THE EFFECT OF REDUCED FUCHSIN ON THE ELECTRODEPOSITION OF NICKEL

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
John Maskal, Jr.
1942

THE EFFECT OF REDUCED FUCHSIN ON THE ELECTRODEPOSITION OF NICKEL

by

John Mashal, Jr.

A THESIS

Submitted to the Graduate School of Michigan
State College of Agriculture and Applied
Science in partial fulfilment of the
requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

1942

Acknowledgements

The author wishes to express his indebtedness to Dr. D. T. Ewing, Professor of Physical Chemistry, for the assistance and timely suggestions given during the course of this investigation. The writer is also indebted to Professor A. J. Clark, Head of the Department of Chemistry of Michigan State College for the grant of an assistantship.

INTRODUCTION

In general bright nickel plating baths contain at least two addition agents, a modifier or semi-brightener and a brightener. The former belongs to a class of organic compounds, usually a sulfonated naphthalene or benzene, which according to F. A. Maurer(1) has the ability to form a colloid with the nickel in solution. The latter, of which reduced fuchsin is an example, has the purpose of imparting a high degree of lustre to the electrodeposit and is usually present in extremely small amounts. The effects of this compound under various conditions of temperature, current density, pH, and modifier concentrations were investigated first in a two liter bath. The results obtained were then applied using a 100 liter bath.

EXPERIMENTAL

The Two Liter Bath

In each case the bath used had the following basic composition:

$NiSO_4 \cdot 7H_2O$	240 grams/liter
$NiCl_2 \cdot 6H_2O$	37.5 "
H_3BO_3	37.5 "

Since a technical grade of materials was used, it was necessary to remove from the solution copper and iron, both or either of which, if present in a high enough concentration (above 0.10% Fe and 0.03% Cu)(2), would cause dark deposits. The purification was accomplished as follows:

To remove iron the pH of the solution was raised to about 5.5 by the addition of ammonium hydroxide and heated at a boiling temperature for one hour. The solution was then cooled slightly and the precipitate of ferric hydroxide filtered off by means of a suction filter.

The copper was then removed by electrolyzing the solution using nickel anodes and a steel cathode for three hours at a temperature of 50 degrees C., pH of 2.0, and a current density of five amperes per square foot. To insure complete removal of the copper several electrolytic nickel plates were suspended for a day in the solution, the nickel replacing the copper by immersion.

The cathodes used throughout were steel panels a tenth of a square foot in area on which copper was plated from a cyanide bath. In preparation for copper plating the steel plates were well-buffed and electrocleaned in a solution of "Anodex", the concentration of which was six ounces per gallon. Likewise, before nickel plating, the copper plates were buffed to a high polish and electrocleaned in an "Anodex" solution of four ounces per gallon. After being electrocleaned the plates were rinsed first in running water which was followed by an acid dip (20% sulfuric acid by volume), and rinsed again in running water.

All pH measurements were made with a

quinhydrone-calomel electrode system used in conjunction with a Leeds-Northrup potentiometer.

Benzene disulfonic acid modifier:

Seven and one-half grams per liter of the modifier was added to the purified solution and several trial runs were made at a pH of 3.5, current density of 30 amperes per square foot and a temperature of 45 degrees C. for thirty minutes. In each case the deposit was semi-bright. 100 milligrams per liter of zinc ion (0.25 grams zinc sulfate) was then added to the bath and several plates made under the same conditions. These plates showed a definite increase in brightness.

TABLE I

Temperature--45 deg. C., C. D.--30 amps/sq.ft., time, 30 minutes

Plate No.	pH	Condition of deposit
7	1.8	Dull, streaked, foggy
8	2.0	Ditto
10	2.2	Bright, no streaks
11	2.6	Ditto
12	3.0	Ditto
13	3.3	Brighter than above
14	4.2	Foggy
15	5.0	Black, loosely adherent
16*	3.8	Very bright

*0.4 milligrams/liter reduced fuchsin added

The operation of this bath beyond Plate 17 consistently yielded deposits which were black and loosely adherent. The cause of these results proved to be an increase in pH from 3.3 to 4.8 during the thirty minute run, which was an indication that the cathode efficiency may have been lower than the anode efficiency.(3) Checking and cleaning the cathode contacts had no effect on the character of the deposit. The bath was then heated with four grams of activated charcoal for an hour, but this treatment also had no effect. The possibility of decomposition of the benzene disulfonic acid as a cause presented itself at the time, but the bath was discarded in order to start work on another modifier.

The table clearly illustrates that the optimum pH range is 2.2 to 2.8, the upper limit giving the best results. The addition of reduced fuchsin improved the brightness of the deposit considerably.

Benzene sulfonic acid(Monsanto B-668)

The following materials were added to the bath:

Benzene sulfonic acid	7.5	grams/liter
Zinc sulfate	0.25	"
Sodium lauryl alcohol sulfate	0.10	"

TABLE II

Temperature--50 to 60 deg. C., Time-- 30 minutes,

Current Density--30 amperes/square foot

Plate No.	pH	Conc. of Reduced Fuchsin(mg./l)	Condition of deposit
1	2.2	1.0	Dull, bright streaks, ductile
2	2.2	1.0	Ditto
3	3.5	1.0	Semi-bright, edges dull, ductile
4	3.5	1.0	Bright, fogged
5	3.5	2.0	Bright, less fogged
6	3.5	2.5	Dull, slightly brittle
7	2.5	2.5	Dull, streaked, brittle
8	3.8	2.5	Dull, brittle
9	3.8	2.5	Ditto
10*	2.2	0.0	Dull, ductile
11	3.8	0.0	Semi-bright, ductile
12	3.8	0.0	Ditto
13	4.7	0.0	Bright, ductile
14	5.2	0.0	Bright, fogged

It is quite evident from the above data that reduced fuchsin does not act as a brightener for this particular case, at least for the pH range 2.2 to 3.8

Sodium naphthalene disulfonate 2, 7 (Eastman-Kodak--Technical):

Materials added:

Zinc sulfate	0.25 grams/liter
Sodium lauryl alcohol sulfate	0.10 "

*Treated bath with activated charcoal to remove brightener

The purpose of the runs shown in the following tables was to obtain first a set of optimum conditions for plating without a brightener. Then knowing this, a set of optimum conditions was found when reduced fuchsin was added.

TABLE III-a*

Plate No.	pH	Current Density Amps/sq ft	Temperature Degrees C.	Condition of deposit
13	1.8	20	55	Semi-bright, dull streaks
14	1.8	30	55	Semi-bright, less streaks
17	1.8	40	55	Ditto
18	1.8	60	55	Semi-bright, no streaks
20	2.0	20	70	Smooth, milky
21	2.0	30	70	Ditto
22	2.2	60	70	Ditto
24	2.2	20	24	Center bright, edges dull
25	2.2	30	24	Ditto, loosely adherent
23	3.2	60	24	Center bright, edges black, loosely adherent
26	3.2	20	55	Bright, slight fog
27	3.2	30	55	Ditto
28	3.2	60	55	Ditto
29	3.2	30	70	Milky, edges bright
30	3.2	60	70	Milky
31	3.05	20	55	Center bright, edges dull
32	3.05	30	55	Ditto

*2 grams/liter sodium naphthalene disulfonate

TABLE III-a (Continued)

Plate No.	pH	Current Density Amps/sq ft	Temperature Degrees C.	Condition of deposit
33	3.95	60	55	Center bright, edges dull
34	5.0	60	55	Center bright, edges black, loosely adherent
35	5.0	60	55	Center bright, edges dull
36	5.0	30	55	Ditto
37	5.0	30	70	Milky

TABLE III-b

4 grams/liter sodium naphthalene disulfonate

Plate No.	pH	Current Density Amps/sq ft	Temperature Degrees C.	Condition of deposit
38	1.4	30	25	Center bright, edges dull, loosely adherent
39	1.4	30	55	Bright, slight fog
44	1.4	60	55	Ditto
45	2.0	30	70	Milky
46	2.0	60	70	Center bright, edges dull
65	3.2	30	55	Ditto
66	3.2	60	55	Ditto
69	3.2	30	70	Bright, fogged
70	3.6	30	55	Bright
51	3.6	60	55	Bright

TABLE III-c

5 grams/liter sodium naphthalene disulfonate

Plate No.	pH	Current Density Amps/sq ft	Temperature Degrees C.	Condition of deposit
53	3.5	30	58	Bright
55	3.5	60	58	Bright
61	3.5	60	58	Bright
57	3.5	30	70	Center fogged, edges dull
4	3.5	60	70	Bright
60*	3.5	30	70	Bright, slight fog
47*	3.5	60	70	Bright
48**	3.5	60	70	Bright

TABLE III-d

10 grams/liter sodium naphthalene disulfonate
Temperature--70 degrees C.

Plate No.	pH	Current Density Amps/sq ft	Condition of deposit
1	3.5	60	Bright, mottled
2	3.5	30	Dull
3	3.5	30	Bright, mottled
4	3.5	30	Foggy, not mottled
5	3.5	60	Mottled
6	3.5	60	Mottled
7	3.5	60	Mottled
8	3.5	60	Mottled
10	3.0	30	Dull, mottled
11	3.0	30	Slightly mottled
9	3.0	60	Slightly fogged, unmottled
12	3.0	30	Ditto

* 6 grams/liter modifier
**3grams/liter modifier

TABLE III-e

(pH--3.0)

Plate No.	Current Density Amps/sq ft	Temp. Deg C.	Modifer* g/l	Condition of deposit
14	30	70	20	Bright
15	60	70	20	Dull, streaky
16	60	70	20	Ditto
20	60	70	20	Dull, black streaks
21	60	55	20	Bright, " "
22	60	55	20	Ditto
23	60	55	20	Bright center, dull edges
24	30	60	30	Bright
25	30	60	30	Dull, black streaks, ductile
27	30	60	30	Bright, ductile
28	30	60	45	Ditto
29	60	60	45	Dull, black streaks
30	30	60	60	Bright, ductile
31	30	60	60	Ditto

*Sodium naphthalene disulfonate

TABLE IV-a

Current density--30 amps/sq ft, Temp.--60 degrees C.

Plate No.	pH	Modifier* g/1	Brightener** mg/1	Condition of deposit
51	2.5	2.0	1.0	Very bright
52	2.5	2.0	1.0	Bright, slight fog
53	2.5	2.0	1.0	Ditto
54	2.5	4.0	1.0	Ditto
55	2.5	4.0	1.0	Ditto
56	2.5	4.0	2.0	Bright, no fog
57	2.5	4.0	2.0	Ditto
58	3.5	4.0	2.0	Ditto
59	3.5	4.0	2.0	Ditto
60	3.5	4.0	2.0	Bright, slight fog

TABLE IV-b***

Plate No.	pH	Modifier* g/1	Brightener** mg/1	Condition of deposit
1	2.5	5.0	0.0	Bright, dull streaks
2'	2.5	5.0	0.0	Ditto
3'	2.5	5.0	0.0	Ditto
4	2.5	5.0	0.0	Dull, streaked
5	3.5	5.0	0.0	Milky
6'	3.5	5.0	0.0	Milky
7	3.5	5.0	1.0	Bright
8	3.5	5.0	1.0	Bright
9	3.5	5.0	2.0	Bright

* Sodium naphthalene disulfonate
** Reduced fuchsin
*** Current density and temperature as in Table IV-a
' Current density--60 amperes/square foot

TABLE IV-b (Continued)

Plate No.	pH	Modifier g/l	Brightener mg/l	Condition of deposit
10	3.5	5.0	2.0	Bright
11	3.3	5.0	4.0	Bright
12	3.3	5.0	4.0	Very bright
13	3.3	5.0	4.0	Very bright
14	3.3	5.0	4.0	Very bright
15	3.3	5.0	4.0	Bright
16	3.3	5.0	6.0	Very bright, brittle
17	2.8	5.0	6.0	Ditto
18	2.8	5.0	6.0	Bright, brittle
19	2.3	5.0	8.0	Ditto
20	2.8	8.0	8.0	Ditto
21	2.8	6.0	6.0	Ditto
22	2.8	20.0	6.0	Bright, slightly brittle
23	2.3	20.0	8.0	Very bright, slightly brittle
24	2.8	30.0	8.0	Ditto
25	2.3	45.0	8.0	Ditto

Some generalizations concerning the character of the deposits can be made from the preceding data. At temperatures of approximately 24 degrees and low pH the deposit is bright in the center and dull and loosely adherent at the edges for current densities of 20 to 60 amperes per square foot. At a pH of 5.0 the edges become black and loosely adherent. Increasing the temperature to 55 degrees (pH of 5.0) gives the same type of deposit as at a low pH and low temperature.

At a temperature of 70 degrees the deposits are all milky, pH and current density having little or no effect on the character of the deposit.

Table III-a shows that the best deposits are obtained at a pH of 3.2 and current densities of 30 and 60 amperes/square foot. The next two tables show that increasing the concentration of the modifier from four to eight grams per liter has no marked effect on the character of the deposit. Increasing the current density from 30 to 60 amperes/square foot has no effect except at a temperature of 70 degrees in which case the higher current density is better.

The purpose of Tables III-d and III-e is to show the effect of concentration of the modifier on the ductility of the deposit. Some difficulty, however, was encountered when the deposits (Table III-d) became mottled. It was suspected that this effect was due to incomplete washing after removal of the copper plate from the electrocleaner. Consequently, Plate 3 was rinsed in the following manner: water, alcohol, water, sulfuric acid, water, alcohol, water, instead of the usual water,, sulfuric acid, water rinse. This treatment reduced the mottled effect a little as is shown by the next plate. Plates 5-11 were rinsed in the same manner, but the deposits were still mottled. Plates 9 and 12 were electrocleaned in a new solution which eliminated the difficulty.

Table III-e shows the effect of current density and concentration of the modifier. Characteristic of a current density of 60 amperes/square foot is the appearance of black streaks on a bright plate. At a current density of 30 amperes/square foot the plates are bright and increase in ductility with an increase in modifier concentration.

From the data in Table IV-a it is evident that bright deposits can be obtained over a pH range of 2.5 to 3.5 and that the minimum concentration of reduced fuchsin is one milligram per liter since Plate 52 was slightly fogged. Increasing the concentration of the modifier from 2 to 4 grams per liter did not eliminate the fogging. However, upon increasing the brightener content to 2 milligrams per liter (assuming that none of it was consumed during the previous runs) the fog disappeared until four runs had been made, after which the fog reappeared. This illustrates conclusively that the brightener is consumed in some manner. It is the belief of F. A. Maurer(1) that the reduced fuchsin is codeposited with the nickel, or more probably is destroyed or changed at the work surface.

The purpose of Table IV-b is to show the optimum concentration of reduced fuchsin and pH range. The brightest plates were obtained at a pH of 3.3 and a concentration of 4 milligrams/liter of the brightener. The bright range, however, lies within the following limits: pH of 2.8 to 3.5 and 1 to 4 milligrams per liter of reduced fuchsin. Increasing the fuchsin content from 4 to 8 milligrams per liter increased the brittleness of the deposit. An increase in the modifier content from 6 to 20 grams per liter, however, reduced the brittleness to a slight extent. Increasing the modifier content up to 45 grams per liter had no visible effect on the brittleness.

As a summary of the foregoing pages the following procedure is proposed for plating bright nickel in the laboratory from a two liter bath:

Dissolve the required amounts (see page one) of nickel salts in two liters of water by heating. Using ammonium hydroxide raise the pH to about 5.5 (electrometric). Heat the solution to boiling temperature for an hour and after allowing to cool slightly, filter off the precipitated iron. The volume of the solution is then brought up to two liters and the pH lowered to 2.0 with the addition of sulfuric acid. The boric acid can then be dissolved in the solution. Plate for an hour to an hour and a half at a current density of 5 amperes per square foot and a temperature of 40 to 50 degrees C. using nickel anodes and a well-buffed and electrocleaned steel plate as a cathode. The last traces of copper can then be removed by suspending several nickel plates in the solution for a day or two.

To this solution the following materials are added:

Zinc ion	100 mg/l
Sodium lauryl alcohol sulfate	0.1 g/l
Sodium naphthalene disulfonate	4-5 g/l
Reduced fuchsin	2.0 mg/l

Plate for thirty minutes on a well-buffed and cleaned copper surface under the following conditions:

Current density	30 amperes/square foot
pH	3.0 to 3.5
Temperature	50 to 60 degrees C.

Since the brightener is consumed during the plating process, it will be necessary to add reduced fuchsin from time to time. The data which follows deals chiefly with the consumption of the brightener.

The 100 Liter Bath

This bath, which is a modified Harshaw type, has the same composition as the two liter bath used previously. Before any plating could be done several preparations were necessary.

The volume of the bath was first carefully adjusted to 100 liters with distilled water. After stirring the solution thoroughly a sample was withdrawn and the pH measured. Representative samples of the bath were obtained by using a piece of twelve mm. glass tubing which was long enough to reach the bottom of the tank. About 150 cc. of the solution was withdrawn in this manner and then a portion of this was used for the necessary measurements. The pH of the solution was found to be 5.5.

The following method was then used to determine how much acid was to be added to the bath to give the desired pH. A dilute solution of C. P. sulfuric acid was prepared by diluting 10 cc of the concentrated acid to one liter in a volumetric flask. Then a 50 cc sample of the bath was titrated with this acid till the solution turned congo red paper blue denoting a pH of 3.0. Knowing the amount of dilute acid required for 50 cc, a simple calculation gave the amount of concentrated acid to be added to the bath. The pH of the bath after making the addition was 3.0.

The reduced fuchsin was prepared by weighing out exactly one gram of the basic dye on an analytical balance. Concentrated hydrochloric acid was then added to the dye till the color changed from red to yellow. The solution was then diluted to exactly one liter with distilled water and four grams of granulated zinc was added in order to carry out the reduction. When the dye is made acid, one of the phenyl groups changes to a quinone structure, which is reduced by the hydrogen to a saturated aliphatic ring.

The condition of the bath was then determined by making several test plates (copper plated steel panels which were one tenth of a square foot in area) at a temperature of 60 degrees C., current density of 30 amperes/square foot, and a pH of 3.0. These test panels were all milky (evidently due to lack of a brightener) and on bending the plate the nickel deposit separated very easily from the copper base, which indicated that the electrocleaner was inefficient (probably due to overuse). A new cleaner ("Anodex" solution of 4 ounces/gallon) remedied the difficulty.

For prolonged operation of the bath (about two to four hours at a current density of 30 amperes per square foot) a cathode of sheet nickel one square foot in area was used. This cathode was prepared by plating a thin coat of bright nickel on a well-buffed copper plate. The plate was then dipped in a chromium plating bath for about three minutes and after being rinsed carefully in running water a heavy coat (current density of 30 amperes/square foot for one hour) of nickel was plated on this surface. The heavier nickel layer was then stripped quite easily from the plate. The purpose of using the nickel cathode was to conserve the nickel which was plated from the bath.

In the table which follows the bath was operated at a current density of 30 amperes per square foot and a temperature of 55 to 60 degrees C. After each run a test panel was made in order to determine how prolonged operation affected the deposit, which is a measure of the consumption of the brightener.

TABLE V

Plate No.	pH	Brightener added mg.	Amp-hours	Test Plate
1	3.0	200	---	Very bright
2	3.0		170	Ditto
3	3.0		345	Foggy
4	3.0		510	Very foggy
5	3.3		690	Ditto
6	3.5	200	80	Very bright
7	3.5		160	Ditto
8	3.5		240	Bright
9	3.5		320	Bright, slight fog
10	3.5		400	Very foggy
11	3.0	200	---	Very bright
12	3.0		60	Ditto
13	3.0		240	Bright
14	3.5		300	Bright, slight fog
15	3.5		400	Very foggy

In each case after the addition of reduced fuchsin it is seen that very bright test plates were obtained up to about 200 ampere-hours. After 240 ampere-hours of operation there was a decrease in the brightness of the deposit and after 300 ampere-hours the test plate was foggy, the fogginess becoming more pronounced as the operation was continued from this point. This transition is shown very readily by Plates 6 through 10, the last one being very similar to the test plates obtained without a brightener.

Assuming that all the brightener has been consumed at this point and that the consumption is directly proportional to the current passed, it was found that the fuchsin was used up at a rate of 0.50 milligrams per ampere-hour. This result is confirmed by the runs 11 through 15. With this fact then it is possible to calculate how much reduced fuchsin must be added to the bath from time to time in order to maintain a bright deposit.

However, a finer check was desired on how the brightener was consumed and the procedure used was as follows: A series of runs was made with a 30 ampere-hour interval and for each interval a test plate and an analysis of the reduced fuchsin content was obtained. The fuchsin analysis was run according to the following method (anon):

Cool sample of bath to 20 degrees C. and pipette 10 cc into a 100 ml beaker; add 3.5 cc saturated ammonium sulfate and 30 cc isopropyl alcohol while stirring (all nickel salts must be precipitated); filter through Gooch crucible into a 6 x 1 test tube; rinse beaker with 5 cc alcohol and pour into Gooch; transfer test tube to water bath at 80-83 degrees C.; add boiling chip and 1 cc 10% ferric chloride solution; keep at this temperature for half hour adding 1 cc ferric chloride solution after fifteen minutes; at the end of boiling period remove test tube from water bath and add one cc 10% ammonium monoacid phosphate; filter through a 60 degree funnel into 50 ml graduate, dilute to 50 cc and compare with standards.

After running one analysis according to the above procedure, it was observed that the color of the solution after filtering the precipitated nickel was pink and that there was no apparent change in the color after completing the analysis. To check this observation the complete procedure was used on a sample of the bath. Then with another portion of the same sample the procedure was run as far as the addition of the ferric chloride solution. The two solutions obtained after dilution to 50 cc showed no visible difference in color. Consequently, all of the analyses were run according to the latter method.

TABLE VI

Plate No.	pH	Brightener added mg.	Amp-hours	Test Plate
1	3.0	100	---	Bright
2	3.0	100	---	Very bright
3	3.0		30	Ditto
4	3.0		60	Ditto
5	3.0		90	Ditto
6	3.0		120	Ditto
7	3.0		150	Ditto
8	3.0		180	Ditto
9	3.2		210	Bright
10	3.4		240	Bright
11	3.4		270	Bright, slight fog
12	3.4	50	---	Bright
13	3.4	50	---	Very bright
14	3.0	100	90	Ditto
15	3.0		150	Ditto
16	3.0		210	Bright
17	3.3		270	Bright

The data in the above table duplicates quite closely the results shown in Table V. After 270 ampere-hours 135 milligrams of the brightener were consumed, the test plate for the run being slightly fogged. The addition of 50 milligrams of reduced fuchsin caused the fogginess to disappear and another 50 milligram addition, bringing the total up to 135 milligrams, produced a test plate that was very bright.

In all cases the test plates were fairly ductile.

The data for the fuchsin analyses which should have appeared in the table was not available due to the fact that neither a relative comparison nor a comparison with colorimetric standard solutions was possible. A Cenco spectrophotolometer and a Bausch and Lomb colorimeter were used to attempt the comparisons, but neither instrument was sensitive enough. However, the results of this study are not conclusive. The colorimetric standards of the fuchsin in isopropyl alcohol which were prepared were pink in color while the unknown solutions were orange. Therefore, a comparison of the two was not feasible.

Had a comparison been possible the amount of fuchsin actually present in the bath after each run could have been calculated from which data it could have been possible to learn if the brightener was consumed linearly as the current was passed.

SUMMARY

1. Reduced fuchsin when used with benzene disulfonic acid modifier, produces a very bright deposit when the concentration is 0.4 milligrams/liter.

2. When benzene sulfonic acid (Monsanto B035) is the modifier, the addition of reduced fuchsin causes dull, streaky deposits which become brittle when the concentration of the brightener is 2.5 milligrams per liter.

3. Using sodium naphthalene disulfonate as a modifier the optimum plating conditions are:

Modifier	4-6 grams/liter
pH	2.3 to 3.5
Current density	30 amps/sq ft
Reduced fuchsin	2-4 mg/liter

4. Reduced fuchsin when present in amounts greater than 4 milligrams/liter causes the deposit to be brittle.

5. Reduced fuchsin is consumed at the rate of 0.50 milligrams per ampere-hour.

REFERENCES

(1) F. A. Maurer, Cleaning and Bright Plating Steel Parts of Electric Irons. Metal Finishing <u>39</u>; 657-61 (1941)

(2) M. R. Thompson and C. T. Thomas, The Effect of Impurities in Nickel Salts Used for Electrodeposition. Trans. Am. Electrochem. Soc. <u>42</u>, 25-29 (1922)

(3) William Blum and George B. Hogaboom, Principles of Electroplating and Electroforming. pp246, (1930), 2nd Ed.

T546 M397 143860

Maskal