White Gold Alloys: Colour Measurement and Grading

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Abstract

A numerical grading system has been established for white gold alloys using the ASTM Yellowness Index D1925, an existing colour quality standard. The Index is calculated from the CIE (International Commission of Illumination) Tri-stimulus values, X, Y and Z, and the scale is linear, so that as the number decreases, the alloy becomes whiter.

This Index provides values that have good correlation with visual assessments and permits easy differentiation of colour without knowledge of an alloys composition. The use of a spectrophotometer instrument provided a quick means of sample colour measurement, with high precision and accuracy.

1 Introduction

In 2003 the MJSA and the World Gold Council started a series of initiatives to define white gold and to improve customer perceptions of white gold products as at the present time there are no international standards defining the colour of white gold alloys, which has permitted several issues to arise, including:

- Different interpretations of what colour constitutes white gold.
- The trend to rhodium plate most commercial white gold jewellery, which misleads the customer as to the natural colour of white gold.
- An inferior colour match being revealed between a Rhodium plate and the metal below when the plate becomes worn.

These issues were discussed at a meeting, led by C.W. Corti's presentation at Expo New York in March 2003 and highlighted some of the concerns in the Industry regarding poor colour matches that occur when a rhodium plate wears off white gold jewellery. Suggestions were made to grade white gold alloys according to their colour (whiteness) and requirement for rhodium plating. To examine these issues, the MJSA and WGC set up a White Gold Task Force in the USA and invited other interested parties, including the Birmingham Assay Office (BAO) and Cookson Precious Metals, to examine the options and offer proposals accordingly. This invitation resulted in the formation of an additional White Gold Task Force in Britain. The authors headed the investigation of the British task force. This paper reports on this work, particularly in terms of defining the degree of whiteness of white gold.

The investigation's scope was to determine:

- How to measure the colour of White Gold alloys and report the value in a single numerical parameter for ease of understanding.
- Devising a series of voluntary standards, permitting the categorisation of white gold alloys in relation to their whiteness and their need to be rhodium plated.

In attempting to define a numerical parameter suitable to grade white gold alloys, the system should provide a single value to allow easy communication of a colour even when a sample is not provided. However, a long-term objective was to define the criteria for the minimum compositional requirements for a white gold alloy to be classified in each of the proposed grades, based on experimental data and elemental composition of each alloy.

The authors were aware of previous treaties work on this subject (1 - 7). The range of methods used to measure gold alloy colours and corresponding data interpretation highlighted the lack of standardisation in the gold technical community.

To understand how to measure and define the colour of White Gold alloys, we need to first understand what exactly is meant by the term 'colour'.

2 What is Colour?

Colour is an occurrence that results from the interaction between light energy, an object and an observer, Figure 1. These three factors are collectively referred to as the 'Observer Situation' (1).

This 'situation' influences how colour is perceived.

- Light Source: Light can be described in terms of the energy it emits at each of the wavelengths in the visible spectrum e.g. a yellowed light emits a greater amount of light between 560 - 590 nanometres.
- Object: An object will reflect some wavelengths of light better than others (absorbing these others). This will change the observers perception of the objects colour e.g. a blue object appears blue because it reflects more blue wavelengths of light, while absorbing the green and red wavelengths of light. This is commonly referred to as 'Spectral Reflectance'.
- Observer: One observer's perception of colour can differ from another observers due to variation and deficiencies in human colour perception.

Colour is only one attribute of 'Appearance', which is described by 2 key categories;

- Chromatic Attributes: Characteristics relating to colour
- Hue: The property by which we differentiate one colour from another e.g. red from blue
- Value: The lightness of a colour when viewed in daylight and marked 0 (black) to 10 (white)
- Chroma: The degree of departure of a colour from a grey of the same value. Colours with a low chroma are weak, while colours with a strong chroma are saturated.
- Geometric Attributes: Characteristics describing how an object modifies the reflected light
- Gloss: The attribute of an objects surface that accounts for lustrous or mirror-like reflection in conjunction with specular reflection (see below)
- Haze: Is the object transparent or translucent to light. If it is and the light is dispersed on passing through the object, this is described as a 'haze' effect
- Texture: Is the object's surface flat and smooth. This will help control light reflection
- Shape: Is the object's surface flat or curved. The shape will also effect the light reflection
- Viewing Angle: Altering the angle at which the object surface is viewed will effect the colours observed
- Surround: The colour of the surroundings a sample is viewed in can influence colour perception as colours of medium value and chroma will appear to change in the direction of lighter, brighter or darker, less saturated colours surrounding them.

These categories both effect the observer's visual perception of an object.

Metallic surfaces, e.g. gold, have a unique colour in their specular reflectance, which is the colour of the metal. Specular reflection occurs when a small fraction of the reflected light (1 - 10%) from the object surface remains unchanged and appears as a white highlight to an observer (a mirror-like reflection).

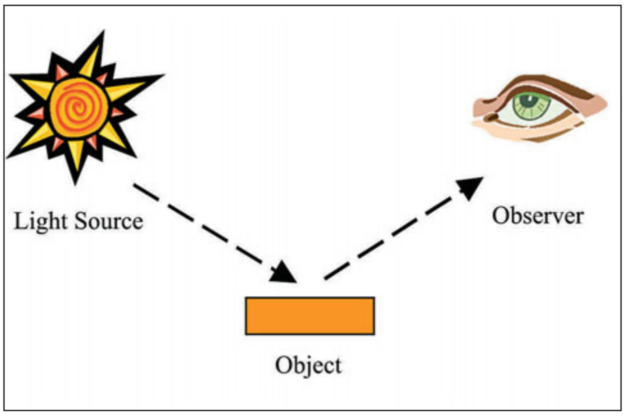

Figure 1
The Observer Situation

2.1 Defining Colour

As the typical human eye can discern seven to ten million colours, we require an ordered method to relay colour information in a useful way. Several mathematical systems exist that can now define colour, providing specific data points or co-ordinates that can describe any colour.

The Munsell Colour Order System (2) was the first system to communicate data in a way that could be readily understood. This system uses the chromatic attributes Hue, Value and Chroma (see above), to specify colours and highlight the relationship between the colours. Other systems have since been developed and include CIE Colour Space and CIELab.

2.1.1 The CIE System

The International Commission on Illumination, commonly abbreviated to CIE, developed a system that took in to account the interaction between the elements shown in 'The Observer Situation', Figure 1, that they believed established the colour of an object. This system subsequently defined a number of key points such as:

- Standard illumination for colour comparison and the conditions for a 'Standard Observer'
- Calculation of the Tristimulus values (X, Y and Z), which describes the response to a specific colour by the human visual system. However, these values were not designed to be a practical means for describing an objects colour but rather a means to determine if two colours having the same tristimulus values matched (using a standard illuminant and observer).
- Converting the Tristimulus values to the more easily understood Chromaticity co-ordinates (x, y and Y), that are often represented on a graph (referred to as a 'colour space')

The chromaticity co-ordinates, x and y, referring to hue and chroma, are a conversion of the tristimulus values and were represented on the CIE 1931 Chromaticity Diagram. The third dimension (projecting out from the paper) is tristimulus Y, or Luminosity, which represents the brightness of the colour.

This diagram mapped out the full range of colours that were perceived by the human visual system. Colours near the

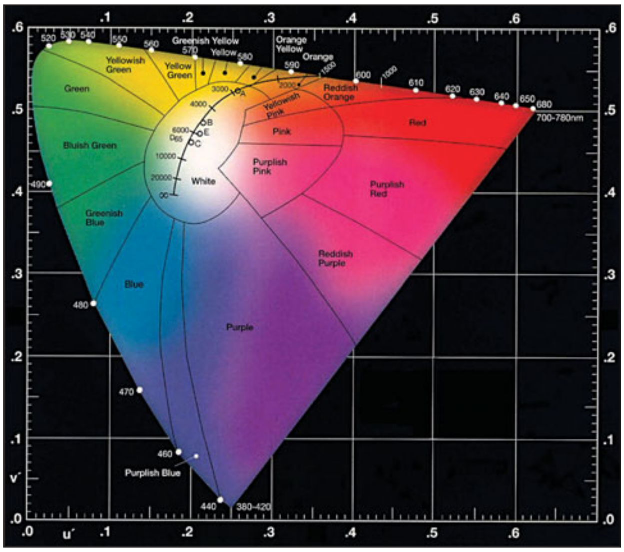

Figure 2

CIE 1976 UCS Chromaticity diagram

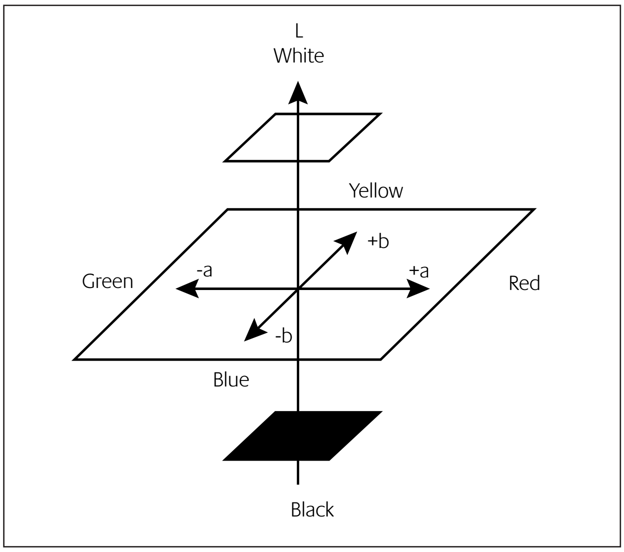

Figure 3

The CIE Lab system of colour definition co-ordinates

centre were considered weak (less saturated) and approaching neutrality (colours of white, black and grey). As a colour moved towards the edge of the diagram, the saturation level increased.

Refinement of this work resulted in the CIE 1976 Uniform Colour Space (3), Figure 2. The shape of the colour space has changed from the 1931 diagram, resulting in equal spatial distances on the graph equating to equal visual colour differences.

This method involved converting the tristimulus values (X, Y and Z) to an alternative set of chromaticity co-ordinates, u' and v'.

$$u' = 4X / (X + 15Y + 3Z)$$
$$v' = 9Y / (X + 15Y + 3Z)$$

2.1.2 The CIELab System

An alternative, popular method for defining colours is the CIELab Colour System. This system is based on the premise of there being three different types of colour receptor in the eye (Red, Blue and Green). When these receptors are excited, the brain interprets the three sets of signals as follows; light or dark, red or green and yellow or blue (4), Figure 3. The co-ordinates selected to represent these signals are

- L*: – Brightness (black if the value is 0, 100 if the colour is white)
- a*: – Red colouring if the value is positive, green colouring if the value is negative
- b*: – Yellow colouring if the value is positive, blue colouring if the value is negative

The magnitude of the value describes the relative strength of the colour.

The colour space provided by the CIELab system was designed to provide a more perceptually uniform colour space than the Tristimulus values and their derivatives.

As the co-ordinates a* and b* approach zero, the colour becomes neutral (White, Black and Grey). As the values for a* and b* rise, the colour saturation increases.

3 Colour Measurement

When measuring a samples colour, standard conditions need to be adopted to ensure essential accuracy and precision. This means using the same lighting conditions, observer position and instrumentation.

3.1 Light Sources and Standard Observer

Early CIE experiments defined the need for standard illuminants (light sources that emitted exact intensities of specific light wavelengths) and a standard observer (a fixed size aperture through which the object is viewed, relative to the observers position. This is described as the angle providing the field of view).

3.2 Sample Preparation

The surface of the sample to be evaluated needs to be carefully prepared prior to examination, in an attempt to minimise any variation.

Variation may result from surface

- Texture
- Uniformity
- Directionality (a homogeneous, non-directional finish is preferred)
- Flatness
- Surround (for visual examinations)
- Size

Additionally, sample storage is important if the sample could be scratched or the surface is subject to change when exposed to temperature, sunlight, moisture and atmospheric gases.

Initial trials using samples with different polished finishes to identify the best sample preparation method demonstrated that objects to be evaluated should have a 6-micron or better diamond polish finish. This simulated the polished surface of a finished article of jewellery or bullion product which ensures a homogeneous, non-directional finish that provides a realistic and repeatable luminosity value, which is essential for accurate measurements and calculations.

The sample was cleaned with cotton wool and a solvent (acetone or methanol) prior to each measurement. Care was taken in the handling and storage of the sample to prevent surface scratches. Some alloys can tarnish over extended periods of time. This time period is shortened through exposure to various conditions e.g. acids and alkalis, sunlight, particular gases etc. Therefore, the sample was stored in a neutral environment and only used when required. After a 3-month period, the sample should be re-polished to ensure a fresh surface for measurement if required as a standard.

3.3 Measurement Instruments

The two instruments most commonly used to measure an objects colour are the human eye and Spectrophotometers (5).

A spectrophotometer is an instrument that emits a powerful pulse of a known illuminant and then measures the reflected light. This data can then be interpreted and converted to the required colour quantification method e.g. CIELab. Accepting the advice of GretagMacbeth, their spectrophotometer, model CE-XTH, was utilised for the experiments.

An instrument as described is always more sensitive than even a trained human eye, detecting minute colour differences.

3.4 Visual Colour Assessment

Assessments using the human eye are subjective for the following reasons (6);

- Differences in illumination – the same light source should be used for all assessments
- Viewing conditions - Angle, background and surround all need to be controlled
- Variation in the human eye, from person to person, as the ability to perceive small colour differences is essential.

Visual assessments should always be used in conjunction with instrument measurements, to ensure a good correlation exists between the two methods.

Daylight is the preferred illuminant for visual assessments as it can be considered neutral.

More specifically North Sky Daylight, the light that enters through a north-facing window, is used for white and near-white colour assessments (10).

The angle at which an object is viewed should be kept the same and a recommended orientation is 0/45. This defines that the object is laid flat and that the light striking the object is from directly above. The observer than assumes a viewing position at 45 degrees to the object (11). A visual assessment should always use a neutral surround (grey, black or white) as this will prevent a number of issues occurring such as chameleon effects, complementary afterimages and simultaneous contrast. Changes in colour are perceived more easily when the background colour is close to or the same as the object colour e.g. light or dark. A white background is best suited for evaluating white and near white coloured objects (12).

Munsell colour charts provide reference colour samples for visual comparison and are in common use today e.g. colour charts that show the colours of various paints.

4 Experimental Trials

The investigation was broken down in to a sequence of trials:

4.1 Colour measurement

The colour of over 70 gold alloy standard samples, of accurately known composition, were measured using a spectrophotometer instrument, model CE-XTH, with illuminant C and a 2-degree observer in an attempt to quantify the colour of white gold alloys. The samples covered 9, 14, 18 and 22ct alloys and the colours white, yellow, pink, red and green. All the samples analysed were prepared according to the sample preparation method outlined previously. The data provided readings for the CIELab co-ordinates, L*, a* and b*, as well as the Tristimulus values, X, Y and Z. The use of L*, a* and b* values in a series of equations to derive numeric values was examined. The measured values were also plotted on a series of graphs (a* versus b*) to examine another means of grading, through the creation of colour boxes. The X, Y and Z values were also used in equations to generate a numerical grading system and were converted to Chromaticity co-ordinates u' and v' (9) so the data could be evaluated on the 1976 UCS Chromaticity diagram, Figure 3.

4.2 Measurement repeatability

Due to the susceptible nature of this measurement method to surface contamination and instrument differences, resulting in variation in measurement readings, a repeatability trial was conducted on a number of samples. This trial examined the reading variations caused by the following

- Calibration
- Sample Preparation
- Method Of Measurements
- Analyst Effect
- Instrument-To-Instrument Effect

The standard deviation of means (standard uncertainty) for each source of variation was calculated and from this data an overall tolerance for each grade was calculated.

4.3 Visual Assessment

A visual assessment was performed on the BAO Standards, samples Au 1 to Au 14, ordering them in terms of yellowness. This involved the use of a controlled light box set to D65 standard of illumination, the setting closest to ‘C’ illumination which had been used as the illuminant in the colour equations. A total of 14 observers in two groups performed the test and ordered the samples accordingly. This assessment, together with accepted colour grading of a standard alloy range that had been specially prepared, was then used to help determine the limits for the grading bands e.g. Premium White.

5 Results

5.1 Colour Measurements

The measured L*, a* and b* values obtained from the spectrophotometer showed some distinct similarities and trends, Table 1. The L* co-ordinate values were uniformly high, with an average of 84.1 (+/- ~9), which supported the visual assessment of the samples being very bright and reflective. The b* co-ordinate values varied considerably from the lowest value, for rhodium, at 2.81, while the lowest value for a commercial white gold alloy (18ct White 1) was 7.38.

The variation in the a* value was larger than expected, from -3.223 for a 9ct alloy, to 1.403 for an 18ct alloy.

The different formulas examined to provide numerical grade resulted in different ordering of the alloys, Table 2.

Plotting the u' and v' Chromaticity co-ordinates against the CIE 1976 UCS Chromaticity diagram (see Figure 2), shows the data falls within the central white region. Rhodium, u = 0.204, v = 0.465, being located at the centre of the white region, while Au 16 (Fine Gold), u = 0.234, v = 0.509, falls at the boundary between the yellow and white zones.

5.2 Repeatability of Results

A number of samples were repeatedly measured in order to obtain statistical measurement data and the samples represented a broad choice of white gold alloys obtainable from several precious metal alloy manufacturers. The results of these measurements and calculated uncertainty data are shown in Table 3 and the results reported under heading '±Tolerance' is an expanded uncertainty calculated using a coverage factor of 2, which gives a level of confidence of approximately 95%, as per accepted international practice.

5.3 Visual Assessment

The visual assessment of the BAO standards, by 14 observers in two groups, resulted in the observers ordering the samples in an order almost identical to the spectrophotometers colour assessment order. In only 3 cases did the order differ and these differences corresponded to samples that possessed similar b values, Table 4.

6 Discussion

6.1 Colour measurements

6.1.1 The requirement for samples to have a polished surface was recognised by both Roberts (1) and German (2). Work later completed by Agarwal (6) highlighted a recognised colour difference between polished and rough finished surfaces. Illumination settings 'C' or D65 have been the settings of choice for a number of previous investigations, with D65 being favoured by German (2) and MacCormack (3) as it most closely matches natural sunlight. The use of a spectrophotometer as the preferred method of spectral measurement has also been recognised by German (2), MacCormack (3) and Agarwal (6).

A variety of means to assess and present colour data of gold alloys have been used, including reflectance curves (1), plotting CIELab results on to alloy compositional diagrams (2) and the use of plain CIELab co-ordinates (5), (6). Roberts (1) did recognise certain benefits of using Tristimulus values (X, Y, Z) for colour perception.

With the high reflectivity of the white gold samples (L* value average of 84.1, +/- ~9), it is possible that their visual assessment could be effected, leading the observer to believe that the sample is whiter than it is. The b* values clearly show the significant perceptible difference in 'whiteness' between white gold alloys and rhodium, fine (pure) silver (4.31) and GW Platinum (5.01), as the human eye can discern an approximate 1-point difference in the b* value. The large variance in a* values was discernible under controlled viewing conditions, highlighting the existing view of colder (blue/green) and warmer (red) white gold colours.

The grading of white gold alloys by a single number scale was dependent on identifying a formula that supported the findings of the visual assessments, a fact that Roberts (1) also supported. Initially, only the b* co-ordinate value was used. This however failed to account for slight colour traits that the human eye registered. It was noted that the presence of a green colour element (- a* value) reduced the perceived yellowness of a sample, while a red colour element (+ a* value) reinforced the yellowness. Therefore, the impact of the a* co-ordinate needed to be reflected in the numeric value and thus the grading. A number of terms and formulas that utilised both the a* and b* co-ordinates were examined.

In general these formulas attempted to control the impact of the a* value on the b* value by establishing the extent of the modification at different levels of the a* value. However, the effect of the a* co-ordinate on the b* co-ordinate could only be estimated due to a lack of alloy readings at specific values of a* and b*. This meant that the formulas, although providing suitable numeric values in line with visual assessment, could not be substantiated.

The equations $b^* + (a^*/3)$ and $\sqrt{(a^{*2} \text{ x } b^{*2})}$ provided simpler but effective data interpretations. The values produced from both equations showed good correlation with visual assessments in the majority of cases, Tables 1 & 2. The $\sqrt{(a^{*2} \text{ x } b^{*2})}$ equation has had application in the colour industry, being more commonly referred to as Chroma or C, one of the three attributes of the Munsell Colour System. The Chroma equation does not satisfy all criteria, as the squaring of the 'a' value will always return a positive value that adds to the b* value. This equation does not reflect the effect of a negative a* value and thus is not suitable for grading White gold alloys, which agrees with MacCormack's findings (3).

Table 1

CIELab coordinates and formulaic results from some of the measured alloys and standards (sorted in ascending order of YI: D1925

Standard	L*	a*	b*	YI D1925	YI 313	√(a^{*2} x b^{*2})	b* +(a*/3)
Rhodium	83.816	0.645	2.817	6.828	4.7	2.89	3.03
Fine Silver	92.65	-0.31	4.305	8.402	6.6	4.32	4.2
95.5 Pt/4.5 Cu	84.604	0.101	5.05	10.927	8.35	5.05	5.08
Palladium	81.063	0.367	6.046	13.638	10.32	6.06	6.17
9ct White 1	92.714	-1.686	8.244	14.679	12.5	8.41	7.68
9ct White 2	92.921	-1.889	9.266	16.35	13.96	9.46	8.64
9ct White 3	93.234	-2.292	9.472	16.358	14.22	9.75	8.71
Au 3	77.255	0.469	7.138	16.611	12.61	7.15	7.29
9ct White 4	90.816	-2.029	11.549	20.685	17.54	11.73	10.87
9ct White 5	89.633	-2.269	11.934	21.398	18.28	12.15	11.18
9ct White 6	93.53	-3.223	13.216	22.169	19.45	13.6	12.14
Au 1	86.463	-0.9	11.577	22.501	18.28	11.61	11.28
9ct Yellow 1	91.647	-0.114	13.143	24.902	19.66	13.14	13.11
Au 5	82.261	-0.786	13.463	27.079	21.89	13.49	13.2
Au 4	77.057	0.253	15.716	33.784	26.5	15.72	15.8
9ct Yellow 2	90.374	-1.588	19.247	34.37	28.19	19.31	18.72
Au 2	85.22	2.2	16.583	34.556	25.78	16.73	17.32
Au 9	78.111	-1.035	7.642	16.138	13.351	7.71	7.3
14ct White 1	83.86	-0.102	8.885	18.539	14.575	8.89	8.85
14ct White 2	81.487	-0.958	9.859	20.136	16.466	9.91	9.54
14ct White 3	80.067	0.985	9.404	21.262	15.964	9.46	9.73
Au 6	75.097	0.772	9.124	21.548	16.316	9.16	9.38
Au 7	76.91	0.884	10.188	23.465	17.775	10.23	10.48
Au 8	79.248	-0.531	15.468	31.903	25.572	15.48	15.29
Au 11	79.653	0.23	7.369	16.48	12.69	7.37	7.45
18ct White 1	80.205	1.287	7.381	17.378	12.64	7.49	7.81
18ct White 2	80.946	1.135	7.884	18.146	13.37	7.97	8.26
18ct White 3	77.046	0.934	7.906	18.719	13.95	7.96	8.22
18ct White 4	84.401	0.306	9.062	19.145	14.78	9.07	9.16
18ct White 5	79.913	1.087	8.658	19.874	14.78	8.73	9.02
Au 12	80.563	-0.45	9.459	19.972	15.97	9.47	9.31
18ct White 6	80.434	1.456	8.696	20.188	14.77	8.82	9.18
18ct White 7	78.219	0.686	9.068	20.683	15.71	9.09	9.3
18ct White 8	81.281	0.42	9.618	20.931	16.12	9.63	9.76
18ct White 9	85.342	-0.104	10.283	20.969	16.52	10.28	10.25
18ct White 10	78.566	0.843	9.505	21.654	16.37	9.54	9.79
18ct White 11	79.252	0.876	10.216	22.978	17.41	10.25	10.51
18ct White 12	77.199	1.817	10.287	24.48	17.89	10.45	10.89
Au 10	77.696	-0.1	13.308	28.609	22.62	13.31	13.27
18ct White 13	80.687	1.403	14.37	31.178	23.59	14.44	14.84
22ct Yellow 1	86.012	4.373	27.426	53.954	39.799	27.77	28.88
22ct Yellow 2	82.018	4.978	32.132	63.453	46.8	32.52	33.79
Au 13	78.949	5.696	34.082	68.634	50.28	34.55	35.98
Au 15	81.642	5.38	36.139	69.708	51.496	36.54	37.93
Au 16	81.98	4.449	38.442	71.784	53.846	38.7	39.93
Au 14	77.223	7.25	35.967	73.837	53.164	36.69	38.38

Table 2

Yellowness Indexes D1925 and E313, b + (a*/3) and √(a^{*2} x b^{*2}) alloy ordering comparisons*

Standard	L*	a*	b*	B* +(a*/3)	Standard	√(a^{*2} x b^{*2})	Standard	YI 313	Standard	YI D1925	Standard
Rhodium	83.816	0.645	2.817	3.03	Rhodium	2.89	Rhodium	4.70	Rhodium	6.828	Rhodium
Fine Silver	92.65	-0.31	4.305	4.20	Fine Silver	4.32	Fine Silver	6.60	Fine Silver	8.402	Fine Silver
95.5 Pt/ 4.5 Cu	84.604	0.101	5.05	5.08	95.5 Pt/ 4.5 Cu	5.05	95.5 Pt/ 4.5 Cu	8.35	95.5 Pt/ 4.5 Cu	10.927	95.5 Pt/ 4.5 Cu
Palladium	81.063	0.367	6.046	6.17	Palladium	6.06	Palladium	10.32	Palladium	13.638	Palladium
Au 3	77.255	0.469	7.138	7.29	Au 3	7.15	Au 3	12.50	9ct White 1	14.679	9ct White 1
Au 11	79.653	0.23	7.369	7.30	Au 9	7.37	Au 11	12.61	Au 3	16.138	Au 9
18ct White 1	80.205	1.287	7.381	7.45	Au 11	7.49	18ct White 1	12.64	18ct White 1	16.350	9ct White 2
Au 9	78.111	-1.035	7.642	7.68	9ct White 1	7.71	Au 9	12.69	Au 11	16.358	9ct White 3
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18ct White 5	79.913	1.087	8.658	8.64	9ct White 2	8.73	18ct White 5	13.96	9ct White 2	18.146	18ct White 2
18ct White 6	80.434	1.456	8.696	8.71	9ct White 3	8.82	18ct White 6	14.22	9ct White 3	18.539	14ct White 1
14ct White 1	83.86	-0.102	8.885	8.85	14ct White 1	8.89	14ct White 1	14.58	14ct White 1	18.719	18ct White 3
18ct White 4	84.401	0.306	9.062	9.02	18ct White 5	9.07	18ct White 4	14.77	18ct White 6	19.145	18ct White 4
18ct White 7	78.219	0.686	9.068	9.16	18ct White 4	9.09	18ct White 7	14.78	18ct White 5	19.874	18ct White 5
Au 6	75.097	0.772	9.124	9.18	18ct White 6	9.16	Au 6	14.78	18ct White 4	19.972	Au 12
9ct White 2	92.921	-1.889	9.266	9.30	18ct White 7	9.46	14ct White 3	15.71	18ct White 7	20.136	14ct White 2
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Au 12	80.563	-0.45	9.459	9.38	Au 6	9.47	Au 12	15.97	Au 12	20.683	18ct White 7
9ct White 3	93.234	-2.292	9.472	9.54	14ct White 2	9.54	18ct White 10	16.12	18ct White 8	20.685	9ct White 4
18ct White 10	78.566	0.843	9.505	9.73	14ct White 3	9.63	18ct White 8	16.32	Au 6	20.931	18ct White 8
18ct White 8	81.281	0.42	9.618	9.76	18ct White 8	9.75	9ct White 3	16.37	18ct White 10	20.969	18ct White 9
14ct White 2	81.487	-0.958	9.859	9.79	18ct White 10	9.91	14ct White 2	16.47	14ct White 2	21.262	14ct White 3
Au 7	76.91	0.884	10.188	10.25	18ct White 9	10.23	Au 7	16.52	18ct White 9	21.398	9ct White 5
18ct White 11	79.252	0.876	10.216	10.48	Au 7	10.25	18ct White 11	17.41	18ct White 11	21.548	Au 6
18ct White 9	85.342	-0.104	10.283	10.51	18ct White 11	10.28	18ct White 9	17.54	9ct White 4	21.654	18ct White 10
18ct White 12	77.199	1.817	10.287	10.87	9ct White 4	10.45	18ct White 12	17.78	Au 7	22.169	9ct White 6
9ct White 4	90.816	-2.029	11.549	10.89	18ct White 12	11.61	Au 1	17.89	18ct White 12	22.501	Au 1
Au 1	86.463	-0.9	11.577	11.18	9ct White 5	11.73	9ct White 4	18.28	Au 1	22.978	18ct White 11
9ct White 5	89.633	-2.269	11.934	11.28	Au 1	12.15	9ct White 5	18.28	9ct White 5	23.465	Au 7
9ct Yellow 1	91.647	-0.114	13.143	12.14	9ct White 6	13.14	9ct Yellow 1	19.45	9ct White 6	24.480	18ct White 12
9ct White 6	93.53	-3.223	13.216	13.11	9ct Yellow 1	13.31	Au 10	19.66	9ct Yellow 1	24.902	9ct Yellow 1
Au 10	77.696	0.1	13.308	13.20	Au 5	13.49	Au 5	21.89	Au 5	27.079	Au 5
Au 5	82.261	-0.786	13.463	13.27	Au 10	13.60	9ct White 6	22.62	Au 10	28.609	Au 10
18ct White 13	80.687	1.403	14.37	14.84	18ct White 13	14.44	18ct White 13	23.59	18ct White 13	31.178	18ct White 13
14ct Red 1	85.373	7.774	15.222	15.29	Au 8	15.48	Au 8	23.81	14ct Red 1	31.903	Au 8
Au 8	79.248	-0.531	15.468	15.80	Au 4	15.72	Au 4	25.57	Au 8	33.784	Au 4
Au 4	77.057	0.253	15.716	17.32	Au 2	16.73	Au 2	25.78	Au 2	34.018	14ct Yellow 1

Table 3
Measurement Uncertainty associated with YI D1925 value

U(X)	U(Y)	U(Z)			
1.4532	1.49853	1.7207			
Trial	**X**	**Y**	**Z**	**YI : D1925**	**Tolerance-+/-**
Rhodium	62.767	63.713	71.69	6.828	0.587
Fine Silver	80.427	82.169	90.606	8.402	0.565
95.5 Pt / 4.5 Cu	64.021	65.233	70.584	10.927	0.931
Palladium	57.608	58.585	62.027	13.638	1.302
9ct White 1	79.862	82.316	85.038	14.679	1.010
9ct White 8	64.607	66.191	68.287	15.58	1.331
Au 9	51.973	53.401	54.63	16.138	1.716
9ct White 2	80.215	82.786	84.094	16.35	1.126
9ct White 3	80.704	83.503	84.568	16.358	1.119
Au 11	55.081	56.069	57.796	16.48	1.659
Au 3	51.135	51.957	53.606	16.611	1.803
18ct White 1	56.469	57.045	58.837	17.378	1.715
18ct White 2	57.717	58.373	59.703	18.146	1.756
14ct White 1	62.524	63.797	64.343	18.539	1.655
14ct White 4	64.207	65.5	66.068	18.554	1.613
18ct White 15	59.788	61.378	61.412	18.625	1.736
18ct White 3	50.969	51.608	52.434	18.719	2.054
18ct White 4	63.726	64.84	65.241	19.145	1.681
18ct White 16	56.463	58.088	57.683	19.158	1.894
18ct White 5	55.878	56.528	56.877	19.874	1.998
Au 12	56.391	57.685	57.226	19.972	1.985
14ct White 2	57.815	59.356	58.539	20.136	1.952
18ct White 6	56.941	57.453	57.817	20.188	1.995
18ct White 7	52.819	53.585	53.326	20.683	2.204
9ct White 4	75.568	78.08	76.015	20.685	1.535
18ct White 8	58.018	58.98	58.413	20.931	2.032
18ct White 9	65.349	66.68	65.721	20.969	1.806
14ct White 3	56.104	56.8	56.355	21.262	2.138
9ct White 5	72.957	75.514	72.855	21.398	1.648
Au 6	47.781	48.433	47.852	21.548	2.547
18ct White 10	53.466	54.179	53.495	21.654	2.288
9ct White 6	80.883	84.184	80.064	22.169	1.543
Au 1	67.177	68.917	66.49	22.501	1.893
18ct White 11	54.649	55.367	53.989	22.978	2.387
Au 7	50.727	51.382	49.881	23.465	2.631
18ct White 12	51.558	51.864	50.281	24.48	2.714
9ct Yellow 1	78.319	79.916	75.8	24.902	1.815
Au 5	59.279	60.781	56.055	27.079	2.629
Au 10	51.644	52.697	48.14	28.609	3.210
18ct White 13	57.368	57.908	52.242	31.178	3.189
Au 8	54.083	55.36	48.646	31.903	3.467

Table 4

Visual assessment of BAO standard alloy samples

Standard	Au	Ag	Cu	Zn	Pd	Ni	X	Y	Z	L*	a*	b*	Yellowness index: D1925	Visual Assessment	Assessed Characterisation
Au 9	57.81		15.31	9.74		16.87	51.973	53.401	54.63	78.111	-1.035	7.642	16.138	1	Premium White
Au 11	74.95				10	15	55.081	56.069	57.796	79.653	0.23	7.369	16.480	2	Premium White
Au 3	37.07	10.57	20.1		32.44		51.135	51.957	53.606	77.255	0.469	7.138	16.611	3	Premium White
Au 12	74.98					24.94	56.391	57.685	57.226	80.563	-0.45	9.459	19.972	4	Standard White
Au 6	44.99	12.54	12.53		24.96		47.781	48.433	47.852	75.097	0.772	9.124	21.548	5	Standard White
Au 1	33.32	66.59					67.177	68.917	66.49	86.463	-0.9	11.577	22.501	7	Standard White
Au 7	57.88	27.68			14.43		50.727	51.382	49.881	76.91	0.884	10.188	23.465	6	Standard White
Au 5	37.14	25.09	23.83	4.92		8.96	59.279	60.781	56.055	82.261	-0.786	13.463	27.079	9	Off-white
Au 10	74.83		9.64	2.6		12.89	51.644	52.697	48.14	77.696	-0.1	13.308	28.609	8	Off-white
Au 8	59.01	7.64	11.98	6.74		14.57	54.083	55.36	48.646	79.248	-0.531	15.468	31.903	11	Off-white
Au 4	37.06	20	10.53			32.43	50.728	51.627	44.802	77.057	0.253	15.716	33.784	10	Off-white
Au 2	33.35	44.65	21.98				66.151	66.44	58.221	85.22	2.2	16.583	34.556	12	Off-white
Au 13	91.67	2.76	5.28				56.061	54.84	32.188	78.949	5.696	34.082	68.634	13	Non-white
Au 15	98.6		1.4				60.762	59.639	34.153	81.642	5.38	36.139	69.708	N/A	Non-white
Au 16	99.99						60.989	60.262	32.837	81.98	4.449	38.442	71.784	N/A	Non-white
Au 14	96		4.02				53.709	51.904	28.701	77.223	7.25	35.967	73.837	4	Non-white

Two additional equations used extensively in the colour industry are the Yellowness Indexes, ASTM E313 and ASTM D1925. These equations are derived from the Tri-stimulus values X, Y and Z. It should be noted that formulas exist to convert the Tri-stimulus values (X, Y and Z) to the CIELab co-ordinates (L*, a* and b*).

The E313 Index is described as "the attribute by which an object colour is judged to depart from a preferred white towards a yellow" and is best used for near white samples that have a dominant or complimentary wavelength between 570 – 580nm. The E313 Yellowness Index calculation is (7)

$$\text{YI: E313} = 100 \times (1 - ((0.847 \times Z)/Y))$$

The E313 Index values showed significant correlation to both the previous equations, $b^* + (a^*/3)$ and $\sqrt{(a^{*2} \times b^{*2})}$, with the

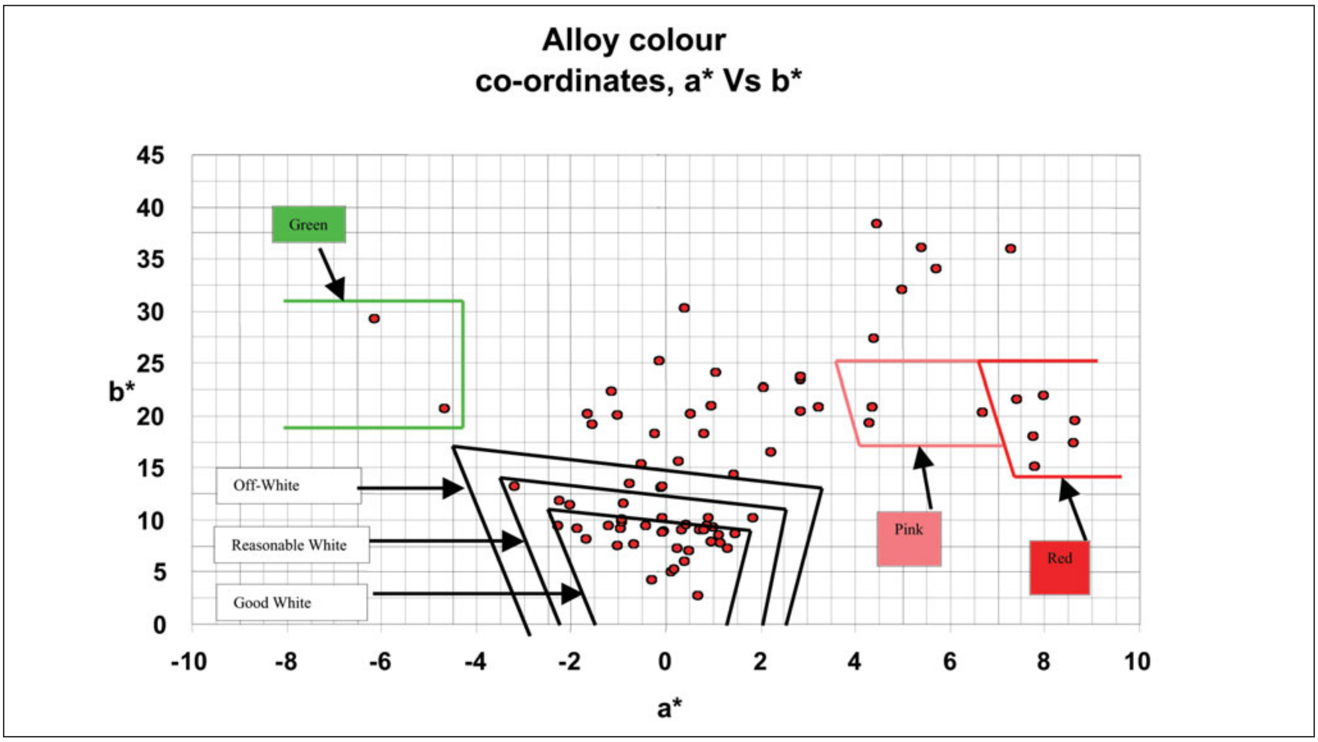

Figure 4

CIELab co-ordinates, a Vs b*, data plotted for all samples. Boxes are potential grades (colour boxes) for all standard colour gold alloys* benefit of being a colour industry standard. However, a comparison of the Yellowness Index values for the alloys measured revealed an issue with regard to the effect of larger a* values not being taken fully into account. For example, the value for alloy 18ct White 13 (a low Palladium white alloy) was 23.59, while the value for alloy 14ct Red 1 was 23.81. The alloys have b co-ordinate values of 14.37 and 15.22, and a* co-ordinate values of 1.4 and 7.77 respectively. Therefore there is little distinction, according to the E313 Yellowness Index, between an 18ct low Palladium White alloy and a 14ct Red alloy. This specific Index only accurately describes premium grade white alloys, where the a* value is small.

The Yellowness Index: D1925 was “developed specifically for determining the yellowness of homogeneous, non-fluorescent near white materials”. The D1925 Yellowness Index is calculated from (8)

$$YI = ((100 \times (1.28 \times X - 1.06 \times Z))/Y)$$

The D1925 Index values displayed several points of correlation to the prior equations, including the E313 Index. However, the ordering of the alloys had shifted so that the 9ct alloys were determined to be whiter than the 18ct alloys. This was supported by a visual assessment of the best 3 examples of the 9ct, 14ct and 18ct alloys. In general the 9ct alloys appeared whiter than the ‘grey’ 18ct alloys, which where in turn whiter than the 14ct alloys. This perceptible whitening of the 9ct alloys is mainly due to the very high level of silver present in these alloys, producing a very high L value, a fact supported by German (2). By referencing L*, a* and b* co-ordinates, we know that the 9ct alloys have a green element to their colouring which serves to deplete the yellow colouring. The 18ct alloys containing Palladium, have a red coloration, which may be what is being perceived as a grey colour. This confirms MacCormack’s previous findings (3).

Referencing the D1925 Index values and comparing these figures to both visual assessments and alloy compositions has enabled grading bands to be identified. The recommended assessment values are shown in Table 5

MacCormack (3) used chroma to grade the colour of the alloys he examined and suggested that an alloy with a chroma value less than 9 was pleasing to the eye and did not require rhodium plating. Referencing Table 2, alloy 18ct White 4 has a YI: D1925 value of 19.145 that corresponds with a chroma value of 9.07. Therefore the grading of Grade 1 white gold alloys to YI: D1925 values of less than 19 agrees with MacCormack’s findings for what is a desirable white gold that does not require rhodium plating.

Another method of colour assessment involved plotting a graph of the measured CIE Lab a* and b* data to produce a co-ordinate map of colours, Figure 4. This method has been employed by others to usually map particular gold alloy colours e.g. white gold alloys (20). This method has the advantages of being able to detail a colour with greater accuracy (separate a* and b* co-ordinates) and any gold colour can be defined. This effectively creates colour boxes for each of the existing gold colours (White, Yellow, Pink, Red and Green), with an intermediate transition zone around or between touching boxes that enables the alloys, whose co-ordinates place them inside this zone, to be described as either colour. These transition zones also need to take into account the tolerances calculated in section 2.

A final method of colour assessment involved converting the Tri-stimulus Values, X, Y and Z, to the Chromaticity co-ordinates u' and v'. This method of colour expression, for gold alloys, clearly lacks the ability to differentiate significantly between the measured colours as all the white alloys examined fall in to the central white region of the colour space, Figure 2.

6.1.2 Every measurement must be evaluated for accuracy and precision to ascertain the uncertainty element. Statistical mathematics can be applied to estimate this uncertainty and this concept was applied to each part of the method used to calculate the ASTM Yellowness Index D1925 Value.

Based upon all of the research and calculations that can be seen in Table 3, the following maximum tolerance limits were considered, Table 6.

The upper limit of the YI:D1925 value is set at 32.0 for the Off-white category as this is the maximum permitted for a white gold. Higher readings will be classed as Non-white gold alloys and therefore the positive component of the tolerance is excluded. The limit value of 32.0 was defined after a review of the YI: D1925 values for commercial alloys showed that a widely accepted straw white, low palladium (7.4%) white gold alloy produced a value of 31.178.

6.1.3 The visual assessment of the BAO standards, by 14 observers in two groups, produced a good correlation of results but neither group managed to arrange all the samples in the correct order, as determined by the b co-ordinate or the D1925 Yellowness Index value, Table 4. The use of 14 observers

Table 5

D1925 Yellowness Index grade bands and maximum tolerances of uncertainty

CATEGORY	GRADE	YI:D1925 VALUE	MAXIMUM TOLERANCE
Grade 1	Good White	< 19.0	+/- 2.0
Grade 2	Reasonable White	19.0 - 24.5	+/- 2.0
Grade 3	Off-white	24.5 - 32.0	- 3 only
Non White	Poor White (Incomplete Bleaching)	> 32.0	

Table 6

Finalised grading proposal

CATEGORY	Grade 1	Grade 2	Grade 3
STANDARD	Good White	Reasonable White	Off White
YI: D1925 VALUE	< 19.0	19.0 - 24.5	24.5 - 32.0
MAXIMUM TOLERANCE	+/- 2.0	+/- 2.0	-3 only
DESCRIPTION	No requirement for rhodium plating	Rhodium plating optional	Will definitely require rhodium plating

Measurement Conditions:

1. Illuminant 'C', observer angle 2^0, Spacular & UV component included
2. CIELab co-ordinates L*= >75.0, a* must be between +3.0 to -3.5

to view the set standards was a method chosen to offset variations in human eye colour perception since the ability to perceive slight colour changes can vary from person to person. The anomalies noted tended to be where the visual rankings were very close e.g. sample Au7 and sample Au1 were ranked 6 and 7 respectively. However, sample Au1 has a slightly lower Yellow index value (closer to white). There may be two potential reasons for this and other similar reversed positions -

- The visual appearance of the two samples was extremely similar, with less than a 1-point change in Yellowness Index co-ordinate values. The human eye struggles to register a change this small so that the perceived order of these samples is interchangeable.
- The difference in their measured values was within the instrumental and measurement variation/tolerance limit, permitting the samples to be interchangeable.

6.2 Metallurgical Considerations

The colour co-ordinates measured can be affected through manipulation of the alloy composition. For example, 9ct alloys typically display the highest L* values, due to the very high silver content (Fine silver has the highest L value of the elements examined, at 92.65) but tend to have a strong green colour element, confirming German's findings (2). The values of a* tend to be negative where a high percentage of silver is present, in the absence of copper (fine silver possesses a negative b value, -0.31).

An examination of the CIELab co-ordinates, L*, a* and b*, together with the alloy elemental compositions, Table 4, provided basic guidelines for alloy compositions to achieve specific colour grading. This data along with data from the other alloys tested provides these guidelines,

All white gold alloys:

- Silver whitens but also colours alloys green
- Palladium whitens but also colours alloys red, confirming MacCormack's findings (3)
- Nickel whitens
- Zinc whitens
- Copper reduces yellowness but increases redness
- Approximate effect of whiteners: 1% silver is equivalent to 1% zinc, 0.6% nickel or 0.5% palladium, agreeing with MacCormack's findings (3)
- Primary Whiteners: The effects of nickel and palladium can be maximised by being added in concert with other alloying elements
- Certain alloying elements inhibit the effect of the primary whiteners

9ct Alloys

- *Grade 1*
  Minimum 62% silver
- *Grade 2*
  Minimum 45% silver

14ct Alloys

- *Grade 1*
  Minimum 26.5% whiteners (of which 16.5% are primary whiteners)
- *Grade 2*
  Minimum 22.5% whiteners (of which 12% are primary whiteners)

18ct Alloys

- *Grade 1*
  Minimum 17.5% whiteners (of which 13.5% are primary whiteners, combined with other alloying elements)
  or
  Minimum 24.5% whiteners (of which 17% are primary whiteners)
- *Grade 2*
  Minimum 19.5% whiteners (of which 7.4% are primary whiteners, combined with other alloying elements)

22ct Alloys

- Cannot be whitened

7 Conclusions

1 The Yellowness Index, ASTM D1925, which is derived from the Tri-stimulus colour co-ordinates, X, Y and Z, produced an acceptable sample ordering, permitting numerical grades to be identified for white gold alloys only. The numeric ordering produced good correlation with visual assessments. The proposed grades are shown in Table 6

2 The CIELab co-ordinate data highlighted some key points

  - L* values are consistently higher for white alloys than for other coloured gold alloys, with values ranging from 75 - 93.

    - b* values varied considerably, from rhodium at 2.81, to the range of white gold alloys, from 7.38 to 14.37. This highlights the distinct difference in perceptible whiteness between rhodium and white gold alloys in general.
    - a* values showed large variations, with many alloys displaying strong red or green aspects. Visual assessments of the alloys confirmed that a green aspect could reduce perceived yellowness, while a red aspect can reinforce it.
    - Formulas employing the CIELab data generally produced good correlation with visual assessments but could not be substantiated.
3. The spectrophotometer instrument used in this study was limited to measuring a 3mm minimum diameter sample. Therefore, another assessment means for items of a smaller size would be required. The proposed Munsell colour charts would satisfy this requirement and, when used in conjunction with controlled lighting and standard observer conditions, will allow for acceptable accuracy for the visual determination of the level of whiteness of an alloy.
4. Samples to be measured should have a 6-micron or better diamond polish finish that would ensure a homogeneous, non-directional finish that provides a realistic and repeatable Y (luminosity) value, which is essential for accurate Yellow Index: D1925 results.
5. The selection of alloying elements to whiten a gold alloy can be complicated by interactions that can occur between the various alloying additions commonly present in gold alloys. These interactions can either enhance or reduce the effects of a whitening agent.
6. To create a system that can specify all gold colours will probably require a graph-based system that will provide a series of distinct colour boxes to classify an alloy. Research suggests that a long-term solution to this problem would involve plotting a graph of the co-ordinates a* vs b* and establishing a tolerance about the proposed grades/colour boxes.

8 Future Work

These proposals have been presented to the MJSA/WGC White Gold Task Force. The proposals have been accepted and have been incorporated into a voluntary US industry guideline for defining white gold alloys and grading within that definition. An additional criteria for defining what is acceptable as a white gold alloy was added after discussion between the European and American White Gold Task Forces. These criteria stipulate that a white gold alloy must have values of L* >75.0 and a* between +3.0 and -3.0.

These definitions have been briefed to the general at Expo NY in March 2005 and are being publicised in the jewellery press. International acceptance of these guidelines is being sought through the international federation, CIBJO.

GretagMacbeth have produced a Munsell colour chart for the different white gold categories, ‘The Whiteness Index’, permitting quick colour comparisons and estimations, making application of the Guidelines easy and practical. The chart uses 7 foil samples of different Yellowness Index values spanning the 3 grades.

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Dippal Manchanda is the Chief Assayer at the Birmingham Assay Office, working on both non-statutory technical projects and day-to-day assay management. He holds a Masters degree (MSc) in inorganic chemistry and has over 20 years experience in assaying and the examination of precious metals and alloys. He is also a Member of the Royal Society of Chemistry, a Chartered Chemist and Chartered Scientist. Since completing his Masters Degree, Dippal has spent his entire career in the field of precious metals and has been involved in several projects including setting up a state of the art Gold/Silver Medallion Manufacturing facility for a Public Sector Undertaking in India. In his role as Chief Assayer, he is responsible for setting, managing and maintaining high analytical standards throughout the Assay Office and providing scientific and technical support on a day-to-day basis to both statutory and non-statutory part of business.

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