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In 1992, Filipe Silva did his final Engineering Degree internship in a Portuguese Jewellery company with more than 200 employees in a project to reduce shrinkage pores in lost wax castings and worked there for 3 years. Since then he did technology consultancy in about 10 Portuguese jewellery companies in different areas but mainly in the waste recovery field. Since 1993 Filipe is a Professor at Minho University, Portugal, working on the mechanics of materials field and on materials and technologies for the jewellery field. In the last 4 years Filipe led a research team on the jewellery field in a project called GRADOURO with two companies in which his team developed new casting processes and developed some other processing techniques like powder metallurgy. He holds 2 patents on jewellery technologies and submitted two other patents on the same field. Among others he is supervising 2 PhD and 5 MSc students in different areas of jewellery applications. He holds a PhD on Mechanics of Materials of Materials from Minho University, Portugal.

New decorative coatings offer a substantial opportunity to improve aesthetics on jewelry components. In order to apply new coatings in jewelry field abrasion and tarnishing resistance are basic requirements. However resistance to abrasion and to tarnishing of the new PVD coatings is still far from being studied for jewelry components. This paper is concerned with abrasion and tarnishing resistance of interference colors in transparent coatings (Me-Ox), as well as of intrinsic colours based on Me-NxOx and dark Me-NxOxCx coatings. All coatings were obtained by reactive sputtering. A comparison of traditional coatings obtained by electroplating (gold and rhodium) and the new coatings will be made. Color change on all coatings will be assessed under common jewelry abrasion and tarnishing conditions.

# Evaluation of new decorative coatings obtained by reactive sputtering for jewelry applications

## Comparative study of abrasion and tarnishing resistance

### 1. Introduction

Decorative PVD coatings have been developed and may replace the traditional gold plating used for 'high-value' jewelry [1] or may add new colors that may offer a substantial opportunity to improve aesthetics on jewelry components. Yellow TiN PVD coatings [2] as well as other materials combinations such as TiOx[3], TiOxNy [4], and TiOxNyCz[5]) offer different colors such as brown, grey, black, red, blue, etc. Because of the higher price of the final product as compared to traditional electroplating coatings, great performance of the PVD coatings is requested. A combination of PVD and electroplating may also be necessary for good coatings performance. PVD coatings have to meet a variety of requirements: attractive color, high wear resistance and good corrosion resistance. Among all the vacuum coating techniques, PVD magnetron sputtering plays a significant role. Actually, several advantages make the cathode sputtering technique more suitable: Its capability of deposition around corners allows three-dimensional geometry parts to be uniformly coated; The possibility of using temperatures lower than 200°C increases the number of substrates to which the PVD process can be applied (plastics, metals, etc); Cathode sputtering easily enables coating using metal applications such as titanium–aluminium, titanium–zirconium, etc, etc. This versatility is only limited by the availability of targets with complex chemical compositions. This allows the obtainment of an almost infinity of colors and textures. For many years, titanium-based PVD coatings have played a major role thanks to their biocompatibility, wide range of available colors and relatively low target price. This paper is concerned with the evaluation of abrasion and tarnishing resistance of interference colors (TiOx), and of different intrinsic colors obtained by different combinations of titanium and gases (TiOxNy, and TiOxNyCz).

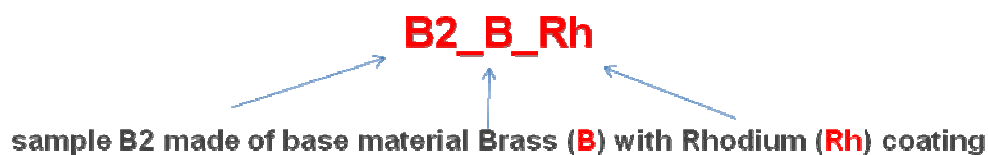
### 2. Materials and Methods

Different common electroplated coatings were tested: Gold and Rhodium platings.

- Two base materials were tested: brass (B) and silver (Ag);
- Two Intermediate coatings were used to improve adherence of coating to base material: Copper (Cu) and Niquel (Ni).

The following legend show the sequence of coatings as presented in the legends of graphs in the text.

#### Example of legend of specimen Electroplated with Rhodium

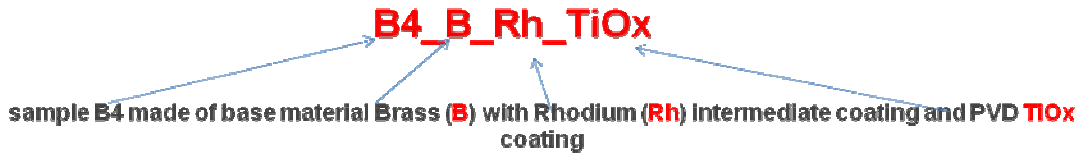


Three PVD systems were tested: TiOx; TiOxNy; and TiOxNyCz

- Three base materials were tested : brass (L), silver (P), and steel (S)
- Two Intermediate coatings were used in some cases (to improve adherence of coating to base material): Copper (Cu), Niquel (Ni).

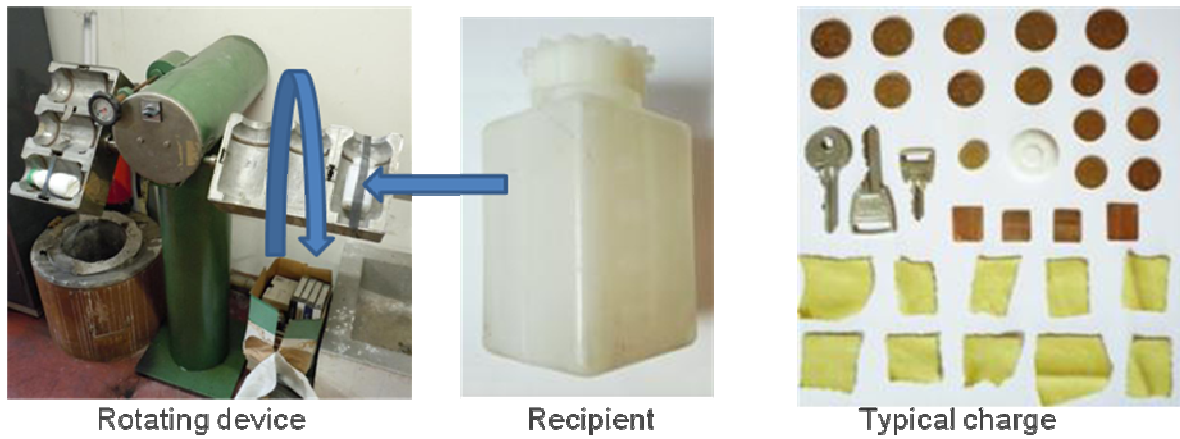
The following legend shows the sequence of coatings as presented in the legends of graphs in the text.

**Example of legend of specimen coated by PVD with Oxide of Titanium**



***Abrasion testing***

Coated pieces were placed inside the recipient along with a charge composed by keys, coins, textile parts, and rotated at 18 r.p.m. for different periods (1 min, 5 min, 10 min, 15 min, 20 min, 25 min, and 30 min) (Fig.1). After each period, scratches (%) and color were measured in each coating.



*Fig. 1. Abrasion testing details.*

Abrasion analysis was performed according to the following scheme as shown on Fig.2. After each period pictures of the samples were taken by using an optical microscope. Then the images were evaluated by using an image software. Scratches percentage on the sample was defined for each sample.

**•Abrasion analysis – scratches quantification**

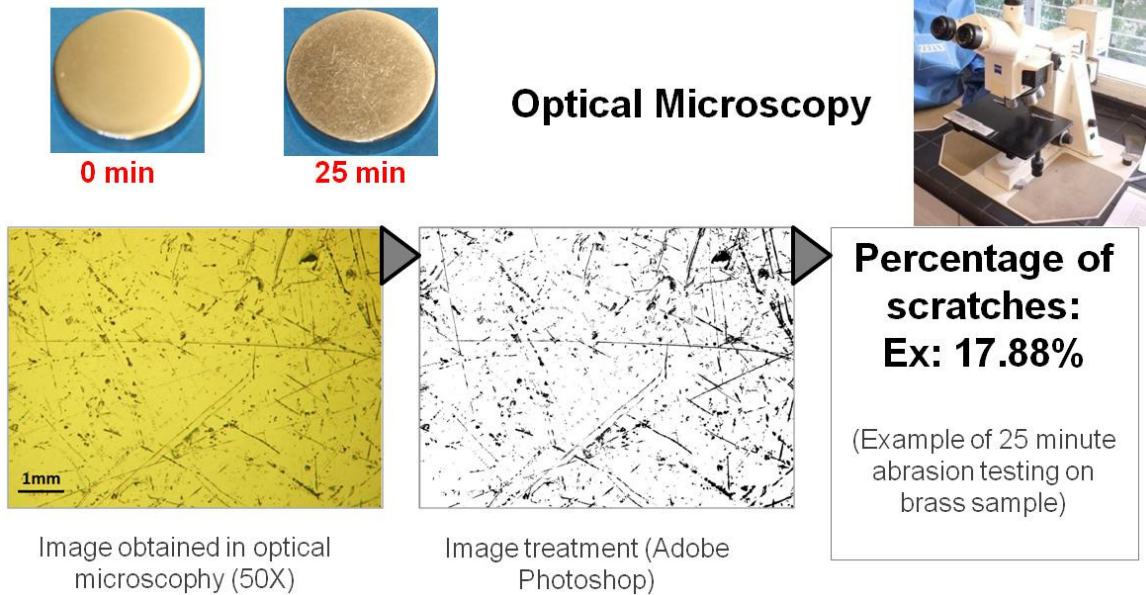


Fig. 2. Abrasion analysis details – scratches quantification.

Color quantification was performed by using a CIELab coordinates system, as shown on Fig.3. Graphs for color evaluation were derived for samples as a function of testing time.

**•Abrasion analysis – colour quantification**  
**- Spectrophotometry**

- Colour coordinates (L\*a\*b\* - CIELab);

Shift in colour was obtained with time

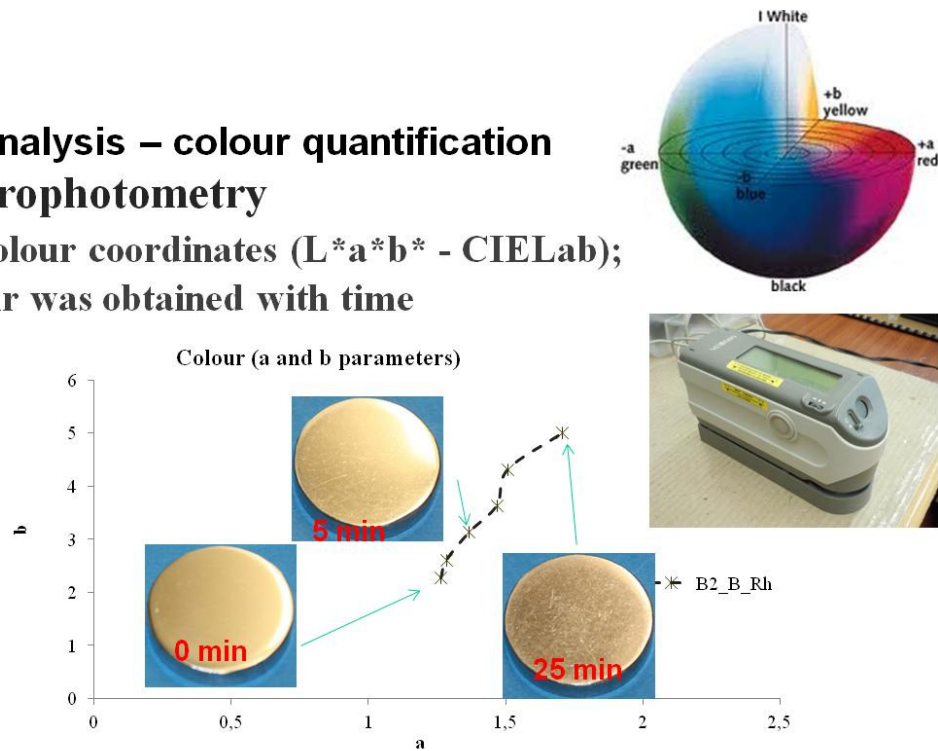


Fig. 3. Abrasion analysis details – color quantification.

### **Tarnishing testing**

Coated pieces were immersed in artificial sweat for different periods (1h, 24h, 5 days, 9 days, 18 days). After each period color was quantified by using a CIELab coordinates system. Graphs for color evaluation were derived for samples as a function of testing time, as shown on Fig.4.

## **•Tarnishing test and analysis - quantification**

**Pieces were immersed in artificial sweat for several periods: 1h, 24h; 5 days, 9 days, 18 days.**

**As for scratches, after each period colour coordinates (L\*a\*b\* - CIELab) were obtained.**

### **- Spectrophotometry**

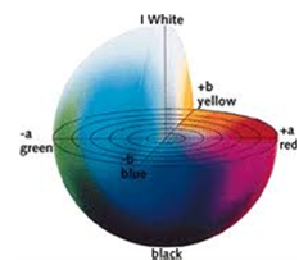


Fig. 4. Tarnishing tests details.

### **Electroplating details**

Electroplating parameters are shown on table 1

Table 1: Electroplating details

Material	Voltage (V)	Temp (°C)	Deposition Time
Au	3,5	60	1 min
Cu	0,6	45	20 s
Ni	1,25	60	1 min
Rh	3	35	40 s

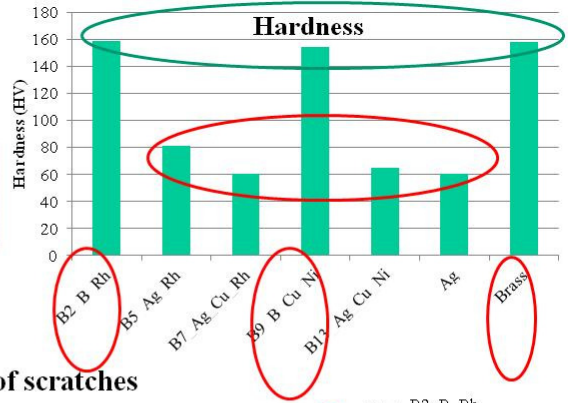
## **3. Results and discussion**

### **Electroplating Coatings**

Results for electroplating coatings are shown on Figs. 5 to 8 for Rhodium and Gold.

**Legend:**

**B2\_B\_Rh** – specimen (B2)\_Brass (B)\_  
(Rhodium) (Rh).



**Percentage of scratches**

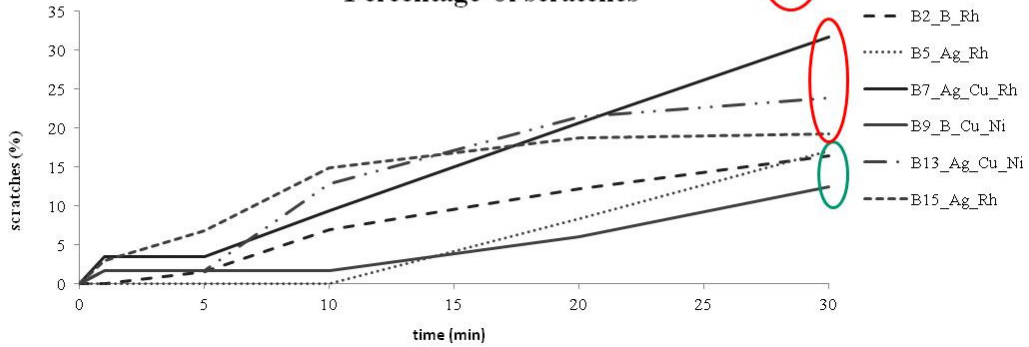
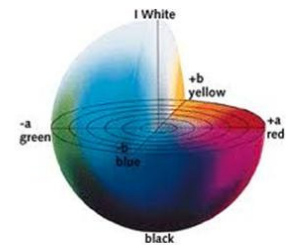
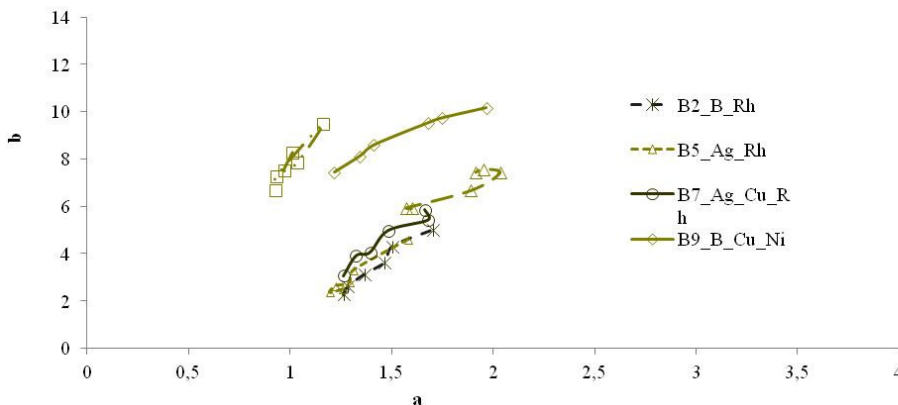


Fig. 5. Scratch and hardness quantification for Rh electroplating coatings.

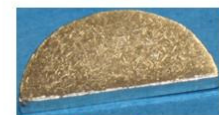
**Colour (a and b parameters)**



**Ex:**



**0 min**



**30 min**

Fig. 6. Color quantification due to scratches for Rh electroplating coatings.

From fig. 5 can be seen that a substantial amount of scratches (10% to 25%) was obtained. It seems that electroplated coatings are very dependent on hardness of base material (Silver or Brass). Harder base materials have less scratches. Regarding color variation from Fig. 6 it is clear that some changes in color were observed in most specimens. This means that some scratches not only plastic deformed the coating but removed the coating bringing into evidence the intermediate coating or the base material.

**Legend: C4\_B\_Cu\_Ni\_Au** – specimen C4\_ (base material Brass) **B\_**(Copper) **Cu\_**(Niquel)**Ni\_**(Gold)**Au**

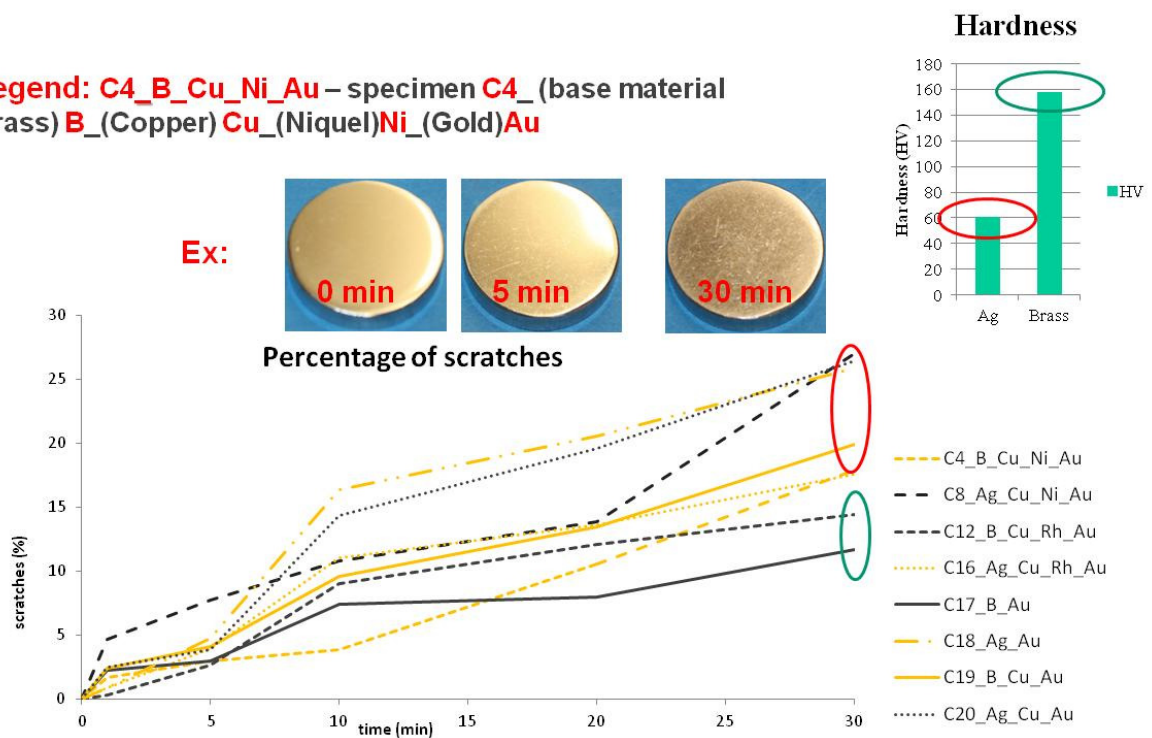


Fig. 7. Scratch and hardness quantification for Au electroplating coatings.

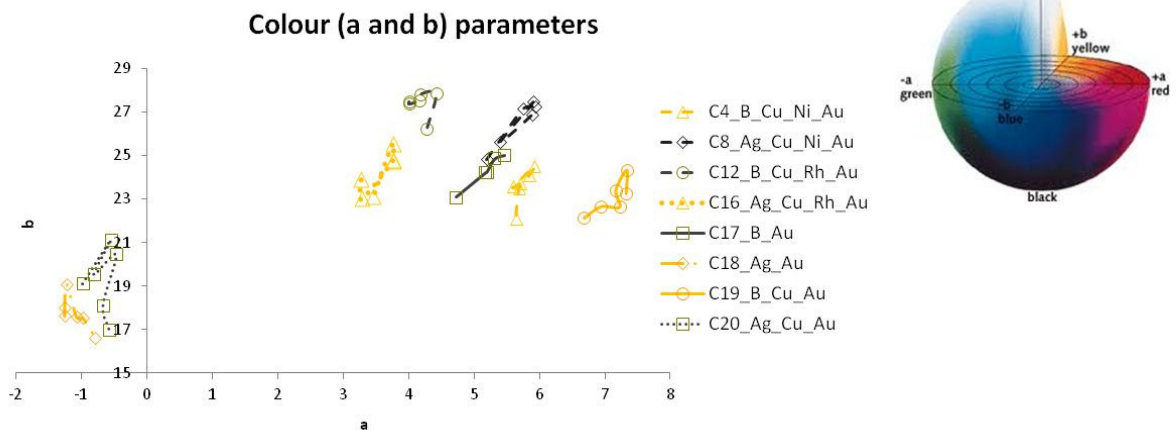


Fig. 8. Color quantification due to scratches for Au electroplating coatings.

It can be observed in Figs 7 and 8 that as with Rhodium, gold coatings show a substantial amount of scratches (10% to 25%). Again it seems that electroplated coatings are more dependent on hardness of base material (Silver or Brass) than on intermediate coatings. Harder base materials have less scratches. Regarding color, as with Rhodium, gold coatings show some changes in color in most specimens. This means that some scratches not only plastic deformed the coating but removed the coating bringing into evidence the intermediate coating or the base material.

## PVD Coatings

### Scratch analysis

Three different coatings were tested: TiOx, TiOxNy, and TiOxNyCz. Details and results for scratch of TiOx coatings are presented in Figs. 9 to 20.

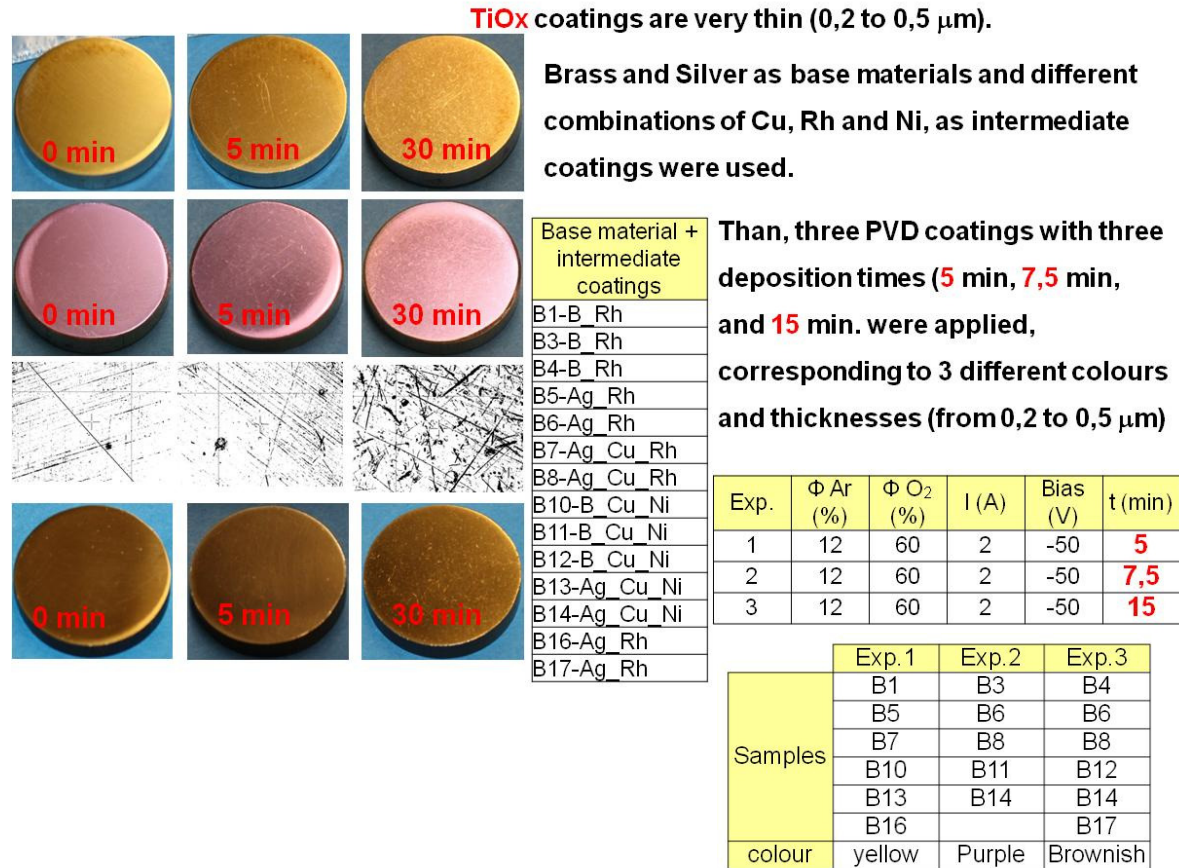


Fig. 8. Testing details for TiOx coatings.

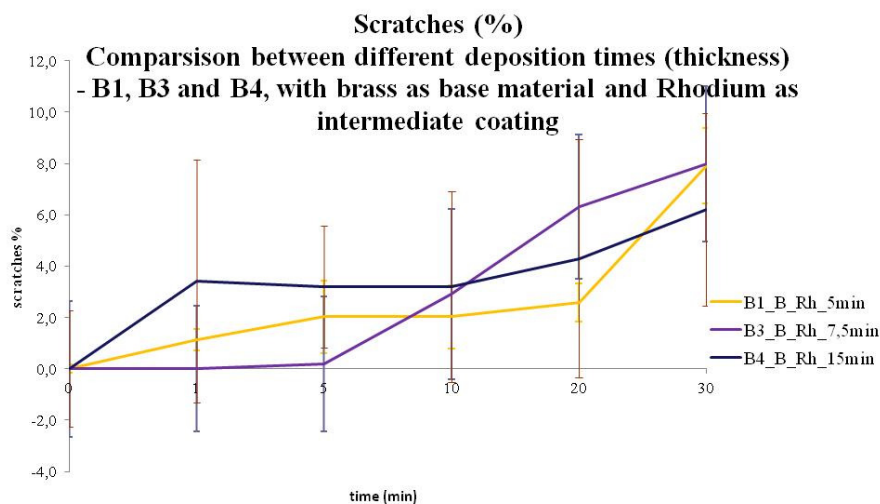


Fig. 9. Scratch quantification for TiOx coatings.



It is observed in Fig. 9 that with brass as base material and Rh as intermediate coating scratches are about 6 to 10% of total area and it seems that there is no substantial difference between coatings with different thicknesses (yellow – 0,2 mm, purple, 0,35 mm, and brownish about 0,5 mm).

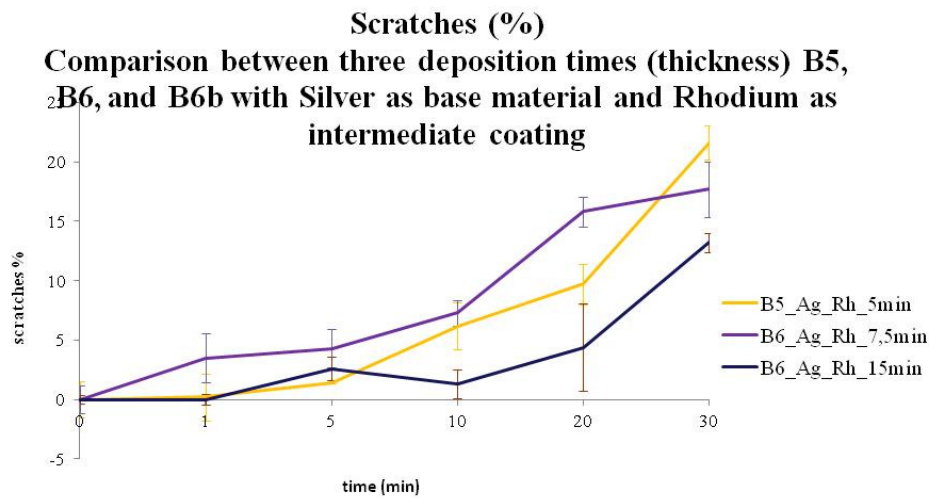


Fig. 10. Scratch quantification for TiOx coatings.

It is observed in Fig. 10 that with silver as base material and Rh as intermediate coatings scratches are about 10 to 20% of total area and it seems that there is a small correlation between coatings with different thicknesses (yellow – 0,2 mm, purple, 0,35 mm, and brownish about 0,5 mm) and scratches (%).

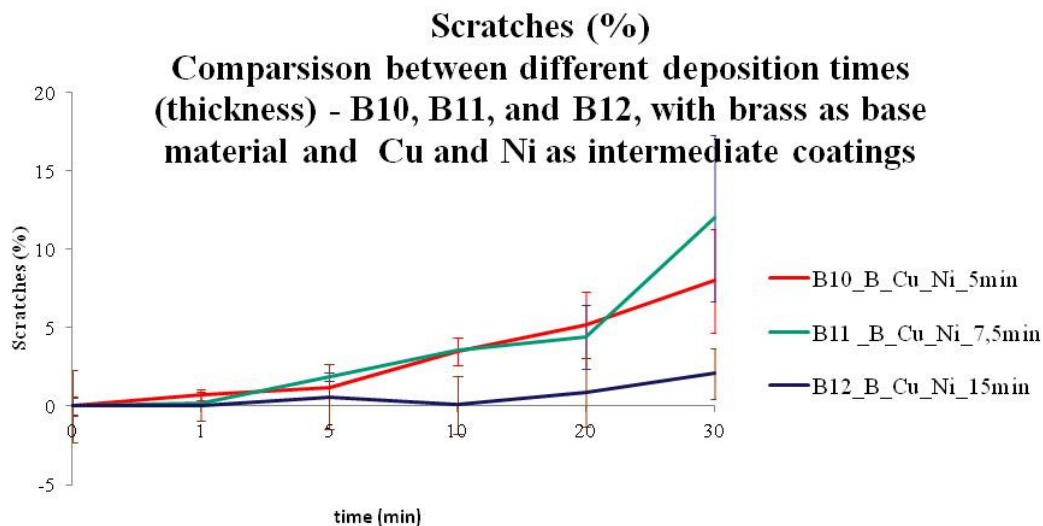


Fig. 11. Scratch quantification for TiOx coatings.

It is observed in Fig. 11 that with brass as base material and Cu and Ni as intermediate coatings scratches are about 4 to 15% of total area and it seems that there is a correlation with coating thickness only for the thickest coating (brownish - 0,5 mm).

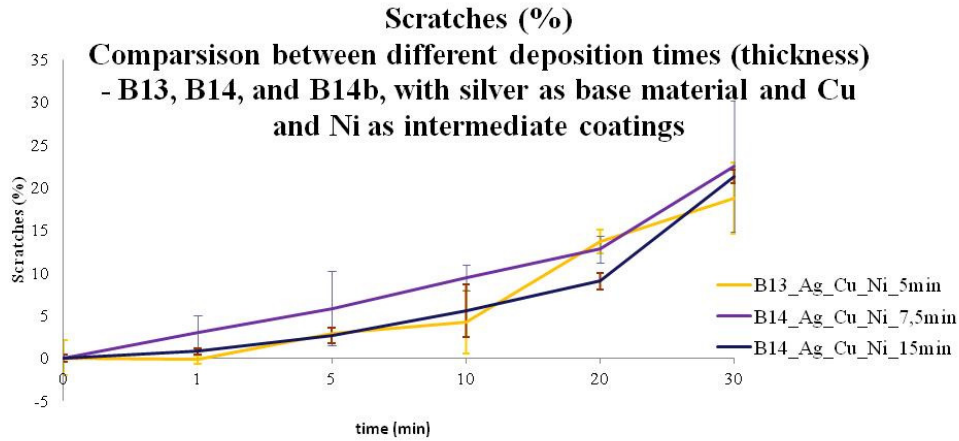


Fig. 12. Scratch quantification for TiOx coatings.

It is observed in Fig. 12 that with silver as base material and Cu and Ni as intermediate coatings scratches are about 15 to 25% of total area and it seems that there is no correlation between coatings with different thicknesses (yellow – 0,2 mm, purple, 0,35 mm, and brownish about 0,5 mm) and scratches (%).

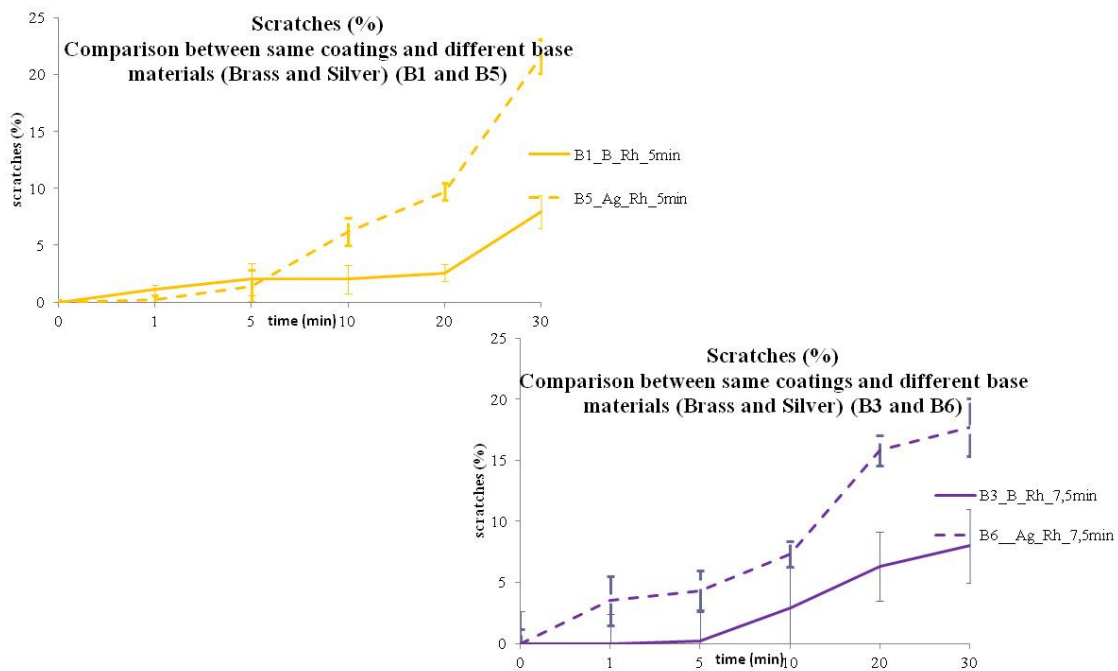


Fig. 13. Scratch quantification for TiOx coatings.

It is observed in Fig. 13 that for the same coatings the hardness of base material (Brass or Silver) is dominant on abrasion resistance.

As a previous conclusion, for TiOx coatings, it seems that:

- abrasion resistance is at about the same order of magnitude of electroplating coatings (10 to 25%)
- It seems again that the hardness of the base material is very influent on coating resistance. With brass as base material scratches vary between 4 to 15% and with silver vary between 15 to 25%.
- Intermediate coatings seem to have a slight influence in terms of abrasion resistance.

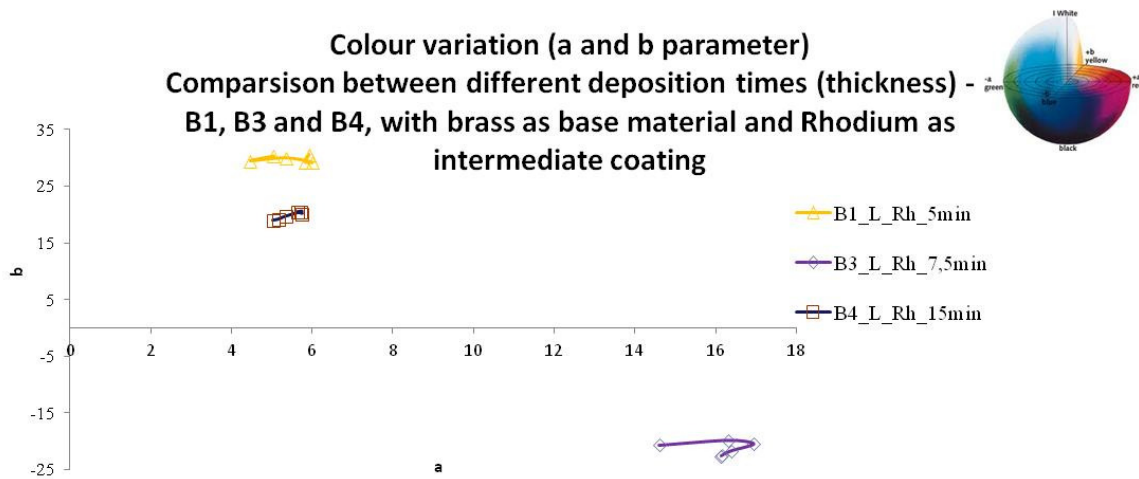


Fig. 14. Color quantification for TiOx coatings.

It is observed in Fig. 14 that as with Rhodium and gold coatings there is a substantial change in color in most specimens. This means that some scratches not only plastic deformed the coating but removed the coating bringing into evidence the intermediate coating or the base material.

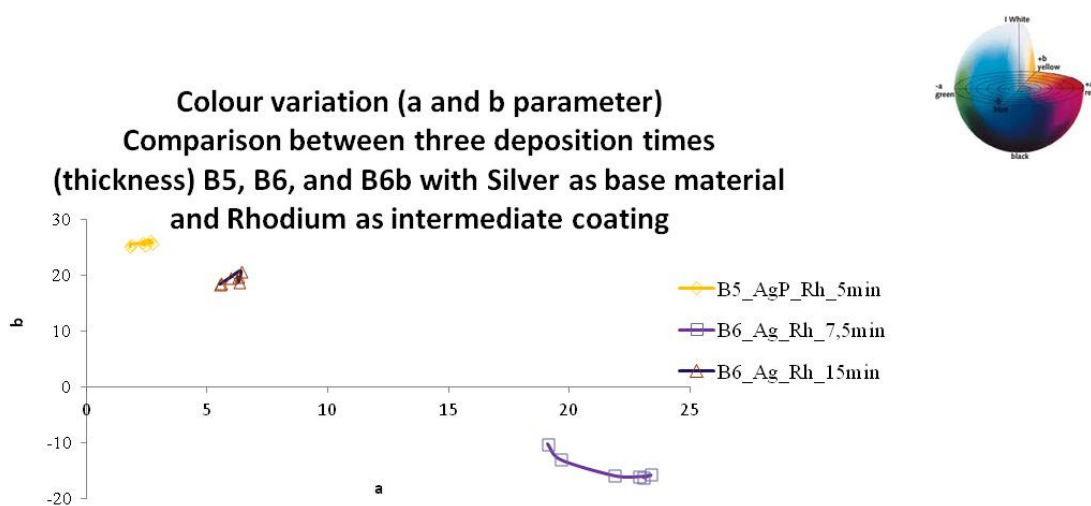


Fig. 15. Color quantification for TiOx coatings.

It is observed in Fig. 15 that as with Rhodium and gold coatings there is a substantial change in color in most specimens. This means that some scratches not only plastic deformed the coating but removed the coating bringing into evidence the intermediate coating or the base material.

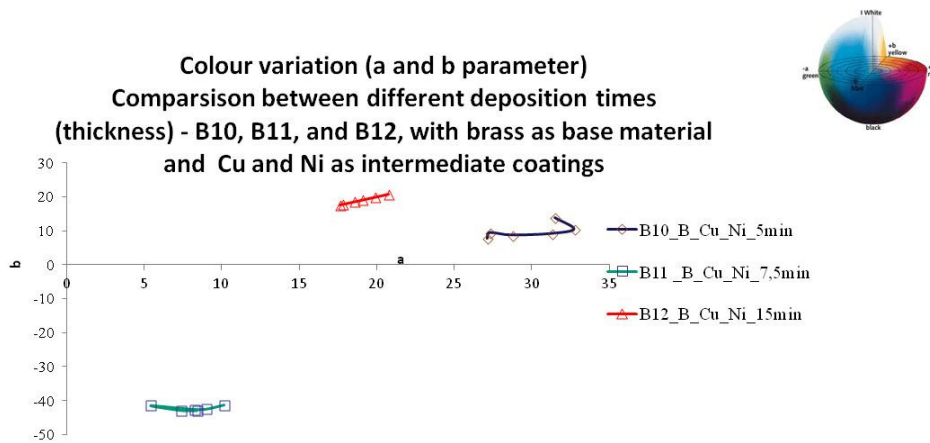


Fig. 16. Color quantification for TiOx coatings.

It is observed in Fig. 16 that as with Rhodium and gold coatings there is a substantial change in color in most specimens. This means that some scratches not only plastic deformed the coating but removed the coating bringing into evidence the intermediate coating or the base material.

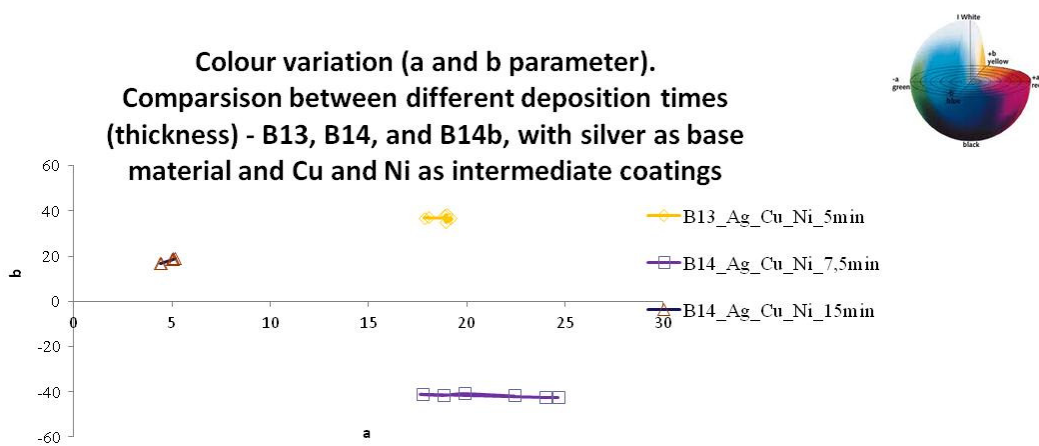


Fig. 17. Color quantification for TiOx coatings.

It is observed in Fig. 17 that as with Rhodium and gold coatings there is a substantial change in color in most specimens. This means that some scratches not only plastic deformed the coating but removed the coating bringing into evidence the intermediate coating or the base material.

As a previous conclusion, for TiOx coatings it seems that color changes due to abrasion in most coatings. This means that some scratches not only plastic deformed the coating but removed the coating bringing into evidence the intermediate coating or the base material.

**TiOxNy** and **TiOxNyCz** coatings are thin films (about 1  $\mu\text{m}$ ) but much thicker than **TiOx** (0,2 to 0,5  $\mu\text{m}$ ).

Brass, Silver, and also steel (**S**), as base materials with and without different combinations of Cu, Rh and Ni, as intermediate coatings were tested.

Then, a PVD coating with one deposition time (60 min) was applied corresponding to a coating thickness of about 1  $\mu\text{m}$ )

samples	Sample	Colour	Base material + intermediate coatings	
	C3	brownish		C3_B_Cu_Ni
	C7	brownish		C7_Ag_Cu_Ni
	C11	brownish		C11_B_Cu_Rh
	C15	brownish		C15_Ag_Cu_Rh
	C17	Blue		C17_S_TiOx
	C18	Black		C18_S_TiOxNxCx
	C19	Dark red		C19_S_TiOxNx

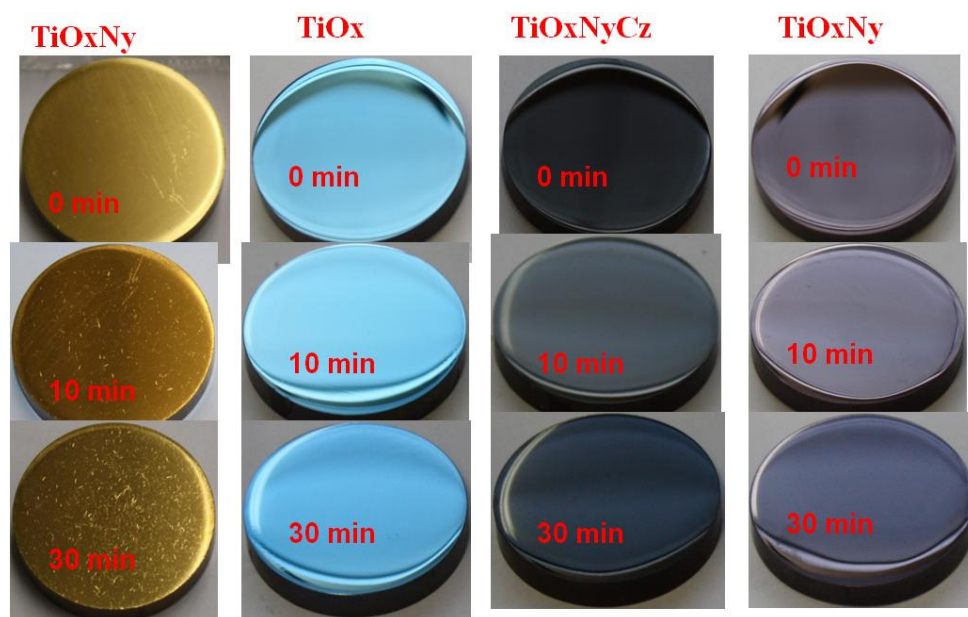


Fig. 18. Testing details for TiOx, TiOxNy and TiOxNyCz coatings.

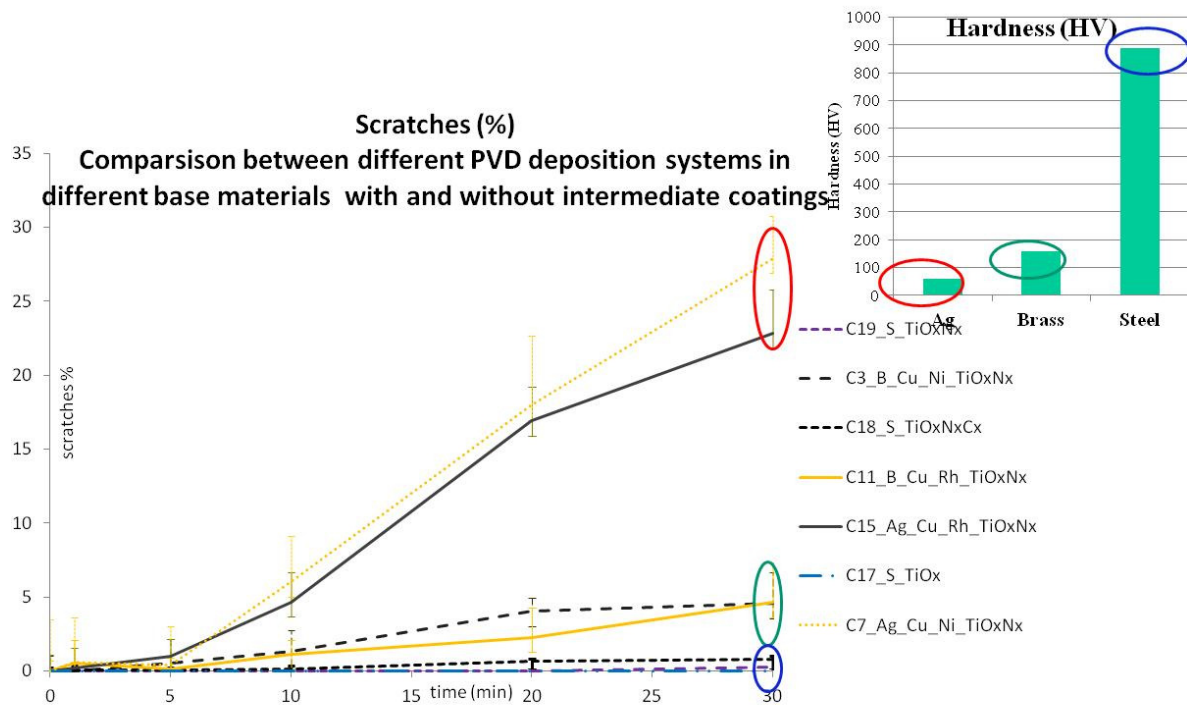


Fig. 19. Scratches and hardness quantification for TiOx, TiOxNy and TiOxNyCz coatings.

It is observed in Fig. 19 that with steel as base material the scratches are almost non-existent (0,2%) while with brass and silver there is a substantial amount of scratches (till 20%). The intermediate coatings are less important on scratches level. This means that the coating does not break when the base material is hard.

The main conclusions that can be drawn till this point are:

- abrasion resistance of PVDs are essentially dependent on hardness of base material; There is a correlation between hardness of base material and % of scratches;
- TiOx may have about 20% scratches in silver but 0,2% in steel;
- It is possible to obtain PVD coatings with nearly no scratches.

**Colour variation (a and b parameter).  
Comparison between different PVD deposition systems in  
different base materials with and without intermediate coatings**

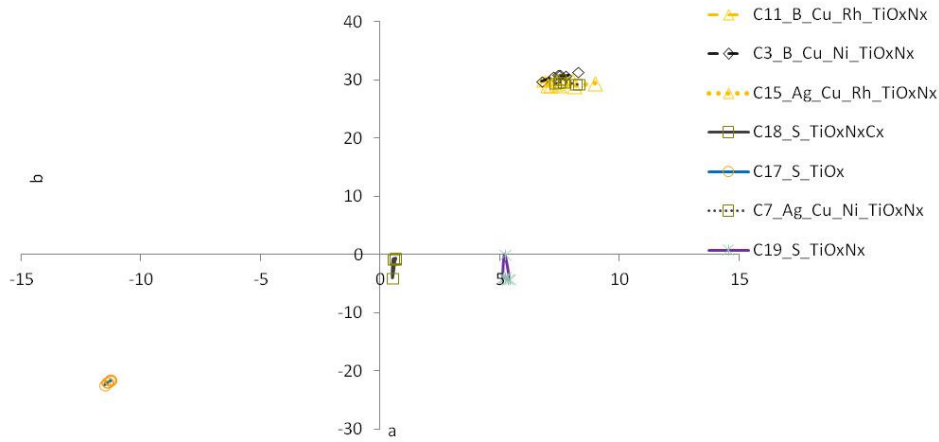
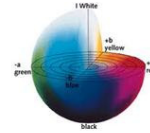


Fig. 20. Color quantification for TiOxNy and TiOxNyCz coatings.

It is observed in Fig. 20 that almost no change in color was observed.

The main conclusion regarding color changes due to abrasion are:

- There is an inverse correlation between hardness of base material and color change; For higher hardness base materials there is no color change of PVD coatings. This means that these materials are very resistant to scratches when base materials are hard.

**Tarnishing**

Tarnishing tests were made on some PVD samples and results are provided in Figs 21 and 22.

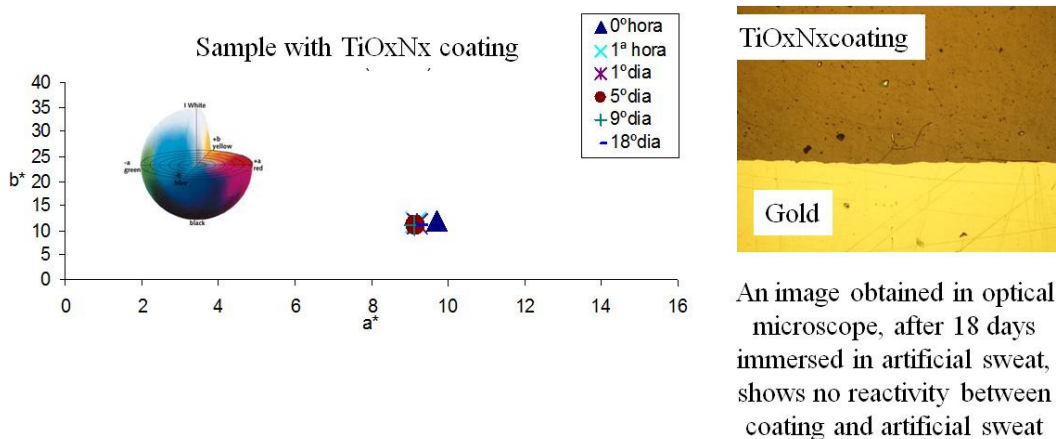


Fig. 21. Color quantification for TiOxNy coating.

It is observed in Fig. 21 that no change in color, after 18 days immersed in artificial sweat, was observed.

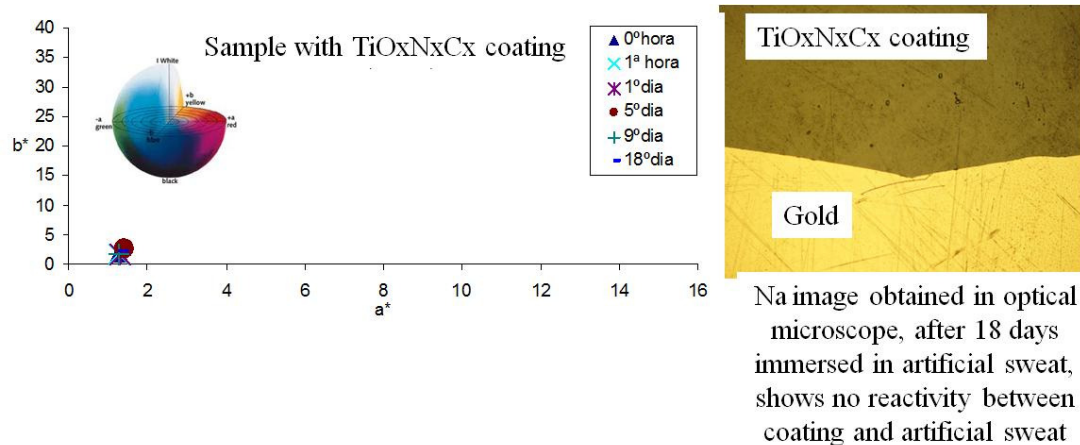


Fig. 22. Color quantification for  $TiO_xNyC_z$  coatings.

It is observed in Fig. 22 that no change in color, after 18 days immersed in artificial sweat, was observed.

From figs 21 and 22 it is clear that PVD coatings are very resistant to artificial sweat in any base material.

## Conclusions

The main conclusions that can be drawn from this study are as follows:

- abrasion resistance of PVD coatings is at about the same order of magnitude of electroplating coatings (10 to 25%) for soft base materials. With brass as base material scratches vary between 4 to 15% and with silver vary between 15 to 25%.
- abrasion resistance of PVDs are essentially dependent on hardness of base material; There is a correlation between hardness of base material and % of scratches;
- Intermediate coatings seem to have a slight influence in terms of abrasion resistance.
- PVD coatings may have nearly no scratches for hard base materials such as steel (0,2% in steel).
- PVD coatings are very resistant to artificial sweat in any base material.



## References

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