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TEST REPORT

Subject:	Author:	
Study of substitutes for rhodium plating on silver alloys: **Characterisation tests on UMICORE's rhodium-ruthenium and rhodium-platinum coatings.**	Sofia BELTRAO, Pierre JOCHUM and Frédéric CHUPIN, Study managers E-mail: s.beltrao@franceclat.fr; p.jochum@franceclat.fr; f.chupin@franceclat.fr	
	Place and date: Besançon, France, 19 December 2022	Distribution: Mr Jean-Pierre BIZE, UMICORE

1) CONTEXT OF THE TESTS

The record high prices of rhodium in recent years have led Francéclat to launch a study into potential alternatives to rhodium plating used in jewellery to protect silver from the effects of sulphidation.

The purpose of this study is to identify potential substitutes and to assess them in terms of colour, sulphidation resistance, perspiration resistance and wear resistance.

This report groups together the results of the tests conducted to characterise two alternative deposits to rhodium plating proposed by UMICORE, a 75/25 ratio rhodium-ruthenium deposit known as RHODUNA ALLOY 1, and a 20/80 ratio rhodium-platinum deposit known as RHODUNA PT 20/80.

The recommended deposit thickness for each solution is 0.1 µm. Furthermore, the application of an intermediate under-layer of either palladium or ruthenium is also proposed.

Silver alloy 935 ‰ plates were sent to UMICORE to be electroplated with each of the solutions to be assessed.

All the plates were pre-coated with a 1-3 µm thick layer of ARGUNA 621 silvering, followed by an intermediate under-layer of either palladium, PALLUNA 457, or ruthenium, RUTHUNA 491, 0.1 µm thick. Two different types of intermediate under-layer were therefore applied, of which the contribution was assessed in parallel with the assessment of the final deposits.
Thus, the four assessed deposit protocols were the following:

- Treatment A: silvering / palladium / rhodium-ruthenium;
- Treatment B: silvering / ruthenium / rhodium-ruthenium;
- Treatment C: silvering / palladium / rhodium-platinum;
- Treatment D: silvering / ruthenium / rhodium-platinum.

Plates coated with a 0.1 µm thick rhodium, RHODUNA DB, deposit also proposed by UMICORE, were characterised in parallel for comparison. Silvering of a thickness of 1 to 3 µm and a 0.1 µm palladium under-layer were applied to the plates prior to the rhodium plating.

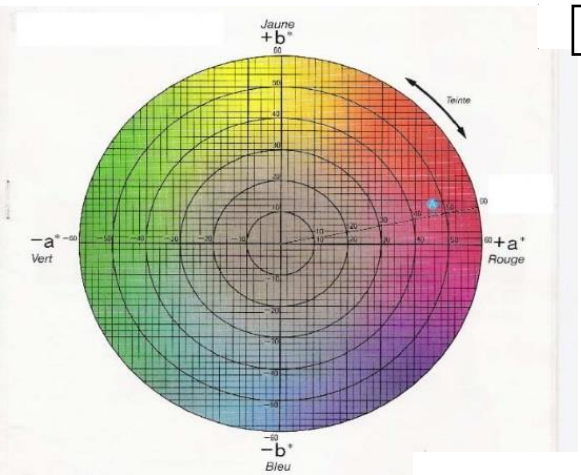
2) COLOUR MEASUREMENT BEFORE TEST

2.1) Test conditions

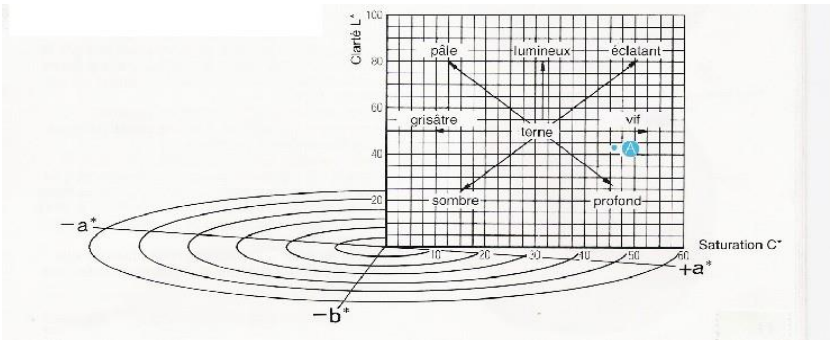
Colour measurements were carried out on six coated plates (per treatment type) in five different zones.

Colour measurements were made in the (L*,a*,b*) system using a MINOLTA CM 2600-d spectrophotometer.

They are expressed by three values: "L*" represents lustre, "a*" the red/green axis and "b*" the blue/yellow axis (axes representing saturation).



For example: A L* = 42.8 a* = 45.04 b* = 9.52



The difference in colour between the rhodium deposit and the alternative deposits is also assessed by calculating the Δ (L*,a*,b*) value according to the formula:

$$\Delta (L^*,a^*,b^*) = \sqrt{((L_r^* - L_a^*)^2+(a_r^* - a_a^*)^2+(b_r^* - b_a^*)^2)}$$

Where L_r^*, a_r^* and b_r^* are the values of L*, a* and b* measured on the plates coated with rhodium and L_a^*, a_a^* and b_a^* are the values of L*, a* and b* measured of the plates coated with an alternative deposit.

This value represents the difference in colour. The higher the value, the greater the colour difference between the two types of deposit.

2.2) Results

The averages of the measured colour values (and their standard deviation in brackets) are given in the following table:

	Colour measurements		
	L*	**a***	**b***
REFERENCE (Pd/Rh)	90.5 (0.1)	0.95 (0.01)	2.02 (0.03)
TREATMENT A (Pd/Rh-Ru)	90.2 (0.1)	0.72 (0.02)	1.59 (0.07)
TREATMENT B (Ru/Rh-Ru)	90.2 (0.2)	0.69 (0.04)	1.55 (0.11)
TREATMENT C (Pd/Rh-Pt)	88.9 (0.2)	0.52 (0.01)	3.39 (0.15)
TREATMENT D (Ru/Rh-Pt)	88.6 (0.4)	0.51 (0.01)	3.50 (0.25)

Colour difference Δ (L*,a*,b*) calculated between the rhodium plating deposit and treatment A (Pd/Rh-Ru): **0.57.**

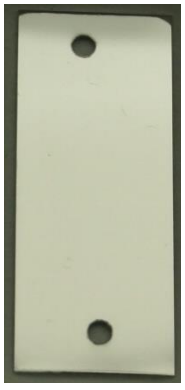
Colour difference Δ (L*,a*,b*) calculated between the rhodium plating deposit and treatment B (Ru/Rh-Ru): **0.62.**

Colour difference Δ (L*,a*,b*) calculated between the rhodium plating deposit and treatment C (Pd/Rh-Pt): **2.15.**

Colour difference Δ (L*,a*,b*) calculated between the rhodium plating deposit and treatment D (Ru/Rh-Pt): **2.45.**

The photos below show a plate coated with each of the deposits.

REFERENCE (Pd/Rh)



TREATMENT A (Pd/Rh-Ru)

TREATMENT B (Ru/Rh-Ru)

TREATMENT C (Pd/Rh-Pt)

TREATMENT D (Ru/Rh-Pt)

The plates coated with the rhodium-ruthenium deposit have a very slightly whiter colour than the rhodium-coated plates (a* and b* closer to 0) regardless of the intermediate under-layer applied (palladium or ruthenium). The calculated colour differences, which are less than 1, correspond to this very slight difference in colour which is not visible to the naked eye**.**

The plates coated with the 20/80 rhodium-platinum deposit have a slightly more yellow colour (higher b* value) and are slightly less bright (lower L* value) than the plates coated with the rhodium deposit. The phenomenon is very slightly less pronounced for the plates coated with a palladium under-layer. **The calculated colour differences, which are slightly higher than 2, are at the limit of what is visible to the naked eye.**

3) SULPHIDATION RESISTANCE

3.1) Test conditions

The sulphidation resistance test was carried out according to a protocol developed in-house.

Two coated plates (per treatment type) and one uncoated plate are placed in a closed chamber containing an ammonium sulphide solution (1 ml of 4% ammonium sulphide + 20 ml of water) for 1 hour.

Colour measurements are made (five per plate) before and after testing and then the Δ (L*,a*,b*) value is calculated according to the formula:

$$\Delta\ (L^*,a^*,b^*) = \sqrt{((L_f^* - L_i^*)^2+(a_f^* - a_i^*)^2+(b_f^* - b_i^*)^2)}$$

Where L_f^*, a_f^* and b_f^* are the values of L*, a* and b* measured after the tests (final) and L_i^*, a_i^* and $b_i^*$are the values of L*, a* and b* measured before the tests (initial).

This value represents the colour variation. The higher the value, the greater the colour variation.

3.2) Results

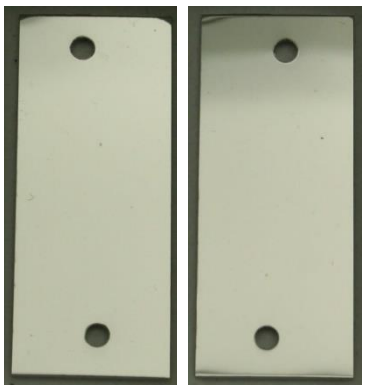
The averages of the measured colour values before and after the sulphidation resistance test with their standard deviation in brackets, as well as the calculated colour variations Δ (L*,a*,b*) are shown in the following table:

	Colour measurements before			Colour measurements after			
	L*	a*	b*	L*	a*	b*	Δ (L*,a*,b*)
SILVER (uncoated)	97.8 (0.2)	0.40 (0.04)	3.09 (0.13)	69.9 (6.3)	1.61 (3.24)	10.58 (5.67)	**28.92**
REFERENCE (Pd/Rh)	90.5 (0.0)	0.95 (0.01)	2.03 (0.02)	90.5 (0.1)	0.93 (0.01)	2.07 (0.04)	**0.06**
TREATMENT A (Pd/Rh-Ru)	90.2 (0.0)	0.74 (0.01)	1.64 (0.03)	90.0 (0.2)	0.66 (0.05)	1.54 (0.09)	**0.27**
TREATMENT B (Ru/Rh-Ru)	90.2 (0.0)	0.71 (0.01)	1.58 (0.03)	90.0 (0.1)	0.64 (0.03)	1.40 (0.07)	**0.26**
TREATMENT C (Pd/Rh-Pt)	88.8 (0.1)	0.53 (0.01)	3.40 (0.10)	88.6 (0.1)	0.51 (0.01)	3.59 (0.08)	**0.25**
TREATMENT D (Ru/Rh-Pt)	88.5 (0.2)	0.53 (0.01)	3.55 (0.19)	88.4 (0.1)	0.54 (0.02)	3.59 (0.12)	**0.07**

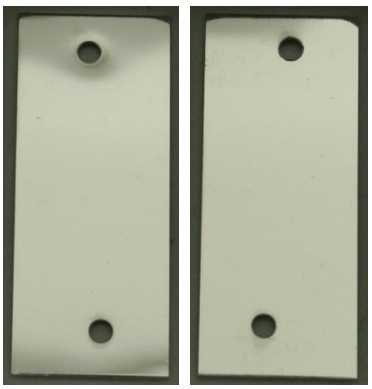
The following photos show the plates after the sulphidation resistance test.

SILVER (uncoated)

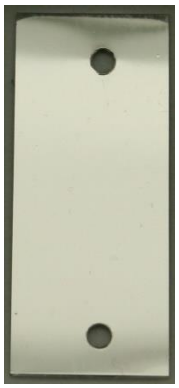
REFERENCE (Pd/Rh)

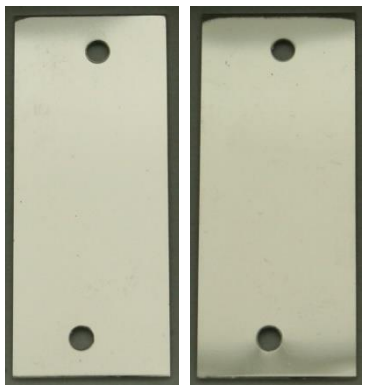


TREATMENT A (Pd/Rh-Ru)

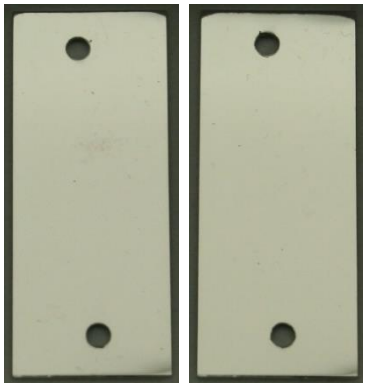


TREATMENT B (Ru/Rh-Ru)





TREATMENT C (Pd/Rh-Pt)



TREATMENT D (Ru/Rh-Pt)

The plates coated with the alternative deposits, either rhodium-ruthenium or rhodium-platinum, are highly resistant to exposure to ammonium sulphide. Indeed, the sulphidation resistance is similar to that of the plates coated with the rhodium deposit. The calculated Δ (L*,a*,b*) values, which are less than 2, are not representative of a significant colour variation that is visible to the naked eye. There is no significant difference resulting from the intermediate under-layer (palladium or ruthenium).

4) PERSPIRATION RESISTANCE

4.1) Test conditions

The test was carried out in accordance with the NF S 80-772 (2010) standard.

Two coated plates (per treatment type) and one uncoated plate are placed on a cotton wool pad saturated with a synthetic perspiration solution (5% lactic acid, 10% sodium chloride and 85% demineralised water), and are then placed in a closed, unalterable chamber and heated to 55°C for 48 hours.

One side of the plate is therefore in direct contact with the perspiration, the other is exposed to the vapour.

Colour measurements are made on each of the two sides of the plates (five measurements per side) before and after testing using the same method as presented in section 2.1 and the colour variation, Δ (L*,a*,b*), is calculated for the sides in contact with the cotton and those exposed to the vapour in the same way as in the sulphidation resistance test.

4.2) Results

Observations after the perspiration resistance test:

- SILVER (uncoated):
  Vapour side: yellowing and corrosion marks
  Cotton side: significant corrosion

- REFERENCE (Pd/Rh):
  Vapour sides: no discolouring or corrosion marks
  Cotton sides: no discolouring or corrosion marks

- TREATMENT A (Pd/Rh-Ru):
  Vapour sides: no discolouring or corrosion marks
  Cotton sides: no discolouring or corrosion marks

- TREATMENT B (Ru/Rh-Ru):
  Vapour sides: no discolouring or corrosion marks
  Cotton sides: no discolouring or corrosion marks

- TREATMENT C (Pd/Rh-Pt):
  Vapour sides: very slight yellowing but no corrosion marks
  Cotton sides: no discolouring or corrosion marks

- TREATMENT D (Ru/Rh-Pt):
  Vapour sides: slight yellowing but no corrosion marks
  Cotton sides: very slight yellowing but no corrosion marks

Colour measurements and photos after the perspiration resistance test:

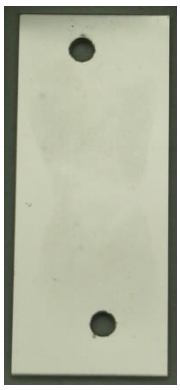
The averages of the measured colour values before and after the perspiration resistance test, with their standard deviation in brackets, as well as the calculated colour variations Δ (L*,a*,b*), are shown in the following tables.

Colour measurements and photos after the perspiration resistance test - **sides exposed to the vapour:**

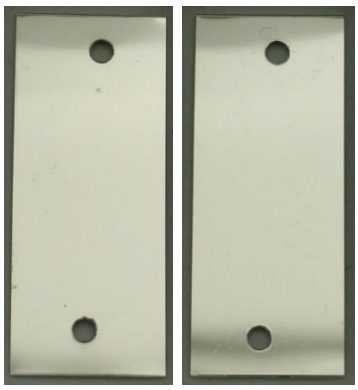
	Colour measurements before			**Colour measurements after**			
	L*	**a***	**b***	**L***	**a***	**b***	**Δ (L*,a*,b*)**
SILVER (uncoated)	98.4 (0.1)	0.30 (0.01)	2.78 (0.05)	86.0 (11.0)	0.55 (0.87)	6.31 (1.28)	**12.90**
REFERENCE (Pd/Rh)	90.5 (0.0)	0.90 (0.00)	2.05 (0.01)	89.9 (0.7)	0.93 (0.02)	2.44 (0.13)	**0.67**
TREATMENT A (Pd/Rh-Ru)	90.1 (0.1)	0.71 (0.02)	1.62 (0.02)	89.7 (0.2)	0.71 (0.03)	2.04 (0.14)	**0.54**
TREATMENT B (Ru/Rh-Ru)	89.8 (0.3)	0.61 (0.06)	1.36 (0.19)	89.8 (0.4)	0.62 (0.05)	1.52 (0.08)	**0.16**
TREATMENT C (Pd/Rh-Pt)	88.6 (0.0)	0.52 (0.01)	3.60 (0.04)	87.5 (0.7)	0.54 (0.03)	4.68 (0.64	**1.52**
TREATMENT D (Ru/Rh-Pt)	88.6 (0.1)	0.51 (0.01)	3.55 (0.04)	86.3 (0.6)	0.49 (0.03)	4.71 (0.41)	**2.57**

The following photos show the plates after the perspiration resistance test - **sides exposed to the vapour**.

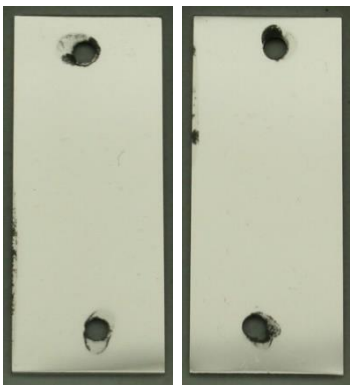
SILVER (uncoated)



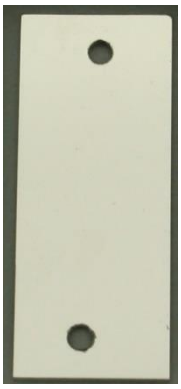
REFERENCE (Pd/Rh)

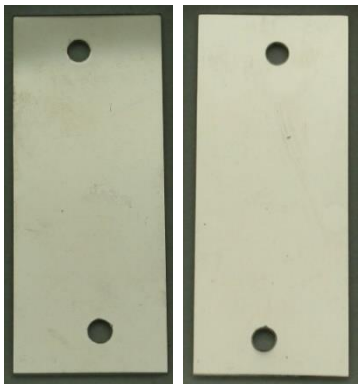


TREATMENT A (Pd/Rh-Ru)

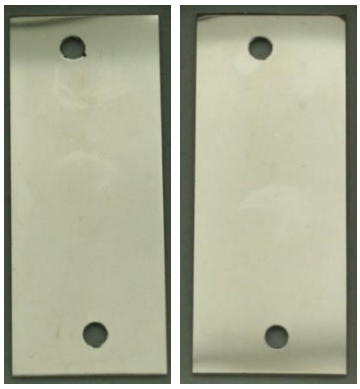


TREATMENT B (Ru/Rh-Ru)





TREATMENT C (Pd/Rh-Pt)



TREATMENT D (Ru/Rh-Pt)

Overall, the plates coated with the rhodium-ruthenium deposit have equivalent resistance to perspiration vapour as plates coated with the rhodium deposit. Only a slight yellowing (slightly higher b* value) is observed which also occurs on the plates coated with the rhodium deposit. The calculated Δ (L*,a*,b*) values, which are less than 2, indicate a colour difference that is not visible to the naked eye. The results are similar regardless of the intermediate under-layer (palladium or ruthenium).

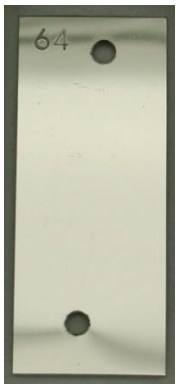
For the plates coated with a 20/80 rhodium-platinum deposit, a slight yellowing is noticeable as confirmed by calculated colour differences which are close to 2. The phenomenon is somewhat more pronounced on plates with a ruthenium under-layer**. The perspiration vapour resistance is however much higher than that of the uncoated plate.**

Colour measurements and photos after the perspiration resistance test - **sides in contact with the cotton:**

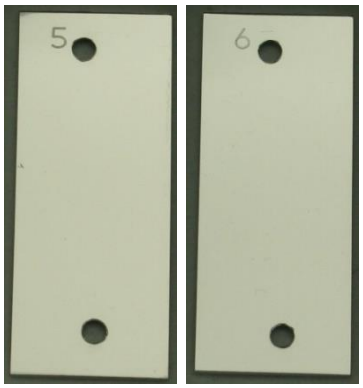
	Colour measurements before			Colour measurements after			
	L*	a*	b*	L*	a*	b*	Δ (L*,a*,b*)
SILVER (uncoated)	97.9 (0.2)	0.30 (0.01)	3.19 (0.24)	78.7 (11.0)	0.39 (1.02)	6.63 (0.39)	**19.59**
REFERENCE (Pd/Rh)	90.5 (0.0)	0.93 (0.02)	2.03 (0.03)	90.3 (0.3)	0.91 (0.01)	2.37 (0.18)	**0.42**
TREATMENT A (Pd/Rh-Ru)	90.1 (0.0)	0.70 (0.01)	1.52 (0.01)	90.0 (0.1)	0.70 (0.01)	1.85 (0.06)	**0.38**
TREATMENT B (Ru/Rh-Ru)	90.2 (0.1)	0.70 (0.02)	1.55 (0.06)	90.3 (0.1)	0.68 (0.02)	1.63 (0.08)	**0.14**
TREATMENT C (Pd/Rh-Pt)	88.7 (0.2)	0.52 (0.01)	3.51 (0.09)	88.3 (0.3)	0.48 (0.02)	4.26 (0.38	**0.86**
TREATMENT D (Ru/Rh-Pt)	88.6 (0.3)	0.52 (0.01)	3.56 (0.22)	87.5 (0.9)	0.49 (0.02)	4.85 (1.15)	**1.70**

The photos below show the plates after the perspiration resistance test - **side in contact with the cotton**.

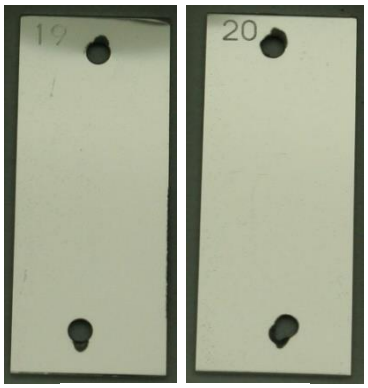
SILVER (uncoated)



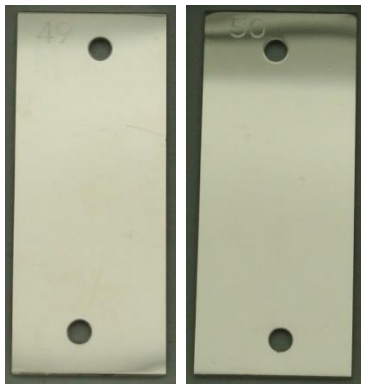
REFERENCE (Pd/Rh)



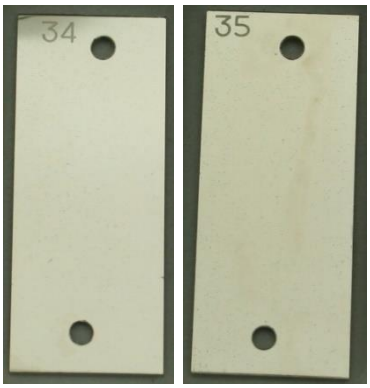
TREATMENT A (Pd/Rh-Ru)



TREATMENT B (Ru/Rh-Ru)



TREATMENT C (Pd/Rh-Pt)



TREATMENT D (Ru/Rh-Pt)

As in the case of exposure to perspiration vapours, the plates coated with the rhodium-ruthenium deposit have equivalent resistance to the contact with perspiration-soaked cotton as the plates coated with the rhodium deposit. Again, only a slight yellowing (slightly higher b* value) is observed which also occurs on the plates coated with the rhodium deposit. The calculated Δ (L*,a*,b*) values, which are less than 2, indicate a colour difference that is not visible to the naked eye. The results are similar regardless of the intermediate under-layer (palladium or ruthenium). **The rhodium-ruthenium deposit therefore has very good perspiration resistance.**

For the plates coated with the 20/80 rhodium-platinum deposit, there is slight yellowing which is barely visible on the plates coated with a ruthenium under-layer. Regardless of the under-layer, the calculated Δ (L*,a*,b*) values are higher than those calculated for the plates coated with the rhodium deposit or those coated with the rhodium-ruthenium deposit. However, the values are still less than 2, and are therefore barely or not at all (for palladium under-layer plates) visible to the naked eye. **The rhodium-platinum deposit has good perspiration resistance.**

5) WEAR RESISTANCE

The plates are wear tested according to the ISO 23160 (2011) standard: the current reference standard for wear, scratch and impact resistance of watch cases and their accessories.

5.1) Test conditions

The plates are tested using a "Turbula", a multi-directional rotating drum. The drum is filled with 4 mm diameter ceramic beads, water and foaming agent.

The wear resistance of the coated plates is assessed using three test durations, namely 2 hours, 5 hours and 10 hours.

Each of the three tests is carried out on two coated plates (per treatment type).

At the end of the tests, a sulphidation test is carried out to reveal any coating deterioration.

Colour measurements are made on each of the coated plates before and after the wear test, followed by the sulphidation test using the same procedure as presented in section 2.1 and the colour variation, Δ (L*,a*,b*), is calculated in the same way as in the sulphidation resistance test.

5.2) Results

5.2.1) Turbula wear test duration 2 hours

Observations:

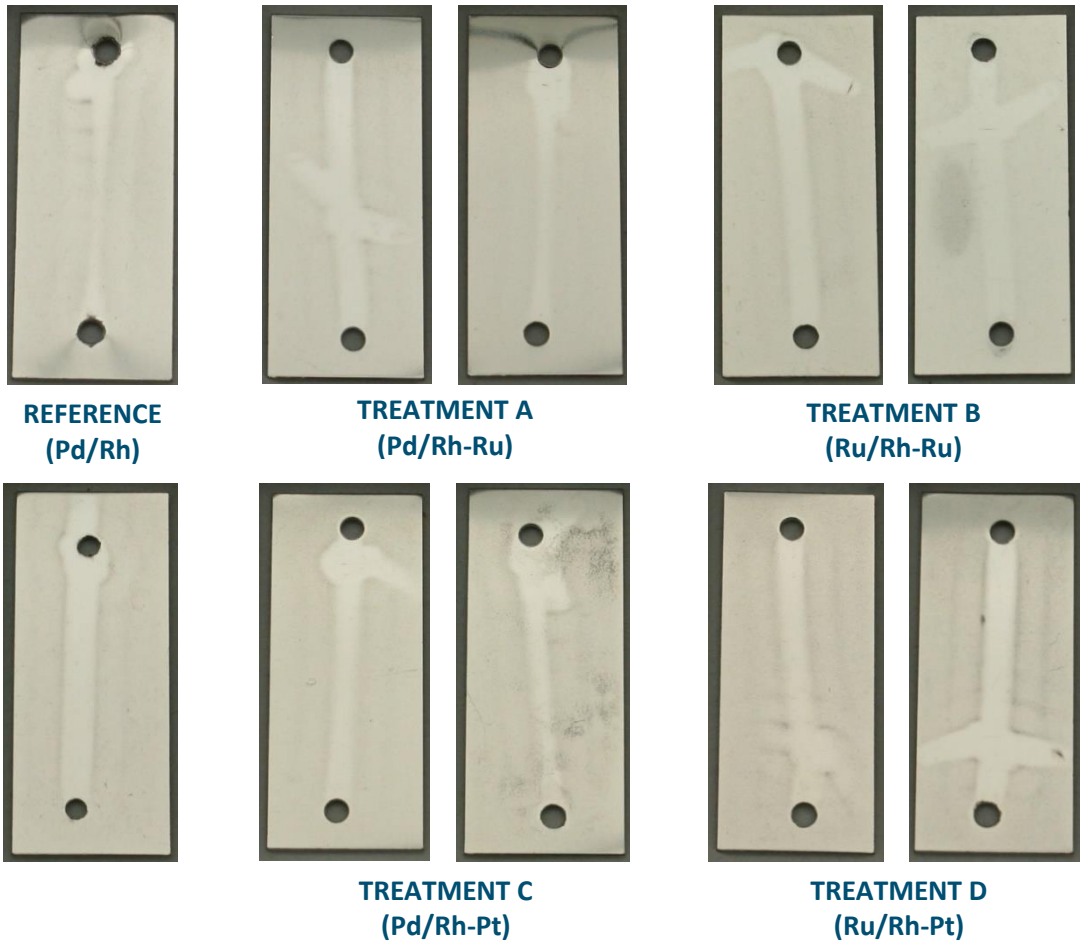
- REFERENCE (Pd/Rh): slight wear marks;
- TREATMENT A (Pd/Rh-Ru): slight wear marks;
- TREATMENT B (Ru/Rh-Ru): slight wear marks;
- TREATMENT C (Pd/Rh-Pt): slight wear marks;
- TREATMENT D (Ru/Rh-Pt): slight wear marks.

Colour measurements and photos after the 2-hour Turbula wear test followed by the ammonium sulphide sulphidation test:

The averages of the measured colour values before and after testing, with their standard deviation in brackets, as well as the calculated colour variations Δ (L*,a*,b*) are shown in the table below.

	Colour measurements before			Colour measurements after			
	L*	**a***	**b***	**L***	**a***	**b***	**Δ (L*,a*,b*)**
REFERENCE (Pd/Rh)	90.5 (0.0)	0.95 (0.01)	2.02 (0.01)	87.5 (0.6)	0.89 (0.04)	2.62 (0.20)	**3.02**
TREATMENT A (Pd/Rh-Ru)	90.2 (0.0)	0.72 (0.03)	1.61 (0.09)	88.4 (0.3)	0.66 (0.03)	2.10 (0.22)	**1.94**
TREATMENT B (Ru/Rh-Ru)	90.2 (0.0)	0.70 (0.02)	1.60 (0.05)	88.3 (0.4)	0.63 (0.07)	2.09 (0.32)	**1.96**
TREATMENT C (Pd/Rh-Pt)	88.9 (0.0)	0.52 (0.02)	3.36 (0.08)	84.9 (1.4)	0.56 (0.07)	3.81 (0.21	**3.96**
TREATMENT D (Ru/Rh-Pt)	88.3 (0.2)	0.52 (0.01)	3.66 (0.18)	84.6 (0.7)	0.51 (0.07)	3.78 (0.29)	**3.69**

The photos below show the plates after the 2 hour Turbula wear test followed by the sulphidation test:



Very slight sulphidation marks are observed on all the plates regardless of the deposit.

The rhodium-ruthenium coated plates are the most resistant to the 2-hour wear test. The colour differences calculated after the sulphidation test are close to 2, i.e. at the limit of what is visible to the naked eye. There is a slight loss of lustre and a small increase in the b* value which indicates slight yellowing. There is no difference in the applied intermediate under-layer (palladium or ruthenium).

The results obtained on the plates coated with the 20/80 rhodium-platinum deposit are slightly worse than those obtained on the plates coated with the rhodium deposit with colour differences calculated at the end of the sulphidation test of around 4 compared to 3 for the plates coated with the rhodium deposit. The colour differences are mainly due to a loss of lustre with a drop in the L* value. An increase in the b* value, which corresponds to yellowing, also occurs, but in similar proportions to that observed on the plates coated with the rhodium deposit. Again, the type of under-layer has no significant influence.

5.2.2) Turbula wear test duration 5 hours

Observations:

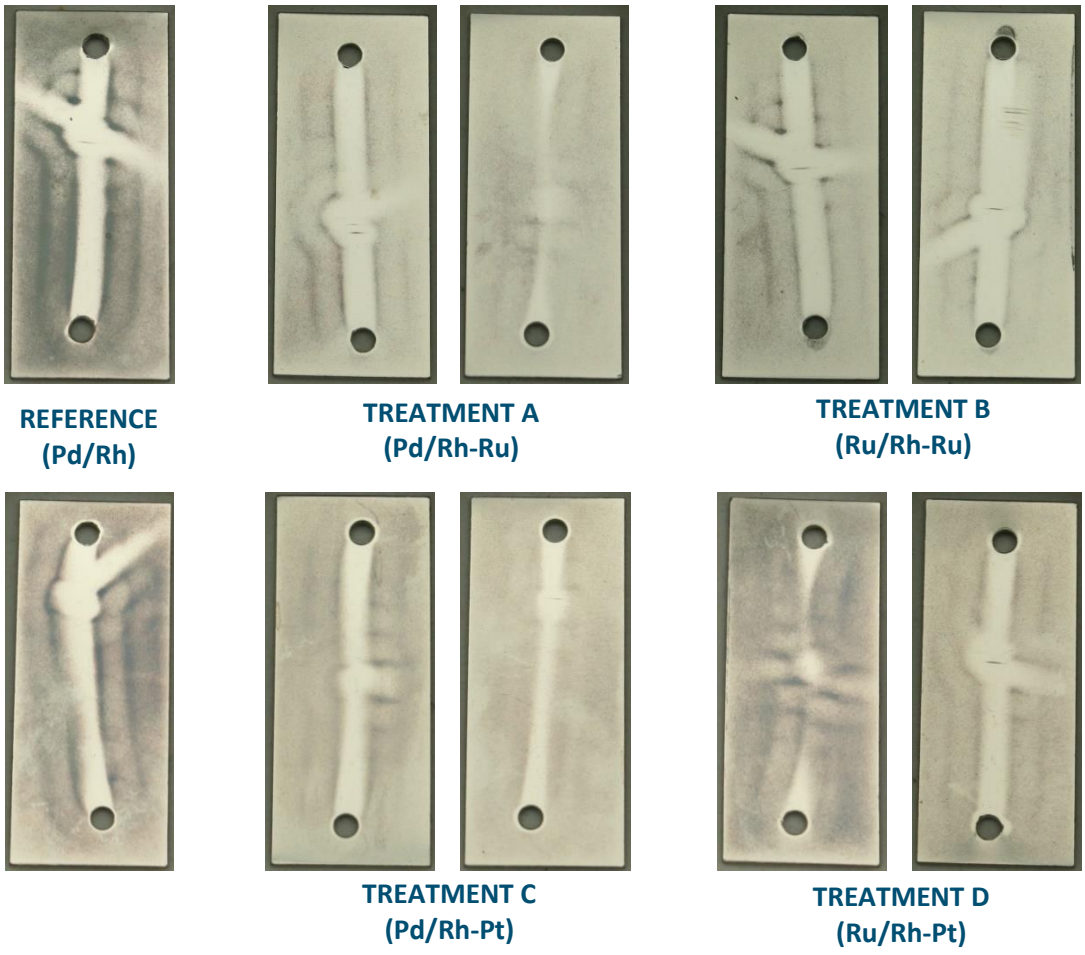
- REFERENCE (Pd/Rh): significant wear marks;
- TREATMENT A (Pd/Rh-Ru): wear marks;
- TREATMENT B (Ru/Rh-Ru): wear marks;
- TREATMENT C (Pd/Rh-Pt): wear marks;
- TREATMENT D (Ru/Rh-Pt): wear marks.

Colour measurements and photos after the 5-hour Turbula wear test followed by the ammonium sulphide sulphidation test:

The averages of the measured colour values before and after testing, with their standard deviation in brackets, as well as the calculated colour variations Δ (L*,a*,b*) are shown in the table below.

	Colour measurements before			**Colour measurements after**			
	L*	**a***	**b***	**L***	**a***	**b***	**Δ (L*,a*,b*)**
REFERENCE (Pd/Rh)	90.5 (0.0)	0.96 (0.01)	2.02 (0.02)	64.4 (4.1)	1.56 (1.14)	-1.60 (1.14)	**26.35**
TREATMENT A (Pd/Rh-Ru)	90.2 (0.1)	0.72 (0.03)	1.58 (0.07)	82.8 (3.8)	1.23 (0.68)	1.60 (0.49)	**7.43**
TREATMENT B (Ru/Rh-Ru)	90.2 (0.0)	0.71 (0.02)	1.58 (0.06)	82.6 (3.6)	1.17 (0.52)	1.51 (0.35)	**7.65**
TREATMENT C (Pd/Rh-Pt)	89.1 (0.1)	0.52 (0.01)	3.18 (0.09)	77.9 (2.5)	1.49 (0.42)	3.20 (0.67)	**11.17**
TREATMENT D (Ru/Rh-Pt)	89.1 (0.2)	0.51 (0.01)	3.15 (0.07)	73.4 (6.0)	1.74 (0.45)	2.07 (1.94)	**15.85**

The photos below show the plates after the 5 hour Turbula wear test followed by the sulphidation test:



At the end of the 5-hour wear test, a clear deterioration of the rhodium deposit is observed, as evidenced by the sulphidation test. Indeed, a significant tarnishing of the plates is observed, resulting in a calculated Δ (L*,a*,b*) value close to 30. The rhodium deposit therefore no longer completely protects the silver alloy plates from sulphidation. Wear on the palladium under-layer is also likely to have occurred.

The two assessed alternative deposits withstand the test much better, especially the rhodium-ruthenium deposit, although some wear is nevertheless observed. The calculated colour differences, around 7.5 for the rhodium-ruthenium coated plates and between 11 and 16 for the rhodium-platinum coated plates, are much lower than those calculated for the rhodium coated plates after the sulphidation test. These are essentially a loss of plate lustre.

For the rhodium-platinum deposits, the results are better when the intermediate under-layer is a palladium deposit.

5.2.3) Turbula wear test duration 10 hours

Observations:

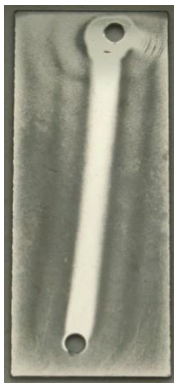
- REFERENCE (Pd/Rh): significant wear marks;
- TREATMENT A (Pd/Rh-Ru): wear marks;
- TREATMENT B (Ru/Rh-Ru): wear marks;
- TREATMENT C (Pd/Rh-Pt): wear marks;
- TREATMENT D (Ru/Rh-Pt): wear marks.

Colour measurements and photos after the 10-hour Turbula wear test followed by the ammonium sulphide sulphidation test:

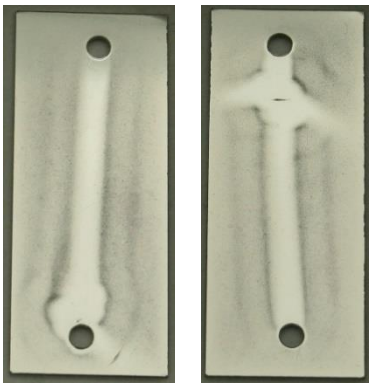
The averages of the measured colour values before and after testing, with their standard deviation in brackets, as well as the calculated colour variations Δ (L*,a*,b*) are shown in the table below.

	Colour measurements before			**Colour measurements after**			
	L*	**a***	**b***	**L***	**a***	**b***	**Δ (L*,a*,b*)**
REFERENCE (Pd/Rh)	90.5 (0.0)	0.95 (0.00)	2.04 (0.03)	60.6 (4.6)	-0.31 (0.75)	-2.28 (1.83)	**30.20**
TREATMENT A (Pd/Rh-Ru)	90.2 (0.1)	0.72 (0.02)	1.57 (0.08)	79.7 (2.1)	0.56 (0.34)	1.28 (0.46)	**10.52**
TREATMENT B (Ru/Rh-Ru)	90.2 (0.1)	0.70 (0.03)	1.56 (0.05)	82.1 (1.5)	0.47 (0.08)	1.40 (0.36)	**8.17**
TREATMENT C (Pd/Rh-Pt)	89.0 (0.1)	0.52 (0.01)	3.31 (0.04)	76.9 (2.8)	0.84 (0.23)	3.63 (0.81	**12.11**
TREATMENT D (Ru/Rh-Pt)	88.7 (0.3)	0.51 (0.01)	3.46 (0.14)	73.7 (2.5)	0.74 (0.56)	2.43 (0.75)	**15.05**

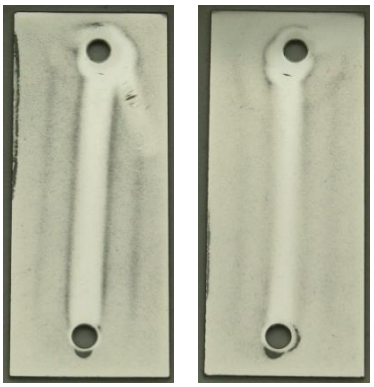
The photos below show the plates after the 10 hour Turbula wear test followed by the sulphidation test:



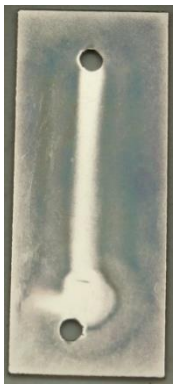
REFERENCE (Pd/Rh)

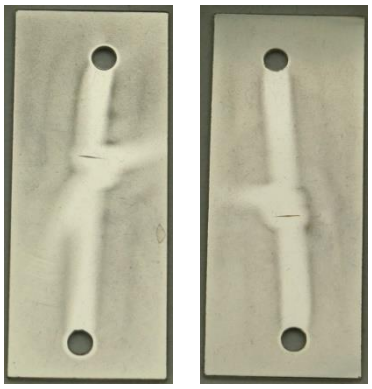


TREATMENT A (Pd/Rh-Ru)

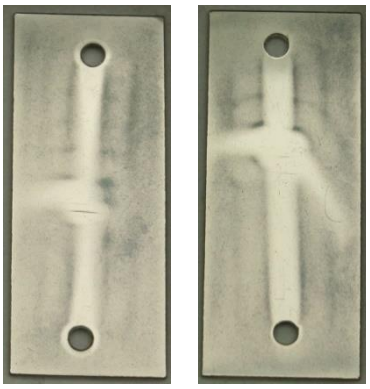


TREATMENT B (Ru/Rh-Ru)





TREATMENT C (Pd/Rh-Pt)



TREATMENT D (Ru/Rh-Pt)

At the end of the 10-hour wear test, the deterioration of the rhodium deposit is slightly greater than at the end of the 5-hour test. The deposit no longer protects the silver from sulphidation. The silvering and the palladium under-layer are also no longer effective.

The two assessed alternative deposits withstand the wear test better than the plates coated with the rhodium deposit.

Indeed, after 10 hours of testing, the results obtained on the plates coated with the rhodium-platinum deposit are similar to those obtained after 5 hours. Once again, the palladium under-coat appears to provide higher wear resistance.

For the plates coated with the rhodium-ruthenium deposit, a slight increase in wear is shown by the colour measurements taken after the sulphidation test. However, they still have the best wear resistance of the three tested deposits.

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6) CONCLUSION

The colour of the plates coated with the rhodium-ruthenium deposit is equivalent to that of the rhodium deposit. The plates coated with the rhodium-platinum deposit have a slightly more yellow colour (higher b* value) and are slightly less bright (lower L* value). The calculated colour differences, which are slightly higher than 2, are, however, at the limit of what is visible to the naked eye. The type of the applied intermediate under-layer has no real influence on the colour of the deposits.

All the assessed deposits protect the silver alloy equally well from the effects of sulphidation. The type of the applied under-layer also has no real influence in this case.

Protection from the effects of perspiration is also provided regardless of the nature of the deposit. However, there is a very slight vulnerability on plates coated with the rhodium-platinum deposit when preceded by a ruthenium under-layer.

The two tested alternative deposits to rhodium have a much higher wear resistance than the rhodium deposit.

The rhodium-ruthenium deposit gives the best results regardless of the type of under-layer. The wear resistance after 10 hours of testing is generally satisfactory, whereas the rhodium deposit is completely worn.

The rhodium-platinum deposit has a slightly lower wear resistance than the rhodium deposit after 2 hours of testing, but the trend is strongly reversed after 5 hours. This is because the rhodium deposit has virtually lost its protective role against sulphidation, whereas the rhodium-platinum deposit still protects the silver alloy plates, especially with a palladium under-layer.

The two types of alternative deposit to rhodium plating assessed are broadly similar to rhodium plating in terms of colour, sulphidation and perspiration resistance. They even have better wear resistance. With the characterisation tests carried out, no significant influence of the nature of the applied under-layer was observed.