

THE MODERNIZATION OF A
PLATING ROOM

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THESIS

THE MODERNIZATION OF A PLATING ROOM

BY

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TABLE OF CONTENTS

THE MODERNIZATION OF A PLATING ROOM

	Page
PLATING ROOM PRACTICE 1935	1
Layouts Figure No. 1, Figure No. 2	2
SILVER PLATING 1935	2
Solutions and Equipment	2
Type of Work Plated	2
Typical Silver Plating Procedure	2
Operator's Effort	5
COPPER PLATING 1935	5
Solutions	5
Typical Procedure for Copper Plating Steel	5
Copper Plating Zinc Alloy Die Castings	6
Operator's Effort	7
NICKEL PLATING 1935	8
Solutions	8
Nickel Plating Procedure	8
Operator's Effort	10
GOLD PLATING 1935	10
Solutions and Equipment	10
Typical Gold Plating Procedure	10
Operator's Effort	11
ZINC PLATING 1935	11
Solutions	11
Typical Zinc Plating Procedure	11
Operator's Effort	12

	Page
BRASS PLATING 1935	12
Solutions	12
Typical Brass Plating Procedure	13
Operator's Effort	13
METHODS OF SOLUTION CONTROL 1935	13
REORGANIZATION AND PROCESS DEVELOPMENT	14
Solution Control	14
Analytical Procedures	15
Acid Copper Solutions	15
Cyanide Copper Solutions	17
Greenspan Bright Copper Solutions	22
Brass and Bronze Solutions	25
Zinc Solutions	27
du Pont Bright Zinc Solutions	30
Nickel Solutions	32
Bright Nickel Solutions	37
Silver Solutions	41
Mercury Solutions	43
Gold Solutions	44
Degreasers	46
Alkaline Cleaners and Acid Solutions	47
Factors	49
Analytical Schedules	50
BRIGHT NICKEL	53
Investigation of Processes	53
Equipment	54
Racking	54
Savings	55



	Page
Purification	56
Solution Composition	58
Operating Conditions	59
BARREL NICKEL PLATING	60
Equipment	60
Old Procedure	61
New Procedure	62
Summary of Improvements	63
PLATING ZINC ALLOY DIE CASTINGS	63
Possible Plating Cycle	63
Preplate Treatment	65
Copper Plating	66
Nickel Plating	66
Revised Procedure	67
Comparison of Costs and Quality	68
BRIGHT COPPER	69
Processes Available	69
Amine Bright Copper	70
Development Work	70
BATCH STAFF PROBLEM	72
Rusting	72
Change in Material	73
AUTOMATIC SILVER PLATING	73
Bright Silver	73
Cleaning	75
Acid Treatment	75
Copper and Nickel Striking	76
Recovery	79



	Page
Plating Cycle	79
Pilot Plant Work	80
Racking	81
Conveyerizing	82
Machine	82
Summary of Silver Developments	83
LAYOUT CHANGES	83
Changes from 1935 to 1940	83
Changes from 1940 to 1941	84
PROJECTED FUTURE DEVELOPMENTS	84
ACKNOWLEDGEMENTS	85
ABSTRACT SECTION	86

THE MODERNIZATION OF A PLATING ROOM

PLATING ROOM PRACTICE 1935

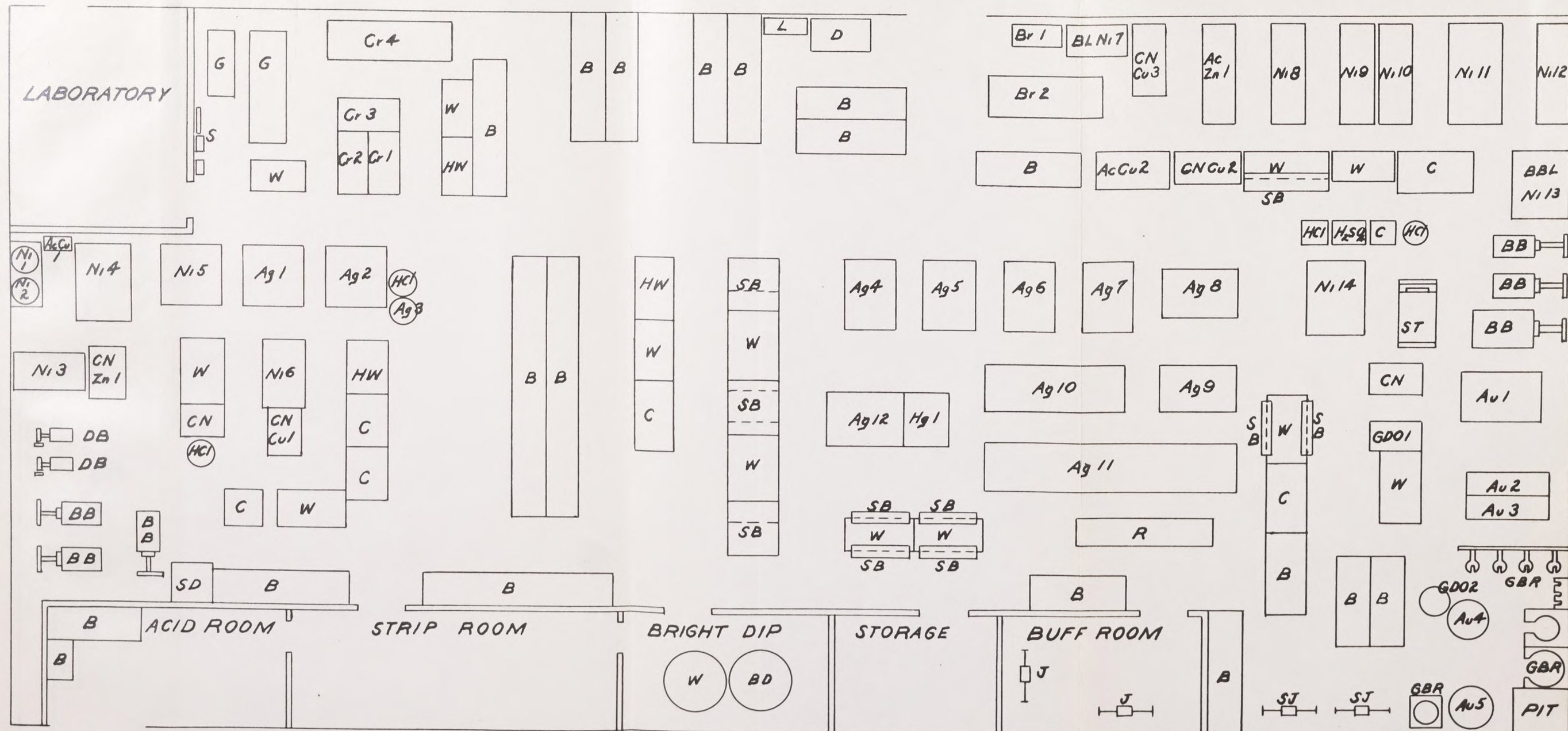
Layouts

This thesis presents general changes in plating room practice and more specifically changes in one plating room over a five year period from 1935 to 1941. Such developments in electrochemical processing necessarily follow, in general, world wide progress in the industry. The manufacture and finishing of band instruments is sufficiently unique that necessarily many special processes have been developed which are not generally used in the electroplating industry.

In order to properly understand the need for modernization and the subsequent improvements it is necessary to describe in detail the equipment and practice as of 1935. Figure No. 1 shows the general plating room layout and location of processing solutions. This plating room was one hundred fifteen feet long by fifty-four feet wide and had a control laboratory in one corner eighteen feet long by thirteen feet wide. A close inspection of the layout shows that a large number of unnecessary steps was taken by various operators particularly in plating nickel. This condition was brought about partly by increasing production demands which resulted in locating solutions at disadvantageous places but mostly by a rather radical change in the type of work plated.

Reference to Figure No. 2 shows the layout of the same plating room in 1929. This layout although inconvenient in minor details shows a plating room very well laid out for the greater bulk of the work done. At that time demands for copper, nickel, and zinc plating were greatly increased due to the purchasing of two drum manufacturing plants. The manufacturing plants were moved to Elkhart and existing solutions were moved in and placed wherever there was room. This condition contributed largely to the

1



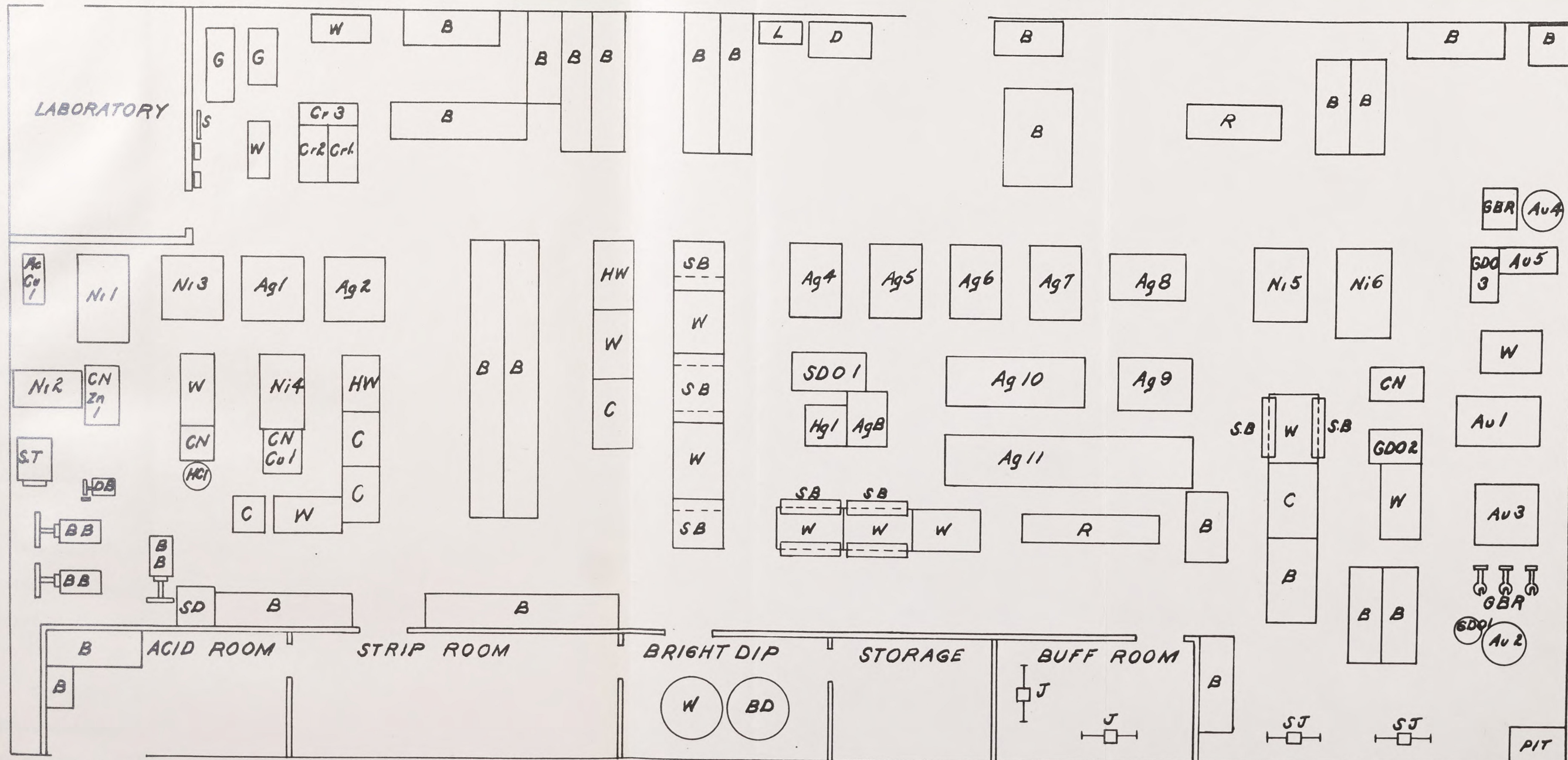
G-GENERATOR
 S-SWITCHBOARD
 B-WORKBENCH
 L-LOCKER
 D-DESK
 R-WORKRACK
 C-ALKALINE CLEANER
 J-BUFF JACK
 W-RINSE TANK
 CN-CYANIDE DIP
 SD-SAWDUST DRIER
 DB-DRYING BARREL

CNCu - CYANIDE COPPER BATH
 AcCu - ACID COPPER BATH
 CNZn - CYANIDE ZINC BATH
 AcZn - ACID ZINC BATH
 Ag - SILVER BATH
 Ni - NICKEL BATH
 BBLNi - BARREL NICKEL BATH
 BLNi - BLACK NICKEL BATH
 Au - GOLD BATH
 Cr - CHROMIUM BATH
 HCl - HYDROCHLORIC ACID DIP

SDO - SILVER DRAG OUT OR RECOVERY
 GDO - GOLD DRAG OUT OR RECOVERY
 GBR - GOLD BELL RACKS
 SJ - SCRATCH BRUSH JACK
 SB - SCRUB BENCH
 BB - BURNISHING BARREL
 ST - SAND TUMBLE BARREL
 BD - BRIGHT DIP
 Hg - MERCURY DIP
 HW - HOT WATER
 H₂SO₄ - SULPHURIC ACID DIP

Fig #1

PLATING ROOM
 CG CONN Ltd
 ELKHART IND
 OCTOBER 1935
 SCALE - $\frac{1}{8}$ " = 1' DRAWN-FKS



G-GENERATOR
 S-SWITCHBOARD
 B-WORK BENCH
 L-LOCKER
 D-DESK
 R-WORK RACK
 C-ALKALINE CLEANER
 J-BUFF JACK
 W-RINSE TANK
 CN-CYANIDE DIP

CNGu-CYANIDE COPPER BATH
 AcCu-ACID COPPER BATH
 CNZn-CYANIDE ZINC BATH
 Ag-SILVER BATH
 Ni-NICKEL BATH
 Au-GOLD BATH
 Cr-CHROMIUM BATH
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 BB-BURNISHING BARREL
 ST-SAND TUMBLE BARREL
 BD-BRIGHT DIP
 Hg-MERCURY DIP

Fig.#2.

PLATING ROOM
 C.G. CONNELL
 ELKHART IND

1929
 DRAWN F.K.S. 1/10/1941.



undesirable layout shown in Figure No. 1.

SILVER PLATING 1935

Solutions and Equipment

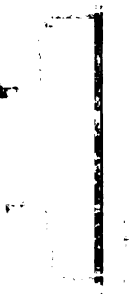
In 1935 silver plating was done in twelve different solutions varying in gallonage from fifty gallons to sixteen hundred gallons. The total silver solution volume was six thousand gallons. Eight of these solutions were operated without agitation while agitation was used in four solutions. In Figure No. 1 silver solutions No. 1 and No. 2 were two hundred fifty gallons each operated with rotary cathode motion. The cathode rail was circular with anodes on the inside and outside. Solution No. 10 was a nine hundred gallon semi-automatic strike. Solution No. 11 was a semi-automatic plating unit of seventeen hundred fifty gallons. Solution No. 3 was a fifty gallon strike which served solutions No. 1 and No. 2. Solution No. 4 was a four hundred gallon strike which served four hundred gallon plating solutions Nos. 5, 6, 7, 8 and 9. Solution No. 12 was a four hundred gallon first strike used where two strikes were necessary before silver plating.

Type of Work Plated

The silver plating operations covered a wide range of base metals. These consisted of copper, nickel, nickel silver, brass, bronze, and steel in the form of sheet, rod, tubing, castings and assemblies of miscellaneous metals. The size of the parts varied from an assembled Sousaphone through the entire range of band instruments to piccolo keys. Nearly all work was wired before plating. Very little racking was done at this time.

Typical Silver Plating Procedure 1935

There were many modifications in plating procedure to take care of the wide variation of work done. The following procedure was typical of the practice.



1. Cork and wire.
2. Clean anodically in alkaline cleaner - 1 min.
3. Bright dip - 1 to 2 sec.

Sulphuric acid - 2 parts.

4. Rinse
5. Hand scrub with pumice.
6. Rinse.
7. Blue dip - 1 to 2 sec.

Hg - .09 to .11 oz./gal.

NaCN (free) - 4-5 oz./gal.

8. Rinse.
9. First silver strike - 1 to 2 min.

Ag - .5 oz. T./gal.

NaCN (free) - 7 to 10 oz./gal.

Tank potential - 6 volts.

Temperature - room.

10. Rinse (optional).
11. Second silver strike - 10 to 15 min.

Ag - .9 to 1.0 oz. T./gal.

NaCN (free) - 6 to 8 oz./gal.

Na₂CO₃ - 4 to 10 oz./gal.

Tank potential - 1.5 to 2 volts.

Temperature - room

12. Silver plate - 1 to 2 hrs.

Ag - 3.0 to 3.5 oz. T./gal.

NaCN (free) - 5 to 7 oz./gal.

Na₂CO₃ - 4 to 10 oz./gal.

Tank potential - .75 to 1 volt.

Temperature - room

13. Rinse.

14. Hot rinse.

The greatest variation from the above procedure was in the case of keys of which some parts were castings. In order to minimize "spotting out" a phenomenon common to brass castings, a nickel strike was used followed by one silver strike before silver plating. In this case bright dipping, blue dipping, and the first silver strike were omitted from the above procedure.

The analysis of the nickel strike solution (No. 5) was as follows:

Ni - 2 oz./gal.

NaCl - 3 oz./gal.

H_3BO_3 - 3 oz./gal.

pH - 5.8 to 6.2 (colorimetric)

Temperature - room

Tank potential - 1 volt

A statement of the current density used has been omitted from all the above operating conditions. Measurement of current densities on objects as deeply recessed as band instruments is futile due to the fact that at no two spots on an instrument is the current density the same. Even average current density measurements are of no value due to the extreme difficulty of obtaining even approximate area estimations. The weight of deposit necessary on each instrument was determined over a period of many years by balancing complaints and refinishing costs against the cost of silver applied to each instrument. Specifications on deposits were written in pennyweights per piece and determined by measuring ampere hours of current flow in each instance. This was usually done with ampere hour meters, sometimes with

only ammeters and a clock.

Operator's Effort

The average operator's time consumed per piece on the average instrument exclusive of the time in processing solutions where the work needed no attention was about twelve minutes. The average number of steps taken per piece were one hundred.

COPPER PLATING 1935

Solutions

At this time both acid copper solutions and cyanide copper solutions were used for copper plating steel. Three cyanide copper solutions were used, No. 1 of two hundred gallons and No. 2 of two hundred gallons for copper striking brass and steel parts before acid copper or nickel plating and No. 3 of two hundred twenty-five gallons for copper plating zinc alloy die castings before running in acid copper.

Typical Procedure for Copper Plating Steel

1. Wire or rack.
2. Soak clean in alkaline cleaner 4-5 min.
3. Clean cathodically in alkaline cleaner 1 min.
4. Rinse.
5. Acid dip 4-5 sec.

1-1 Hydrochloric acid

6. Rinse.
7. Copper strike (cyanide copper No. 1 or No. 2)

Cu - .2 - .3 oz./gal.

NaCN (free) - .2 - .3 oz./gal.

Na₂CO₃ - 2 to 10 oz./gal.

Time - 4 to 5 min.

Tank potential - 4 to 6 volts.

Temperature - 80-90°C.

8. Rinse.

9. Copper plate (acid copper #2)

Cu - 3 to 4 oz./gal.

H₂SO₄ - 2 to 3 oz./gal.

Time 1 hr.

Temperature - room

Tank potential - .75 to 1.5 volts.

10. Rinse.

11. Hot rinse.

The procedure for slowly building up worn sections in acid copper solution

No. 1 was the same as above. The solution analysis was as follows:

Cu - 3 to 4 oz./gal.

H₂SO₄ - .5 oz./gal.

Time - 12 to 48 hrs.

Temperature - room

Tank potential - .75 to 1.5 volts.

Copper Plating Zinc Alloy Die Castings

The procedure for plating zinc alloy die castings was as follows:

1. Wipe off hard packed buff dirt.

2. Wire.

3. Soak in alkaline cleaner - 1 min.

4. Cathodically clean in alkaline cleaner - 15 sec.

Tri sodium phosphate - 3 oz./gal.

Sodium carbonate - 3 oz./gal.

Temperature - 80 to 90° C.

5. Rinse

6. Acid dip - 5 sec.

Sulphuric acid - 3% by wt.

7. Copper plate (Cyanide Copper #3)

Cu - 2.5 to 3.0 oz./gal.

NaCN - 2-3 oz./gal.

Na_2CO_3 - 2.0 to 10 oz./gal.

Temperature - 40°C.

Tank potential - 1 to 1.5 volt.

Agitation - Cathode Oscillation.

Stroke - 4 in.

Twenty cycles per minute.

Time - 15 min.

8. Rinse.

9. Copper plate (acid Copper #2).

Same formula and conditions as Page No. 5

10. Rinse.

11. Unwire.

12. Copper buff.

13. Wire.

14. Clean as before (Steps 3 and 4).

15. Rinse.

16. Acid dip as before (Step 6).

17. Rinse.

18. Nickel plate, same solution and conditions as given under nickel plating on Page No. 9

19. Rinse and dry.

20. Nickel buff

Operator's Effort

The average operator's time consumed per rack or per batch of wired work in copper plating steel was about twenty minutes exclusive of the time that the work was in processing solutions requiring no attention.

The use of the word batch is in connection with wired work and means the number of wires that could conveniently be handled at once. In the case of racked work from one to two racks were handled at once.

NICKEL PLATING 1935

Solutions

In 1935 the nickel plating was done in fourteen solutions varying in capacity from seventy-five gallons to four hundred twenty gallons. The total volume of solution used was three thousand seventy-five gallons. These were all cold solutions operated without agitation except in special instances.

The work plated was principally brass and copper plated steel. A small amount of steel was nickel plated direct. Copper plated die castings were nickel plated. Aluminum tubing and castings were also nickel plated. The size and configuration varied tremendously. The largest pieces were bugle lyra frames measuring about thirty inches long by twenty inches wide made from hollow tubing, drum shells up to fourteen inches in diameter by six inches deep, and chime tubes up to six feet long. The work graded down to small screws of which fifty or sixty were put on a wire. Nearly all work was wired although racks were used in some cases.

Nickel Plating Procedure for Copper, Brass, Copper Plated Steel, and Steel and Copper Plated Die Castings.

1. Wire or rack.
2. Soak in alkaline cleaner - 5 minutes.
3. Cathodically clean in alkaline cleaner - 1 min.
4. Rinse.
5. Acid dip 4 to 5 sec.

1 to 1 Hydrochloric acid

6. Copper strike (cyanide copper No. 1 or No. 2).

Same formula as on Page No. 5

Time - 2 to 15 sec.

7. Rinse.

8. Nickel plate Solutions (Nos. 3, 4, 8, 9, 10, 11, 12, or 14.)

Ni - 3.0 oz./gal.

NaCl - 3.0 oz./gal.

H_3BO_3 - 3.0 oz./gal.

pH - 5.8 to 6.1 colorimetric

Temperature - room

Agitation - none

Tank potential - 1 to 1.5 volts.

Current density - 1 to 5 amp./sq. ft.

Time - 1 to 2 hrs.

9. Rinse and dry.

10. Buff

The copper strike was used in the above sequence and others, not for the protective value afforded by such a very thin film of metal, but for two other reasons. The alkalinity of the solution by virtue of its cyanide content was found to be a good detergent. It corrected slight imperfections in the previous cleaning steps by removing slight grease films, tarnish films, and insoluble soap films induced by immersing work from the alkaline cleaner in a cold, hard water rinse. The above removal was aided by large quantities of hydrogen liberated on the work surface which tended to tear and pry the dirt off mechanically in the same way as in an electric cleaner. The other reason for using a copper strike was to cover soft solder used in assembling parts over which nickel has a well known poor adhesion but over which copper has a much better adhesion.

Operator's Effort

The operator's time consumed in nickel plating work per batch was about twenty minutes exclusive of the time the work was in the tank requiring no attention. The average number of steps taken per batch of work was one hundred ten.

GOLD PLATING 1935

Solutions and Equipment

There were five gold plating solutions in use at this time. Only one of these, a three hundred gallon solution, was used to plate entire horns. This was equipped with a double oscillating work rod which was so constructed that each piece could be run individually on one of six separate ampere hour meters. In this way the exact quantity of gold plated on each piece could be controlled to specifications. The other four solutions were ten gallon crocks, one of which was used for sponging and the others for heating gold solutions to gold plate the inside of horn bells. This was done by corking the throat of the bell, supporting the horn upright with the bell end up, and placing a circular rubber around the rim of the bell to keep solution from dripping out when the bell was filled above the rim. After filling with warm gold solution a cathode contact was made on the horn with a bulldog clip and a platinum anode was inserted. The current flow was regulated on small bells by the depth the anodes were inserted. On large bells a sheostat and ampere hour meter were used together with a rotating anode to give solution agitation. The basis metal in most cases was the same as in silver. (Page No. 2)

Typical Gold Plating Procedure 1935

1. Before gold plating the horns were first silver plated as on
Page No. 3
2. Scratch brush.
3. Soak cleaner - 2 to 3 min.

4. Scrub - (Pumice).

5. Gold plate.

Au - 4-5 dwt./gal.

NaCN (free) - .1 to .5 oz./gal.

Na₂CO₃ - 6 to 8 oz./gal.

Na₃PO₄ - .25 oz./gal.

Temperature - 40° C - 50° C

Tank potential - 1 to 1 1/2 volt.

Time - Depending upon specifications.

Operator's Effort

The average time consumed in gold plating a typical horn such as a cornet or trumpet exclusive of the time the horn was in the solution requiring no attention was fifteen minutes. The average time consumed for a bell only was five minutes. The average number of steps taken in either operation was about thirty.

ZINC PLATING 1935

Solution

Only one zinc plating solution was used to plate zinc finishes. The other solution, the cyanide zinc bath, was used to strike aluminum before attempting to nickel plate. The solution for zinc finishes was an acid zinc solution operated without agitation. The work plated in this solution was principally steel flesh hoops around which drum heads were tacked. These finished hoops did not show and all that was desired was to rust proof the steel.

Typical Zinc Plating Procedure 1935

1. Soak clean - 4 to 5 min.
2. Cathodically clean - 1 min.
3. Rinse.
4. Acid dip - 15 sec.

1-1 HCl

5. Rinse.
6. Copper flash - 1 min.
7. Rinse.
8. Nickel flash - 5 min.
9. Rinse.
10. Zinc plate - 15 min.

Zn - 6-7 oz./gal.

pH - 4.5

The author never learned just why the above plating procedure was used. It appears to be an excellent example of tradition in plating room practice. The zinc solution contained quantities of other materials than those mentioned, particularly aluminum salts, added probably for buffering action.

Operator's Effort

The average time required in zinc plating one batch of work exclusive of the time the work required no attention was twenty minutes. The average number of steps taken was about one hundred thirty.

BRASS PLATING 1935

Solutions

There were two brass solutions operated at this time, one small one of thirty gallons which was used to put a special brass finish on aluminum bugle lyra bars and a four hundred gallon solution which was used for applying ornamental brass finish on steel drum parts. This brass finish called "nobby gold" was subsequently lacquered with clear lacquer. In 1935 the "nobby gold" finish was nearly a thing of the past, and very little brass plating was done. The special finish on the aluminum bars was discontinued shortly thereafter. The two brass solutions were of very nearly the same analysis the small one being slightly lower in free cyanide.

Typical Brass Plating Procedure 1935

1. Soak clean - 5 min.
2. Cathodically clean - 1 min.
3. Rinse
4. Acid dip - 15 sec.

1-1 HCl

5. Copper strike (solution #2) - 5 to 10 sec.
6. Rinse
7. Brass plate

Cu - 4.0 oz./gal.

Zn - 1.5 oz./gal.

NaCN - 3.5 oz./gal.

Na_2CO_3 - 4 to 10 oz./gal.

Temperature - 35°C to 45°C

Time - 1 to 1 1/2 hrs.

Agitation - none

Tank potential - 1 to 1 1/2 volts

Operator's Effort

The average number of steps taken in brass plating one batch of work was one hundred ten. The operator's time consumed was about twenty minutes.

METHODS OF SOLUTION CONTROL 1935

During a few depression years prior to 1935 no chemist was employed by the company. No standard methods of analysis or solution control were used. What little was done was performed by one of the operators who had no technical training and little chemical knowledge. No definite schedules were followed as to frequency of analysis. In many cases an analysis was run only if a solution was giving trouble. In spite of these inadequacies as late as 1935 a good job of plating was being done even though a steady

flow of production due to solution troubles, was not had at all times. The author wishes to pay tribute, with all humility, at this time to the old practical forman plater, today nearly a thing of the past, who armed only with a thermometer and hydrometer, a sense of smell and taste, no knowledge of chemistry, denied at times the use of the essential ammeter, still applied electrodeposits sufficiently well to build a ground work for the present day large industry.

REORGANIZATION AND PROCESS DEVELOPMENT

Solution Control

The author has collected, tested and used many procedures for the analysis of plating solutions. The procedures have come from so many sources that due credit cannot here be given for each specific scheme. Only a few modifications are due to personal ingenuity. The following procedures are given because it is believed that this will be the first time as complete a scheme for as many solutions has been collected and and correlated. These procedures are in places, of questionable accuracy but have all been used in actual solution control and have been found sufficiently accurate for routine control work.

PROCEDURE FOR ACID COPPER SOLUTIONS

I. Copper

A. Solutions

1. $\text{Na}_2\text{S}_2\text{O}_3$.1 N. 25 gr./L.
 - a. Weigh accurately app. .2 gr. Cu.
 - b. Dissolve in 5cc HNO_3 , boil to expell NO_2 .
 - c. Cool, add 25cc H_2O , add NH_4OH to deep blue.
 - d. Add 10cc HAc (Acetic acid) to strongly acid, light blue
 - e. Boil 1-2 minutes, cool, dilute to 150 cc.
 - f. Add 3 gr. KI, 2 cc starch solution.
 - g. Titrate with $\text{Na}_2\text{S}_2\text{O}_3$ to end of blue color.
 - h.
$$\frac{\text{gm Cu}}{\text{cc Na}_2\text{S}_2\text{O}_3} = f = \text{gm Cu/cc Na}_2\text{S}_2\text{O}_3$$

B. Procedure

1. 5cc of plating solution, add 5 cc H_2SO_4 , few drops HNO_3 , heat to SO_3 fumes.
2. Follow above procedure from step (c) on.
3. After addition of HAc add 6 cc 50% KF solution.
4. $(\text{cc Na}_2\text{S}_2\text{O}_3) (\text{factor}) (26.8) = \text{Oz. Cu/gal.}$

II. Determination of copper in plating solutions by Electrolysis

A. Procedure

1. 10 cc sample of acid copper solution, add 3 cc H_2SO_4 , add few drops HNO_3 , evaporate to copious fumes of SO_3 . Treat as below from step three on.
2. 10 cc sample of strong copper cyanide solutions, 25 cc sample of weak solutions. Add 8 cc H_2SO_4 , caution, under hood, few drops HNO_3 , evaporate to copius fumes of SO_3 . If solution does not clear up upon evaporation, add few drops more HNO_3 and continue evaporation.

3. After evaporation, add few drops more HNO_3 dilute to 150 cc.
Cover with split watch glass. Electrolyze over night at $1\frac{1}{2}$ to $3\frac{1}{4}$ amp. or 3 amps. for $3\frac{1}{2}$ hours. Wash down sides of beaker and cover glasses with water. Continue electrolysis until there is no test for copper with fresh H_2S water.
4. 10 cc sample, (wt. deposit) (13.4) = oz. Cu./gal.
5 cc sample, (wt. deposit) (26.8) = oz. Cu./gal.

III. Sulphuric Acid

A. Solutions

1. Methyl orange indicator.
2. Sodium Hydroxide .1 N. 4 gm/L.
 - a. Standardize as given on Page No. 47
 - b. 1 cc .1 N. NaOH = .0049 gm H_2SO_4 .
 - c. gm H_2SO_4 = 1 cc NaOH soln. is factor.

B. Procedure

1. 10 cc plating solution dilute to 100 cc.
2. Add M. O., titrate with NaOH to slight yellow.
3. (ccNaOH) (factor) (13.4) = oz. H_2SO_4 /gal.

PROCEDURE FOR CYANIDE COPPER SOLUTIONS

I. Copper

A. Solutions

1. $\text{Na}_2\text{S}_2\text{O}_3$ same as acid copper. (Page No. 15)

B. Procedure

1. 10cc of cyanide copper solution, dilute to 100cc.
2. Add few cc sat. Na_2S solution.
3. Make slightly acid with .5 N. HCl (avoid excess)
4. Filter, wash thoroughly with hot water.
5. Place paper and ppt. in beaker, add 5 cc HNO_3 .
6. Heat to expel NO_2 , cool.
7. Add NH_4OH to deep blue, make acid with acetic acid, boil 1-2 min.
8. Cool, dilute, add 2-3 gr. KI (excess), titrate with $\text{Na}_2\text{S}_2\text{O}_3$
9. $(\text{cc } \text{Na}_2\text{S}_2\text{O}_3) (\text{factor}) (13.4) = \text{oz. Cu/gal.}$

C. Optional Method

1. 10cc sample of plating solution.
2. Add 10cc H_2SO_4 and 1/2 cc HNO_3 under well ventilated hood.
3. Boil to expel HCN fumes until dense white fumes of SO_3 are copiously evolved.
4. Dilute with 25cc water, add 5cc of bromine water to oxidize arsenic and antimony, boil off excess.
5. Follow above procedure from step (7) on - add 5 cc 50% KF after addition of acetic acid to reduce iron concentration.

II. Free Cyanide

A. Solutions

1. AgNO_3 .01 N. weigh exactly 1.6989 gr. AgNO_3 . Make up to 1L.

B. Procedure

1. 10cc cyanide plating solution dilute to 150cc.
2. Add few drops 2% KI solution, titrate with AgNO_3 to faint cloud.

$$3. (\text{cc AgNO}_3) (.0134) = \text{oz. NaCN/gal.}$$

Note - For copper solutions containing over .5 oz. NaCN/gal.

use $1/10 \text{ AgNO}_3$.

III. Carbonate

A. Solutions

1. HCl about .2 N. 16cc concentrated acid/L. Standardize against standard NaOH or very pure Na_2CO_3 with methyl orange indicator.

$$\frac{\text{Gr. Na}_2\text{CO}_3}{\text{cc HCl}} = \text{gr. Na}_2\text{CO}_3/\text{cc HCl solution (factor)}$$

$$1\text{cc N}/10 \text{ HCl} = .0053 \text{ gr. Na}_2\text{CO}_3 = (\text{factor})$$

B. Procedure

1. 10cc plating solution. Add 1 cc NH_4OH dilute to 50cc.
2. Heat nearly to boiling, add excess BaCl_2 solution.
3. Filter, wash with hot water several times.
4. Put ppt. and paper in beaker, dissolve in standard HCl, titrate excess with NaOH using M. O. (See note).
5. $(\text{cc HCl-HCl equivalent of NaOH}) (\text{factor}) (13.4) = \text{oz. Na}_2\text{CO}_3/\text{gal.}$

Note - In step 4 when dissolving ppt. add 10-15cc standard HCl in excess after M. O. turns red. Let stand for 10-15 min. before back titrating with NaOH.

IV. Rochelle Salts

A. Solutions

1. Oxalic Acid .1 N.
 - a. Weigh out exactly 6.305 gm $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Dilute to 1L.
2. Potassium permanganate.
 - a. Weigh out approximately 3.16 gm. KMnO_4 . Make up to 1L.
 - b. Standardize against oxalic acid solution by the same method as given in the procedure.

$$\frac{(\text{weight of oxalic acid used}) (1000)}{(\text{cc } \text{KMnO}_4 (63))} = \text{Normality of } \text{KMnO}_4$$

B. Procedure

1. 5cc of plating solution, transfer to a 250cc beaker, add 2cc of concentrated hydrochloric acid.
2. Boil 20 min., do not allow the volume to fall below 2cc. This operation should be carried out in a hood to avoid inhaling the hydrocyanide acid which is evolved.
3. The solution should be clear and have the greenish color characteristic of copper chloride.
4. Dilute to 50cc with distilled water, and add about 2 grams of zinc dust or granulated zinc.
5. Shake periodically for about 30 min. to precipitate all the copper.
6. Filter and wash the precipitate thoroughly with distilled water. At this stage, the solution should be colorless and clear.
7. Add 5cc of concentrated sulphuric acid and several crystals of manganous sulphate (less than 1 gram) to the combined filtrate and washings.
8. Heat almost to boiling.
9. When the solution has reached the proper temperature and the crystals have dissolved titrate with tenth normal potassium permanganate solution, with stirring, until an excess of a few cc has been added.
10. The solution at this point shows a brownish turbidity due to the presence of precipitated manganese dioxide.
11. Clear the solution with 5 or 10cc of tenth normal oxalic acid.
12. Heat almost to boiling once more.
13. Add more permanganate solution until the pink color which appears on the addition of each drop persists for at least 1 min.

14. One cc of tenth normal potassium permanganate is equivalent to 0.0047 gram (0.11163 oz.) of Rochelle salt ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$).
15. Calculate the Rochelle salt from the total amount of tenth normal potassium permanganate solution and the amount of tenth normal oxalic acid used. For a 5cc sample, this difference, when multiplied by 0.94, gives the result in grams/liter, or by 0.125 oz./gal.

$$(\text{cc } .1 \text{ N. KMnO}_4 - \text{KMnO}_4 \text{ equiv. of oxalic acid}) (.125) =$$
 oz. Rochelle salts/gal.
16. This method for determining tartrate in cyanide copper plating solution gives reproducible results, and is accurate enough for control purposes.

V. Rochelle Salts (Optional Method)

A. Solutions

1. Sodium hydroxide .1 N. See acid copper Page No. 16
2. Thymolphthalein indicator.

B. Procedure

1. 10cc sample of plating solution in 250cc beaker.
2. Add 10cc concentrated hydrochloric acid, 15cc distilled water, and boil until liquid is greenish in color and free from turbidity.
3. Add 10cc of a 15% solution of sodium sulphide, while stirring, let settle, and filter. Wash with small amounts of distilled water to which has been added a few drops of sodium sulphide and sufficient hydrochloric acid to render wash water faintly acid to litmus paper.
4. Boil the filtrate collected in a 250cc beaker until its volume is reduced approximately 1/3 and add 35% potassium carbonate.
 Note - If precipitate is evident at this stage filter before adding potassium carbonate.

5. Evaporate until volume is reduced by $1/2$ and add glacial acetic acid until solution is just acid to litmus.
6. Continue to evaporate until the volume has reached 20 or 25cc, remove from hot plate, stir in 7cc of glacial acetic acid and let stand 15 min. with occasional stirring.
7. Add 100cc of 95% ethyl alcohol and let stand 15 min. with occasional stirring.
8. Filter and wash four times with 25cc portions of ethyl alcohol or until the washings are neutral to litmus paper.
9. Transfer filter paper to beaker in which ppt. was made, add 150cc distilled water, 5 drops thymolphthalein indicator and heat to boiling.
10. Titrate with .1 N. sodium hydroxide until one drop produces a faint blue color. The number of cc's multiplied by .378 equals oz./gal. Rochelle salts in plating solutions.

Note - Where over 6 oz./gal. of Rochelle salts or over $1/2$ oz./gal. of iron is present, a 5cc sample should be taken instead of 10cc portion.

GREENSPAN FRIGHT COPPER

I. Copper

A. Solutions

1. KI soln. 30%
2. $\text{Na}_2\text{S}_2\text{O}_3$.1 N. Make up and standardize as on Page No. 15

B. Procedure

1. 10cc sample of soln. in 300cc Kjeldahl flask.
2. Add .5 gm HgSO_4
3. Boil to light green color or colorless
4. Add 10cc H_2SO_4 (conc.)
5. Heat cautiously until foaming ceases, and then hotter to fumes of SO_3
6. Cool, dilute to 125cc
7. Add NH_4OH (conc.) to deep blue color.
8. Add 10cc HAc (glacial) to strongly acid
9. Add 10cc KI soln. (30%)
10. Add few drops starch solution and titrate with .1 N. $\text{Na}_2\text{S}_2\text{O}_3$ to end of blue color
11. (cc .1 N. $\text{Na}_2\text{S}_2\text{O}_3$) (.68) = oz. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ /gal.

II. Total Sulphate

A. Solutions

1. BaCl_2 10%

B. Procedure

1. 5cc sample, dilute to 300cc
2. Neutralize with HCl , add 5cc HCl excess (conc.)
3. Heat to boiling, add dropwise while stirring 10cc BaCl_2 soln. 10%
4. Keep hot several hours or allow to stand overnight
5. Filter through gooch crucible
6. Wash, dry, ignite, and weigh

7. (wt. BaSO_4 ppt.) (37.7) = total sulphate as oz. $(\text{NH}_4)_2\text{SO}_4/\text{gal.}$

III. Ammonium Sulphate (Combined ammonia)

A. Procedure

1. (Value for copper sulphate) (.53) = Ammonium sulphate equivalent
2. (Total sulphate II B 7) - (Amm. Sulp. Equiv. III A 1) =
Ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$

IV. Total Ammonia (As ammonium sulphate

A. Procedure

1. 10cc sample, dilute to 150cc in 300cc flask
2. Add 2 gm NaOH pellets and several pieces of broken porcelain
3. Connect to a condenser through a Hempel fractionating column
10" to 12" long as quickly as possible.
4. Distill slowly until volume is reduced to about 1/3
5. Collect distillate in a 600cc beaker containing 50cc .1 N. HCl
6. Vapor in distillation should not be over 100°C to avoid loss
of amine
7. Flush condenser into beaker with distilled water
8. Add 1cc bromocresol purple indicator .04% or 3 or 4 drops of
methyl red.
9. Titrate with .1 N. NaOH to color change
10. (cc .1 N. - cc .1 N. HCl) (.176) = total ammonium oz./gal. as
ammonium sulphate

V. Free Ammonia

1. (Total ammonia - Combined ammonia) (.86) = oz. 26% aqua ammonie/gal.

VI. Total Nitrogen

A. Procedure

1. 5cc sample, place in Kjeldahl flask
2. Dilute to 25cc, add 5-1 H_2SC_4 to disappearance of blue color, then

add 10cc conc. H_2SO_4

3. Add .2 gm $HgSO_4$ and 5 gm anhydrous Na_2SO_4
4. Heat to fumes of SO_3 and continue with strong flame for 1 hr.
5. Put several small pieces broken porcelain or one piece granulated zinc in the flask and enough 50% NaOH to make mixture alkaline
6. Connect quickly to condenser and adapter dipping into 600cc beaker containing 250cc water and 50cc .1 N. HCl
7. Distill until volume is reduced to 100cc
8. Flush out condenser into beaker with distilled water
9. Add 1cc .04% bromocresol purple indicator or 3 or 4 drops of methyl red indicator, titrate with .1 N. NaOH solution until indicator changes color
10. (cc .1 N. HCl - cc .1 N. NaOH) (.88) = total nitrogen as oz./gal. ammonium sulphate

VII. Amine

1. (oz./gal. total nitrogen - oz./gal. total ammonia) (.0665) - oz. diethylenetriamine/gal.

PROCEDURE FOR EPASS AND BRONZE SOLUTIONS

I. Copper

A. Solutions

1. Same as cyanide copper. Page No. 17

B. Procedure

1. 10cc sample, add 10cc H_2SO_4 and $1/2$ cc HNO_3 , boil to SO_3 fumes.
(Under hood)
2. Boil, cool, add NH_4OH to deep blue
3. Add HAc to strongly acid, boil 1-2 minutes
4. Cool, dilute to 150cc, add 3 gr. KI
5. Titrate with $Na_2S_2O_3$ and starch
6. $(ccNa_2S_2O_3) (factor) (13.4) = oz. Cu/gal.$

II. Zinc

A. Solutions

1. Same as for zinc solutions Page No. 27

B. Procedure

1. 10cc sample, dilute to 50cc, heat to $60^\circ C$
2. Heat gently, add excess sat. Na_2S solution, stir, heat few minutes, filter, wash with warm water. The zinc ppt. should be white at this point, if not, add NaCN to whiten it.
3. Return the ppt. and paper to beaker, add 20cc 1-1 HCl, boil 10 min., cool
4. Just neutralize with NH_4OH , make just acid with 1-1 HCl, add 3cc concentrated HCl excess
5. Dilute to 150cc, heat nearly to boiling, add 1cc $FeSO_4$ solution
6. Titrate hot with $K_4Fe(CN)_6$ from blue to green
7. $(Factor) (cc K_4Fe(CN)_6) (13.4) = oz. Zn/gal.$

III. Free cyanide

A. Solutions

1. $\text{Cu}(\text{NO}_3)_2$

- a. 24.16 gr. $\text{Cu}(\text{NO}_3)_2$ in 1 L. water
- b. Weigh accurately app. .5 gr. KCN (pure)
- c. Dissolve in 100cc water
- d. Add 10cc NH_4OH , titrate with $\text{Cu}(\text{NO}_3)_2$ solution until blue color persists 1 min.
- e.
$$\frac{(\text{gr. KCN}) (.753)}{(\text{cc Cu}(\text{NO}_3)_2)} = \text{Gr. NaCN/cc solution (factor)}$$

B. Procedure

1. 10cc sample of plating solution
2. Dilute to 50cc, add 10cc NH_4OH
3. Titrate with $\text{Cu}(\text{NO}_3)_2$ until blue color persists 1 min.
4. $(\text{cc Cu}(\text{NO}_3)_2) (\text{factor}) (13.4) = \text{oz. NaCN/gal.}$

IV. Carbonate

A. Same as Cyanide Copper, Page No. 17

V. Notes

1. It is impossible to get a good end point if there is not sufficient zinc present to use several cc of $\text{K}_4\text{Fe}(\text{CN})_6$ solution. In this case add a known amount of zinc as ZnCl_2 to the solution before titrating and subtract that amount from the answer.

PROCEDURE FOR ZINC SOLUTIONS

I. Zinc

A. Solutions

1. $K_4Fe(CN)_6$

- a. 44 gr. $K_4Fe(CN)_6$) 1 L. water
- b. .3 gr. $K_3Fe(CN)_6$
- c. Age six weeks
- d. Standardize against .2 gr. Zn dissolved in 20cc 1-1 HCl as given in procedure from step B 3 on, or standard zinc solution
- e. $\frac{(\text{gm Zn})}{(\text{cc } K_4Fe(CN)_6)} = \text{gm Zn} / \text{1cc } K_4Fe(CN)_6 \text{ soln. (factor)}$

2. $FeSO_4$

- a. 3 gr. $FeSO_4$
- b. 10cc HCl
- c. 1 L water

B. Procedure

1. 10cc sample of cyanide zinc solution, 5cc sample of acid zinc solution
2. To the cyanide solution add 10cc HCl (under hood), boil 10 min., cool
3. To either solution dilute to 100cc add NH_4OH to just alkaline then 1-1 HCl to just acid
4. Add 3cc concentrated HCl excess
5. Dilute to 200cc, heat almost boiling, add 1cc $FeSO_4$ solution
6. Titrate with $K_4Fe(CN)_6$ solution to color change from blue to green
7. $(\text{cc } K_4Fe(CN)_6) (\text{factor}) (13.4) = \text{oz. Zn/gal. (cyanide)}$
 $(\text{cc } K_4Fe(CN)_6) (\text{factor}) (26.8) = \text{oz. Zn/gal. (acid)}$
8. See note on zinc in brass solutions. Page No. 26

II. Total Cyanide

A. Solutions

1. 10% KI solution
2. .1 N. AgNO_3 solution
3. 10% NaOH solution

B. Procedure

1. 5cc sample of plating solution
2. Add about 5cc of 10% NaOH and few drops of 10% KI solution
3. Titrate with .1 N. AgNO_3 to faint, permanent, yellow turbidity.
Stir vigorously during titration
4. Add a little more NaOH, if the turbidity disappears, continue titration until a permanent turbidity is produced
5. (cc AgNO_3) (.262) \pm oz. NaCN/gal.

C. Notes

1. The total cyanide is determined because in the presence of NaOH, not even a good approximation of free cyanide can be obtained.
2. Titration is not affected by aluminum salts or tartrates, but the result is high in the presence of ammonium hydroxide.
3. Sodium zincate (Na_2ZnO_2) and the double zinc sodium cyanide ($\text{Na}_2\text{Zn}(\text{CN})_4$) are both present in the zinc plating solution so that it is difficult to calculate the uncombined sodium cyanide with any degree of accuracy

III. Total Alkali

A. Solutions

1. Potassium ferrocyanide as used for zinc titration.
2. Silver nitrate as used for total cyanide titration
3. .1 N. hydrochloric acid

B. Procedure

1. 5 cc of plating solution

2. Dilute to 150cc, add slightly more than enough K_4FeCN_6 to ppt. the zinc (slightly more than 1/2 that required in I).
3. Add slightly more $AgNO_3$ than amount required in II.
4. Add few drops of phenolphthalein, titrate with N/10 HCl until pink disappears for a few minutes.
5. By this method, the total alkaline hydroxide plus one half the carbonate is determined.
6. 1cc .1 N. HCl = .004 gr. NaOH
 (.004) (26.8) (cc .1 N. HCl) = oz. NaOH/gal. (Uncorrected)
7. (oz. Na_2CO_3 /gal.) (.377) = oz. NaOH/gal. (Correction)
8. (oz. NaOH/gal. step 6) - (oz. NaOH/gal. step 7) = oz. NaOH/gal. (Corrected)

C. Notes

1. Correction is not necessary unless Na_2CO_3 or $ZnCO_3$ has been added or unless the solution is old
2. In the above titration, the carbonates have been changed to bicarbonates.
3. The calculation (step 7) allows for only one half the carbonate content as found in IV

IV. Carbonate

- A. Same as for cyanide copper solutions. Page No. 18.

V. Acidity

- A. The acidity of acid zinc solutions may be titrated in the absence of weak acids, but it is better to measure the pH either by electrometric or colorimetric methods.

ANALYSIS OF DU PONT ZINC

- I. Zinc (Same as for cyanide zinc solutions Page No. 27)
- II. Total Cyanide Determination (Same as for cyanide zinc solutions Page No. 28)
- III. Caustic Soda Determination

A. Solutions

1. .1 N. H_2SO_4 50 gm/L.
 - a. Standardize against standard NaOH solution
2. Sulpho-orange indicator

B. Procedure

1. Pipette a 10cc sample into a 250ml Erlenmeyer flask
2. Add 10cc water and 1 gram sodium cyanide and 5 drops sulpho-orange indicator
3. Titrate with 1 N. Sulphuric acid to a color change from red-orange to yellow green or lemon color as end point.

CAUTION

1. This method involves the titration of acid into a cyanide solution. Avoid adding excess acid. At the proper end-point the solution will still be alkaline.
2. Use granular sodium cyanide rather than a solution of NaCN because NaCN slowly decomposes into ammonia and in an aqueous solution which would make results high.
3. The titration should be made in good light so the color changes can be accurately noted.
4. Sodium cyanide must be added so that all of the zinc which is present is in the form of $\text{Na}_2\text{Zn}(\text{CN})_4$ (Sodium zinc cyanide) and not as Na_2ZnO_2 (sodium zincate) since the zincate is not titrated. Results will be low if insufficient NaCN is added.

5. Calculations

$$(\text{cc NH}_2\text{SO}_4) (.536) = \text{oz. NaOH/gal.}$$

IV. Carbonate Determination (Same as for cyanide copper solutions Page No. 18)

PROCEDURE FOR NICKEL SOLUTIONS

I. Nickel

A. Solutions

1. AgNO_3 .1 N.

a. Same as free cyanide for Cu Page No. 17

2. KCN .2 N app.

a. Weigh accurately about 10 gr. KCN, make up to 1L.

b. Dissolve about .1 gr. pure nickel weighed accurately in
5cc HNO_3 c. Heat to expell NO_2 , dilute to 25cc (H_2O), add 10cc NH_4OH
dilute to 150cc

d. Add few drops KI solution (10%)

e. Add .1 N AgNO_3 until permanent cloud

f. Titrate with KCN until cloud disappears

g. Bring back with AgNO_3 , finish titration with KCN to clear
solutionh. Compare solutions (1cc $\text{AgNO}_3 = X$ cc KCN) using KI indicator

$$\frac{(\text{wt. Sample})}{(\text{cc KCN}) - (\text{AgNO}_3 \text{ equiv. of KCN})} = \text{wt. Ni/cc KCN (factor)}$$

i. 1cc .1 N KCN = .001467 gr. Ni

B. Procedure

1. 5cc sample of plating solution, dilute to 50cc (H_2O)2. Add few drops of tartaric acid, add 5cc NH_4OH , dilute to 200cc
(H_2O)

3. Add few drops KI and titrate as above

4. (cc KCN - KCN equiv. of AgNO_3) (factor) (26.8) = oz. Ni/gal.

Factor = .001467 XN

II. Optional Method for Nickel

A. Solutions

1. Ammonium hydroxide C. P.
2. Dimethylglyoxime 1% alcoholic solution.

B. Procedure

1. Take 10cc sample of nickel solution (25cc if nickel content is less than 2 oz./gal.), add 5cc H_2SO_4 , evaporate to SO_3 fumes, cool, neutralize with NH_4OH
2. Add 2 gr. of $(\text{NH}_4)_2\text{SO}_4$ and 20cc of NH_4OH , dilute to 100cc
3. Electrolyze at .2-.25 amp., if not agitated, for at least 4 hrs. using platinum electrodes
4. When the blue color of the solution has disappeared and a drop of the solution produces no pink color with dimethylglyoxime, the electrolysis is complete.
5. Wash, dry, and weigh the cathode. The increase in weight is the nickel in the original sample.
6. (wt. Ni) (13.4) = Ni oz./gal.

III. Chloride

A. Solutions

1. AgNO_3 .1 N 16.989 gr./L
2. K_2CrO_4 10% solution

B. Procedure

1. Take 5cc sample of nickel solution, dilute to 100cc
2. Add 1cc K_2CrO_4 solution, titrate with AgNO_3 (.1 N) to light buff color
3. (cc AgNO_3) (.156) = oz. Na/Cl/gal.
 (cc AgNO_3) (.1434) = oz. NH_4Cl /gal.
 (cc AgNO_3) (.1735) = oz. NiCl_2 /gal.
 (cc AgNO_3) (.316) = oz. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ /gal.

IV. Sulphate

A. Solutions

1. BaCl_2 10%

B. Procedure

1. 5cc sample of nickel solution dilute to 200cc
2. Add 10cc C. P. HCl , 10cc alcohol, boil
3. Add excess 10% BaCl_2 solution (20cc for 30 oz. $\text{Na}_2\text{SO}_4/\text{gal.}$) slowly, stir, keep hot for 2 hrs.
4. Filter, wash free from chlorides, ignite in gooch
5. (wt. BaSO_4) (16.26) = oz. $\text{Na}_2\text{SO}_4/\text{gal.}$)
(wt. BaSO_4) (13.82) = oz. $\text{MgSO}_4/\text{gal.}$)) Total sulphate
6. (wt. Ni oz./gal.) (2.42) = oz. $\text{Na}_2\text{SO}_4/\text{gal.}$ (Combined)
7. (wt. total Na_2SO_4) - (wt. combined Na_2SO_4) = oz./gal. Na_2SO_4

V. Magnesium Sulphate

A. Solutions

1. Dimethylglyoxime 1% alcoholic solution
2. Sodium amonium phosphate 10% solution

B. Procedure

1. 10cc of nickel solution
2. Add 50cc NH_4OH
3. Electrolyze at 1.5 amperes until there is no trace of Ni with dimethylglyoxime
4. Add 15cc 10% sodium ammonium phosphate
5. Stir for 30 minutes; or let stand for 3 hrs.
6. Filter through gooch and blast
7. Weigh as $\text{Mg}_2\text{P}_2\text{O}_7$ and calculate to MgSO_4
(wt. ppt.) (2.1212) (13.4) = oz. $\text{MgSO}_4/\text{gal.}$

VI. Boric Acid

A. Solutions

1. NaOH .1 N 4 gm./L. Standardize as on Page No. 47
2. Bromcresol purple .04 gm./50cc alcohol

B. Procedure

1. 5cc sample plating solution
2. Add mannite to make thin paste
3. Add 10 drops bromcresol purple indicator
4. Titrate with NaOH solution to purple end point
5. (cc .1 N NaOH) (.166) = oz. H_3PO_3 /gal.

VII. Boric Acid (Optional Method)

A. Solutions

1. NaOH .1 N 4 gm./L. Standardize as on Page No. 47
2. Indicator-Heat 100cc glycerine to 100°-120° F, add .02 gm. methyl red, dissolve. Solution when made up should be a bright lusterous red.

B. Procedure

1. 25cc sample plating solution
2. Add 25cc neutral glycerine
3. Titrate with standard NaOH until a drop from end of stirring rod, produces an orange color when mixed with a drop of the indicator on the spot plate.
4. If the titration is carried too far the color is yellow instead of orange.
5. 30.1cc .1 N NaOH = 1 oz./gal. H_3BO_3 (25cc sample)
6. $\frac{(\text{cc } .1 \text{ N NaOH used})}{(30.1)} = \text{oz. } H_3BO_3/\text{gal.}$

VIII. Zinc as an Impurity

A. Solutions

1. HCl (1-4)
2. H_2SO_4 (1-1)
3. H_2SO_4 (1-4)
4. NaOH (20%)

5. $K_4Fe(CN)_6$ soln. as in zinc analysis Page No. 27

B. Procedure

1. Take 100cc sample of nickel solution in 600cc beaker add 300 cc cold water.
2. Pass a rapid stream of H_2S gas through the solution for 40 min., filter, wash well with cold water.
3. Without puchering the paper dissolve the ZnS of the ppt. with cold HCl (1-4) into original beaker, add 15cc H_2SO_4 (1-1), evaporate to dryness.
4. Dissolve salts in beaker with 100cc water neutralize with $NaOH$ (20%), acidify with H_2SO_4 (1-4) and add 3cc H_2SO_4 (5%) in excess.
5. Dilute to 200cc with cold water and reppt. with H_2S for 40 min.
6. Wash and dissolve ppt. as before, neutralize with NH_4OH make just acid with HCl and add 2cc HCl (concentrated) in excess.
7. Titrate solution with $K_4Fe(CN)_6$ exactly as done in analysis of zinc solution from step (I-B-5) on Page No. 27
8. $(cc\ K_4Fe(CN)_6) (factor) (1.34) = oz./gal.$

METHODS OF ANALYSIS FOR FRIGHT NICKEL SOLUTION

I. Nickel

Same as white nickel, Page No. 32

II. Cobalt

A. Solutions

1. Sulphuric acid (1-5)
2. Sodium Hydroxide (conc.)
3. Starch solution
4. Sodium thiosulphate .1 N. Standardize against pure copper given under copper solutions. $1\text{cc N/10 Na}_2\text{S}_2\text{O}_3 = .00636\text{ gm. Cu}$ Page No.

B. Procedure

1. 10cc sample of plating solution, dilute to 100cc
2. Acidify with H_2SO_4 (1-5) (litmus) and add 5cc excess
3. Add 2 gm. dry sodium perborate
4. After perborate has dissolved add sufficient NaOH solution to make solution strongly alkaline (litmus).
5. Boil for 10-15 min. to decompose excess perborate.
6. Cool to room temperature and add about 1 gm. KI
7. After solution of KI acidify with H_2SO_4 (1-5) (litmus)
8. Allow to stand and stir until precipitate is completely dissolved. If the subsequent titration is attempted before the slow reaction liberating iodine is complete, the results will be low.
9. After ppt. is all dissolved titrate with $\text{Na}_2\text{S}_2\text{O}_3$ solution and starch indicator.
10. $(\text{cc } .1\text{ N Na}_2\text{S}_2\text{O}_3) (.375) = \text{oz. CoSO}_4 \cdot 7\text{H}_2\text{O/gal.}$

III. Chloride

Same as white nickel Page No. 33

IV. Boric Acid

A. Solutions

1. From cresol purple (.04%) alcoholic
2. Sodium hydroxide .1 N

B. Procedure

1. 5cc sample, add 25cc glycerine and 25cc water
2. Add 1cc (.04%) brom cresol purple
3. Titrate with standard NaOH solution to dark green then purple
4. (cc .1 N NaOH) (.166) = H_3PO_3 /gal.

V. Formaldehyde

A. Solutions

1. Sodium bisulphite (1%)
2. Iodine solution .1 N. Dissolve 20-25 gm. KI and 13 gm. I_2 in 1 L. water. Standardize against standard $Na_2S_2O_3$.
3. Normality I_2 soln. =
$$\frac{(cc Na_2S_2O_3) (Normality Na_2S_2O_3)}{2(cc I_2 soln.)}$$

B. Procedure

1. 10cc sample plating solution dilute to 50cc
2. Add exactly 10cc of the bisulphite solution and allow mixture to stand 15 minutes. Tightly stoppered in iodine flask.
3. While above is standing pipette another exact 10cc sample of the bisulphite solution to another flask.
4. Dilute to 50cc and titrate with standard iodine solution (.1 N) and starch indicator to first blue color
5. Titrate the mixture (step 2) in exactly the same way
6. (cc I_2 .1 N step 4) - (cc I_2 .1 N step 5) = cc I_2 .1 N equivalent to HCHO in sample
7. (cc .1 N I_2) (.05) = oz./gal. 40% HCHO in solution

VI. Sodium Formate

A. Solutions

1. Sodium formate std. exactly 27.5 gm/L
2. Sulphuric acid (std.) (N) 4 gm./L Standardize as on Page No.

B. Procedure

1. 5cc sample of nickel solution dilute to exactly 100cc
2. Add with pipette exactly 5cc normal H_2SO_4 and exactly 5cc standard sodium formate solution
3. The electrometric pH should now be 2.7 (-.294 mv. 25°C quinhydrone)
4. If the pH of the mixture is below 2.7 titrate with sodium formate to this pH
5. The number of cc of standard sodium formate used is the number of oz./gal. required to bring the solution up to the proper analysis of 5 oz./gal.

VII. Ammonium Sulphate

A. Solution

1. Sulphuric acid (1-5)
2. Sulphuric acid .1 N standardize as on Page No. 18
3. Sodium hydroxide .1 N standardize as on Page No. 47
4. Brom cresol purple (.04%)

B. Procedure

1. 10cc plating solution dilute to 150cc in a 300cc Kjeldahl flask
2. Acidify with dilute H_2SO_4 , add 5cc excess
3. Add 2 gm. dry sodium perborate, dissolve
4. Put in flask several small pieces broken porcelain, add 3 gm. NaOH pellets
5. Place the distillation trap in position quickly and connect with adapter which dips into a 600cc beaker containing 300cc

water and 25cc .1 N sulphuric acid. The end of the adaptor must dip below the surface of the liquid to prevent loss of ammonia.

6. Distill until the volume of solution in the Kjeldahl flask is reduced to approximately 100cc
7. When distillation is over, remove trap from condenser and flush out with distilled water. All washings go into beaker
8. Add 1cc of brom cresol purple indicator, and titrate with .1 N NaOH until indicator changes color.
9. $(\text{cc } .1 \text{ N H}_2\text{SO}_4 \text{ used}) - (\text{cc } .1 \text{ N NaOH used}) = \text{cc } .1 \text{ N H}_2\text{SO}_4 \text{ equivalent to NH}_3$
10. $(.088) (\text{cc } .1 \text{ N H}_2\text{SO}_4 \text{ equivalent to NH}_3) = \text{oz. (NH}_4)_2 \text{SO}_4 / \text{gal.}$

PROCEDURE FOR SILVER SOLUTIONS

I. Silver

A. Solutions

1. NH_4CNS $1/3$ N app.
 - a. Weigh 22 gr. (app.) NH_4CNS , make up to 1 L.
 - b. Weigh (accurately) about .5 gr. pure silver
 - c. Dissolve in 5cc CP HNO_3 and a few drops of water
 - d. Dilute to 150cc add a few drops of 10% $\text{Fe}(\text{NO}_3)_3$
 - e. Titrate with NH_4CNS to a faint red color
 - f.
$$\frac{\text{Wt. sample}}{(\text{cc } \text{NH}_4\text{CNS used})} = \text{gr. Ag/cc } \text{NH}_4\text{CNS solution (factor)}$$

B. Analysis

1. 10cc of silver plating solution, dilute to 50cc
2. Heat gently, add excess (10cc) of $(\text{NH}_4)_2\text{S}$, continue heating for few minutes. Stir several times, do not boil
3. Filter and wash with hot water
4. Place ppt. and paper in beaker, dissolve in HNO_3 (7cc), boil to expell NO_2
5. Dilute to 150cc (H_2O), add $\text{Fe}(\text{NO}_3)_3$, titrate as above
6. $(\text{cc } \text{NH}_4\text{CNS}) (\text{factor}) (12.2) = \text{oz. T. Ag/gal.}$

II. Free Cyanide

A. Solutions

1. AgNO_3 - .1 N exactly 17 gm./L.

B. Procedure

1. 5cc plating solution, dilute to 150cc
2. Add few drops KI solution
3. Titrate with AgNO_3 to faint cloud
4. $(\text{cc } \text{AgNO}_3) (.2614) = \text{oz. NaCN/gal.}$

III. Carbonate

A. Solutions

1. N/5 HCl)
2. N/5 NaOH) Standardize as in acid copper Page No. 16

B. Analysis

1. 5cc sample, dilute to 100cc with boiling water
2. Add excess (20cc) Barium Chloride solution (10%)
3. Filter ppt., wash thoroughly with hot water
4. Dissolve ppt. in excess acid, let stand 10 min.
5. Titrate excess acid with standard alkali
6. (cc HCl used) - (HCl equiv. of NaOH) = cc HCl used
 (cc HCl) (factor) (26.8) = oz. Na_2CO_3 /gal.
 1cc N/10 HCl = .00531 gr. Na_2CO_3

IV. Chloride

A. Solutions

1. 1-1 Nitric acid

B. Analysis

1. Boil 5cc solution with 25cc 1-1 HNO_3 under hood until no further decomposition occurs, cool, dilute to 100cc. Add AgNO_3 until chlorides are completely precipitated.
2. Filter on weighed gooch, wash. Dry at 110-115°C to constant wt.
3. Wt. AgCl X 10.76 = oz. NaCl/gal.

DETERMINATION OF MERCURY IN BLUE DIP

I. Mercury

A. Solutions

1. NH_4CNS as used for silver determination, Page No. 41
diluted exactly 1-10 (.02N)
2. Ferric nitrate indicator, acidified with boiled HNO_3

B. Procedure

1. 25cc of plating solution
2. Add 10cc H_2SO_4 (caution) to destroy cyanide in solution
3. Add .5 gr. KMnO_4 , heat to fumes, add oxalic acid until solution becomes colorless
4. Heat to fumes again, cool, dilute to 100cc
5. Titrate with NH_4CNS (1-10) and 10cc Ferric nitrate indicator to first red cloud after white cloud and needle crystals.
6. (cc diluted solution) (factor for Ag of undiluted reagent)
(.499) = oz. Hg/gal.

II. Free Cyanide

- A. Same as silver Page No. 41 Factor .1307 (10cc sample)

PROCEDURE FOR GOLD SOLUTIONS

I. Gold

A. Procedure

1. Take 50cc sample of plating solution, heat, add 3 gr. NaCN, dissolve, heat gently
2. Add excess pure zinc dust to ppt. gold, stir well, let stand for five hours or over night
3. Wash thoroughly to remove cyanide (decant)
4. Add excess HCl to remove zinc, decant
5. Wash until free from chlorides
6. Add concentrated HNO_3 to remove other impurities
7. Wash, filter, wash
8. Ignite paper in weighed crucible, weigh
9. (wt.) (48.8) = dwt. Au/gal.

II. Free Cyanide

A. Procedure

1. Take 10cc sample, dilute to 100cc
2. Add few drops of KI, titrate with 100N AgNO_3
3. (cc AgNO_3) (.01307) = oz. NaCN/gal.

III. Gold (Optional)

A. Solutions

1. $\text{Na}_2\text{S}_2\text{O}_3$.01 N
 - a. 2.5 gr./L
 - b. Weigh app. .05 gm. Au, dissolve in aqua regia (10cc)
 - c. Carefully exaporate to a syrup over a water bath
 - d. Add 150cc water, 5 gr. KI, and starch solution
 - e. Titrate with .01 N $\text{Na}_2\text{S}_2\text{O}_3$ to disappearance of blue color
 - f.
$$\frac{(\text{wt. Au})}{(\text{cc } \text{Na}_2\text{S}_2\text{O}_3)} = \text{factor}$$

B. Procedure

1. 10cc plating solution
2. Add 15cc HCl (under hood), evaporate to a syrup over a water bath
3. Add 150cc water, 5 gr. KI, and starch solution
4. Titrate with N/100 $\text{Na}_2\text{S}_2\text{O}_3$ to disappearance of all color
5. $(\text{cc } \text{Na}_2\text{S}_2\text{O}_3) (\text{factor}) (244) = \text{dwt./gal.}$

Note - A dilute iodine solution N/100 may be used to back titrate if necessary. The end point of the $\text{Na}_2\text{S}_2\text{O}_3$ titration is not sharp, therefore it is desirable to dryness or the gold will be precipitated.

PROCEDURE OF DETERMINING ACIDITY OF DEGREASERS

I. Acid

A. Solutions

1. N/10 HCl Standardize as on Page No. 47
2. Methyl Orange indicator

B. Procedure

1. Filter solvent through gooch if very dirty. Pipette 100cc sample into separatory funnel. Add 100cc water. Add few drops methyl orange
2. Shake vigorously several minutes
3. Draw off water portion, add methyl orange and titrate with N/10 HCl
4. If the solution turns red when methyl orange is added, this denotes acidity and an unhealthy degreaser condition
5. The titration for a healthy degreaser condition should be run between $1\frac{1}{2}$ cc and $2\frac{1}{2}$ cc N/10 HCl

PROCEDURE FOR ALKALINE CLEANERS AND ACID DIPS

I. Total Alkali

A. Solutions

1. NaOH .2 N

- a. 9 gr. NaOH/L water
- b. Weigh accurately app. .5 gr. oxalic acid, dissolve in 100cc water
- c. Add few drops P. P. solution, titrate with NaOH solution to light red.
- d.
$$\frac{(\text{wt. of oxalic acid})}{(\text{vol. used})(.063)} = \text{N of NaOH}$$

2. HCl .2 N

- a. 17cc concentrated/L water
- b. Compare against NaOH solution using P. P. or M. O. indicator
- c.
$$\frac{(\text{N of NaOH})(\text{cc used})}{(\text{cc HCl used})} = \text{N HCl}$$

B. Procedure

1. 10cc of cleaning solution
2. Add few drops M. O., dilute to 100cc
3. Titrate with HCl solution to end point
4. Back titrate with NaOH if necessary
5. 1cc 1/10 N HCl = .004 gr. NaOH
6. (gr. NaOH) (13.4) = oz./gal. NaOH
7. (oz./gal. NaOH) (1.325) = oz./gal. Na₂CO₃

II. Acid

A. Solutions - same as I

B. Procedure

1. 5cc acid dip solution
2. Add few drops of M. O., dilute to 100cc
3. Titrate with NaOH solution to color change. Back titrate with

HCl if necessary.

4. 1cc .1 N NaOH = .00490 gr. H_2SO_4

(gr. H_2SO_4) (1.285) = gr. HNO_3

(gr. H_2SO_4) (.745) = gr. HCl

FACTORS

1. (N) (cc) = (N) (cc)
2. (N) (gr. eq. wt.) = gr./L
3. (gr. NaCH) (1.325) = gr. Na_2CO_3
4. (gr. NaOH) (2.100) = gr. NaHCO_3
5. (gr. NaHCO_3) (.476) = NaOH
6. (gr. NaOH) (1.225) = gr. H_2SO_4
7. (gr. NaOH) (1.575) = gr. HNO_3
8. (gr. NaOH) (.911) = gr. HCl
9. (gr. H_2SO_4) (1.286) = gr. HNO_3
10. (gr. H_2SO_4) (.745) = gr. HCl
11.
$$\frac{(\text{gr. Pure St.})}{(\text{Vol.}) (\text{Mill. Eq. Wt. of St.})} = \text{Normality}$$
12. (gr./L) (.134) = oz./gal.
13. (gr./L) (.122) = oz. T./gal.
14. (gr./L) (2.44) = dwt./gal.
15.
$$\frac{(\text{Sp. Gr. of Metal})}{12} = \text{oz./sq. ft. for .001"}$$
16. 1 oz. av. = 28.35 gr.
17. 1 oz. T. = 31.10 gr.
18. 1 qt. = .946 L
19. (gr. AgNO_3) (.635) = gr. Ag
20. (gr. KCN) (.753) = gr. NaCN
21. (1cc N/10 $\text{Na}_2\text{S}_2\text{O}_3$) = .00636 gm. Co
22. 1cc N/10 KMnO_4 = .005584 gm. Fe
23. 1cc N/10 KMnO_4 = .006003 gm. Sb
24. ($\text{Mg}_2\text{P}_2\text{O}_7$) (.2184) = Mg
25. ($\text{Mg}_2\text{P}_2\text{O}_7$) (2.12138) = $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
26. (cc NaOH N/10) (.0049) = gr. H_2SO_4
27. 16cc H_2SO_4 = 1 oz. wt.

ANALYTICAL SCHEDULES

The following is a condensed schedule of routine analytical solution control work. The intervals between analyses have been established by individual solution performance and use. The chart is given only to show how the schedule was set up in this case, not to be indicative of the frequency analyses might be necessary in other shops, even those using the same solutions. The chart is set up for a period of one month.

	Monday	Tuesday	Wednesday
First Week	All alkaline cleaners for P&H alkalinity, surface tension and Feaume Acid dips Caustic dips Mercury solutions Boiler water	Electroforming solutions All copper solutions All degreasers for stabilization Check all heating coils for leaks Cold nickel solutions for pH only	Boiler water
Second Week	Same as first week	Electroforming solutions Copper solutions for cyanide All nickel solutions except bright nickel All degreasers for stabilization Check all heating coils for leaks	Boiler water
Third Week	Same as first week	Electroforming solutions Copper solutions for cyanide Bright nickel Bright copper All degreasers for stabilization Check all heating coils for leaks	Boiler water
Fourth Week	Same as first week	Electroforming solutions Copper solutions for cyanide Degreasers for Prass solution Zinc solution Check all heating coils for leaks	Boiler water

	Thursday	Friday	Miscellaneous
First Week	Electroforming solutions	Silver solutions Boiler water	Every day pH on Barrel nickel Bright nickel Conveyer nickel strike
			Three months
Second Week	Electroforming solutions	Silver solutions Silver recovery solutions Boiler water	Carbonates on all cyanide plating solutions Rochelle salts on all cyanide copper solutions
			Keep following solutions prepared at all times
Third Week	Electroforming solutions	Silver solutions Boiler water	Cadmium brightener for barrel nickel Carbon disulphide brightener for sil- ver Mercury solution
Fourth Week	Electroforming solutions	Silver solutions Boiler water	Once monthly at end of month gold solutions

BRIGHT NICKEL

Investigation of Processes

In 1937 bright nickel seemed to be well enough established as a reliable commercial process to warrant thorough investigation as to its possibilities in band instrument work. There were at that time two basic processes for producing heavy bright deposits (19) of nickel, that covered by the Schlotter patent, and that covered by the Weisberg-Stoddard patent. (60) (61) (62)

The Schlotter solution was a modified hot Watts solution wherein the brightening agents were furnished in a concentrate form and no good scheme of analysis had been worked out for them at that time. The plater operating such a solution had no knowledge of the ingredients of the brighteners and in case of trouble often had to depend on service men to find and correct the difficulty. The plate was truly bright although inclined to be brittle and difficultly buffed when buffing was necessary.

The Wiesberg-Stoddard solution was a process in which the codeposition of nickel and cobalt (71) was employed. All of the solution ingredients were known and rapid analytical schemes were worked out for the plater. Trouble could be looked for and found by individuals responsible for plating. The plate produced by this process was truly bright. It was not only harder than either the conventional cold nickel deposit or the hot Watts nickel deposit but was also very tough and could be easily buffed when necessary. The solution was more susceptible to impurities than the Schlotter solution, but could be easily purified. The solution worked best using greater agitation than the Schlotter solution but the permissible current density range was wider. Both the initial cost and running expense for royalties and anodes were higher than with the Schlotter solution.

It was decided, however, that if a bright nickel process was to be used

at all that it should run as trouble free as possible and that it was essential to be able to analyze for all ingredients. If a savings was to be realized it should be sufficient to make slightly higher solution and operating costs be a negligible item.

It was accordingly decided to install the Weisberg-Stoddard process. This did not necessarily mean that this particular process was superior to the other. It only meant that for our own application of bright nickel it was believed to be better.

Equipment

The equipment necessary for a six hundred gallon solution was as follows:

1. 1-rubber lined steel tank 84" X 42"
2. 3-1" anode rails 90" long
3. 2-Nelson patent cathode rails
4. 1-rubber covered steel center anode rod support
5. 1-800 ampere rheostat
6. 1-60 gal. purification tank
7. 1-low speed Alsop stirrer
8. 1-duriron pump
9. 1-industrial 14" X 28" filter, duriron and rubber throughout
10. 1-motorized valve and thermostat
11. 55-Cobolt-nickel anodes
12. Rubber pipe for air agitation
13. 1-duriron heat exchanger

Racking

The greatest part of the development work was proper racking to avoid shading of parts. Due to the high current density used the racks had to be made of heavier metal. In order to save metal they were covered with

rack coating material except at the contact points. A rack material which was found to be highly satisfactory was Korolac, a copolymer vinyl resin. The procedure developed for rack coating was to grind or otherwise remove all sharp corners, apply one coat by dipping, wrap tightly with narrow bias cotton tape, and apply three or four coats over the tape. This procedure was later extended to include all other racks used in plating.

Savings

After the process had been used for some time and had been adapted to substantially all nickel plating operations on brass and steel the following observations were made.

The nickel buffing operations had been cut from five full time operators to one operator working about half time together with one low priced operator to wipe water marks and to fan slight clouds sometimes unavoidably obtained. Savings were made on every part processed. These savings graded down from a high of twenty cents a piece for bugle lyra frames, representing four hundred dollars per year on this part only, to a few cents per hundred for very small parts.

In addition to the above savings a distinct increase in quality was obtained. The plated work was blue white in color instead of a yellow white and had a greater resistance to tarnish than the conventional nickel deposits. In buffing very angular and deeply recessed band instrument parts there always had been trouble in cutting through, the sharp corners. Whenever some pieces were cut through, the rest were always very thin at those points which resulted in earlier breakdown than if no metal had been removed by buffing. This trouble was completely eliminated with bright nickel and resulted in savings difficult to estimate, but nevertheless real, in customer good will and in the lowering of complaints.

The nickel plating rates also were lowered partly due to the speed the

operator could plate the work and partly due to a rearrangement of the plating room which resulted in about thirty steps taken per batch of work or about eighty less steps than previously. Due to the speed nickel could be plated from the bright nickel solution several old solutions were discarded which greatly cut down analysis and maintenance expenses.

The extra expense involved was a higher price of anodes which amounted to about five hundred dollars per year for the first three years and thereafter was cut to amount to about two hundred dollars per year. This expense was well justified in view of the savings realized.

Purification

Two methods of solution purification (53) were successfully used, the chemical purification and the elcetrochemical purification. The chemical (37) purification, or Lipscomb purification, was performed as follows:

1. Raise pH to 6.4 - 6.5 colorimetric
2. Heat to 150°F
3. Add 1/4 lb. ferrous sulphate per 100 gal. of solution, and stir thoroughly
4. Add 1 pt. of 100 volume hydrogen peroxide per 100 gal. of solution
5. Allow to stand at 150°F with constant stirring for at least six hours
6. Filter out suspended matter
7. Heat filtrate to 160°F with stirring for one hour to release peroxide
8. Adjust pH to operating range
9. Lead, zinc, tin, iron, and copper is removed

This method had the advantage that it removed all impurities rather completely. It had the disadvantage of being rather time consuming. The

solution was out of production while being purified and at times was somewhat erratic when first placed back in service.

The electrochemical (63) purification method was continuous and when used in conjunction with proper filter procedure was far more satisfactory. The solution which was continuously filtered was returned through a purification tank of about one tenth the capacity of the plating tank. This tank was equipped with nickel anodes and cathodes of sheet brass or steel. The cathode area was as large as was possible to get in that size tank. A fixed resistance allowed current to pass during plating operations at the rate of two or three amperes per square foot. At this current density impurities such as lead, tin, iron, and copper were plated out on the cathodes in a much higher proportion to nickel than at the higher current densities at which bright nickel was plated. It was found that a solution may be kept substantially free from these metallic impurities in that way even though deeply recessed work with soft soldered seams was being plated. At times when the purification unit was inadequate the main plating solution was dummed in the same way during off hours. All organic contamination encountered in over three years of operation was removed in the filter (1) (9) (41) proper by a mixture of activated carbon (26) and activated clay. In operation the filter plates were precoated with a diatomaceous earth (42) hyflo, one third superfiltro, an activated clay, and one third darco, an activated carbon. It was found that recharging the filter every two weeks was sufficient to maintain flow rates and to keep the solution free from organic impurities. Again, this was a specific case and might not be often enough in some solutions under some conditions.

Solution Composition

The nominal solution composition and the function of each ingredient is as follows:

<u>Ingredient</u>	<u>Amount</u>	<u>Function</u>
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	32 oz./gal.	To furnish metal
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	6 oz./gal.	To promote anode corrosion
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	2 oz./gal.	To furnish metal
$\text{Ni}(\text{OCH})_2$	6 oz./gal.)	Buffer, brightener
or NaOoch	5 oz./gal.)	
or HCOOH	3 oz./gal.)	
H_3PO_3	4 oz./gal.	Regulates pH of cathode film, permits higher current density
$(\text{NH}_4)_2\text{SO}_4$.33 oz./gal.	Gives depth of color
HCHO	.33 oz./gal.	Activates brightening influence of formate

Operating Conditions

The solution analysis, operating conditions and permissible variations are as follows:

<u>Ingredient</u>	<u>Amount</u>	<u>Permissible Variation</u>
Ni	8.6 oz./gal.	7.0 oz./gal. up
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	6.0 oz./gal.	5.5 to 6.5 oz./gal.
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	2.0 oz./gal.	.5 to 3 oz./gal.
HCOONa	5.0 oz./gal.	1 oz./gal. up
$(\text{NH}_4)_2\text{SO}_4$.33 oz./gal.	.2 to .7 oz./gal.
HCHO	.33 oz./gal.	.25 oz./gal. up
pH	3.7 electrometric	3.6 to 3.9
Current density	40 amp./sq.ft.	10 to 100 amp./sq.ft.
Temperature	60°C	55°C to 65°C
Agitation	Air	Rapid cathode oscillation

In some cases there could be wider variations than noted above, however, trouble in one way or another was apt to be encountered. It was found that the presence of sodium salts induces harder deposits. Nickel formate was accordingly used for additions instead of sodium formate, and formic acid was used to lower pH. When necessary, nickel hydroxide or carbonate was used to raise the pH, thus avoiding further additions of sodium salts.

BARREL NICKEL PLATING

A study of Figure No. 1 shows that in 1935 the barrel plating operations (8) were scattered all over the plating room. This had an effect of slowing production, as well as making the work difficult for the operator. At this time barrel nickel work produced was not entirely satisfactory in appearance and there were also numerous complaints due to an early breakdown of the finish. Increases in sales also made necessary increases in production facilities.

Equipment

The problem of advantageously grouping the equipment was first attacked. At the same time the bright nickel was installed a complete plating room arrangement was made, whereby all barrel plating equipment was moved to one end of the plating room and segregated by a partition. This partition was erected primarily to keep flying drying compound from settling in other solutions. The grouping of the equipment cut down the operator's steps from one hundred ninety to eighty per load of work.

The new equipment found necessary was to replace the old single barrel plater with a new modern double barrel plater. An additional burnishing barrel was also purchased. A study was made to determine the proper barrel speed for each type of piece. The burnishing balls, cones, and stars were found to be badly rusted, shipped, and broken, which resulted in scratches on the work. New burnishing material was provided to replace worn out

and inadequate material, thus the appearance of the work was improved.

Old Procedure

It was found that the rusting of barrel nickel plated parts was due to both inadequate thicknesses of nickel and to improper application of metal. The old barrel nickel plating procedure was as follows:

1. Sand or pumice tumble, where necessary, 12 to 48 hrs.
2. Ball burnish 1 hr. to 40 hrs., depending on finish, in neutral soap solution (40)
3. Clean in baskets by oscillating up and down in hot alkaline cleaner for 1 min.
4. Rinse
5. Pickle in 1-1 HCl solution for 30 sec.
6. Rinse
7. Barrel nickel plate in following solution

Ni - 3 to 4.5 oz./gal.

NaCl - 3 oz./gal.

H_2BO_3 - 3 oz./gal.

pH - 6.0 to 6.2 colorimetric

Temperature - room

Time - 20 to 30 min.

Current - 30 to 50 amp./load

Often the above cleaning procedure did not properly clean the work (34) before plating. The work picked up dirt, grease, and insoluble calcium and magnesium soap films from dirty barrels and dirty burnishing balls. An extreme effort was made to clean up the barrels and balls and to keep them that way by carefully cleaning the work before burnishing in a three phase degreaser, using stabilized trichlorethylene solvent followed by an alkaline cleaning. It was found that insoluble soap films could largely

be avoided by incorporating a small amount of a sulphonated alcohol (25) (43) (51) called orvus in both the cleaner and the burnishing soap. Small quantities of orvus amounting to about one half of one percent of the weight of the other cleaning compounds was found to be sufficient.

New Procedure

The nickel solution was changed to a hot solution, higher in metal, with a higher permissible current density. The time of plating was also increased. The operating pH of the solution was lowered to prevent the codeposition of basic nickel compounds with nickel. Drying methods after plating were also improved by substituting corn cob meal for sawdust in drying the work. Sawdust had a tendency to sour and become soggy much quicker than the corn cob meal. These advantages compensated for the slightly higher cost of the meal.

The plating procedure as revised was as follows:

1. Degrease (58) (69)
2. Clean in hot alkaline cleaner by oscillating by hand
3. Sand or pumice tumble 12 to 48 hrs.
4. Ball burnish 1 to 40 hrs. depending on finish in neutral soap and orvus
5. Clean in hot alkaline cleaner
6. Rinse
7. Pickle in 1-1 HCl solution for 30 sec.
8. Rinse
9. Barrel nickel plate in following solution

Nickel Metal - 6.5 to 7 oz./gal.

Chloride as nickel chloride - 4 to 5 oz./gal.

Poric acid - 4 oz./gal.

pH - 5.8 mas. (colorimetric)

Temperature - 45° to 50°C

Time - 1 hr.

Current - 75 to 100 amp./load

Size of load was about one third more than in old method.

Summary of Improvements

The following is a brief summary of the improvements made on barrel nickel plating operations:

1. Advantageous grouping of equipment
2. Purchase of properly designed new equipment
3. Erection of a partition to prevent contamination of the other solutions
4. Reduction in operator's effort of one hundred ten steps per load
5. Adjustment of burnishing barrel speed
6. Provision of proper burnishing materials
7. Elimination of grease, dirt and insoluble soap formation from process
8. Elimination of broken or chipped materials
9. Modification of plating solution to provide much greater thicknesses of nickel and increase permissible loads
10. Use of a degreaser
11. Use of better drying material

PLATING ZINC ALLOY DIE CASTINGS

A great deal has been written of the plating of zinc alloy die castings. (3) (4) (57) A large number of procedures have been recommended. All procedures and recommendations were carefully studied and most of them tried, at least experimentally, in a search for the highest quality at the lowest cost. A rather complete report of our work on die cast plating is given here.

Possible Plating Cycles

There are three generally accepted schemes for applying nickel deposits

to die castings, each of which has a number of variations. The three systems may be called the nickel direct system, the copper-nickel system, and the nickel-copper-nickel system. All three systems are satisfactory from a corrosion standpoint if the layers of copper plus nickel are of equal thicknesses and are properly applied in all three cases. There seems to be little difference between the corrosion resistance of .001" of properly applied nickel alone and an aggregate of the same thickness of copper plus nickel. It is difficult, however, to obtain a thickness of nickel directly over zinc to meet specification plating for outdoor exposure without running the danger of brittle deposits from the cold, high sulphate nickel solutions from which they are plated. With high sulphate solutions the common sulphate ion provided by sodium or magnesium sulphate reduces the tendency of nickel to deposit by immersion in black spongy deposits by reducing the nickel ion concentration. Even if this precaution is taken there is always danger of deposition by immersion in recesses where the current cannot throw nickel, or where the current density is low. An added difficulty is that during this deposition an equivalent amount of zinc is dissolved by the solution. Zinc in nickel solutions rapidly poisons them making necessary purification or a new solution, both of which are expensive and time consuming.

The copper-nickel system eliminates the necessity of high sulphate nickel solutions and permits the use of conventional warm or bright high speed nickel processes. This system also minimizes the danger of cracking of the plate and to a large extent prevents solution contamination by zinc. The major objection to this method is that the thickness of copper next to the die cast base metal must be at least .0002" thick after the buffing operation. With less copper than this minimum thickness the absorption of the copper by the zinc to form hard and brittle copper-zinc

alloys in the beta and gamma ranges, increases the danger of peeling as the absorption layer approaches the nickel plate. A die casting is considered immune to this defect if the copper deposit is at least .002" thick at its thinnest point. The copper absorption undoubtedly continues during the life of the part but the rate apparently slows down to a negligible value after a short time. The difficulty is to apply enough copper to irregularly shaped objects so that the operator doing the buffing leaves at least the minimum required thickness. Another draw back to this method is the additional expense of plating and buffing the copper deposit.

The nickel-copper-nickel system minimizes the difficulties encountered in both the above systems in that a thin coating of nickel, not enough to crack or check, is first applied in a high sulphate solution, then as much copper as necessary to properly buff. After buffing a finish coating of nickel from any standard solution may be applied. This method is considered best from the standpoint of quality and service but is seldom used because of the comparatively high labor and solution cost, therefore it will not be considered further in this discussion.

Preplate Treatment

The plating procedure for zinc alloy castings before work was started to improve the process was given on Page No. 6

That procedure in the light of present day knowledge has many obvious flaws. These will be taken up in the order they were attacked. Cleaning was first studied. Many proprietary cleaners were tried and some used successfully. It was found, however, that a cleaning solution (34) made up using 3 oz./gal. Na_3PO_4 and 3 oz./gal. Na_2CO_3 to which was added 1/2 pt./100 gal. of a sulphonated alcohol called orvus (51) was as successful as any tried and a great deal cheaper. It was also found that wiping could be eliminated by degreasing the parts properly in a three phase trichlorethylene

degreaser (29) (58) (69) before alkaline cleaning and that the time of cleaning could be greatly reduced. In this connection it was found that over cleaning produced as many or more rejects as under cleaning. (2)

An acid dipping technique was successfully used wherein the work was immersed in a hydrochloric acid solution containing nickel sulphate compounded in the following proportions:

HCl - 1.5% by wt.

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ - 10 oz./gal.

The first dip produced a deposit of nickel on the zinc alloy by immersion. The acid undercut the surface through porosity in the immersion deposited nickel which left shallow pits to which subsequent deposit mechanically interlocked. Obviously, the undercutting operation could not either be too shallow or too deep or an inferior finish would be produced.

Copper Plating

The copper plating operation was modified several times. The use of acid copper was early abandoned due to the severe attack of the zinc by the acid in deep recesses. For a time a Rochelle copper deposit (21) was produced upon which nickel was plated without the preliminary copper buffing. It was difficult to hold an order of smoothness sufficient to finish and at times great difficulty was encountered in nickel buffing. Bright copper was installed as soon as enough knowledge was available. This was done by first applying a thin strike or flash of Rochelle copper and then plating to thickness in a Greenspan bright copper solution. (24) (23)

Nickel Plating

Bright nickel was used directly over the above bright copper deposit as soon as bright nickel was available. By plating bright nickel over unbuffed copper one of the major objections to the copper-nickel system was eliminated. No copper was removed by Buffing and minimum thicknesses of copper were much easier to maintain. The deposit of bright copper-

bright nickel were often smooth enough that a wiping operation to remove watermarks was all that was required. It was found, however, that a fan-ning operation using a soft wheel and rouge was as cheap as wiping and also removed slight clouds sometimes produced in the compound deposits.

Revised Procedure

The final plating sequence established for zinc alloy die castings was as follows:

1. Degrease - Three phase degreaser
2. Rack
3. Soak clean

Na_2CO_3 - 3 oz./gal.

Na_3PO_4 - 3 oz./gal.

Orvus - 1/2 pt./100 gal.

Temperature - 180°F - 212°F

Time - 15 sec.

4. Cathodically clean

Same solution

Time - 15 sec.

5. Rinse

6. Nickel acid dip

HCl - 1.5% by wt.

$\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$ - 10 oz./gal.

Time - 3 sec.

Temperature - room

7. Rinse

8. Rochelle copper strike

Time - 3 min.

Temperature - 50° - 55°C

Tank potential - 4 volts

9. Rinse
10. Rinse
11. Bright copper plate

Formula on Page No. 70

Temperature - 60°C

Time - 17 min.

Current density - 30-40 amp./sq.ft.

Tank potential - 2 1/2 to 4 volts

12. Rinse
13. Acid dip 1.5-2% HCl by wt.

Time - 2-3 sec.

14. Rinse
15. Bright nickel plate

Formula on Page No. 59

Temperature - 60°C

Time - 15 min.

Tank potential - 3 volts

16. Rinse
17. Hot rinse
18. Unrack
19. Nickel fan

Comparison of Costs and Quality

In order to get a comparison of costs before and after the above developments one part was taken as a fair example. The complete finishing cost for labor and overhead before the above changes were made was eight dollars per one hundred parts. The cost after the process was improved for the same one hundred parts was seven dollars. This saving was made over a period when wages went up about twenty percent. The

changes definitely improved the quality in several ways. The rejects from peeling and blistering were greatly reduced. Due to the fact that copper was not buffed at all no metal was removed in this operation and minimum thicknesses were easily maintained. Little nickel was removed in the fanning operation after plating and few, if any, losses are realized from cutting through the deposit on sharp corners. More nickel was applied and the harder bright nickel deposit was found to be less porous and more resistant to corrosion.

BRIGHT COPPER

Processes Available

During the die casting problem the necessity of a bright copper solution was realized. There were at that time only two commercial bright copper processes known to the author. These were the Zialite process (5) and the duPont process. (46) Experimental solutions of both processes were installed and operated. The Zialite process was found to have too low a limiting current density to be useful for this application. The duPont process was successful but for two outstanding faults difficult to eliminate. Burning on the high current density areas was very pronounced if the limiting current density was only slightly exceeded. The greatest trouble was realized from roughness of the deposit even if electrolytic anodes were used. The maximum brightness obtainable in steady operation was also not believed to be sufficient for this application.

It was learned that Greenspan and Weisberg had been working on a bright

¹ The author's opinion on any proprietary process discussed in this paper is only in respect to the specific application in which it was tried and should not influence the reader in any way as to its usefulness for any other application or to the industry in general.

copper process and had it developed to the place where it was ready for commercial trials. An agreement was reached whereby the development work was to be done in our plant under production conditions on zinc alloy die castings. (23) (24)

Amine Bright Copper

The formula submitted as the best found in the laboratory was as follows:

Copper sulphate - 13.5 oz./gal.

Ammonium sulphate - 2.75 oz./gal

Diethylene Triamine - 11/0 oz./gal.

Ammonia - 4.5 fl. oz./gal.

Tergatol penetrant 03 - .25 oz./gal.

It was found that neither iron nor lead lined tanks were suitable. A three hundred gallon solution was therefore prepared in a rubber lined steel tank. The tank was equipped with a cathode rocker which had a four inch stroke with twenty four cycles per minute. A nickel silver heating coil was used which in operation was made slightly cathodic through a suitable resistance to prevent stray fields from corroding the coil and starting leaks. The anodes were conventional rolled copper anodes. A filter was provided and was tried both with constant and intermittent filtration. Periodic filtrations were found to be suitable.

Development Work

The experimental work on bright copper consisted of studying the following factors: Cleaning methods, acid dipping, procedures, Rochelle copper strike, all operating conditions such as current density, temperature, filtration, agitation, and bath composition, the subsequent bright nickel plating conditions, and drying methods. In all, about eighty trials were made before production runs were started.

Observations on each variable were made and recorded. These observations follow in a condensed form. The cleaning and preplate cycle as out-

lined in the above procedure under zinc alloy die castings must be closely followed to avoid trouble. The time of the Rochelle strike is important and must be at least two minutes to completely cover the die casting.

The solution concentration may vary over rather wide limits and still produce bright deposits. The ammonia content may vary widely with no detrimental effect, however, with low ammonia it is necessary to use greater agitation. A high ammonia content permits higher current densities. The copper concentration is not critical. The solution has been successfully operated from one half to twice the nominal copper content. However, the ratio of the copper to sulphate should be rather closely maintained for very bright deposits.

The temperature can be varied from 45°C to 75°C and except for the fact that the higher temperatures permit higher current densities in the bright range, bright plates may be secured within the above limits.

The maximum and minimum permissible current density is determined by the variables of temperature, ammonia content, racking and agitation. Brilliant deposits can be produced between 10 amperes per square foot and 130 amperes per square foot. The optimum range is between 40 and 70 amperes per square foot for the general run of work.

Pitting was the trouble most frequently encountered. Filtering through diatomaceous earth frequently helped. The use of willow charcoal and activated clay in filtering along with the filter aid was also found to be valuable. Additions of the wetting agent also helped. Adjustment of copper to sulphate ratio was found to be important to suppress pitting.

Dull deposits and roughness always were overcome by the addition of ammonia or amine if the racking and solution filtration had been properly carried out.

The bright copper process has been singularly successful over long time heavy production. A substantial part of the savings and increase

in quality realized in the above die casting problem was due to its success.

BATON STAFF PROBLEM

Rusting

This problem and its solution is described here because it is a typical case of one of many problems encountered in plating room practice not involving a change in plating procedures. It often happens, as in this case, that a change in material solves a serious problem.

Baton staffs were made from a tube of .750" X .680" X 28-3/4" long steel into which were soldered two end plugs, one solid, and one hollow. The hollow plug was threaded on the inside to receive a baton ball. These staffs were polished, bright nickel plated and chromium plated.

Many complaints were received from the trade due to rusting of the inside of the staff which weakened it to the extent that it easily fractured when dropped or otherwise abused. This rusting was traced to the processing solutions which removed protective grease and scale films from the inside of the staffs and perhaps left residual chemicals and moisture. The following modifications in procedure were unsuccessfully tried to eliminate the trouble.

1. Building racks vented to above the surface of the solutions to equalize the internal pressure in the staffs and to prevent the entry of solutions into them by the partial vacuum otherwise created when the work was transferred from a hot to a cold solution.
2. Carefully drying out the inside after plating with alcohol and air.
3. Coating the inside of the staffs with beeswax dissolved in carbon tetrachloride.
4. Coating the inside of the staffs with rust proof oil.

Change in Material

None of the above efforts eliminated the rusting difficulty and complaints were nearly as numerous as before.

An investigation was carried out to determine the possibility of a more corrosion resistant material. After many trials it was found that very hard drawn nickel silver, containing 15% nickel, was strong enough even though a thinner wall stock had to be used to obtain the same weight. The weight factor was very important in this particular instance.

The nickel silver was a much more expensive material. Consequently a study of possible processing changes was made to approximate, if possible, the same production cost as when steel tubing was used. The oiling, some of the polishing operations, water testing for leaks, drying with alcohol and air, and nickel buffing could be eliminated by using nickel silver. Other operations could be minimized due to the superior finish of nickel silver and its better workability.

The net savings in labor and overhead effected by the use of nickel silver per 100 staffs was \$15.24. The added material cost was \$17.20 per 100 staffs. This left an increase in cost per 100 staffs of \$1.96 or about two cents each which was a very small price to pay for the elimination of a very serious difficulty. Where previously dozens of staffs were returned and had to be replaced before the change in material not a single case has come to the author's attention in over a year of production of many thousands of the new staffs.

AUTOMATIC SILVER PLATING

Bright Silver

A thorough investigation of silver plating was started which rather thoroughly covered all phases of the subject. The objects of the investigation were as follows: (18) (38) (45) (50) (52)

1. To find a more rapid method of depositing silver.

2. To find a silver process to produce deposits of mirror brilliance
3. To improve preplate methods to eliminate hand work such as scrubbing
4. To find a method of depositing silver more resistant to severe perspiration conditions.
5. To devise racking technique to replace wiring
6. To conveyerize all operations if possible

The subject of bright silver and rapid silver seemed to go hand in hand and were investigated first. A search of patent literature was made. Several patents were found which claimed addition agents to the regular cyanide-carbonate solution or a modification thereof which would produce bright deposits. Mercaptans, urea, thiourea, thiosemicarbazide, and derivatives of the above compounds were faithfully tried according to instructions. Varying degrees of bright silver was obtained and in some cases brilliant silver was plated. The bright ranges were either too narrow, the limiting current densities too low, or the baths themselves too unstable to be of use in our application.

Accordingly work on bright silver was abandoned and work was continued on finding a stable silver solution with a high permissible current density. Many addition agents and many different bath formulations were tested in one and five gallon laboratory solutions. A silver bath was found which cut silver plating time to about one fourth that of previous practice. This bath formula was as follows: (28) (66)

Ag - 2.00 to 2.25 oz./gal.

NaCN (free) - 2.3 - 3.0 oz./gal.

KNO₃ - 16 oz./gal.

Na₂CO₃ - 3 oz./gal. max. (32) (33)

Temperature - 30°C - 35°C

Agitation - cathode oscillation

Current density is not mentioned in the above formula nor will it be mentioned in the following discussion of silver plating, for the same reason as explained on Page No. 4 Sodium cyanide was used to maintain the cyanide content because of price considerations. Potassium cyanide worked equally as well. Drag out was found to keep the ratio of sodium to potassium salts sufficiently in balance to prevent trouble due to a high sodium salt content. (36) (55)

Cleaning

It was found that grease and dirt could be entirely removed from the work by a soak cleaning cycle of six minutes followed by a cathodic electric cleaning cycle of two minutes in a cleaner of the following formulation:

NaOH - 50 parts

Na₂CO₃ - 40 parts

NaCl - 25 parts

Na₃PO₄ - 40 parts

Na₃PO₄ - 400 parts

The above mixture was made up 6 oz./gal. and a wetting agent (orvus) (25) was added in the ratio of one pint per one hundred gallons of cleaning solution. The solutions were operated hot (185° to 210°F). Staining of the brass surface, when it occurred, was eliminated by small additions of ammonium chloride. This addition agent, due to hydrolysis slightly, reduced free alkalinity of the solution. (7) (10) (11) (12) (29) (34) (16) (43) (47) (48) (51) (56) (64) (67) (68)

Acid Treatment

In the previous silver plating procedure (Page No. 3) hand scrubbing and bright dipping was necessary to insure the removal of dirt, grease, and tarnish. The above alkaline treatment adequately removed the dirt. The

next problem was to remove the tarnish, scale, and oxides without bright dipping. A bright dip operation would have been difficult to conveyerize due to the extremely short immersion time permissible. Bright dip fumes would have been very detrimental to machine parts. The use of a bright dip on horn parts due to rapid metal attack, was also undesirable.

After many trials of different acids and acid combinations it was found that a 32° Fe. sulphuric acid solution in which the work was made the cathode at 50 to 100 amperes per square foot performed very efficiently. Scale, tarnish, and oxides were removed in a maximum time of three minutes. In operation, this solution acted as an ordinary acid solution in removing scale chemically. The large quantities of nascent hydrogen evolved on the work surface reduced oxides to the metallic state electrochemically. The tearing and prying action of the liberated hydrogen also aided in the removal of loose material. (13) (39) (44) (54)

Copper and Nickel Striking

Silver, even in cyanide solutions, has a very decided tendency to deposit on copper or copper base alloys by simple immersion whereby non-adherent silver deposits are produced and equivalent amounts of the base metal go into solution. This tendency may be overcome or minimized in a number of ways in silver plating copper base alloys.

1. By using a series of silver strikes starting with low silver content and high free cyanide and working up to the plating solution formula. The current density in the strikes must be high and the time must be short.
2. By using a mercury or "blue dip" which deposits a film of mercury on the work. The amalgam formed is said to aid in the adhesion of the silver plate probably because it resists the deposit of silver by immersion and forms a layer of silver amalgam.

3. By preplating with nickel upon which silver has little or no tendency to deposit by immersion.

The series of silver strikes was undesirable insofar as conveyerizing was concerned due to the problem of solution control and the number of tanks necessary. The use of mercury on any nonferrous metal is undesirable wherever avoidable due to the fact that mercury actively predisposes season cracking, especially upon thin hard rolled sections predominant in band instruments. A mercury dip was to be avoided if possible also from the standpoint of the very short immersion time difficult to obtain on a full automatic machine.

The nickel undercoat was decided upon as the most logical undercoat to use. Tests were run on the corrosion resistance of silver over a thin pore free deposit of nickel using the standard silver plate over brass as a control. The tests were performed by oscillating a test plate at constant load and constant speed over a felt pad which was soaked with a synthetic perspiration of one of the two following formulae:

1. Acid synthetic perspiration

Sodium chloride - 2.65 gm./L

Urea - .75 gm./L

Make pH 5.3 (electrometric) with acetic acid

2. Alkaline synthetic perspiration

Ammonium chloride - .839 gm./L

Sodium chloride - 1.732 gm./L

Ammonium hydroxide sp.gr..88 - .42 cc/L

Make pH 7.5 (electrometric) with acetic acid

It was found that with the nickel undercoating the silver resisted corrosion nearly twice as long as silver alone with all other conditions the same.

The horns and horn parts which were silver plated were assembled largely with soft solder over which nickel has a well known poor adhesion. If nickel were to be used as an undercoating some way had to be found to overcome this difficulty. Two methods were tried.

The first was that of using a nickel solution which had been rather extensively used to plate stainless steel. The solution of the following composition was also found to be suitable for depositing adherent nickel on soft soldered joints.

Nickel chloride - 27 oz./gal.

Hydrochloric acid - 16 fl. oz./gal.

Current density - 50 to 75 amp./sq.ft.

Temperature - room

Time - 1 to 4 min.

In use this solution was found to have sufficient throwing power to cover deep recesses. This may have been partly due to the local cell action between the solder and the brass or the constituents thereof which generated a potential sufficient to successfully oppose the plating potential in recesses. This solution was consequently abandoned although it was perfectly satisfactory in every other respect. (20) (65)

The second method used for applying nickel to brass before silver plating was to first apply a copper strike followed by a modified hot Watts nickel. (22) Copper applied from a cyanide solution or Rochelle copper solution was known to adhere well to soft solder as well as to have a high throwing power. (21) (70) The copper strike was also found to have the same distinct advantage of connecting slight imperfections in the previous cleaning steps as in the nickel plating procedure Page No. 9

The formula of the nickel solution used was as follows:

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ - 27 oz./gal.

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ - 6 oz./gal.

H_3PO_3 - 4 oz./gal.

Na_2SO_4 - 5 oz./gal.

pH - 5.8 (colorimetric)

Tank potential - 2.5 - 3.5 volts

Temperature - 60°C

Agitation - Cathode oscillation

The magnesium sulphate was added to improve throwing power.

Recovery

Work was done to find the most efficient way to recover silver from rinse water without the use of elaborate counter flow systems. This proved to be a very simple problem. It was found that if a steel rinse tank contained a quantity of zinc borings and turnings any silver entering the tank was rapidly and completely deposited on the zinc by immersion. The resultant impure cement silver periodically was sent to a reliable refiner for recovery. (6) (27) (49)

Plating Cycle

The new silver plating cycle was as follows:

1. Rack
2. Alkaline clean-still 6 min.
3. Alkaline clean-cathodically 2 min.
4. Rinse
5. Electric acid 3 min.
6. Rinse
7. Copper strike 1 min.
8. Rinse
9. Nickel strike 3 min.
10. Rinse
11. Silver strike 2 min.

12. Silver plate 15 min.
13. Recovery
14. Recovery
15. Hot rinse
16. Unrack

Pilot Plant Work

After the above cycle had been worked out in the laboratory, tolerances and optimum operating conditions established, and corrosion tests performed, a pilot plant was set up to do production work. The complete cycle was carried out using fifty gallon solutions which were prepared in steel drums and stoneware crocks. This plant was sufficiently large to silver plate cornets, trumpets, and metal clarinets as well as smaller parts such as accessories. A total of one thousand horns were plated wherein a complete record was made on each horn of instrument number, method of degreasing, if any, time, temperature, current flow, voltage in each solution including cleaners, and complete daily analyses of each solution. In this plant minor variations in plating technique, material handling, and solution composition were worked out. It was also in this pilot plant that it was definitely established that it would be practical to conveyerize silver plating operations.

No study of racking methods for horns, particularly the larger ones, could be made in the small pilot plant. Also no definite proof could be established that the procedure worked out for the smaller horns would be satisfactory for larger horns such as baritones and sousaphones in respect to throwing power. Another pilot plant was built wherein three hundred gallon solutions were prepared. The same care in recording data was used here as in the previous pilot plant. A total of three thousand band instruments of all sizes were plated which resulted in only minor modifications in plating technique.

Racking

The racking problem was very carefully studied and sample racks were made for each piece. All racks were made of one half inch round brass rod covered with koralac rack coating material and bias cotton tape which was subsequently impregnated with koralac. The koralac was a special copolymer vinyl resin especially compounded for plating racks and its use was found to be very successful in every plating and cleaning solution except trichlorethylene degreaser solvent. Brass rod was used instead of copper because it was a stock item and did not have to be a special order. It was found to be as good if a sufficiently large size was used to carry the current.

No special racking technique was needed on small horns and parts except to devise ways to obtain approximately the same effective cathode area on each rack. In the cases of the larger horns special anodes had to be used to obtain deposits in recesses such as the inside of horn bells and around valve sections. Pure strip nickel was found to be nearly an ideal material as it was substantially insoluble in all processing solutions. It was only necessary to use an electrical connection from the special anodes to the positive side of the plating line while the work was in the silver strike solution. In the other solutions, copper strike, nickel strike, and silver plate, the special anodes performed the unique function of bipolarity without direct electrical connection. These anodes in places were rather close to the regular tank anodes. In the absence of direct electrical connection they were cathodic at these points. At the points where they were close to the horn, that is in the recesses, they were anodic. The electrical resistance in the metal was less than in the solution, therefore considerable current was conducted by them.

This is the only application to the author's knowledge where the well known phenomena of bipolarity has been used in a practical plating room process. Another well known electrochemical application of bipolarity is in the series refining of copper.

Conveyerizing

A complete study was made of possible savings which might result in an automatic silver plating machine using the new cycle. An itemized list of the factors considered is given without the specific savings in each case.

1. Labor
2. Drag out (13)
3. Brushes
4. Pumice
5. Sulphuric acid
6. Nitric acid
7. Reclamation charges
8. Increased quality

The above study proved that the cost of an automatic machine could easily be justified. The cost could be written off at the rate of about one third per year.

Machine

The plating machine decided upon was a Hanson-Van Winkle-Munning elevator type conveyer. The machine was equiped with a hydraulic lift, a hydraulic index, electric timer, and an agitation mechanism which gave variable cathode oscillation transverse to the work travel. The machine had an overall length of sixty six feet ten inches, was eight feet wide and eight feet six inches high. The distance between carrier centers was three feet and the lift was four feet. The machine was equiped with forty carriers and at normal operating speed turned out one rack per minute. This could be varied

from twenty seconds to three and one half minutes insofar as the machine was concerned but only from one half minute to about two minutes in actual practice because of plating specifications.

Summary of Silver Developments

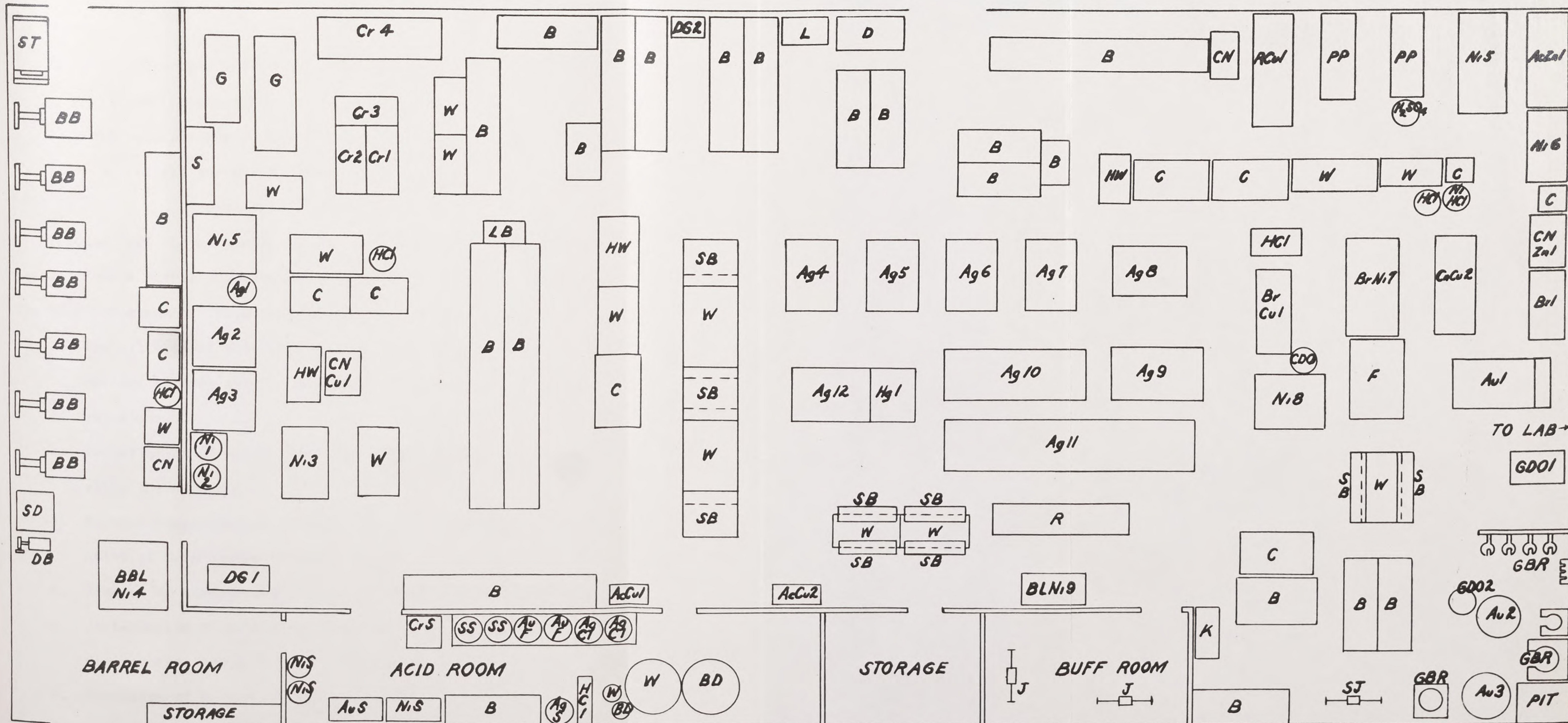
All of the objects given on Page No. 73 except bright silver were achieved. Costs were cut, quality increased, time decreased, hand work eliminated, racking developed, and a brighter more easily finished product was obtained.

LAYOUT CHANGES

Changes from 1935 to 1940

Figures No. 1 and No. 2 have already been explained. Figure No. 1 is a layout of the plating room in 1935. Several changes were made between 1935 and 1940 due to changes in processing already explained in detail and other changes of a less important nature. The following are the layout changes during this period and the general effect on the efficiency of plating room operation. Figure No. 3 shows the layout in 1940.

1. The control laboratory was moved to a new building on the opposite end of the plating room, was greatly enlarged, and modernized.
2. The ball burnishing, and barrel nickel plating operations were gathered to one location and segregated as already noted with a resultant saving of one hundred ten steps per load.
3. Degreasing systems were installed. (58) (69)
4. Solutions were advantageously grouped so that miscellaneous plating operations, repairing, and stripping was more efficiently performed.
5. Bright nickel was installed subsequently retiring several cold nickel solutions. Steps saved in nickel plating were eighty steps per batch.
6. The gold plating solutions were reduced due to less production demands. (35)



G-GENERATOR

S-SWITCHBOARD

L-LOCKER

D-DESK

R-WORKRACK

C-ALKALINE CLEANER

J-BUFF JACK

W-RINSE TANK

F-PUMP, FILTER, PURIFICATION

K-KOROLAC

B-WORKBENCH

SD-SAWDUST DRIER

CNGu - CYANIDE COPPER BATH

RCu - ROCHELLE COPPER BATH

BrCu - BRIGHT COPPER BATH

AcCu - ACID COPPER BATH

CDO - COPPER RECOVERY

Ni - NICKEL BATH

BBLNi - BARREL NICKEL BATH

BLNi - BLACK NICKEL BATH

BrNi - BRIGHT NICKEL BATH

NiS - NICKEL STRIP

NiHCl - NICKEL ACID DIP

Cr - CHROMIUM BATH

CNZn - CYANIDE ZINC BATH

AcZn - ACID ZINC BATH

Ag - SILVER BATH

AgS - SILVER STRIP

AgCl - SILVER CHLORIDE

SDO - SILVER RECOVERY

PP - PILOT PLANT-RAPID SILVER

Au - GOLD BATH

GDO - GOLD RECOVERY

AuS - GOLD STRIP

AuF - GOLD FULMINATE STORAGE

GBR - GOLD BELL RACKS

CrS - CHROMIUM STRIP

HCl - HYDROCHLORIC ACID DIP

BD - BRIGHT DIP

Hg - MERCURY DIP

H₂SO₄ - SULPHURIC ACID DIP

CN - CYANIDE DIP

BB - BURNISHING BARREL

ST - SAND TUMBLE BARREL

DB - DRYING BARREL

SJ - SCRATCH BRUSH JACK

SB - SCRUB BENCH

HW - HOT WATER

LB - LIGHT BOX

DG - DEGREASER

SS - SOLDERING ACID STORAGE

Fig #3

PLATING ROOM

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JANUARY 1940

SCALE $\frac{1}{8}"=1'$ DRAWN-F.K.S.

7. Acid copper plating was practically eliminated and Rochelle salt cyanide solutions substituted.
8. Acid zinc plating was abandoned and a bright du Pont cyanide zinc process was substituted.

Changes from 1940 to 1941

In June 1940 the automatic silver plating machine was installed which necessitated a rather complete rearrangement as shown by Figure No. 4.

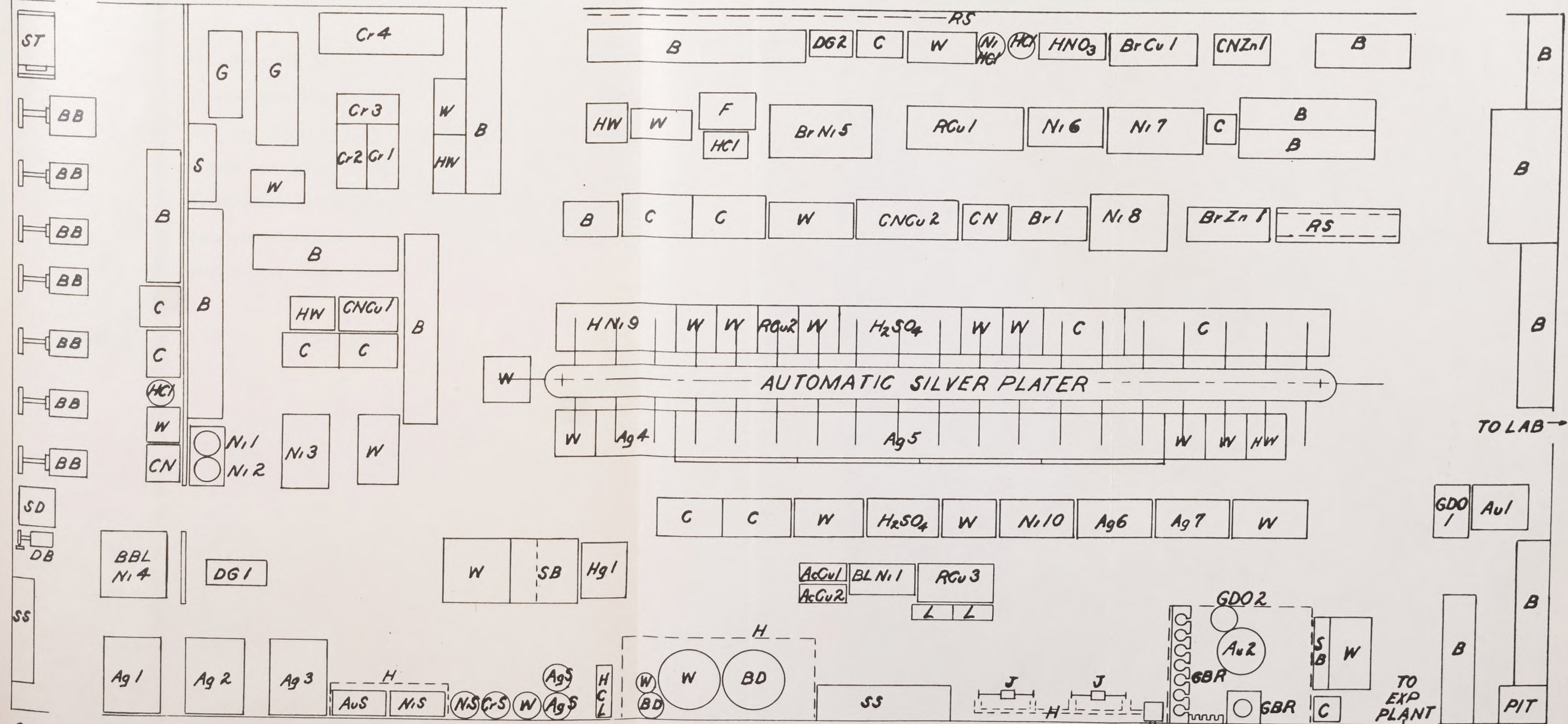
The more important of these changes are as follows:

1. Installation of automatic silver plating machine resulting in savings already noted. Retiring of several old type silver solutions.
2. Installation of pilot plant for silver not yet removed paralleling the automatic.
3. Further consolidation of gold plating operations and installation of drip basins to catch splash.
4. Removal of unnecessary partitions which produced congestion.
5. Installation of extensive blower and dust systems on bright dip, strips, and buff jacks where noted by dotted lines. (15) (54)
6. Provision of better storage facilities.
7. Change in doors to avoid congestion in flow of work in and out of plating room.
8. Grouping of copper, nickel, zinc, and brass plating systems in three lines, resulting in increased production speed and decreased material handling.

PROJECTED FUTURE DEVELOPMENTS

Work is at present going forward to perfect plating room practice in a number of ways.

1. Printed procedures for each plating cycle specifying



G-GENERATOR
 S-SWITCHBOARD
 L-LOCKER
 R-WORKRACK
 C-ALKALINE CLEANER
 J-BUFF JACK
 W-RINSE TANK
 B-WORK BENCH
 SD-SAWDUST DRIER
 Cr-CHROMIUM BATH

CNCu - CYANIDE COPPER BATH
 RCu - ROCHELLE COPPER BATH
 BrCu - BRIGHT COPPER BATH
 AcCu - ACID COPPER BATH
 Ni - NICKEL BATH
 BBLNi - BARREL NICKEL BATH
 BLNi - BLACK NICKEL BATH
 BrNi - BRIGHT NICKEL BATH
 NiS - NICKEL STRIP
 NiHCL - NICKEL ACID DIP
 CNZn - CYANIDE ZINC BATH
 BrZn - BRIGHT ZINC BATH
 Ag - SILVER BATH
 AgS - SILVER STRIP
 Au - GOLD BATH
 GDO - GOLD RECOVERY
 AuS - GOLD STRIP
 GBR - GOLD BELL RACKS
 CrS - CHROMIUM STRIP
 HCl - HYDROCHLORIC ACID

BD - BRIGHT DIP
 Hg - MERCURY DIP
 H2SO4 - SULPHURIC ACID DIP
 CN - CYANIDE DIP
 BB - BURNISHING BARREL
 ST - SANDTUMBLE BARREL
 DB - DRYING BARREL
 SB - SCRUB BENCH
 HW - HOT WATER
 DG - DEGREASER

SS - STORAGE
 RS - RACK STORAGE
 H - HOOD & BLOWER

Fig #4

PLATING ROOM
 C.G. CONN Ltd.
 ELKHART IND
 MARCH 1941
 SCALE $\frac{1}{8}'' = 1'$ DRAWN-EKS.

all variables to be placed on cards in holders and located conveniently near the operators work place.

2. Complete study of metal deposited on each part to obtain more accurate costs.
3. Development of technique for studying dragout losses.
4. Constant search for better methods, better processes, better metal and a better product.

ABSTRACTS

- (1) Amberg, R. J.
Filter Aids for Filtration
Met. Ind. 556-12-38
- (2) Anderson, E. A. and Reinhard, C. E.
Alkaline Cleaning and Copper Plating
Mo. Rev. 175-3-40
- (3) Anderson, E. A.
How Zinc Alloy Die Castings are Plated Commercially
Mo. Rev. 437-6-38
- (4) Anderson, E. A., Reinhard, C. E., and Kittleberger
The Plating of Zinc Alloy Die Castings and Polled Zinc
Met. Cl. Fin. 721-9-37
- (5) Anonymous
Zinc Bright Copper Solution
Pro. Fin. 40-8-38
- (6) Anonymous
Recovering Precious Metals
Met. Ind. 184-5-36
- (7) Ashelrod, R. S. and Erukhimova, N. A.
Electrolytic Cleaning in Alkaline Solutions
Mo. Rev. 476-6-40
- (8) Beaver, H. L.
Series of Articles on Barrel Finishing
Pro. Fin. 1937 to 1941
- (9) Belke, W. E.
Development of Filters for Plating Solutions
Met. Ind. 27-1-39

- (10) Camel, L. C.
Alkaline Cleaning
Mo. Rev. 777-11-39
- (11) Cleveland, T. K.
Alkalis for Metal Cleaning
Met. Fin. 478-9-40
- (12) Cleveland, T. K.
Solution for Metal Cleaning
Mo. Rev. 432-6-40
- (13) Conley, C. C.
Determination of Drag-Out Loss
Mo. Rev. 355-5-39
- (14) Cosgrove, J. M.
The Electrodeposition of Nickel on Zinc
Mo. Rev. 7-12-36
- (15) Delorme, E. C.
Ventilation of Acid Dipping and Electroplating Rooms
Mo. Rev. 112-2-38
- (16) Dodd, S. R.
Alkaline Cleaning
Met. Fin. 331-6-40
- (17) Egeberg, E. G. and Promisel, N. E.
Brightening Agent for Silver
Met. Fin. 331-6-40
- (18) Egeberg, E. C. and Promisel, N. E.
Silver Plating of Hollow Ware
Pro. Fin. 5-4-37
- (19) Egeberg, E. G. and Promisel, N. E.
Brightness of Electrodeposits and its Measurement

Met. Ind. 166-4-37

- (20) Flowers, L. C.

Throwing Power and Current Distribution in Plating Baths

Mo. Rev. 47-11-36

48-12-36

44-1-37

- (21) Graham, A. K. and Read, H. J.

A Study of the Rochelle Salt Copper Plating Bath

Met. Ind. 559-11-37 (Series of Articles)

- (22) Graham, A. K. and Read, H. J.

Anodic Behavior in Cyanide Copper Plating Baths

Met. Cl. Fin. 734-11-38

- (23) Greenspan, L.

New Copper Plating Process

Met. Ind. 227-5-40

- (24) Greenspan, L.

Electrodeposition of Bright Copper

Elec. Soc. Preprint 78-13

- (25) Hall, N.

Wetting Agent Action and Control

Pro. Fin. 52-6-40

- (26) Helbig, W. A.

Activated Carbon in Electroplating Solutions

Met. Ind. 553-12-38

- (27) Hickman, K., Weyerts, W. and Goehler, O. E.

Electrolysis of Silver Bearing Solutions for the Recovery of Silver

Met. Ind. 349-9-36

- (28) Hirsch, S., Snyder, H., Jackson, R. and Verrelle, N.

Effect of Free Sodium Cyanide and of Sodium Carbonate on the

Cathode Efficiency of a Silver Plating Solution.

Pro A. E. S. 70-37

- (29) Hogaboom, G. B.

Practical Pointers on the Use of Solvents and Alkaline Solutions
in Metal Cleaning

Abr. Cl. Meth. 20-12-36

- (30) Hogaboom, G. B.

Alkali Cleaner and Acids on Lead

Met. Cl. Fin. 740-11-38

- (31) Hogaboom, G. B.

Plating Economy Demands Control of Drag-Out Losses from Plating
Solutions

Mo. Rev. 48-12-36

- (32) Hogaboom, G. B.

Removal of Carbonates from Metal Cyanide Solutions

Met. Ind. 64-2-37

- (33) Hull, R. O.

The Removal of Carbonate from Cyanide Plating Solutions by
Gypsum

Pro. A. E. P. 164-37

- (34) Kaye, A. L.

Colloidal and Surface Aspects of Metal Cleaning and Finishing

Met. Cl. Fin. 9-1-36

- (35) Kushner, J. B.

Modern Gold Plating

Pro. Fin. 30-9-40 (Series of Articles)

- (36) Kushner, J. B.

Measurement of Drag Out

Met. Ind. 320-7-39

- (37) Mattacotti, V.

Impurities in Plating Solutions

Met. Ind. 259-6-39

- (38) Nesle, F. C.

A Resume of Silver Plating

Pro. A. E. P. 104-37

- (39) Meyer, W. R.

Bright Dipping of Non-ferrous Metals

Met. Ind. 401-9-39

- (40) Meyer, W. R.

Barrel Furnishing

Met. Ind. 101-3-36

- (41) Meyer, W. R.

Filtration of Electroplating Solutions

Met. Ind. 117-3-39

- (42) Meyer, W. R.

Methods of Mixing Filter Aids

Met. Ind. 558-12-38

- (43) Meyer, W. R.

Cleaning of Metals

Abr. Cl. Meth. 9-8-36

- (44) Muscio, G.

Bright and Matte Dipping

Pro. A. E. P. 262-38

- (45) Nicol, A. E.

Variables in Silver Plating Solution

Met. Ind. (Lond.) 275-3-40

- (46) Oplinger, F. F.
The Development of a Process for High Speed
Copper Plating from Cyanide Solutions
Mo. Rev. 181-3-39
- (47) Reese, T. W.
Analyzing and Controlling Metal Cleaning Operations
Mo. Rev. 83-2-37
- (48) Finker, E. C.
Surface Films in Metal Cleaning
Met. Ind. 20-1-40
- (49) Savage, Frank K.
Recovery of Gold and Silver from Plating Solutions
Met. Ind. 160-4-39
- (50) Savage, F. K.
Finishing Band Instruments
Met. Ind. 132-3-40
- (51) Savage, F. K.
Alkaline Cleaners and Wetting Agents
Mo. Rev. 445-6-33
- (52) Savage, F. K. and Pfefferle, P. R.
Automatic Silver Plating
Mo. Rev. 101-2-41
- (53) Smith, C. W.
Purification and Filtration of Plating Solutions
Mo. Rev. 687-10-39
- (54) Smith H.
Fume Exhaust Design
Pro. A. E. P. 241-38

- (55) Soderberg, G.
Drag Out
Mo. Rev. 156-3-37
- (56) Strachan, E. K.
Plater's Cleaning Compounds
Pro. Fin. 21-8-38
- (57) Towner, O. T.
Finishing of Die Cast Products
Mo. Rev. 671-10-39
- (58) Wallace, E. V. D.
Vapor Phase Degreasing
Pro. Fin. 16-3-37
- (59) Weiner, R.
Experiments on the Electroplating of Bright Silver
Mo. Rev. 487-6-40
- (60) Weisberg, L.
Recent History of Certain Cobalt-Nickel Alloy Plating Solutions
Elec. Soc. Preprint 77-18
- (61) Weisberg, L.
Cobalt-Nickel Plating Solutions
Met. Fin. 318-6-40
- (62) Weisberg, L.
Commercial Deposition of Cobalt-Nickel Alloys
Met. Ind. 236-5-38
- (63) Weisberg, L.
Purifying Nickel Plating Solutions by Electrolysis
Met. Ind. 451-9-37
- (64) West, A. C.
Electric Cleaners
Mo. Rev. 262-4-40

(65) Wood, D.

Commercial and Practical Aspects of Throwing Power as a Factor
in the Character of Deposits.

Mo. Rev. 11-7-36

(66) Wood, D.

Something New in Silver Plating

Met. Ind. 166-4-38

(67) Young, C. P. F.

Metal Cleaning

Abr. Cl. Meth. 7-1-37

(68) Young, C. B. F.

Metal Cleaning, Principles and Practice

Met. Ind. 446-9-37

(69) Young, C. B. F.

Solvent Degreasing

Pro. Fin. 62-10-37

(70) Young, C. B. F.

Study of Cyanide Copper Plating Paths

Met. Ind. 560-12-38

(71) Young, C. B. F.

Nickel-Cobalt Alloy from Acid Sulphate Solutions

Met. Ind. 179-5-36

Abbreviations

Abr. Cl. Meth.	-	Abrasive & Cleaning Methods
Elec. Soc.	-	Electrochemical Society Bulletin
Met. Cl. Fin.	-	Metal Cleaning & Finishing
Met. Ind.	-	Metal Industry New York
Met. Ind. (Lond.)	-	Metal Industry London
Mo. Rev.	-	Monthly Review American Electroplater's Society
Pro. A. E. S.	-	Annual Proceedings of American Electroplater's Society
Pro. Fin.	-	Products Finishing

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