature and can be relieved either by a 24-48 hour room temperature holding period or by traditional baking procedures.

   Finishing methods such as electroplating in which the steel parts are constantly cathodic, however, can produce irreparable damage to the parts. No amount of time nor baking can alleviate the damage.

   Mass spectrometry studies indicate that no correlation between evoluable hydrogen content and prospensity toward brittle failure of hardened steel parts exists.

2. Mechanical cleaning action from the media which definitely aids in scale removal and shortens the time of the preplate cycle.

3. Ability to plate tangling and flat parts completely and evenly. The impact media tends to keep tangling parts and flat parts which normally mask from making contact with others, allowing complete plating deposition.

4. A system that consumes all chemistry during each process cycle eliminating bath maintenance.

5. Ability to change metal coatings from batch to batch in the same equipment.

6. Non-complex waste treatment procedures; no cyanides or chelating agents are used in the process.

7. Ability to plate powder metallurgy without impregnation. In electroplating, the porosity of powder metallurgy parts is responsible for the entrapment of cleaning and plating solutions. The pores act as thermal pumps, forcing the solutions into the part interior or to the outside, depending on the temperature difference between plating bath and part. These solutions often break down, leaving potentially harmful deposits that eventaully bleed out to ruin the finish and form premature corrosion products. Porous surfaces also make it difficult to obtain smooth or continuous electroplating. Therefore, it becomes necessary to impregnate the powder metallurgy parts with resins, plastics or wax before they can be electroplated. The

impregnation step is costly and time-consuming, but it is not necessary prior to mechanical plating. In fact, mechanical plating of powder metallurgy is basically the same as plating of other metals. Once it has been established that the powder metallurgy part is of sufficient density, is oil-free and is not impregnated, normal procedures are followed.

8. Attractive economics especially for coating in the 0.0003" (0.0076mm) and higher range.

9. Good adhesion and uniformity of coating on interior and exterior of part.

Advantages and Benefits:

Mechanical Glavanizing Provides:

1. Ability to deposit heavy coatings in the 0.002" to 0.003" (0.05 to 0.076mm) range.

2. Batch-to-batch and part-to-part uniformity.

3. Simple and easy control of plating thickness.

4. Freedom from hydrogen embrittlement.

5. Room temperature process - no detempering of parts and metal baths or noxious fumes.

6. Elimination of "stickers". In the molten metal/hot dip process, parts often stick together requiring (in some cases) 100% inspection after processing.

7. Simple waste treatment.

8. No re-tap after plating. In the molten-metal dip process, internal threaded components must either be plated and re-tapped to clean out thread roots, or plated as blanks and then thread tapped. Neither method provides corrosion protection for threaded areas. With the Mechanical Galvanizing Process, normally, overtapped internal threaded components are plated per standard procedure. Plating protection is provided in all recessed areas, and there are no problems with ease of assembly or thread fit.

9. Low energy requirements attractive economics.

10. Ability to deposit multi-metal or alloy coatings for increased corrosion protection. In salt spray testing the addition of 25% tin metal powder to the heavy zinc coating (0.021 in. or 0.53mm) provides up to 400 additional hours of corrosion protection (Table 1).

11. Smoother and improved appearance over the molten metal dip coating application.

Equipment:

Mechanical plating and galvanizing equipment is basically a multi-sided rotating open-end barrel. Machines range in size from 1 to 30 ft. 3 barrels with the large barrels having the capability to coat 2,000-4,000 lbs./load. Parts are loaded with a jib crane or other suitable loading mechanism into the plating barrel. Surface preparation and plating operations are carried out in an inclinable rotating barrel. The plating barrels are open-end for greater productivity and ease of control. When the plate cycle is completed, the mixture of coated parts and glass impact beads are then discharged from the plating barrel into a surge hopper. The capacity of the surge hopper is large enough to receive the entire load within 2-5 minutes. Thus, freeing the plating barrels so that another load of glass impact beads and parts is dropped into the plating barrel and plating begins while the first load of parts and glass impact beads is separated. Separation of the parts from the impact beads is accomplished with a vibrating screen separator or magnetic belt or combination of these. Upon separation of the media from the parts, the media is diverted into a media sump. From the sump, the slurry of media is transferred via pneumatic pump or Auger system to an overhead reservoir for usage in the next coating run. After separation, the parts are either dried or chromated and dried.

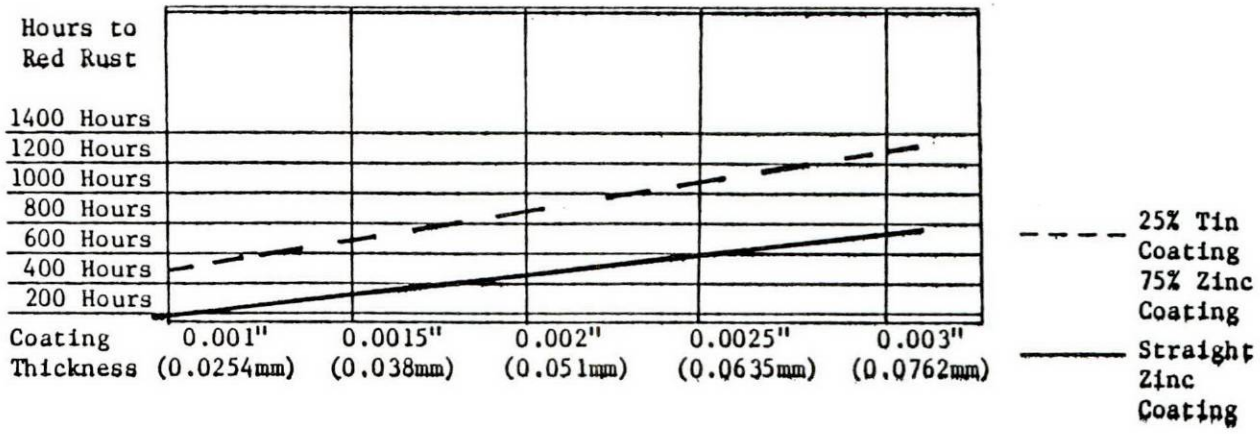
Plate Characteristics:

Mechanical plating thickness is independent of plating time and is controlled by the amount of metal powder used per load. It is significant that a fairly heavy plate can be plated in the same time as a light plate. Uniformity of thickness from part to part generally falls within $\pm$ 10%. Variation in plating thickness on a given part exhibits a reverse pattern from that experienced with electroplating. On mechanically plated parts, the plating is somewhat thinner on sharp edges and projections. Holes, grooves and recesses (areas of low current density in electroplating) generally receive adequate thickness by mechanical plating. Of utmost significance is the fact that since no electric current is used, no hydrogen is evolved in the process. With the use of the proper surface-preparation materials and promoter chemicals, hydrogen embrittlement of hardened-steel parts is, therefore, eliminated.

The surfaces of mechanically plated and galvanized parts exhibit a bright nonspecular appearance. The mirror-birght surface possible with electro-plate is not achieved, but the appearanace is much brighter and smoother than is produced by hot-dip galvanizing. Thus eliminating many of the problems associated with the hot-dip galvanized coating on fasteners such as non-uniform coating, parts sticking together, clogged threads, etc. Postplating treatments such as dichromating can be applied. The performance of Mechanical Plating in areas of corrosion protection can be specifically tailored to end-user requirements. Slat-spray date are available which details various finishes lasting from 24 to 20,000 hours of exposure time (Table 2).

The Mechanical Plating process has the unique capability of producing multi-metal finishes by co-depositing a mixture of metal powders. Many factors must be put into perspective when selecting a finish for a given application. To meet end user needs, requirements and demands, a considerable amount of time and effort has been devoted to developing multiple metal coatings. Examples are the Cadmium/Tin coatings used widely throughout the Automotive and Marine Industry. They are initially developed as alternatives to straight Cadmium coatings, and have several inherent and desirable characteristics. Straight Cadmium coatings, when given a post-plate chromate for increased corrosion protection, take on an iridescent or straw-colored appearance. However, Cadmium/Tin coatings, when given the same iridescent chromate treatment, remain silver-colored but take on the corrosion protection provided by the post-plate treatment. The Tin does not accept the iridescent color but the overall coating does exhibit increased corrosion protection. Results reveal a finish that has the corrosion protection equal to or better than straight Cadmium, that remains silver where brighter coatings are called for, has similar Cadmium and is cheaper than straight Cadmium to produce.

Table 1 - Corrosion Resistance of Mechanically Galvanized Coatings
Salt Spray Test Results - ASTM B117



An additional and very important benefit is a 50% reduction in Cadmium consumption. While continuing to maintain the integrity of the protective finish, the overall Cadmium usage has been significantly reduced, the end user does not suffer product deficiency and the loss of Cadmium into the environment is minimized.

Automotive engineers are constantly adapting lighter metals for weight reduction, subsequently reducing gas consumption and pollution. Aluminum is successfully replacing steel in many applications and continues to be looked at favorable as a viable means to further help the industry produce lighter weight vehicles.

Cadmium/Tin coated fasteners have proven superior to Zinc coated fasteners in corrosion tests against Aluminum. The Cadium/Tin coatings last longer and have minimal destructive electrolytic action with Aluminum. After 1000-hour salt spray test, bolt-washer assemblies plated with Zinc with yellow chromate then fastened in chromated 6061 Aluminum channel, were severely corroded and the Aluminum was pitted due to galvanic corrosion. Similar bolt-washer assemblies mechanically plated with a 50/50 Cadmium/Tin combination with a yellow chromate revealed virtually no corrosion. The 6061 chromated Aluminum channel was also essentially corrosion-free. (See figure 3A & 3B).

Another application for Cadmium/Tin coatings within the transportation industry is for fasteners used in the construction of over-the-road tractors and trailers. Various mechanically plated Cadmium/Tin fasteners are used to attach and secure Aluminum, Aluminum to Steel and Aluminum to Plywood. Subject to destructive environments in all types of roadway circumstances, these fasteners are an excellent demonstration of the coatings effectiveness.

Table 2 - Corrosion Resistance of Mechanically Plated Coatings
Salt Spray Test Results, A. S. T. M. B117 - 62

Time in Hours to Red Rust

TYPE OF COATING	THICKNESS, MILS					
	0.2	0.25	0.3	0.4	0.5	1.0
Plain Zinc	36		48		96	192
Zinc + Clear Chromate	36		48		96	192
Zinc + Colored Chromate	108-336		120-384		168-480	264-650
Plain Cadmium	50		120	200	320	
Cadmium + Chromate	200-500		500-2000		2,000-20,000	
Cadmium/Tin (50/50)	50		120	200	320	
Cadmium/Tin (50/50) + Chromate	200-500		500-2000		2,000-20,000	

Cadmium/Zinc is yet another co-deposit coating that is proving very promising in the metal finishing field. This finish, still undergoing rigid testing, was primarily developed as a high performance coating for components that fasten dissimilar or bimetallic surfaces. The trenchant posture of this coating is the fact that up to 75% of Cadmium can be eliminated from a given procedure with no deterioration in end use affects. Plating costs to produce the Cadmium/Zinc coatings are significantly less than straight Cadmium or Cadmium/Tin coatings.

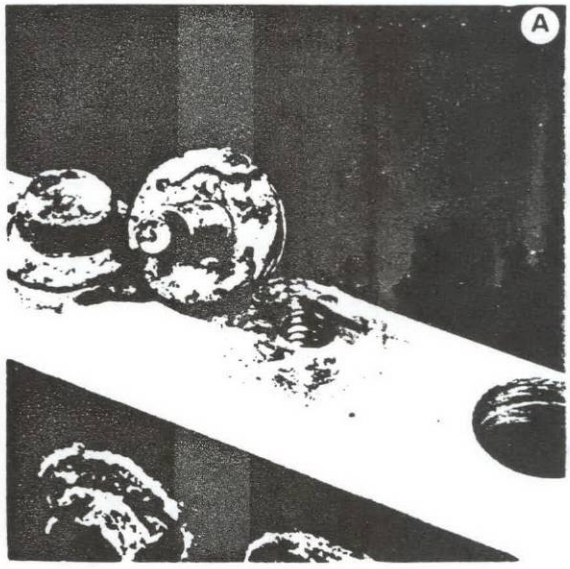


Fig. 3a- Zinc mechanically plated bolt/ washer assemblies reveal severe corrosion damage after 1000-h salt spray test. The aluminum channel (6061) also reveals corrosion damage

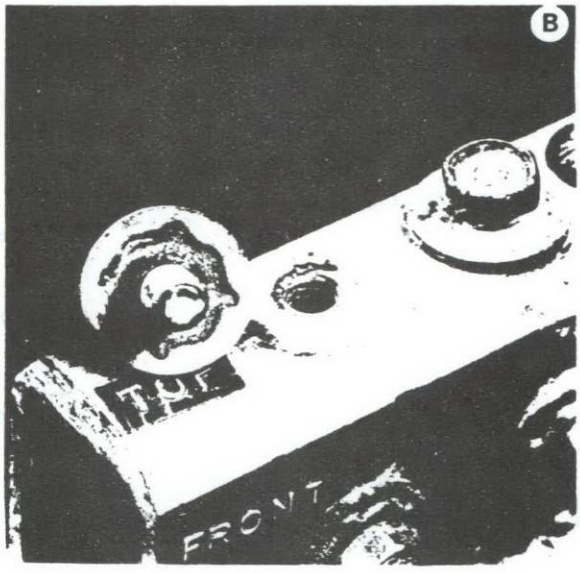


Fig. 3b- Cadmium/tin mechanically plated bolt/ washer assemblies reveal virtually no corrosion after 1000-h salt spray test. The aluminum channel (6061) also is virtually corrosion free

Summary:

Mechanical Plating and Galvanizing utilizes mechanical energy to provide parts that can be batch-handled with various protective finishes. The part types, along with selected glass bead impact media and finely divided metal powder, are barrel-tumbled in a chemically controlled aqueous environment. The metal powder added is cold-welded to the part types which provides the parts with an adherent, sacrificially protective metallic coating.

Mechanical Plating provides the end-user with product reliability, freedom from hydrogen embrittlement, consistent corrosion protection, uniform controlled coatings, proper torque drive relationships, tailor-made coatings

for specific corrosion and bimetallic fastening situations and competitive economics.

Mechanical Galvanizing provides a high performance coating that will provide sacrificial protection in rural, industrial and marine environments for 10 to 30 years or greater. Through the usage of the system usage of the system, zinc oating weights 1 oz./ft. 2-1.65 oz./ft. 2 are achievable and being widely accepted as an alternative to hot-dip galvanizing by construction pole line hardware, highway maintenance and nail industries.

R-4

Decorative and Functional Finishes Session R

Quality Appearance of Electroplated Parts By Spectrocolorimetry

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QUALITY APPEARANCE OF ELECTROPLATED PARTS BY SPECTROCOLORIMETRY

By
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From Lambert - Beer's law and Nessler tubes to electronic sophistication, the measurement of color, absorbance and reflectance has become a standard in the scientific community. Among instruments being used are spectrophotometers with light sources of infrared, visible and ultraviolet, colorimeters for color comparison and variable source sophisticated equipment. They are used for mixing and matching paint and painted surfaces. Colorimetric devices are used extensively in the paper industry for controlling white and colored paper stock and colored printing. Spectrophotometers are used for monitoring dye systems in many industries. Laboratories are using various spectrophotometers for research, process control and analysis. Our laboratory has developed a unique concept in light measuring techniques.

It is important to us to have a quality lock body that is both bright and corrosion resistant. The lock bodies (the laminated section) have historically been cadmium plated and the appearance has been determined by visual inspection. There have always been major disagreements between what is acceptable and unacceptable. People's perception of color varies considerably depending on days and lighting conditions. The general criteria is to have the brightest and blue-whitest lock body possible. The average thickness of the cadmium plate is .00030 - .00060" and the parts are bright dipped in a clear chromate conversion coating. It became necessary to devise some standard of quality appearance that everyone could agree on. A metering device that could read both color and brightness on an opaque surface was pursued. Among various instruments on the market, a spectrocolorimeter (1) seemed to meet our needs. The instrument has a visible light source that simulates daylight and an alternate light source that would simulate typical fluorescent indoor light conditions. It is programmable to read both the standard tri-stimulus values and specific color coordinates. (2) Tri-stimulus are the L,a,b (HUNTER) or the L,a,b, (CIELAB). A chart of this is included. Further, the spectrocolorimeter can compare how far away a color is from white. Using a small spot reflectance port, a lock body can be put on the instrument and readings determined for brightness and yellowness. The readings are printed out on tape to give "L" values for brightness (reflectance), "a" values for green-red, "b" values for blue-yellow, D1925 readings as a comparison to a yellow standard, E 313 for additional yellow standards and WI 313 comparison to white.(3)

Footnotes:

(1) Manufactured by Hunter Lab, Reston, Virginia

(2) Unit can be programmed to read colorimetric differences in XYZ, Lab, Xxy, or CIELAB scales from a product standard or from a standard entered through the keyboard.

(3) Yellow Indices ASTM D 1925-70, E 313-73 and whiteness Index AATC 110-1979, ASTM E 313-73.

L,a,b, COLOR SOLID

CIE 1976 $L^* a^* b^*$ (CIELAB)

$L^* = 116 (Y/Yo)^{1/3} - 16$

$a^* = 500 [(X/Xo)^{1/3} - (Y/Yo)^{1/3}]$

$b^* = 200 [(Y/Yo)^{1/3} - (Z/Zo)^{1/3}]$

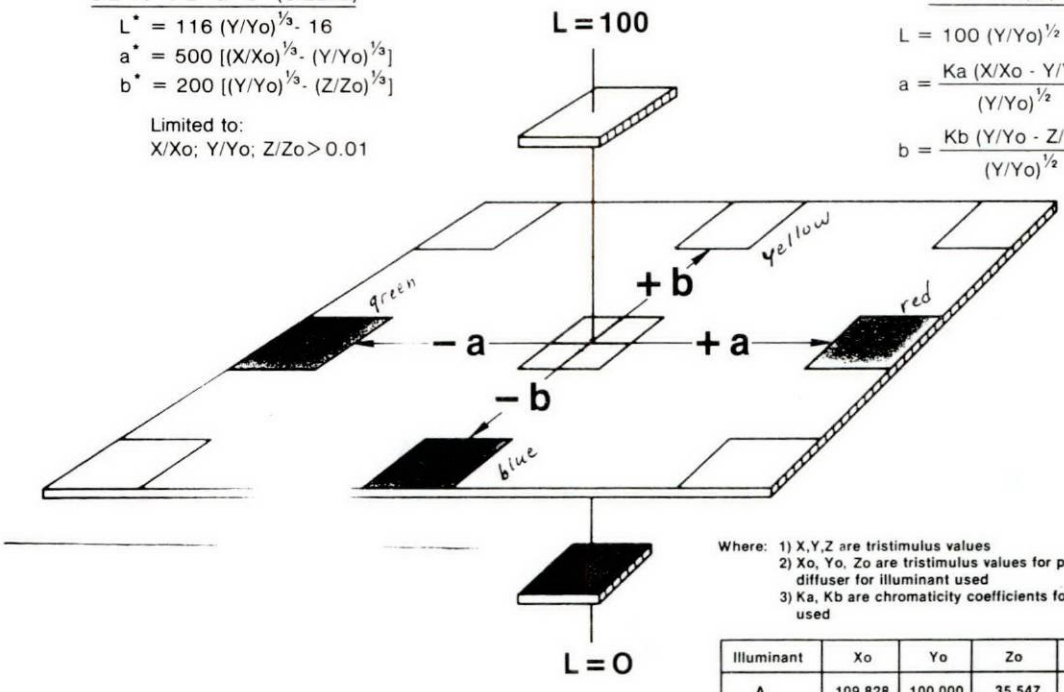
Limited to:
X/Xo; Y/Yo; Z/Zo > 0.01

HUNTER L, a, b

$L = 100 (Y/Yo)^{1/2}$

$$a = \frac{Ka (X/Xo - Y/Yo)}{(Y/Yo)^{1/2}}$$

$$b = \frac{Kb (Y/Yo - Z/Zo)}{(Y/Yo)^{1/2}}$$



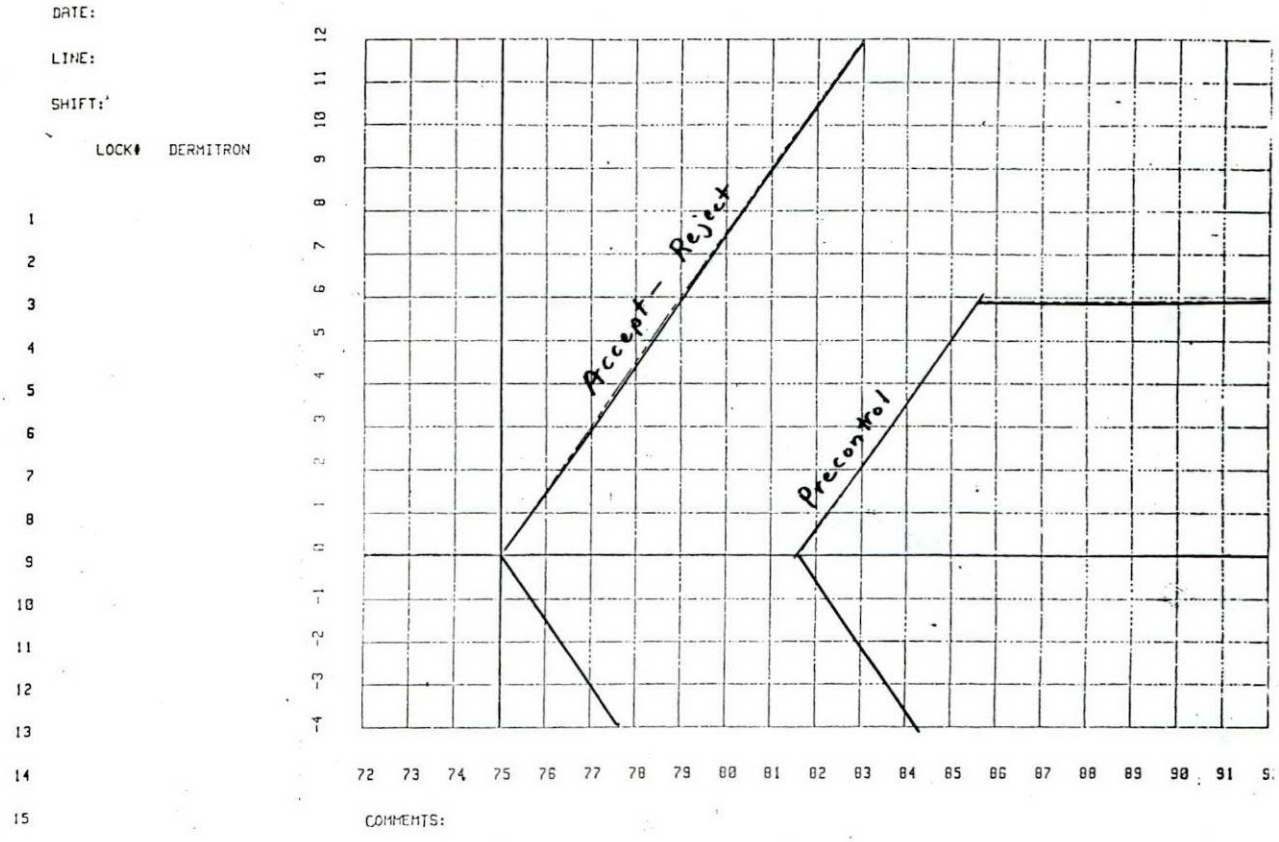
Where: 1) X,Y,Z are tristimulus values
2) Xo, Yo, Zo are tristimulus values for perfect diffuser for illuminant used
3) Ka, Kb are chromaticity coefficients for illuminant used

Illuminant	Xo	Yo	Zo	Ka	Kb
A	109.828	100.000	35.547	185	38
C	98.041	100.000	118.103	175	70
D_{65}	95.018	100.000	108.845	172	67

We started the project by taking 20 lock bodies identified visually as unacceptable and 20 lock bodies indentified visually as acceptable and making readings on the unit. The "a" readings did not seem to vary much between the acceptable and unacceptable parts. But the "L", "b", "D1925", "E313" and "WI313" readings varied considerably. Because we were not sure how refined and controllable our readings could be to our plating conditions, we chose to plot "L" readings on a horizontal scale and "b" readings on a vertical scale graph. All the unacceptable parts had "L" readings of less than 79 and "b" readings from 6-9. All the acceptable parts had "L' readings from 80-82 and "b" readings less than 7. It was interesting to find at this point that parts with higher "L" values (brightness) could tolerate higher "b" values (yellowness) than duller parts and still look good. So we drew a diagonal line between the groups and called that our accept-reject line with all parts to the left reject and all parts to the right accept. See accompanying graph. We then took lock bodies from the plating line and plotted their "L" and "b" readings on the graph. Again, what we had determined visually as good and bad parts fell on the appropriate side of the line. Then, Quality Control ran a statistical analysis of how many parts with how many readings would give us an indication of the plating quality of the lock bodies. This turned out to be 10 readings on 5 lock bodies every 5 loads. We plate 300 lb. loads at 5 1/2 minute automatic cycle with 2 shifts. We felt that the number of readings and sampling would be manageable and accurate. Each group of 5 samples was averaged and plotted.

After a week or two of collecting numbers, the big question was, "What causes the color and brightness to vary?". The plating process was divided into three phases - (a) before plating, (b) plating tank and (c) after plate. All of the conditions of each phase were identified and recorded. The before plate process consists of cleaning and pickling. Concentrations of the cleaners (soak and electro cleaners) and acid pickle (acid salts) and temperature were varied one at a time and recorded. The plating bath metal, cyanide and caustic levels were varied one at a time and recorded along with temperature, brightener level (according to Hull cell tests) and contaminants. The after plate process consists of a mild nitric neutralization dip and a clear chromate. Temperature, pH and concentrations of these were recorded. Samples of the lock bodies before and after all of the changes were taken and recorded. The computer people ran regression analyses on all parameters versus the color and brightness of the lock bodies. Thickness of the cadmium plate was also recorded and plotted against color and brightness. From these regression analyses, significant parameters and ideal conditions were identified. These model conditions were incorporated into the line and measured daily. The cadmium plating bath typically was run at 1.8 - 2.5 oz/gal metal, 2.5 oz/gal caustic and cyanide at a 5.5 ratio to metal. The ideal conditions identified by the regression analyses was the metal at 2.0-2.2 oz/gal, 2.0 oz/gal caustic and the cyanide ratio at 6.0 - 7.0 times the metal. The thickness of the plating was marginally significant. Plating below .0001" and above .0010" was found to give less brightness and/or more yellow than the middle range of .0003 - .0008". The appearance that we determined as most appealing was a low number on the "b" scale and higher than 82 on the "L" scale. The rectifiers were set to an amperage that would give us the middle range of plating thickness (time was consistent because the line is automatic). At this point, our range became very narrow. The "D 1925" value (yellow standard) became

QUALITY GRAPH



a truer measurement of small yellow changes so we changed our graph to "D 1925" readings on the vertical scale, and "L" readings on the horizontal scale. After maintaining model conditions on the plating line and plotting "L" and "D" values on the graphs for several weeks, we had enough historic information to fine tune even more. We set a range that we called precontrol limits. We found that we could plate all lock bodies above 82 on the "L" scale and less than 6 on the "D" scale. The second line on the enclosed graph shows this range. If the parts start approaching the precontrol limits, corrective action is taken. We varied inflow and temperatures on the rinse tanks (again dividing the line into preplate, plate and after plate). Because the total volume of water available to the line is controlled by our waste-treatment, we could increase to one area and decrease to another. We also have a maximum flow going to cyanide reduction and cadmium precipitation. Our maximum for this is 1 1/2 - 2 gals. per minute with two counterflow tanks and a drag-in/drag-out tank. Our lock bodies are laminated steel plates held together by rivets with a problem of entrapment and poor rinsability. We chose to retain the maximum flow on the plate phase and found no significant improvement by increasing temperature. We found that increasing the flow substantially gave us a significant improvement on the color and brightness (lower "D" and higher "L" values). Our preplate cycle has a counterflow rinse after cleaning and an inflow rinse after acid pickle. We feed the acid rinse into the cleaner rinse which has no clean water inflow. The volume of water in this phase and temperature of the water had little, if any, significance on the color and brightness of the final product. We chose to keep this flow minimal, hoping to pick up some flow in our after plate phase. We increased the inflow into our final rinse and added a counterflow rinse (it was a stagnant hot water rinse). The increased rinsing proved to lower our "D" (less yellow) and raise our "L" (brighter). We varied the temperatures on the individual rinse tanks and found no particular improvement. Also in the after plate cycle is a mild nitric acid neutralization dip and tri-valent chromate conversion coating. The concentration of the nitric was varied from .25 - 1.0%. The most effective concentration was 0.5%. Below 0.5%, the lock bodies retained more yellow and above 0.5%, the lock bodies clouded up. The chromate conversion concentration (4) and temperature were also varied. The chromate was controlled at 0.5 - 1.0 oz/gal. The ideal turned out at 0.5 oz/gal and cold. The recommended operating temperature is 75 - 90°F. The chromate was made up with cold water and run at 50 - 60°F with better results than warm. The "L" value didn't change much but the "D" values were significantly lower when cold. The pH of the conversion coating was also found to make a difference. When new, the pH is 1.8. When the pH goes beyond 2.5, the yellow increases dramatically. So a dump schedule and fresh make up was obtained by following pH versus color. Another interesting fine tuning project that succeeded was to monitor the nickel (contained in the brightener), copper and zinc contamination in the plating bath versus color and brightness. The copper was a problem and kept on increasing. At the level of 350 ppm, the yellow was noticeable on both the Hull cell panel and the parts; although they were not rejects, the value was increasing. It was found that the yellow increased

Footnotes:
(4) Kenvert 126-S

when both the nickel and copper were high. After searching for the source of copper contamination, we found that the spring on the inside of the lock was dissolving in the plating solution. It had been customary to leave the barrels full during the third shift shutdown and over weekends. We did not want to lose production time daily, so we settled for emptying the line on weekends and the copper contamination was reduced. Zinc contamination is relatively low (around 250 ppm) and seems stable. It does not seem to have any effect on the finished plate.

The nickel level had previously been around 20 ppm and maintained there by rotating between a no-nickel and nickel brightener system. (5) The vendor runs atomic absorption weekly to determine the nickel level (they also monitor the copper and zinc). The nickel was gradually increased to 35 ppm and both the "L" and "D" values increased. After adjusting the nickel level (and reducing the copper somewhat), it was found that 25 - 30 ppm nickel gave us a maximum "L" without "D" values increasing. My Hull cell panels are read daily on the spectrocolorimeter and brightener adjustments are made accordingly. With most parameters identified and controlled, we can consistently expect our lock bodies to have 85 - 89 "L" readings and 0 - 4 "D" readings. A plating line that was plagued with problems now has almost no rejects and a better quality product. Further, the numbers tell the exact color and appearance and there are no individual discrepancies to deal with. As the readings are taken and plotted, an alert goes out to Quality Control, the plating supervisor and the chemist when they start to approach the precontrol limits. Because of our rigorous identification of parameters on the plating line, corrective action is relatively easy. While the line is still running good parts, the water, pH, temperature, etc., can be checked to quickly identify the problem and correct it.

This type of spectrocolorimetric analysis can be used for general applications of appearance and process control in monitoring plating quality. The same project of setting standards, identifying variables, monitoring line conditions and ease of trouble shooting can be adapted to bright nickel, zinc, chromium, copper, bronze, gold, brass, tin and antiquing. The advantages of consistent appearance quality are:

1) Different components of an assembly would match.
2) Different parts displayed side by side would be visually identical.
3) The same parts run at different times would have equal excellence.
4) Conversion coatings would be consistent in brightness and color.
5) Antiquing could be adjusted to exactly the same color each time.
6) Different processes could be matched up - such as gold and brass.

The cost of the instrument is minimal compared to the cost of rework and rejects. This procedure is going to save over $100,000 in one year of operation. The unit is easily programmed and operated. We have trained employees on the plating line to operate and record data on the instrument.

Seminars are available several times a year to teach people about the basics of spectrophotometry and applications of color measurements. Although this

Footnotes:
(5) Electrochemical Products, Inc.

is the first application to electroplated parts, the adaptation as a tool for quality control of appearance and monitoring device is perfectly attuned for all plating applications. We are pleased with the success of using the spectrocolorimeter for the following reasons:

1) No rejected parts due to color quality.
2) Better productivity because the line is not tied up in the replate process.
3) Savings of more than $100,000 due to early diagnosis of problems and correction.

As you can see, because of increased productivity, improved quality and economic benefits, we will continue to utilize this process application.

I will be happy to answer any questions, give more information or consult with other electroplaters on applications.

Jeanne D. Kitazaki CEF
Chemical Process Engineer
Master Lock Company

R-5

Decorative and Functional Finishes
Session R

Advances in Zinc Phosphate Coatings

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ADVANCES IN ZINC PHOSPHATE COATINGS

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ABSTRACT

Significant advances have been made in zinc phosphate coatings for auto bodies and appliances. A new generation of zinc phosphate processes and coatings has been developed to improve corrosion resistance and durability of paint finishes.

INTRODUCTION

Today, there is an ever increasing demand for improving the durability of autos and appliances against premature rust perforation and paint peeling. The manufacturers are meeting this challange by improving the materials of construction, pretreatment and the paint finish. The prepaint process and chemicals have been modified to meet the challange.

FACTORS FOR CONSIDERATION

One of the most significant changes in materials of construction has been the increased use of galvanized steel. Galvanized steel parts are an integral part of auto bodies and appliances and are processed simultaneously with the cold rolled steel in the same prepaint system. A common zinc phosphate bath is used for both the galvanized steel and the cold rolled steel.

The condition of the galvanized steel surface, as received from the mill, can have a significant effect on phosphating. Chrome treatments on the galvanized surface are to be avoided since they interfere with phosphating. Also, phosphating is dependent on the type of coated alloys.

An increasing amount of attention is also being given to the condition of the steel surface received from the steel mill. Numerous articles have been published on the detrimental effect to phosphating of carbon residues on a steel surface. Carbon residue is one of the most difficult soils to remove from steel and if not removed can lead to voids in the zinc phosphate coating predisposing the surface to corrosion failure. Despite the quality control precautions, some carbon often remains on the surface and must be removed before zinc phosphating.

One of the techniques used for removing carbon is prewiping auto bodies with emulsion cleaners before entering the prepaint cleaning systems.

One of the important changes in the paint system has been the application of electrocoat primers as a base for top coats. The prepaint systems has been modified to include final deionized water rinses to remove chemical residues that could interfere with electrocoat baths. Chromate carry-over from the final possivating rinses is of particular concern in electrocoat baths.

Other significant changes have been made in the prepaint systems for auto bodies to increase the penetration of the zinc phosphate coating into crevices created by over lapping seams and bends. These crevices are where corrosion starts. A common practice to improve crevice coating is to dip the bottom of the auto bodies, which are most susceptible to corrosion, into the zinc phosphating bath at the same time as the upper body is sprayed using a common bath. Therefore, the same bath has to have the capability to apply a satisfactory zinc phosphate coating by both immersion and spray.

A discussion of the prepaint system is not complete unless we stress the importance of the cleaning stages preceeding a zinc phosphating bath. A satisfactory zinc phosphate coating will not form on a surface that is not clean. To enhance cleaning, immersion is often combined with spray application. Currently, ultrasonic energy is being considered for immersion cleaning to enhance the cleaning of crevices. The scrubbing action of ultrasonic energy can also eliminate the need for spray cleaning to shorten the prepaint line.

In order to clean a surface it is necessary to match the cleaner to the soils. The soils are residues of the metal forming compounds left on the surface; such as, drawing compounds, coolants, and rust preventives. Today, an increasing amount of attention is being given to cleanability in the selection of these materials. The selection can be optimized if the drawing compounds, coolants, rust preventives, and cleaners are available from the same vendor who can match the products for cleanability. This is particularly important since the cleaning and phosphating products have a proprietory composition making it difficult to match products from different vendors.

Totally ignoring the cleanability of drawing compounds and cleaners and leaving the soils on a surface for a long time can cause polymerization and hardening that can lead to a condition where the soil can not be removed by any prepaint cleaner. Such soils have to be removed by precleaning before entering the prepaint phosphating system.

ZINC PHOSPHATE COATINGS

Zinc phosphating baths are tailor made for specific prepaint processes. We will limit our presentation to the type of zinc phosphates commonly used in a complex prepaint line simultaneously processing both

steel and galvanized steel parts in a common bath as a base for electrocoat paint primer.

The steps in a typical multistage prepaint system are shown in Table 1. Two spray cleaning stages are used followed by two spray rinses to clean the surface. Next a proprietary titanium activating rinse is sprayed on the clean surface to prepare the surface for zinc phosphating. The activiting step is particularly important for galvanized surfaces to provide nucleation for the formation of fine grained zinc phosphate coatings. The zinc phosphate coating is formed by the zinc phosphating bath which can be a combination of immersion or spray. The phosphate coating is thoroughly rinsed in two stages to remove unreacted phosphate chemicals from the surface. The rinsed phosphate coating is then treated with a proprietory chrome passivating rinse. Best results are obtained with a reactive chrome rinse that forms a polymer film on the surface to seal the pores and to enhance corrosion resistance. This is followed by a deionized water rinse to remove any unreacted chrome from the surface so it will not contaminate the electrocoat primer tank.

Zinc phosphate coatings formed by the foregoing process pass the industry standard tests for salt spray, scab corrosion, gravelometer, paint adhesion, and water resistance tests. These methods correlate well with the newer and more rapid assesments of the quality of a zinc phosphate coating from SEM (scanning electron microscope) photomicrographs and chemical analysis of the coatings by EDS (energy dispersive spectroscopy).

SEM photomicrographs show differences in the phosphate coating morphology when coatings are obtained by a conventional zinc phosphate versus a new type of zinc phosphate on steel (Figure 1). The new type of coating has much finer crystals and lower porosity than the conventional coating. This results in superior resistance to salt spray, scab corrosion, improved paint adhesion, and water resistance.

EDS chemical analysis of the zinc phosphate coating shows that the conventional coating is iron rich with a phosphophilite structure that gives acceptable performance. By contrast the new type of zinc phosphate coating is rich in alkaline earth metals. It has much finer crystals and reduced porosity and gives superior performance.

The new alkaline earth rich phosphate coating also produced better results on galvanized steel. SEM photomicrographs show that the new coating is much finer and less porous than the conventional coating. This results in improved performance (Figure 2).

Maintaining the quality of the zinc phosphate coating in a prepaint line is of utmost importance. The existing quality control tests, such as salt spray and scab corrosion tests, require several weeks for completion. By contrast the newer SEM and EDS techniques can give an indication of the coating quality in less than one hour. In trained hands the SEM and EDS are valuable tools for detection of phosphate

problems and rapid correction. An increasing number of manufacturers and some phosphate suppliers have SEM and EDS equipment to help maintain quality zinc phosphate coatings.

SUMMARY

Improved alkaline earth rich zinc phosphate coatings are available for steel and galvanized steel as a pretreatment for auto bodies and appliances to enhance durability of the total finish. To optimize performance it is necessary to consider the entire process including the surface of the metal from the mill and the drawing compounds and coolants that have to be removed as soil in the prepaint system. Performance can be enhanced by modifying the prepaint system to use immersion instead of spray to penetrate crevices with phosphate coating to improve corrosion protection. Coating of crevices can be further enhanced by adding ultrasonic energy to critical stages in the prepaint line. Quality of the zinc phosphate coating can be monitered and maintained by use of SEM and EDS for surveillence and trouble shooting.

TABLE 1

TYPICAL PRETREATMENT PROCESS

STAGE	
1	Clean, Spray
2	Clean, Dip or Spray
3	Water Rinse, Spray
4	Water Rinse, Spray
5	Grain Refine, Spray
6	Phosphate, Dip and/or Spray
7	Water Rinse, Spray
8	Water Rinse, Spray
9	Reactive Chrome Seal, Spray
10	Deionized Water Rinse, Spray
11	Deionized Water Rinse, Spray

FIGURE 1 AND FIGURE 2

SEM photomicrographs (1500X) show differences in morphology between conventional zinc phosphate (A) and new zinc phosphate (B).

FIGURE 1 Substrate is SAE 1010 Steel

A Conventional



B New

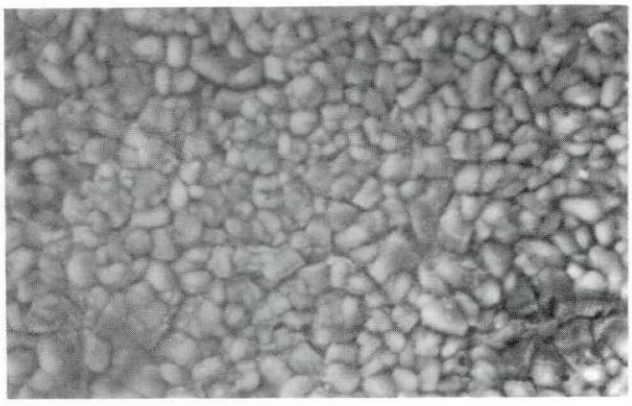
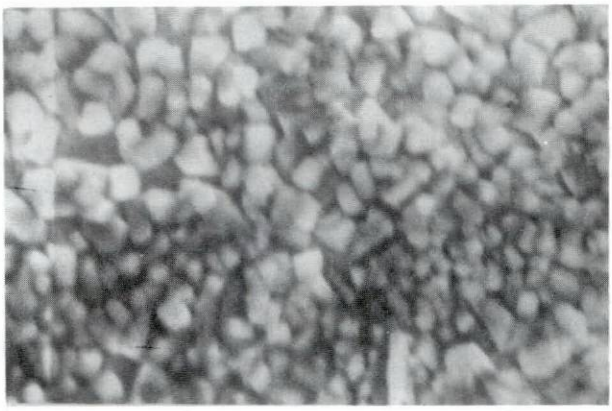


FIGURE 2 Substrate is Galvanized Steel

A Conventional



B New

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