Economical Alternative for Nickel-free Gold Coatings

P. Parthasarathy,

Surface Chem Finishers, 46-47, Doddanna Indl. Estate, Peenya II Stage, Viswaneedam Post, BANGALORE 560 091

European Economic Community, by the directive 76/769 of European Union (E.U). bans the use of nickel containing articles coming into contact with skin, if the rate of nickel release from these articles are more than 0.5 $\mu g/cm^2$ of exposed area per week [1]. These articles cover gold / silver plated jewellery items (such as ear rings, necklaces, bracelets & chains) as well as watch case parts & straps and spectacle frames containing nickel as under coats.

European dermotologists are of the opinion that 10 to 20% of the female and 1 to 10% of the male population suffer from nickel dermatitis [2]. Based on a study conducted in a public hospital in Spain [3], it is found that 29.4% of men and 54% of women have tested positive of nickel contact allergy. The allergic skin sensitisation to nickel is caused mainly due to sweat and once sensitisation occurs, it remains for the rest of the life of the affected person. The sensitisation is more pronounced in cases of nickel containing jewellery used in pierced earrings and in watch parts that come in contact with our skin.

There is no clear-cut guideline from EU for a test to determine the amount of nickel released by a watch component in a week [4]. It is interesting to note the effect of gold jewellery on skin contact and the formation of black patches on skin have been studied [5].

Test for Nickel Release Limit

One method (Danish test given below) has been suggested [6].

Danish-Test for Nickel Alloys For Possible Nickel-Allergy

Reagents

- 1% Solution of dimethylglyoxime in Ethyl alcohol
- 10% ammonium hydroxide solution in water

Method of Analysis

Two drops of each solution are placed on a cotton swab stock which is rubbed against the item under test for 30 seconds by an even movement. The colour of area ranging from faint rose to heavy cherry red is taken as an indication that the liberation of Nickel exceeds 0.5 micro gm/cm^2/ week.

Another method (given below) uses synthetic sweat. This is being used by Hong Kong platers [7] to test the presence of nickel ions.

Synthetic Perspiration Test

Composition of Synthetic Perspiration

NaCl	-	20 gm/ltr
NH_4Cl	-	17.5 gm/ltr
Urea	-	5 gm/ltr
Acetic acid	-	2.5 gm/ltr
Lactic acid	-	15 gm/ltr
NaOH	-	To adjust pH 4.7

The Test

The vessel shall be filled with the solution to a depth of about 10 mm. The samples shall be

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suspended on a glass hook at a distance of 30 mm from the liquid and the walls of the vessel. temperature shall be 40 ±2°C.

In this test the watch parts are soaked in the above solution for seven days and then tested for the presence of nickel ions. Here only the average Ni content over the entire surface is obtained but in reality the upper portion of a watch part does not come into skin contact.

However many other companies - particularly in Europe, North America and Japan - are contemplating on enforcing a ban and regulations on nickel containing coatings. Therefore the demand for nickel free coatings in jewellery and watch industries are growing rapidly.

ALTERNATIVES

Nickel has been a proven under coat since long [8] for decorative gold and silver plating because of its excellent properties of leveling and brilliant luster as well as its functioning as an effective diffusion barrier layer, exhibiting good corrosion resistance properties. Therefore the coatings which can substitute nickel should offer similar or improved characteristics with respect to brightness, corrosion and wear resistance so that the decorative function of the gold top coat lasts longer. This paper deals with, experiments on some nickel-free undercoats and evaluating the same for its corrosion and wear characteristics, with due consideration of the process.

The first alternative for nickel-free coating in watch industry can be **Plasma Vapour Deposition (PVD)** process of coating TiN (0.5-1.0 micron) followed by gold (0.1-0.2 micron). However, an effective diffusion barrier is required to be coated for brass/ zinc alloy base metals by wet process before PVD coating [9]. A nickel-free undercoat by wet plating is required before PVD can be attempted. It is to be noted here that, the PVD coating cost mainly depends on the high cost of equipments and its import. In most of the cases, 75-80% of the customer's cost is absorbed by the plant's machine hour cost alone, and the real precious metal value the customer gets is very low. On the contrary, in conventional wet gold plating, almost 75% of the cost paid by the customer is for the precious metal itself.

EXPERIMENTAL

The experiments were conducted on watch bezel parts of brass metal with various under coats (Table 1). Pretreatment of the base metal in all the cases were done with utmost care to ensure good performance of the subsequent coatings. Absence of bright nickel necessitates, a suitable coating, that can offer the brightness and good leveling property as well as a diffusion barrier, for which bright acid copper is chosen even though the acid copper alone has poor corrosion performance without any suitable top coats. A thickness of 5 micron of acid copper is plated after a cyanide copper flash in all cases.

In process A of the study (Table 1), pure palladium of thickness of 0.2 microns is coated over the acid copper to prevent migration of copper ions. Since the pure palladium offers practically a pore-free coating [10]. It impedes the diffusion of copper and also it is white in colour. Bath Composition For Palladium Deposition is given below.

Table 1

Various Nickel-free Process Layouts

Base Metal: Brass

Acid Copper 5 micron in every case is followed by	
Process A	Pd Co-2 Micron
Process B	Cu-Sn Alloy 3 micron
Cu-Sn Alloy	Silver(2 micron)
	Palladium (0.2 micron)
Followed by Gold (1.2 micron) in every case	

Process B deals with acid copper followed by copper-tin alloy (white bronze) coating to a thickness of 3 micron (Bath composition given below). Copper-tin offers excellent hardness and corrosion behaviour and has brilliant white colour. Under the name Speculum, these metallurgical alloys have been used since ancient time and rank among the oldest known.

Composition of The Pd Plating Bath

Palladium Diamino Dichloride (as Pd) g/lit	8-12
Conducting salts g/ltr	90
Complexing agents g/ltr	10
pH electrometric	9.5
Density of Bath Be at 25°C	9.0
Temperature °C	55 - 60
Cathode Current Density A/dm²	0.3 - 0.6
Anodes	Pt - Ti
Time to deposit 1 micron (at 0.5 A/dm²)	6 - 8 min
Agitation	Required
Hardness of coating Hv	240

Process C deals with acid copper 5 micron followed by silver plating about 3 microns (Bath composition given below), with a silver strike in between. Beneath gold layer, silver is far superior to nickel - a fact that can be attributed to the blocking of existing pores [11]. However the drawback is the migration of silver and hence the possibility of formation of silver sulfide over gold layers. This phenomena necessitates overcoating of silver with palladium of 0.2 micron before gold plating.

Copper-Tin Alloy Plating Bath Composition

Copper Salt (as Cu) g/ltr	9
Tin Salt (as Tin) g/ltr	45
Free Cyanide g/ltr	12
pH electrometric	12-13
Temperature °C	60
Cathode Current Density A/dm²	1.0-2.0
Anodes	Graphite
Time to deposit 1 µm (at 1.5 A/dm²)	3 min
Agitation	Required
Hardness of coating Hv	550

Silver Plating Bath

Silver Metal g/ltr	45
KCN g/ltr	90
Potassium carbonate g/ltr	20
Brightners	As required
pH	12.0-12.5
Anodes	Silver
Cathode Current Density A/dm²	1.0
Agitation	Essential
Hardness Hv	110
Time to Deposit 1 µm (at 1 A/dm²)	1 min. 30 sec

In all the 3 cases the watch bezels are finally over coated with 23.5 Kt hard acid gold to a thickness of 1 and 2 microns after the usual gold flash plating. Post treatment of gold plated parts are most important factor in respect of pore sealing. A hot demineralised water rinse at 90°C for 5 min followed by ultrasonic cleaning at 65°C for 2 min were followed.

In certain quarters yellow bronze (80 Cu % - 20 Tin %) is being favoured as nickel-free undercoat. But this coating has poor corrosion and tarnish resistance. In addition, the yellow colour could mislead the customer as the top coated gold wears out. Also yellow bronze baths are difficult to control. Bright tin [12] could be another option, but the coatings are too soft.

EVALUATION

The parts plated from the above three processes were subjected to various corrosion and wear testing. The adhesion of these coating layers were tested by Thermal shock method [13] - by heating the parts at 250°C for 60 minutes and quenching in water. The parts are inspected for blisters and peel-off. There has been no adhesion failure in all the three cases. The thickness of various coatings were ascertained by weight-area method taking into account the various deposit densities.

Corrosion Testing

Corrosion is evaluated by Porosity testing by nitric acid vapour test [14], ammonia vapour test and by Synthetic perspiration test. Procedures are given below.

HNO_3 Vapour Test

Samples are thoroughly cleaned before they are taken for testing. The ambient temperature of the specimens and solution shall be 23±3°C during the test period. Nitric acid is added to the chamber and sealed with a cover. After 30 min, the cover is lifted, the samples are loaded using suitable fixtures, and the cover resealed. Unless otherwise specified, the test duration is 1 h±10 min for gold coatings on copper or copper alloys and 2 h± 10 min for nickel substrates and under plates. The samples are removed at the end of test and oven-dried at 125±5°C for 30±5 min. Fresh nitric acid solution is used for each test.

NH_3 Porosity Test

Ammonia solution (10%) is added to the chamber and the cover resealed. After 30 min, the cover

Table 2

Corrosion Testing

TEST PROCEDURE	PROCESS A Acid Cu+Pd followed by Gold(1.2 mg) in each case	PROCESS B Acid Cu+Sn	PROCESS C Acid Cu+Ag+Pd+	Conventional Ni (7micron
Nitric Acid Vapour 1hr exposure	Mild corrosion	No corrosion	No corrosion	Mild Corrosion
Ammonia Vapour 24 hr exposure	Mild corrosion	No corrosion	No corrosion	No Corrosion
Syn. Perspiration 5 hours at 40°C. 16 hr Room temp	No corrosion	No corrosion	No corrosion	No corrosion

is lifted, the samples are loaded using suitable fixtures and the cover resealed. The test duration is 24 hrs. The samples are removed at the end of test and oven-dried at 125±5°C for 30± min. Fresh ammonia solution is used for each test.

The parts are tested simultaneously along with conventional bright nickel (7 microns) + gold plated. The results are shown in Table 2.

Wear Testing

The standard test procedures, such as ISO 3160/3 : Watch cases and their accessories - Gold alloy coverings - part three. Abrasion resistance test on a type of coating applies to samples of flat shapes with specially prepared coatings subjected to an abrasive medium. Extensive work has been done using *A rider flat device* to evaluate the wear of gold coatings [15]. By these methods, it becomes difficult to assess wear to that of finished product. Therefore a simple

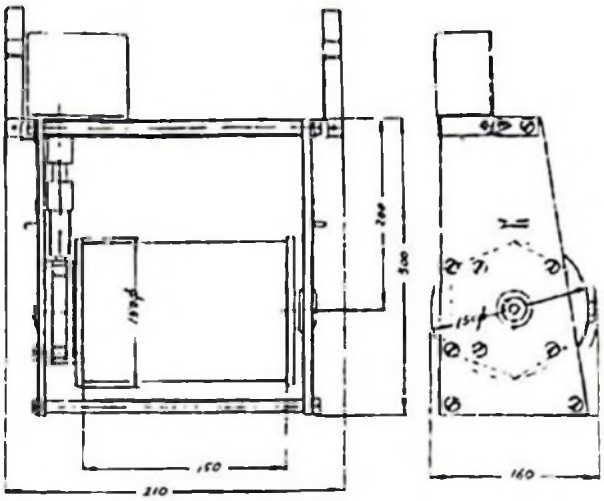


Fig 1 Wear Testing Equipment
Test Conditions: Media - Glass beads: Size - 3 mm dia: Quantity - 1 litre by volume: RPM - 12

method of evaluation of wear is done as per Fig 1, which can be done easily by any well equipped plating shop. The extent of wear is evaluated by weight loss of the coatings. The results are summarized in Table 3. In order to assess the wear in a more realistic

Table 3

Wear Test Results
Speciman Acid Cu 5µ, Pd 0.2µ, Cu-Sn 3µ Ag-3µ, Ni-7µ

Time	Process A Acid Cu+Pd+Au		Process B Acid Cu+Cu-Sn+Au		Process C Acid Cu+Ag+Pd+Au		Ni plated 7 mg + Au	
In Water								
Au micron	1	2	1	2	1	2	1	2
24 hr	2 mg	3 mg	1 mg	2 mg	Nochange	1 mg	4 mg	4 mg
48 hr	4 mg	5 mg	3 mg	5 mg	2 mg	2 mg	6 mg	7 mg
Wear test with Synthetic Perspiration Solution								
24 hr	4 mg	4 mg	2 mg	2 mg	2 mg	2 mg	4 mg	3 mg
48 hr	6 mg	5 mg	3 mg	5 mg	3 mg	4 mg	6 mg	6 mg

way, the studies were conducted with the same equipment and by using synthetic sweat solution in place of water and the results are also included in Table 3.

DISCUSSION

From the data presented in the study, it is obvious that process A (acid copper + palladium + gold) is best suited for inexpensive costume jewellery and parts of low cost watchs with some compromise on performance characteristics; process B (acid copper + copper-tin + gold) fits medium range market with copper-tin coating cost being marginally higher than conventional nickel plating cost. Process C (acid copper + bright silver + palladium + gold) may be ideal for high end watch market, with double precious metals as undercoats.

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