

ELECTROCHEMICAL PRECIPITATION OF GOLD COATINGS WITH INCREASED HARDNESS

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Increase in the durability of gold coating is very important for jewelry articles, apparatus construction, and so on.

It is possible to increase the coating strength either by means of introducing an additive which increases the hardness or by changing the galvanic process conditions for metal deposition. According to literature data [1-3], the presence of nickel salts in the electrolyte acts to increase the hardness of the gold deposit. There have been a few recipes [4-7] for gold plating with nickel additives; however, there has been no systematic investigation of gold-nickel baths and of the coatings obtained in them to the present time. Neither the electrochemical behavior of these baths nor the effect of the galvanic regime on the deposit properties have been studied.

The purpose of the present work was to determine the optimum conditions for depositing gold from gold-nickel baths. The microhardness and abrasion resistance of the coating served as criteria of quality in the coatings obtained.

EXPERIMENTAL

Conditions and method of working. The gold electrodeposition process was conducted in an electrolyte having the following composition: Au (calculated as the metal) 4 g/liter, KCN (free) 16 g/liter; K_2CO_3 was present to the extent of 5 g/liter.

Nickel was added to the above described electrolyte, in the form of a nickel cyanide complex, to the extent of 0.5-4.0 g/liter (calculated as metal).

The experiments were conducted in an electrolyzer of the accumulator type having a volume of 75 ml, operated in a thermostat. The direct current source was a storage battery. The series circuit contained a milliammeter, rheostat, and coulometer. As a cathode base we used sheet brass, Mark L-62. The brass samples were 10 X 15 mm in size. The surface of the samples was thoroughly ground and then polished on a felt wheel with crocus paste. Platinum anodes were located on both sides of the cathode at the same spacing from it (30 mm). Before electrodeposition the cathode base was degreased in dichloroethane, washed in a 4-5% soda solution containing soap, rubbed with a magnesium oxide paste, and (immediately before immersion in the bath) pickled in 15% sulfuric acid.

After electrolysis the deposited gold was polished by hand rubbing with rouge.

Testing the gold coating for its microhardness was performed by an impression method using a PMT-3 microhardness tester.

To obtain comparable data, the tests were performed on samples having the same deposit thickness, equal to 4μ and an impression diagonal of 20μ . Under these conditions the hardness of the base does not show an effect on the coating hardness and the effect of work-hardening is almost completely absent.

The wear-resistance of the coating was determined using a device the main element of which was a brass drum pressed tightly on a cloth. The measure of wear-resistance was the number of rotations of the drum necessary to remove a layer of gold of definite thickness (2μ) to the base metal at a constant pressure on the sample (500 g).

The base metal (copper) was developed using GOST (All-Union Standard) 3247-46.

Measurement of cathode potentials was by the direct method using an "Etalon" type PV-2 potentiometer.

The electrolyte was systematically analyzed for its content of gold, nickel, potassium cyanide, and potassium carbonate. The cathode deposit was analyzed for its nickel content. The gold was determined by attack with sulfuric acid followed by cupellation; nickel, by colorimetry. The free cyanide content was determined using a volumetric method with silver nitrate. Potassium carbonate was determined by titration with hydrochloric acid in the

presence of methyl orange after adding excess silver nitrate and heating the solution to coagulate the precipitate.

Microhardness of Gold-Nickel Coatings

Effect of electrolyte nickel content on the microhardness of the gold deposit. Experiments on investigating the effect of nickel on the microhardness of gold coatings were performed with current densities of 1.0, 1.5, 2.0, and 3.0 A/dm² and at temperatures of 70 and 42°C.

The experimental data are presented in Table 1.

TABLE 1

Effect of Electrolyte Nickel Content on the Microhardness of Gold-Nickel Coatings under Varying Conditions of Their Deposition

Cathode current density (A/dm ²)	Electrolyte nickel concentration (g/liter)	Microhardness of the coating H _{20μ} (kg/mm ²)	Change in microhardness of gold-nickel coatings (%) based on hardness of a gold coating without nickel)
1.0*	0.5	116	108
	1.0	127	118
	2.0	132	122
	3.0	131	121
	4.0	135	125
1.5*	0.5	120	111
	1.0	132	123
	2.0	151	140
	3.0	141	131
	4.0	137	128
2.0*	0.5	149	138
	1.0	158	146
	2.0	172	159
	3.0	158	146
	4.0	153	141
3.0*	1.0	158	146
	2.0	158	146
	3.0	163	151
	4.0	176	163
1.5**	0.5	163	151
	1.0	167	155
	2.0	172	159
	3.0	163	151
2.0**	1.0	167	155
	2.0	172	159
	3.0	172	159
	4.0	172	159

The change in microhardness of the gold-nickel coatings as dependent on the conditions of deposition is expressed as a percentage of the microhardness of a gold coating without nickel added. The microhardness of a gold coating deposited from a bath containing 4 g/liter Au and 16 g/liter KCN at a temperature of 70°C and a current density of 0.3 A/dm² was equal to H_{20μ} = 108 kg/mm².

It can be seen from the data of Table 1 that adding nickel to the electrolyte to the extent of 0.5-4.0 g/liter significantly increases the microhardness of gold coatings.

The highest microhardness value was obtained with nickel contents of 2-4 g/liter with a current density of 2-3 A/dm². The color of the gold-nickel coating after polishing was not different from that of a gold coating without a nickel additive.

Effect of current density on microhardness of gold-nickel deposits. Based on the data of Table 1 we constructed the graph (Fig. 1) characterizing the effect of current density on microhardness of Au-Ni coatings.

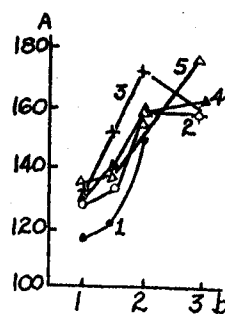


Fig. 1. Effect of current density on microhardness of gold-nickel coatings at a temperature of 70°C. A) microhardness (kg/mm²); B) current density (A/dm²). Ni content (g/liter): 1) 0.5; 2) 1.0; 3) 2.0; 4) 3.0; 5) 4.0.

With increase in current density from 1 to 2 A/dm² the microhardness increases sharply. At 2 A/dm² the curve has a discontinuity, and with further increase in the current density to 3 A/dm² the microhardness either remains the same (1 g/liter Ni), or falls (2 g/liter Ni), or continues to increase slowly (3 g/liter Ni).

* Bath composition: Au 4 g/liter, KCN 16 g/liter, at a temperature of 70°C.

** Bath composition: Au 4 g/liter KCN 16 g/liter, at a temperature of 42°C.

The effect of current density on microhardness of gold coatings was likewise studied by us on deposits obtained from baths containing 2 g/liter Au and 4 g/liter Ni.

The test data are given in Table 2.

TABLE 2

Effect of Current Density on Microhardness of Gold-Nickel Coatings. Bath composition: Au 2 g/liter, Ni 4 g/liter, and KCN 16 g/liter; temperature 70° C.

Cathode current density (A/dm ²)	Microhardness of the coating H _{20μ} (kg/mm ²)	Change in microhardness of gold-nickel coatings (% based on hardness of a gold coating without nickel)
1.0	163	151
2.0	195	180
3.0	195	180
4.0	185	171

current density, reaching a maximum (195 kg/mm²) at 2-3 A/dm². The comparative values for microhardness of gold-nickel coatings given in Tables 1 and 2 show the utility of the latter; however, because of their color (brownish tint) they do not satisfy requirements of appearance.

Effect of temperature of microhardness of gold-nickel coatings. By comparing the data of Table 1 obtained at temperatures of 42 and 70° C, it can be seen that reducing the temperature over these limits leads to increase in microhardness; however, a very dark gold deposit is obtained after electrolysis.

Effect of electrolyte potassium cyanide concentration on microhardness of gold-nickel coatings. The effect of potassium cyanide was studied with an electrolyte containing Au 4 g/liter and Ni 2 g/liter at a temperature of 70° C with D_C = 2 A/dm².

Results of the tests are given in Table 3.

The data of Table 3 show that increasing KCN concentration does not increase the microhardness.

Effect of electrolyte potash concentration on microhardness of gold-nickel coatings. The effect of potash was studied over the wide concentration limits of from 4.9 to 103.4 g/liter.

The experimental data were obtained with a bath containing 4 g/liter Au, 2 g/liter Ni, and 15 g/liter KCN, at a temperature of 70° C with D_C = 2 A/dm², and are given in Table 4.

TABLE 4

Effect of Potash on Microhardness of Gold-Nickel Coatings

K ₂ CO ₃ content (g/liter)	Microhardness H _{20μ} (kg/mm ²)	Remarks
4.9	168	The color of the coating was no different from that from a pure Au bath.
15.5	170	
29.7	167	
96.1	167	
103.4	155	

TABLE 5

Effect of Gold on Microhardness of Gold-Nickel Coatings

Au electrolyte concentration (g/liter)	Microhardness H _{20μ} (kg/mm ²)	Remarks
1.0	190	Coating color was yellow with a brown tint
2.0	185	The same
3.0	163	Pale yellow color
4.0	153	Yellow color
5.0	152	The same

It can be seen from the data of Table 4 that increasing the K₂CO₃ content to 103.4 g/liter has an insignificant effect on reducing coating microhardness.

* The color of the coating was no different from that of pure gold in all of the tests.

** Scaly deposit

Effect of Electrolyte Gold Concentration on Microhardness of Au-Ni Coatings

The effect of gold concentration was studied in an electrolyte containing 3.85 g/liter Ni with a current density of 2 A/dm² at a temperature of 70°C. The gold concentration was varied over the limits from 1 to 5 g/liter.

Test results are given in Table 5.

It can be seen from the data of Table 5 that increasing the electrolyte gold content from 1 to 5 g/liter leads to a decrease in microhardness from 190 to 152 kg/mm². The coating color varies from yellow with a brownish tone to normal.

Wear-Resistance of Gold-Nickel Coatings

The method of determining wear resistance of gold coatings has been described above. The tests for wear resistance were performed under a loading on the sample of 500 g.

The test data are presented in Table 6.

TABLE 6

Results of Testing Wear Resistance of Gold Coatings

Electrolyte composition (g/liter)			Current density (A/dm ²)	Temperature (°C)	Coating thickness (μ)	Number of rotations of the wear drum	Wear resistance of gold-nickel coatings (% of wear resistance of pure gold coating)
Au	Ni	KCN					
4.0	0	16.0	0.3	70	2	1400*	100
4.0	1.0	16.0	2.0	70	2	2300	164
4.0	2.0	16.0	2.0	70	2	2300	164

* This number is the average of 8-10 tests.

It can be seen from the data of Table 6 that the wear resistance of gold-nickel coatings is 1.64 times greater than the wear resistance of gold coatings without nickel added.

Current Yield During Deposition of Coatings from Gold-Nickel Baths

Effect of nickel concentration. The effect of nickel concentration on current yield was determined under the following conditions: bath composition 4 g/liter Au and 15 g/liter KCN, $D_c = 2$ A/dm², at a temperature of 70°C.

The experimental data are presented in Table 7.

TABLE 7

Effect of Nickel Concentration on Current Yield

Nickel concentration (g/liter)	Current yield (%)
0.5	24.9
0.5	23.5
1.0	21.0
2.0	25.0
2.0	20.9
3.0	20.9
4.0	20.7

TABLE 8

Effect of Gold Concentration on Current Yield

Gold concentration (g/liter)	Current yield (%)
1.0	7.7
2.0	9.6
3.0	13.8
4.0	20.7
5.0	22.1

It can be seen from the data of Table 7 that the electrolyte nickel concentration has almost no effect on current yield, which varies within the limits from 20.7 to 25.0%.

Effect of gold concentration. The effect of gold concentration on current yield was studied under the following deposition conditions: bath composition Ni 3.85 g/liter and KCN 17.9 g/liter, $D_c = 2$ A/dm², at a temperature of 70°C. The test data are given in Table 8.

The data of Table 8 show that increasing the gold concentration from 1.0 to 5.0 g/liter increases current yield from 7.7 to 22.1%.

Effect of potassium cyanide concentration. The effect of KCN concentration on current yield was investigated with the following electrolyte composition and process regime: Au 4 g/liter, Ni 2 g/liter, K_2CO_3 7.5 g/liter, $D_c = 2 \text{ A/dm}^2$, at a temperature of 70°C.

The experimental data are given in Table 9.

TABLE 9

Effect of Potassium Cyanide Concentration on Current Yield

KCN concentration (g/liter)	Current yield (%)
8.8	26.2
8.8	22.3
29.5	18.6
50.8	12.1

TABLE 10

Effect of Potash Concentration on Current Yield

K_2CO_3 concentration (g/liter)	Current yield (%)
4.9	22.5
12.1	18.0
62.7	16.7
103.4	13.0

As is shown by the data of Table 9, the current yield falls from 26.2 to 12.1% with increase in KCN concentration from 8.8 to 50.8 g/liter.

Effect of potash concentration. The effect of K_2CO_3 on current yield was studied in an electrolyte containing: 4 g/liter Au and 12.5 g/liter KCN; $D_c = 2 \text{ A/dm}^2$, at a temperature of 70°C.

Results of these experiments are given in Table 10.

Increase in K_2CO_3 concentration from 4.9 to 103.4 g/liter reduces the current yield from 22.5 to 13.0%.

Effect of temperature on current yield was studied over the temperature interval from 16 to 70°C under the following conditions: Au 4 g/liter, Ni 1.6 g/liter, KCN 8.8 g/liter; $D_c = 2 \text{ A/dm}^2$.

Results of the experiments are given in Table 11.

TABLE 11

Effect of Temperature on Current Yield

Temperature (°C)	Current yield (%)
16	16.0
33	15.8
42	18.0
70	22.0

TABLE 12

Effect of Current Density on Current Yield

Current density (A/dm^2)	Current yield (%)
1.0	22.9
1.5	25.0
2.0	20.9
3.0	23.3

Changing temperature from 16 to 70°C increases current yield from 16 to 22%.

Effect of current density on current yield in gold-nickel baths. The effect of current density was studied in an electrolyte containing: Au 4 g/liter, Ni 2 g/liter, and KCN 8-12 g/liter; the temperature was 70°C.

The results of experiments performed are presented in Table 12.

Change in current density over range 1-3 A/dm^2 hardly shows any effect on current yield.

Cathode Polarization

We studied the shapes of polarization curves (Fig. 2) obtained in baths of varying composition.

Curve 1 was obtained in a bath containing Au 4 g/liter and KCN 11 g/liter at a temperature of 70°C without addition of nickel.

Curve 2 was obtained under the same conditions as was curve 1, but in presence of 2.5 g/liter Ni and with a KCN content of 20.3 g/liter.

Curve 3 was obtained with an electrolyte content of 2.95 g/liter Ni and 15.97 g/liter KCN at a temperature of 70°C.

Curves 1 and 2 consist of two parts connected by a portion with a limiting current. The first part of both curves corresponds to separating the metal (gold), the second part - to separating the metal and hydrogen (for curve 1 it is $\text{Au} + \text{H}_2$, for curve 2 it is $\text{Au} + \text{Ni} + \text{H}_2$).

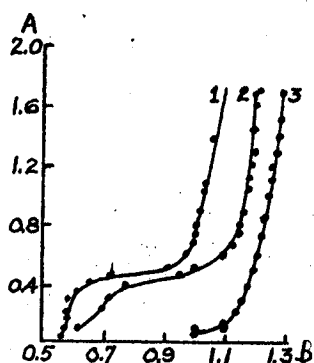


Fig. 2. Cathodic polarization in cyanide, gold, and nickel solutions at 70° C. A) Current density (A/dm^2); B) Cathode potential (V). Bath composition: (g/liter): 1) Au 4, KCN 11; 2) Au 4, Ni 2.5, KCN 20.3; 3) Ni 2.95, KCN 15.97.

In curve 3, evolution of hydrogen begins already at low current densities; here transition from deposition of metal to evolution of hydrogen takes place without a region showing a limiting current.

Analysis of coatings obtained from an electrolyte containing 4 g/liter gold, 2 g/liter nickel, and 8-12 g/liter KCN, showed that: 1) nickel was not detected in deposits obtained with a current density of $0.2 \text{ A}/\text{dm}^2$, and 2) with a current density of $2 \text{ A}/\text{dm}^2$ the deposit contains 0.32-0.40% Ni based on the weight of the gold deposit. Deposits obtained from baths containing 2 g/liter Au and 4 g/liter Ni showed nickel contents of 1.90-1.93%.

DISCUSSION OF RESULTS

We investigated the effect of adding nickel on microhardness and wear resistance of gold coatings.

The effects of other factors were also determined on current yield in gold-nickel baths, and polarization curves were plotted.

It was found that already with a content of 2 g/liter nickel and 4 g/liter gold with a current density of $2 \text{ A}/\text{dm}^2$, the microhardness of the deposit was approximately 1.6 times greater than the microhardness of pure gold deposited using a current density of $D_c = 0.3 \text{ A}/\text{dm}^2$ at a temperature

of 70° C; in this the coatings obtained were sufficiently smooth and could not be distinguished from pure gold coatings after polishing.

When using a bath containing 4 g/liter Ni and 2 g/liter Au, the microhardness was even higher (about 1.8 times), however the color of the coating did not meet requirements applicable to decorative coatings.

Tests on wear resistance gave good similarity to data on microhardness. Thus, a deposit obtained from a bath with 4 g/liter Au and 2 g/liter Ni with a current density $D_c = 2 \text{ A}/\text{dm}^2$ at a temperature of 70° increased the resistance to abrasion by 1.6 fold as compared with a deposit of gold from a normal bath (4 g/liter Au, $D_c = 0.3 \text{ A}/\text{dm}^2$, at a temperature of 70° C).

Comparison of the polarization curves indicates that adding nickel shifts the potential for hydrogen evolution into the region of higher electronegative values; this enables us to conduct the metal deposition process in a wider interval of current densities.

The current yield in a gold-nickel bath does not exceed 30%. The strongest variations in current yield are shown by change in Au and KCN concentrations. With increase in the Au concentration and with decrease in free KCN concentration, the current yield falls.

The effect of potash is shown at very high concentrations (100 g/liter). Changes in nickel concentration and in temperature have almost no effect on current yield.

Despite the fact that the current yield in the gold-nickel bath is about 3 times smaller than in a gold bath without addition of nickel, it should be noted that the attainable current density is about 6 times greater, and that consequently, the rate of plating the metal is some 2 times greater than in an ordinary bath.

SUMMARY

1. The following electrolyte is recommended for gold plating: gold chloride (calculated as metal) 4 g/liter, nickel cyanide (calculated as the metal) 2 g/liter, potassium cyanide (free) 16 g/liter, current density $2 \text{ A}/\text{dm}^2$, temperature 70° C. Insoluble anodes (platinum).

2. The microhardness and wear resistance of coatings obtained from this electrolyte are 1.6 times greater than those from an electrolyte without nickel added.

3. The coating color is not different from usual.

4. The rate of deposition is increased about 2 fold.

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