Quantitative Characterization of Rhodium and other Platinum Group Metal Electrodeposits.

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Electrodeposits of platinum group metals, such as rhodium, have often been compared for "whiteness" and "brightness" although these terms are poorly defined. The objectives of this paper are to establish a more precise terminology for defining the appearance of these deposits and indicate the influence of addition agents on this feature for rhodium. A comparison of various platinum group metal deposits is also presented using these terms.

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Introduction

The Platinum Group Metals (PGM) are referred to as precious metals because they are both rare and noble. Their rarity causes them to be valuable and their nobility implies that they are corrosion and tarnish resistant. These intrinsic properties have led to their use as both decorative and electronic finishes. Electroplating processes have been developed for most of these metals, the most commonly plated ones being palladium, palladium alloys, rhodium, platinum and ruthenium.

Palladium, palladium-nickel and palladium-cobalt with a gold-flash are well established as contact finishes and are preferred to hard gold plating in many electronic applications.[1, 2, 3] These deposits have also found extensive decorative use on watchcases and straps, eyeglass frames and costume jewelry.[4, 5]

Rhodium deposits are extremely hard and the metal has a high resistance to spark erosion. These properties have made it an ideal finish for the contact areas of reed switches and other relatively high load electronic contacts. Ruthenium is also applied to similar contacts, though generally those that operate at lower loads. Due to its "blue-white" color, rhodium has long been favored as a decorative finish for jewelry items. Of all the white metals, other than silver, rhodium is considered to be the whitest.

The corrosion protection of surfaces subjected to very high temperatures can be achieved by plating them with platinum. An excellent example of this application is the turbine blades used in aircraft engines. Some insoluble anodes are manufactured by electroplating titanium or niobium with platinum.

The appearance of an electrodeposit is of paramount importance in decorative applications but can be important in more functional uses also. In some cases a lack of "brightness" is indicative of a problem (e.g. on contacts which are to withstand significant sliding wear); in other cases obtaining bright deposits from a process that should be producing "dull" ones may indicate solution contamination. In any case, it is highly desirable to be able to define deposit appearance objectively.

Electroplated rhodium was chosen as the first deposit for investigation using techniques and considerations described in a previous paper.[6] Decorative deposits of this metal are often compared for "brightness" and "whiteness", the comparisons being totally subjective. Disputes occur due to differences between two observers' interpretation of the terminology.

Table 1. Rhodium Plating Solutions.

Solution Number	Rhodium, g/L	Sulfuric Acid, ml/L	Additive Designation	Additive Concentration, ml/L
1	2	25	None	None
2	2	25	A	40
3	2	25	A	120
4	2	25	A	200
5	2	25	B	3
6	2	25	B	6
7	2	25	B	9
8	2	25	C	10
9	2	25	C	20
10	2	25	C	30
11	5	25	D	150

Notes:
a. Solution #1 is without any additives.
b. Additive A is used for general-purpose applications.
c. Additive B is used for decorative applications.
d. Additive C is used for decorative applications.
e. Additive D is used for electronic applications where low stress at higher thickness is required.
f. All solutions were operated at 45°C.

Table 2. Palladium, Platinum and Ruthenium Plating Solution Parameters.

Solution Number	Metal	Solution Type	Solution pH	Operating Temp, °C
12	Pt @ 12 g/L	Hydroxide	12+	80
13	Ru @ 5 g/L	Nitrilo-chloride	1.5 – 2.0	70
14	Pd @ 10 g/L	Ammoniacal	7.5	35

Experimental

A single batch of rhodium sulfate concentrate was used to prepare the plating solutions listed in Table 1.

It was decided to plate sets of panels at approximately 0.25 µm (0.000010 inch) and 1.0 µm (0.000040 inch), typical values for decorative and electronic applications respectively. Since current density may have an effect on deposit appearance, two plating conditions were selected, 1.1 A/dm (10 A/ft) and 2.2 A/dm (20 A/ft). Two panels were plated at each condition making 8 samples processed in each solution formula.

In order to evaluate the influence of grain refiners and brighteners, three additives in common use were selected (referred to here as A, B and C). Each was introduced to a standard rhodium plating solution at 3 concentrations and 8 panels were plated as described above at each concentration. Additionally, a stress-reducing additive (D) was introduced to a rhodium solution typical of those used to plate dull, low stress deposits for special electronic applications. Again 8 panels were plated, making a total of 88 samples in all.

Finally deposits of platinum, palladium and ruthenium were prepared on similar substrates for direct comparison with rhodium. Solution parameters are listed in Table 2, and the entire sample matrix is presented in Table 3.

The plated samples were prepared using polished brass panels. These were 0.5 mm (0.020 inch) thick so that they were rigid and flat. The surfaces were polished to an average roughness (Ra) of approximately 110 Å.

Pretreatment consisted of an electrolytic degrease and a mild acid dip. No pre-plates were used except for the usual gold strike under the ruthenium.

The reflectivity of each panel was measured in 2 places using a spectrophotometer, these measurements included the specular component of the reflected light. We chose to identify the "whiteness" of these deposits according to the CIE 1976 method.[7]

In this system there are 3 components used to quantify the color of the surface under test. These are L*, the "lightness" where 0 is black, 50 is gray and 100 is white; a*, the red-green component; and b*, the blue-yellow component. See Figure 1.

Results and Discussion

It was realized that the red-green component of these results was of little significance and that the color of these deposits is adequately described by L* and b*.

Table 4 summarizes the reflectivity results by using an average of 4 readings per set of conditions.

Figures 2 through 6 illustrate the data graphically by plotting "L" against "b*". Note that all the original data points have been used to create these figures.

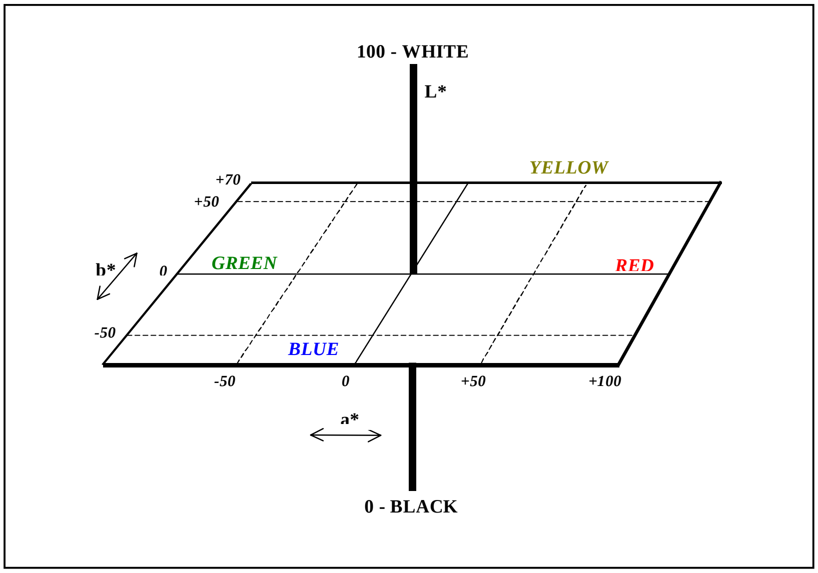

Figure 1. The Hunter *L*, *a*, *b* diagram on which the CIE 1976 *L, *a**, *b** system is based.**

Table 3. Test panel matrix showing current density and resulting deposit thickness.

Solution Number		**Panel Numbers**							
		1	2	3	4	5	6	7	8
1	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.275 (11)	0.25 (10)	1.025 (41)	1.05 (42)	0.3 (12)	0.3 (12)	1.1 (44)	1.025 (41)
2	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.175 (7)	0.275 (11)	1.075 (43)	1.125 (45)	0.3 (12)	0.3 (12)	1.1 (44)	0.975 (39)
3	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.3 (12)	0.375 (15)	1.05 (42)	1.05 (42)	0.3 (12)	0.275 (11)	1.05 (42)	1.0 (40)
4	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.3 (12)	0.275 (11)	1.0 (40)	0.975 (39)	0.25 (10)	0.25 (10)	1.075 (43)	1.025 (41)
5	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.25 (10)	0.25 (10)	1.0 (40)	1.0 (40)	0.3 (12)	0.3 (12)	1.075 (43)	1.025 (41)
6	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.2 (8)	0.25 (10)	1.025 (41)	1.0 (40)	0.25 (10)	0.25 (10)	1.0 (40)	0.975 (39)
7	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.225 (9)	0.25 (10)	1.0 (40)	1.025 (41)	0.275 (11)	0.275 (11)	1.025 (41)	1.025 (41)
8	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.3 (12)	0.3 (12)	1.125 (45)	0.925 (37)	0.3 (12)	0.275 (11)	0.95 (38)	0.9 (36)
9	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.275 (11)	0.25 (10)	1.075 (43)	0.9 (36)	0.3 (12)	0.25 (10)	1.0 (40)	0.95 (38)
10	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.3 (12)	0.275 (11)	1.0 (40)	1.0 (40)	0.325 (13)	0.275 (11)	1.0 (40)	1.025 (41)
11	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.3 (12)	0.3 (12)	1.075 (43)	1.05 (42)	0.3 (12)	0.3 (12)	1.0 (40)	1.0 (40)
12	A/dm^2 (A/ft^2)	0.9 (8)	0.9 (8)	0.9 (8)	0.9 (8)	0.4 (4)	0.4 (4)	0.4 (4)	0.4 (4)
	µm (µin)	0.25 (10)	0.25 (10)	0.95 (38)	0.925 (37)	0.225 (9)	0.225 (9)	0.925 (37)	0.95 (38)
13	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.25 (10)	0.25 (10)	0.85 (34)	0.85 (34)	0.275 (11)	0.275 (11)	0.85 (34)	0.775 (31)
14	A/dm^2 (A/ft^2)	2.2 (20)	2.2 (20)	2.2 (20)	2.2 (20)	1.1 (10)	1.1 (10)	1.1 (10)	1.1 (10)
	µm (µin)	0.325 (13)	0.3 (12)	1.075 (43)	1.025 (41)	0.275 (11)	0.25 (10)	1.125 (45)	1.1 (44)

Table 4. Spectrophotometric results.

Solution Number	Panel Numbers	CD (A/ft^2)	Nominal Thickness (μin)	"L*"	"b*"
1	1 & 2	20	10	87.66	4.66
(Rh)	3 & 4	20	40	87.55	4.87
	5 & 6	10	10	86.57	5.70
	7 & 8	10	40	85.15	7.22
2	1 & 2	20	10	82.35	5.81
(Rh)	3 & 4	20	40	66.43	11.65
	5 & 6	10	10	78.00	8.34
	7 & 8	10	40	62.44	10.94
3	1 & 2	20	10	84.95	4.35
(Rh)	3 & 4	20	40	75.94	5.13
	5 & 6	10	10	86.17	3.58
	7 & 8	10	40	85.48	2.65
4	1 & 2	20	10	86.05	3.60
(Rh)	3 & 4	20	40	84.18	4.02
	5 & 6	10	10	86.98	3.01
	7 & 8	10	40	87.30	2.33
5	1 & 2	20	10	88.80	3.77
(Rh)	3 & 4	20	40	88.99	3.74
	5 & 6	10	10	88.38	4.14
	7 & 8	10	40	88.31	4.46
6	1 & 2	20	10	88.64	3.89
(Rh)	3 & 4	20	40	89.10	3.58
	5 & 6	10	10	88.17	4.40
	7 & 8	10	40	88.36	4.23
7	1 & 2	20	10	89.48	3.07
(Rh)	3 & 4	20	40	89.47	3.17
	5 & 6	10	10	89.16	3.43
	7 & 8	10	40	89.04	3.58
8	1 & 2	20	10	88.31	4.51
(Rh)	3 & 4	20	40	81.64	7.58
	5 & 6	10	10	85.25	6.53
	7 & 8	10	40	78.50	9.79
9	1 & 2	20	10	85.65	6.65
(Rh)	3 & 4	20	40	80.14	8.38
	5 & 6	10	10	85.45	6.46
	7 & 8	10	40	81.90	8.83
10	1 & 2	20	10	89.60	2.84
(Rh)	3 & 4	20	40	89.59	3.03
	5 & 6	10	10	88.94	3.53
	7 & 8	10	40	87.23	5.52
11	1 & 2	20	10	88.92	3.02
(Rh)	3 & 4	20	40	78.71	3.65
	5 & 6	10	10	89.16	2.98
	7 & 8	10	40	78.04	5.96
12	1 & 2	8	10	76.86	4.04
(Pt)	3 & 4	8	40	77.19	3.78
	5 & 6	4	10	77.74	4.23
	7 & 8	4	40	77.49	3.82
13	1 & 2	20	10	74.33	3.17
(Ru)	3 & 4	20	40	73.62	2.91
	5 & 6	10	10	73.78	3.45
	7 & 8	10	40	74.03	3.24
14	1 & 2	20	10	82.53	4.59
(Pd)	3 & 4	20	40	82.43	4.46
	5 & 6	10	10	81.67	4.90
	7 & 8	10	40	82.84	4.30

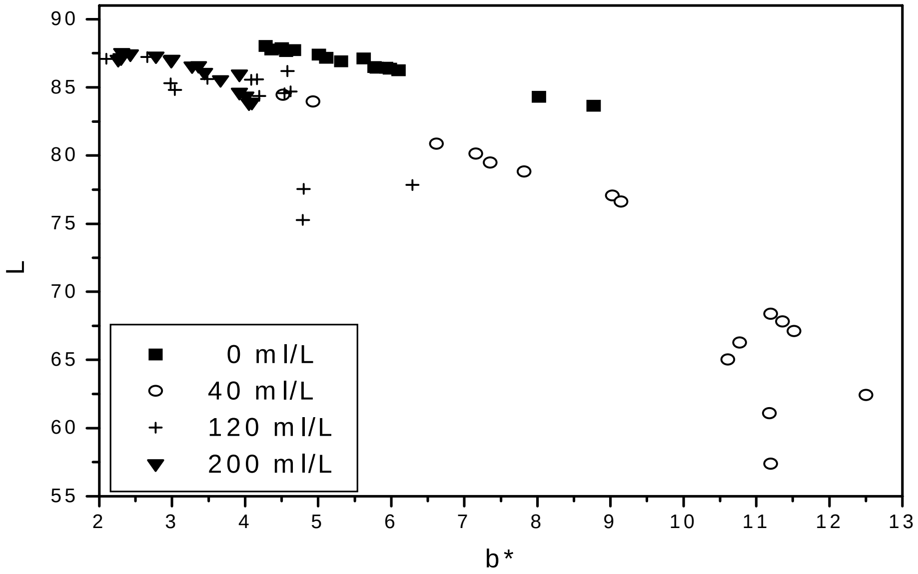

Figure 2. The effect of Additive A on the appearance of Rh.

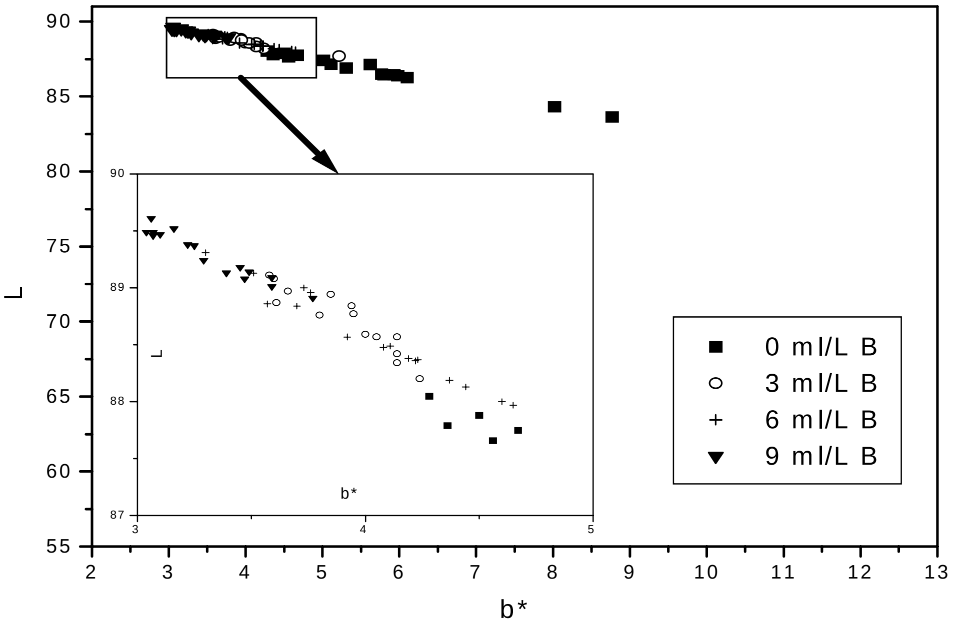

Figure 3. The effect of Additive B on the appearance of Rh.

The effect of Additive A, a grain refiner, is shown in Figure 2 and it is clear that greater than 120 ml/L is required in order to produce deposits that are tending towards "whiteness" ("L" approaches 100 and "b*" tends toward 0). In fact, the rhodium deposits are a little "lighter" in color when this additive is absent altogether. It is interesting to note that Additives A and C (see Figures 2 and 4), both grain refiners, cause deposits to be less bright when used at lower concentrations, especially when the deposit thickness is increased.

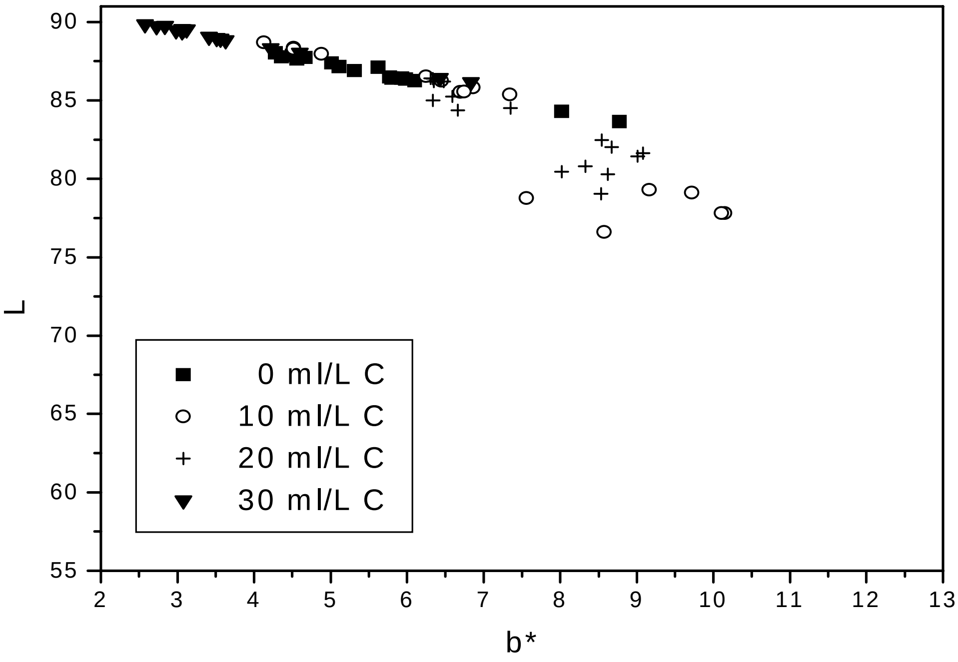

Figure 4. The effect of Additive C on the appearance of rhodium.

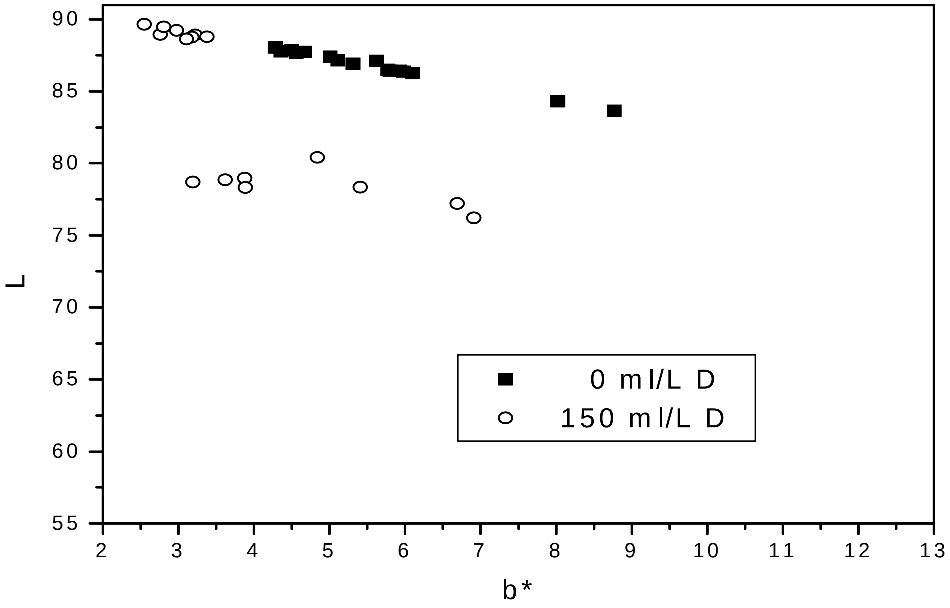

Figure 5. The effect of Additive D on the appearance of low stress rhodium.

Additive B is considered to be a true brightener and this is confirmed by these results. Note in Figure 3 the increasing "whiteness" of the deposits as Additive B concentration increases.

Additive D is used to reduce the deposit stress for specific applications of rhodium and thus was not expected to increase deposit brightness. Figure 5 confirms that only at low deposit thickness is there any increase in whiteness over deposits produced without any additive. All thicker deposits are less bright, those plated at higher current density are "bluer" in appearance.

Perhaps of greatest interest is Figure 6, which compares deposits of rhodium, palladium, platinum and ruthenium. Much has been talked about the comparative merits of these metals as decorative finishes, mostly in subjective terminology. Here we can define the differences in appearance. As expected rhodium is the "whitest finish" of these PGMs and ruthenium is the "darkest". Palladium has long been recognized as a challenger to rhodium's position in decorative finishing.

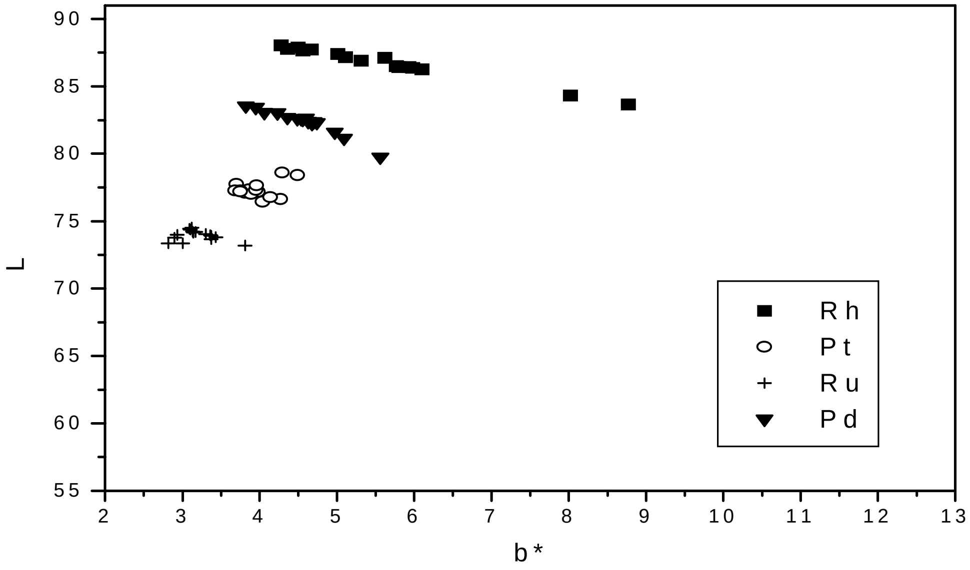

Figure 6. A comparison of the deposit appearance of rhodium, palladium, platinum and ruthenium.

Conclusions

Electrodeposits of rhodium and other platinum group metals have been quantitatively compared using spectrophotometric analysis of light reflected from their surfaces.

The effect of various additives in rhodium plating solutions has been assessed by the same technique.

This technique provides both supplier and user of these processes with a useful quality control tool.

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