## **Bright "White" Rhodium Plating**

#### Title: Bright "white" Rhodium Plating of Decorative Components

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Rhodium plating has been used for many years to provide a bright white finish on decorative components. This paper will describe two new processes for these applications, super white and ultra white as well as describing the development of processes in this market. The operating conditions of these two new processes will be described together with the results obtained from processes in the field. The difference between super white and ultra white will also be described.

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## Introduction

The use of Rhodium plating as a "white" finish for decorative plated items has been a well established process for many years. Over time attempts have been made to standardise the colour/whiteness of the Rhodium deposit. This paper is an attempt to clarify a measurement technique of the "whiteness" in comparison with the most sophisticated technique available, the human eye.

#### **History Of Rhodium Plating**

Rhodium, (*Greek - Rhodon, Rose*), is one of the rarest elements, it constitutes only around  $1 \times 10^{-7}$  of the earth's crust.

Rhodium was discovered in 1803-4 by Woolaston<sup>2</sup>, in crude platinum ore believed to be obtained from South America.

It is found in small quantities associated with all native platinum; in the minerals, rhodite, sperrylite, iridosamine and in some nickel-copper ores.

Rhodium occurs naturally with other platinum metals, the rivers sands of the Urals and also in North and South America.

The annual world production of rhodium is only around 7 - 8 tons.

Its scarcity, difficulties with extraction and purification, combined with the fact that the other precious metals were more abundant, easier to work with and satisfied the industrial demands, meant that progress on the electrochemical nature of rhodium was slow.

No significant work was carried out until the late 1920s when the chemistry of rhodium began to be explored on many fronts.

Practical methods for separation of the metal were described by Wichers and Gilchrist in 1928<sup>3</sup>, from that date onwards, many references exist related to rhodium as workers began to explore the electrochemical properties.

Keitel and Zschiegner<sup>4</sup> were among the early workers and developed a solution analogous to their platinum bath with the rhodium in the form of dinitro-diammino nitrite (US patent 1,779,436 and 1,779,457 [1930]).

Also among the early workers were Fink and Lambros<sup>5</sup> (1933) who explored the possibility of a bath using rhodium hydroxide in a sulphuric acid electrolyte. They also explored the addition of supplementary organic acids.

Atkinson and Raper<sup>6</sup> (1934) proposed an acid bath using rhodium amminonitrite which could incorporate additions of sodium nitrite to enhance the conductivity and help to stabilise the rhodium amminonitrite in the electrolyte.

As technology developed, then many workers<sup>7,8,9</sup> explored the chemistry and two basic electrolytes emerged, based on either Rhodium Sulphate in a Sulphuric Acid electrolyte or Rhodium Phosphate in a Phosphoric Acid Electrolyte.

Reid<sup>8</sup> and Rhodes<sup>10</sup> investigated a variety of electrolytes and some examples are shown in Table I.

It can be seen that the rhodium metal content of these earlier baths was significantly higher than the presently available commercial plating baths, which normally will operate at below 5 g/l rhodium for economic reasons rather than any intrinsic technical benefit.

A general trend that was observed by Reid<sup>8</sup> was that sulphate baths always exhibited a higher cathode efficiency than the phosphate baths and that sulphate baths also exhibited lower internal stress and marginally higher hardness values.

Sulphamate baths showed some positive aspects, but did not generate sufficient commercial interest for their parameters to be fully optimised.

Addition agents to maintain the whiteness of rhodium were explored in the early stages of process development<sup>11</sup>, many of these additives were organic material believed to enhance the whiteness of the rhodium deposit, some of these organics were patented<sup>12</sup>.

The purity of the rhodium used in the manufacture of the plating syrup is known to have a significant effect on the final whiteness of the electrodeposit, metallic impurities, in particular, will degrade the whiteness of the final rhodium electrodeposit. Any metallic contaminants introduced to the plating bath during production plating will also serve to degrade the whiteness. This subject will be referred to later.

A common contaminant in costume jewellery production is nickel which traditionally has been a common undercoat for costume jewellery items, normally a rhodium bath will show a decrease in whiteness with increase in nickel concentration.

European legislation to reduce the usage of nickel<sup>13</sup> in many of these applications may reduce the possibility of this contaminant.

Three types of rhodium baths have emerged as the most established processes  $^{14}$ .

Some typical formulations used for decorative applications are shown below.

1.	Sulphate bath	
	Rhodium (as sulphate concentrate)	2 g/l
	Sulphuric Acid (conc.)	20 ml/l
2.	Phosphate-Sulphate	
	Rhodium (as phosphate concentrate)	2 g/l
	Sulphuric Acid (conc.)	20 ml/l
3.	Phosphate bath	
	Rhodium (as phosphate concentrate)	2 g/l
	Phosphoric Acid, ortho 85%	40 ml/l
		2

All of these baths are operated in the range 1 - 4 A/dm<sup>2</sup>, using platinum or platinised titanium anodes.

The sulphate bath has been found to exhibit a lower stress<sup>15</sup> and as such is often the basis for industrial applications where a thicker deposit (1.0 - 5.0 microns) of rhodium is often employed.

Rhodium, as plated, is a highly stressed deposit, so for these thicknesses a stress reducer is often employed in proprietary formulations, some examples are selenic acid and magnesium sulphamate<sup>14</sup>.

Rhodium baths due to their very nature are very susceptible to contamination, both organic and metallic. In decorative baths this can show itself as a darkening of the deposit and by exhibiting stress in industrial deposits.

Steps should be therefore be taken to ensure any carryover or drag-in of contamination from preceding plating stages is eliminated, this can be by use of fully effective rinsing techniques and employing clean de-ionised or distilled water rinses immediately prior to the rhodium bath.

It should be remembered that rhodium baths are acidic and will readily attack many base metals if they are exposed to the solution, care should be taken in tank design to eliminate any exposed metal parts from contact with the solution.

Rhodium is one of the Platinum Group of metals. Some of the basic physical properties of rhodium are shown in the following Table II.

## **Examining Colour**

An infinite number of colours surround us in our everyday lives. We all take colour pretty much for granted and it has a wide range of roles in our daily lives.

A colour expression often though means ten different colours to ten different people. If you show the same plated item to different people you are bound to get different answers describing the colour.

Colour is a matter of perception and subjective interpretation. Even if they are looking at the same plated item different people will draw on different references and experiences to express colour in different words.

Words for expressing colour have always changed with the times. Words like "electric" to describe a colour could not have been used before the invention of electricity. Adjectives such as "bright", "dull" and "deep" are often used to improve the description.

Therefore verbal expression of colour is still not accurate enough. How then shall colours be expressed to avoid misunderstandings?

Even when we just look around, a wide variety of colours leap into our eyes. We are surrounded by an infinite variety of colours in our daily lives. However, unlike length or weight, there is no physical scale for measuring colour, making it unlikely that everyone will answer in the same way when asked what a certain colour is. For example, if we say "blue ocean" or "blue sky" to people, each individual will imagine different blue colours, because their colour sensitivity and past experiences will be different.

This is the problem with colour. If there was a standard method by which colours could be accurately expressed and understood colour communication could be smoother, simpler and exact.

Such precise colour communication could if applied to rhodium plated items eliminate colour related problems.

So let's study a little and determine what kind of colour information would be useful.

#### Factors that affect how a colour looks.

#### **Light-source differences**

Most people have experienced how sunlight, fluorescent light, tungsten light, etc.: each type of illumination will make the same plated item look different.

#### **Observer differences**

The sensitivity of each individual's eyes is slightly different; even for people considered to have "normal" colour vision, there may be some bias toward red or blue. Also, a person's eyesight generally changes with age. Therefore the same colour can appear to be different to different people.

#### **Size differences**

Colours covering a large area tend to appear brighter and more vivid than colours covering a smaller area. This is referred to as area effect. Selecting objects which will have a large area based on colour samples having a small area may result in mistakes.

#### **Background differences**

If a plated item is placed in front of a bright background, it will appear duller than when it was placed in front of a dark background. This is referred to as contrast effect, and is undesirable for accurately judging colour.

#### **Directional differences**

Often when looking at a plated item, viewing from a slightly different angle can make the item appear brighter or darker. This is due to the directional characteristics of the plated item. The angle from which the object is viewed, and also the angle from which it is illuminated, must be constant for accurate colour identification.

#### **The Principles of Colour.**

#### Hue. Lightness. Saturation.

#### Hue Red. Yellow, Green, Blue... Hues form the colour wheel.

Apples are red, lemons are yellow, the sky is blue; that's how we all think of colour in everyday language. Hue is the term used in the world of colour for the classifications of red, yellow, blue, etc. Also, although yellow and red are two completely different hues, mixing yellow and red together results in orange (which is sometimes referred to as yellow-red), mixing yellow and green results in yellow-green, mixing blue and green results in blue-green, and so on. The continuum of these hues results in the colour wheel shown in Figure 1.

#### **Lightness** Bright colours, dark colours. The lightness of colours changes vertically.

Colours can be separated into bright and dark colours when their lightnesses (how bright they are) are compared. Take, for example, the yellows of a lemon and a grapefruit. Without a doubt, the yellow of the lemon is much brighter. How about the yellow of a lemon and the red of a sweet cherry. Again, the yellow of the lemon is brighter, right? This lightness can be measured independently of hue. Now take a look at Figure 2. This figure is a cross section of Figure 1, cut along a straight line between A (Green) and B (Red-purple). As the figure shows, lightness increases toward the top and decreases toward the bottom.

#### **Saturation** Vivid colours, dull colours. Saturation changes outward from the centre.

Going back to yellow, how do you compare the yellows of a lemon and a pear? You might say the yellow of the lemon is brighter, but more to the point in this case, it is vivid, while the yellow of the pear is dull. This is another big difference, but this time one of colour saturation or vividness. This attribute is completely separate from those of both hue and lightness. If we look at Figure 2 again, we can see that saturation changes for red-purple and green respectively as the horizontal distance from the centre changes. Colours are dull near the centre and become more vivid as we move away from the centre. Figure 3 shows general adjectives used to describe the lightness and saturation of colours. To see what the words express, look back at Figure 2 again.

# By creating scales for hue, lightness, and saturation, we can measure colour numerically.

#### History of expressing colours numerically.

Various people in the past have devised methods, often using complex formulas, for quantifying colour and expressing it numerically with the aim of making it possible for anyone to communicate colours more easily and more accurately. These methods attempt to provide a way of expressing colours numerically, in much the same way that we express length or weight. For example, in 1905 the American artist A. H. Munsell<sup>(17)</sup> devised a method for expressing colours which utilised a great number of paper colour chips classified according to their hue (Munsell Hue), lightness (Munsell Value), and saturation (Munsell Chroma) for visual comparison with a specimen colour. Later, after a variety of further experiments, this system was updated to create the Munsell Renotation System, which is the Munsell system presently in use. In this system, any given colour is expressed as a letter/number combination (H V/C) in terms of its hue (H), value (V), and chroma (C) as visually evaluated using the Munsell Colour Charts. Other methods for expressing colour, the Commission International de l'Eclairage (CIE).

The two most widely known of these methods are the Yxy colour space, devised in  $1931^{(18)}$  based on the tristimulus values XYZ defined by CIE, and the L\*a\*b\* colour space, devised in  $1976^{(19)}$  to provide more uniform colour differences in relation to visual differences. Colour spaces\* such as these are now used throughout the world for colour communication.

\* Colour space<sup>(20)</sup> Method for expressing the colour of an object or a light source using some kind of notation, such as numbers

#### The L\*a\*b\* colour space method.

The L\*a\*b\* colour space (also referred to as CIELAB) is presently one of the most popular colour space for measuring object colour and is widely used in virtually all fields. It is one of

the uniform colour spaces defined by CIE in 1976 in order to reduce one of the major problems of the original Yxy colour space: that equal distances on the x, y chromaticity diagram did not correspond to equal perceived colour differences. In this colour space, L\* indicates lightness and a\* and b\* are the chromaticity co-ordinates. Figure 1 shows the a\*, b\* chromaticity diagram. In this diagram, the a\* and b\* indicate colour directions: +a\* is the red direction, -a\* is the green direction, +b\* is the yellow direction, and -b\* is the blue direction. The centre is achromatic; as the a\* and b\* values increase and the point moves out from the centre, the saturation of the colour increases. Figure 1 is a view of this solid cut horizontally at a constant L\* value.

#### **Plating Test Procedure**

Three solution formulations were chosen to evaluate for their colour differences. They were as follows :

- 1) Rhodium Phosphate, Sulphuric Acid Type. Standard Rhodium No Additive.
- 2) Rhodium Sulphate, Sulphuric Acid Type. Pure Rhodium With Additive A (Super White).
- 3) Rhodium Sulphate, Sulphuric Acid Type. Pure Rhodium With Additive B (Ultra White).

The test panels were evaluated for their differences with Current Density, Thickness of Deposit and for low levels of contaminants.

The formulation for each bath was as in Table III and the results of the colour measurements tabulated in Table IV.

#### <u>The method of Colour Measurement using the Minolta</u> <u>Chromameter CR200</u>

This procedure relates to standard white plate calibration.

Absolute colour measurements are made in  $L^* = a^* = b^*$  co-ordinates in the Munsell colour system.

L*	=	Light/Darkness			
+a*	=	Red.	-a*	=	Green
+b*	=	Yellow.	-b*	=	Blue

#### Equipment

Minolta Chromameter CR200, Measuring Head, AC adaptor and White calibration plate.

#### **Calibration**

Interval - before use. Slide power switch on. Display should show:

END	Y94.20
x .3156 y.3330	

If not, press COLOUR SPACE SELECT to obtain.

Place measuring head on the white calibration plate and press CALIBRATE and wait for the 3 flashes of the pulsed Xenon arc lamp. Do not remove the measuring head until the 3 flashes have pulsed. The Minolta will average the 3 readings and the display should now show:

CAL. Choo	Y94.20
x .3156 y.3330	

If the calibration is incorrect, move the cursor marked  $\leftarrow / \rightarrow$ , and then enter the corrected values for Y, x, y.

When the correct values for Y, x, y have been entered, press COLOUR SPACE SELECT to give the L\*,  $a^*$ ,  $b^*$  display. The Chromameter is now ready for use.

#### COLOUR EVALUATION OF RHODIUM: Phosphate, Super White & Ultra White.

<u>Minolta - L\*a\*b\* results</u> (Results for 0.5 & 1.0 micron compared)

- 1) Colour difference (Delta E) between Phosphate & Super White = 0.73 & 1.21 according to the classification is small.
- Colour difference (Delta E) between Super White & Ultra White = 0.46 & 0.94 according to the classification is again seen as small.

Up to 0.2	-	Not perceptible
0.2 - 0.5	-	Very small
0.5 - 1.5	-	Small
1.5 - 3.0	-	Distinct
3.0 - 6.0	-	Very distinct
6.0 - 12.0	-	Great
above 12	-	Large

#### Visual Results

A number people were separately shown panels of Phosphate type, Super White & Ultra White that were labelled as **A,B & C** 

and asked their opinion on the colour difference. The results were as follows :

A = Phosphate B = Super White C = Ultra White.

1) 20 % Could not see any difference between any of the three panels.

Of the other 80% the following was established.

- A has a yellow / orange tinge. Obvious difference in lightness between A & B or A & C. A slight yellow tinge is also seen in B. There is a subtle difference in colour for panel C compared to panel B.
- 3) A has a gold tinge. Panels B & C look slightly lighter & greyer in appearance. No difference seen between panels B & C.
- 4) A is darker in appearance than B or C. Only a subtle difference in lightness is seen between B & C.
- 5) A looks yellow / brown in colour compared with B & C. No significant difference seen between B & C.

#### **CONCLUSIONS**

\* The results from the Minolta fails to pick up the colour differences, that the human eye can quite clearly see ie. between **Phosphate & Super White** or **Phosphate & Ultra White**.

- \* However, If you look at the 0.5 & 1.0 micron thickness results, the Minolta does appear to have picked up a **very small** difference between Phoshate Type, Super White and Ultra White.
- \* Out of the contaminants added to the solution (Ni,Cu,Fe, and Ag) at 20ppm and 100ppm, only the Ag (at low ppms) seemed to have any effect on the colour, causing it to darken or turn black. It is well known that as nickel contamination in the Rhodium bath increases the deposit will gradually darken. Due to the acidic nature of the bath this is inevitable.
- \* The **human eye** is more accurate than the Minolta, as most people can see a definite difference in colour between Phosphate, and the other two Rhodiums. The Minolta's numerical results are all very close, and does not pick up any significant difference.
- \* Studies have shown that over 90% of humanity have a fairly close correlation of colour discimination, so there can be a general agreement as to colour matches in most cases. The minolta only appears to pick up on the greyness in the panels, and does not see any significant differences in the colour between the panels. The human eye therefore still seems the more reliable method of establishing the "colour or whiteness". Unfortunately we still are subject to subject to human preferences, therefore there will perhaps always be the discussion on how white is a "white" Rhodium. White, Grey-White, Yellow-White and Blue-White all seem to be relevant.

## Table I

### Some Examples of Early Rhodium Electrolytes Investigated by Reid and Rhodes

Electrolyte Type	Unit	Rhodium Concentration	Free Acid Concentration
Sulphate	g/l	10 - 50	10 - 100
Phosphate	g/l	10 - 50	30
Sulphate - Phosphate (Mixed Acid)	g/l	20	10 - 100
Fluoborate	g/l	20 - 90	25
Sulphamate	g/l	20 - 50	30

## Table II

## **Properties of Rhodium**

Property	Unit	Value
Chemical Symbol	-	Rh
Atomic Number	-	45
Atomic Weight	-	102.905
Specific Gravity at 25°C	-	12.41
Hardness	Hv	700 – 800
Physical State at 25°C	-	Solid, metal
Melting Point	°C	1964 ± 3
Boiling Point	°C	$3695 \pm 100$
Electronegativity	Pauling	2.28
Crystal Structure	-	Face Centred Cubic
Weight Deposited / ampere hour @ 100% Cathode Efficiency	g	1.28

## <u>Table III</u>

Formulation of the Solutions.

Electrolyte Type	Phosphate	Sulphate (Super White)	Sulphate (Ultra White)
Rhodium Concentration	2g/l	2g/l	2g/l
Sulphuric Acid Concentration	20m/l	25ml/l	15ml/l
Phosphoric Acid Concentration	20g/l	-	-
Additive	Х	Y	Y
Temperature <sup>o</sup> C	40	25	25

#### COLOUR EVALUATION OF RHODIUM PLATING SOLUTIONS TABLE IV

All colour measurments obtained using the Minolta Chromameter CR200, using the L\*a\*b\* Colour Notation System.

C\* = Colour Tone Delta E = The degree of colour difference

		I	hodium P	hospate Ty	pe			Rhoćium Sulphate Type (Super White)								Rhodium Sulphate Type (Ultra White)						
		L*	a*	b*	Delta E	Diff. from Std.	Chroma $C^*= a^2 + b^2$	L*	a*	b*	Delta E	Diff. from Std.	$Chroma C^* = a^2 + b^2$	Phosphate Compared with SW	L*	a*	b*	Delta E	Diff. from Std.	Chroma b <sup>2</sup>		
Standard 0.1 microns		73.89	0.96	1.85	73.92	- = darker than std. + = lighter than std.	2.08 Very Pale Grey	73.06	0.97	1.76	73.09	- = darker than std. + = lighter than std.	2.00 Very Pale Grey	0.83	74.59	0.95	1.51	74.61	- = darker than std. + = lighter than std.	1.23 Pale Gr		
Change in C.D	1 A/dm <sup>2</sup>	73.12	1.14	2.59	73.17	-0.75	2.83 Very Pale Grey	72.66	1.00	2.21	72.70	-0.39	2.42 Very Pale Grey	0.47	74.36	1.10	1.51	74.38	-0.23	1.23 Grey		
	2 A/dm <sup>2</sup>	73.30	1.03	2.14	73.34	-0.58	2.37 Very Pale Grey	72.38	1.28	1.90	72.42	-0.67	2.29 Very Pale Grey	0.92	74.16	1.28	1.41	74.18	-0.43	1.90 Grey		
	3 A/dm <sup>2</sup>	73.44	1.03	2.47	73.49	-0.43	2.68 Very Pale Grey	73.28	1.13	1.77	73.31	0.22	2.10 Very Pale Grey	0.18	74.51	1.08	1.34	74.53	-0.08	1.72 Grey		
	4 A/dm <sup>2</sup>	73.28	1.01	2.21	73.32	-0.60	2.43 Very Pale Grey	74.10	1.18	1.59	74.13	1.04	1.98 Very Pale Grey	0.81	74.71	1.08	1.23	74.73	0.12	1.64 Grey		
	5 A/dm <sup>2</sup>	73.87	1.05	1.60	73.89	-0.03	1.91 Very Pale Grey	73.42	1.20	1.61	73.45	0.36	2.01 Very Pale Grey	0.44	74.49	0.96	1.42	74.51	-0.1	1.71 Grey		
Change in Thickness	microns 0.10	73.89	0.96	1.85	73.92	std.	2.08 Very Pale Grey	73.06	0.97	1.76	73.09	std.	2.00 Very Pale Grey	0.83	74.59	0.95	1.51	74.61	std.	1.23 Grey		
	0.25	72.85	0.95	2.72	72.91	-1.01	2.88 Very Pale Grey	73.47	1.15	1.70	73.50	0.41	2.05 Very Pale Grey	0.59	74.14	1.03	1.73	74.17	-0.44	2.01 Grey		
	0.50	72.60	0.95	2.79	72.66	-1.26	2.95 Very Pale Grey	73.38	1.23	0.72	73.39	0.30	1.42 Very Pale Grey	0.73	73.83	0.98	1.60	73.85	-0.76	1.88 Grey		
	1.00	71.89	1.24	2.84	71.96	-1.96	3.10 Very Pale Grey	73.14	1.14	1.89	73.17	0.08	2.21 Very Pale Grey	1.21	74.08	1.07	1.68	74.11	-0.44	1.99 Grey		
Added Impurities	20ppm Nickel	74.27	1.15	1.50	74.29	0.37	1.89 Very Pale Grey	75.12	0.77	1.07	75.13	2.04	1.32 Very Pale Grey	0.84	74.52	1.10	1.30	74.54	-0.07	1.70 Grey		
	100 ppm Nickel	74.44	1.21	1.41	74.46	0.54	1.86 Very Pale Grey	73.28	0.97	1.59	73.30	0.21	1.86 Very Pale Grey	1.16	74.10	1.10	1.51	74.12	-0.49	1.87 Grey		
	20ppm Copper	74.11	0.84	1.42	74.13	0.21	1.65 Very Pale Grey	73.70	1.12	1.49	73.72	0.63	1.86 Very Pale Grey	0.43	74.47	0.94	1.65	74.49	-0.12	1.90 Grey		
	100 ppm Copper	72.84	0.73	1.85	72.87	-1.05	2.0 Very Pale Grey	72.19	1.04	2.04	72.23	0.86	2.29 Very Pale Grey	0.64	73.65	0.92	1.80	73.68	-1.03	2.02 Grey		
	20 ppm Iron	73.91	1.03	1.55	73.93	0.01	1.86 Very Pale Grey	73.69	1.17	1.45	73.71	0.62	1.86 Very Pale Grey	0.22	73.56	0.83	1.92	73.58	-1.03	2.09 Grey		

100 ppm <b>Iron</b>	74.34	0.93	1.29	74.36	0.44	1.59 Very Pale Grey	73.43	1.16	1.59	73.46	0.37	1.97 Very Pale Grey	0.93	72.24	0.89	2.15	72.27	-2.34	2.33	Grey
20ppm <b>Silver</b>	74.57	0.85	0.81	74.58	0.66	1.17 Very Pale Grey	73.77	1.09	1.43	73.79	0.70	1.80 Very Pale Grey	0.79	72.40	0.77	2.61	72.45	-2.16	2.72	Grey
100 ppm Silver	23.92	1.72	3.92	24.30	49.62	5.2 Very Dark Grey / Black	70.33	1.08	3.85	70.44	-2.65	4.00 Greyish / Dark	46.14	65.90	0.73	2.32	65.94	-8.67	2.43	Dark



#### **References**

- 1. The Merck Index 12<sup>th</sup> Edition (1996).
- 2. Phil. Trans 94.419.(1804).
- 3. Wichers & Gilchrist Trans Am Mining Metallurgical Eng 76,619, (1928).
- 4. W. Keitel and H.E. Zschiegner Elektrochem, 39.948-58 (1930).
- 5. C.G. Fink and G.C. Lambros Trans Electrochem. Soc.63 181-6 (1933).
- 6. R.H. Atkinson and A.R. Raper Metal Ind.(N.Y.) 32,119-21 (1934).
- 7. K. Schumpelt Electrochem.Soc 80,495 (1941).
- 8. F.H. Reid Bull.Inst.Metal Finishing 6,107-42 (1956).
- 9. H.J. Wiesner Proc.Amer.Electroplat.Soc 39,79-99 (1952).
- 10. E.A. Parker Plating, 1955,42,882-92 (1955).
- 11. S. Dorner and L. Froels Galvanotechnik.49.539 (1948).
- 12. Baker, US Pat 2,057,475 (1936).
- 13. S.J. Hemsley & J.F. Sargent Nickel Free Plating Technology for Decorative Applications. AESF SURFIN98 Conference Minneapolis 185-193 (1998).
- 14. Frederick.A.Lowenheim, Modern Electroplating, Electrochemical Society, Princeton NJ. Page 351 Third Edition (1974).
- 15. F.H. Reid, Metall.Rev, 8,167 (1963).
- 16. G.R. Smith, C.B. Kenahan, R.L. Andrews and D. Schlain, Plating, 56,805 (1969).
- 17. A.H.Munsell (1905) Method of expressing colours.
- 18. CIE (1931) Method of expressing colours.
- 19. CIE (1976) Method of expressing colours.
- 20. Minolta Handbook (1993) P colour contamination.