Multifuctional behaviour of nanostructured porcelain enamels

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Abstract

Nanoscience represents an enabling technology for many different industrial applications. The multifunctional behaviour of materials at nanoscale permits the development of new products with high added value and innovative chemical-physical features as antibacterial, photocatalytic and high resistance surfaces. The aim of this work is to show the multifunctional behaviour of a porcelain enamel after treatment with a mix of liquid dispersion of different nanomaterials.

The applicaton of a liquid suspension of Ag^0, TiO_2, ZrO_2, Al_2O_3, CeO_2 nanoparticles developed by Colorobbia Italia on the top of enamels before or after the thermal treatment leads to a complex nanostructured surfaces showing a mix of different behaviour like antibacterial, self cleaning, depollution, anti scratch ecc.. The compatibility of the liquid nanosupensions permits a fine tuning of the characteristics on the basis of the final product requirements. In our research activity, different types of nanosuspensions were applied on enamels and the nanostructured surfaces were evaluated by SEM-FEG-STEM microscopy, AFM atomic force microscopy. The antibacterial activity has been tested on two different microorganism (*E-Coli* and *Staphilococcus Aureus*) while the self cleanliness was established with the drop pendant method. The degradation kinetic of NOx and VOC's under light irradiation and the surface resistance was also established.

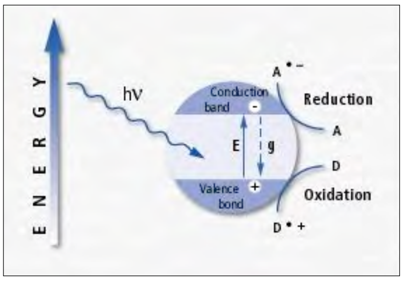
The preliminary results are very promising and show the possibility to combine different functionality on the same enamel surface with a fine tuning of the final characteristics due to the mutual compatibility of the different nanostructured suspensions.

Introduction

In the last years nanomaterial technology rapidly grows on intriguing reality in materials science. The “nano dimension” permits the development of multifunctional material. Cericol manufactured a set of nanosuspensions; among these, suspensions suitable for enamels treatment were developed. Thanks to the nanostructured, the new coating surfaces show self-cleaning (with nano titania treatment), anti-bacterial (with nano silver or zinc treatment) and anti-scratch (with nano zirconia treatment) features. The nanoparticles dispersions used in this work were obtained by a “bottom-up” polyols synthesis [1] which allows nano dispersion of metal nanoparticles in organic or even water solvent through a rapid nucleation of metal precursors. The process involves an initial nucleation step, followed by a controlled heating allowing a crystal growth. The monitoring of reaction kinetics and the choice of solvents and complexing agents permits the size and shape control. The nano suspensions obtained are stable for long periods (> 12 months) without showing aggregation phenomena of nano particles and changes in chemical characteristics.

Nano titania particles in anatase crystal form exploit a photocatalysis behaviour under UVA-light irradiation [2, 3, 4, 5, 6] The nanometric size increase the efficiency of photocatalysis. The nanostructured titania on enamelled surfaces generates coating with self-cleaning properties and a strong tendency to increase wettability ("superhydrophilicity" phenomenon) (fig.2). The hydrophilicity estimation was carried out through contact angle measure (fig.3). The surface can be considered hydrophilic if the angle is lower than 15°.

The coating lifetime was evaluated by an appropriate equipment constituted by a mobile arm upon which a soft sponge in order to simulate a hand-wash is installed.



$$TiO_2 + h\nu \rightarrow TiO_2(e^-, h^+)$$
$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet}$$
$$TiO_2(h^+) + Rad \rightarrow TiO_2 + Rad^{\bullet}$$
$$H_2O + TiO_2(h^+) \rightarrow {}^{\bullet}OH + H^+ + TiO_2$$

Fig. 1. Scheme of nano-titania photoexcitation

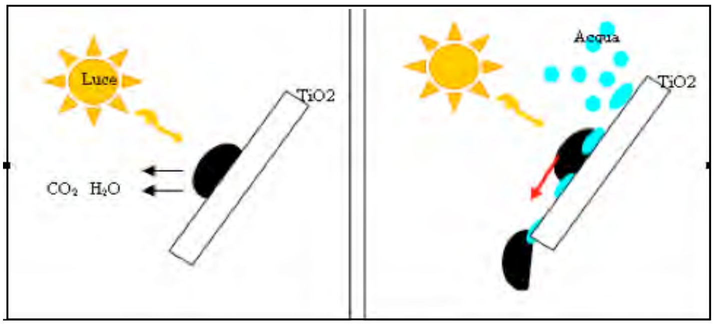


Fig. 2. Photo oxidation and superhydrophilicity processes of nano TiO_2 coating

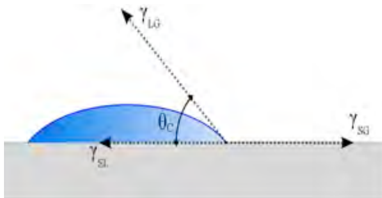


Fig. 3. Contact angle determination

Nano silver and nano zinc oxide ca be nanostructured giving bacteriostatic or bactericide features to enamelled surfaces. Ag^+ ions bind with cell membranes molecules and cause a functional and metabolic deficit that entailing the cellular death. The mechanism of Ag^+ release from nanometallic films (fig.5) requires the water or umidity presence : in this conditions, it is supposed a metallic-ionic silver equilibrium: $Ag^0 \rightarrow Ag^+ + e^-$. Moreover it is established that the antibacterial nanometric silver efficiency manifests itself with a few ppb already, an amount absolutely lower than normal concentrations of silver salt (e.g. silver nitrate).

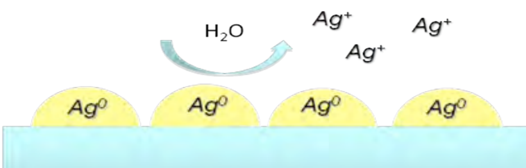


Fig 5: Mechanism of release of Ag + ions from the metal film

As the nano silver, nano zinc oxide particles have an antimicrobial effect. To date, the mechanism of action of ZnO nanoparticles against bacteria is not completely clear: some studies sustain that the antibacterial properties depend on the disruption of cell membrane activity [7] while other works suggest that the production of reactive oxygen species like hydrogen peroxide (H_2O_2) could be toxic for bacterial cells.

Metallic silver and zinc oxide nanoparticles have been shown to have a good antibacterial activities against many type of bacterial strains, like *Escherichia coli* and *Staphylococcus aureus* [8]. To evaluate their antibacterial effect, on the samples with antibacterial treatment, biological tests have been carried out according to an internal protocol of analysis, following an international method.

Porcelain enamels are subject to undergo scratching easily. In order to improve the scratch resistance of these materials, on their surface it has been realized a zirconium dioxide coating. The ZrO_2 is very well-known for its good fracture resistance; the nano particles can form a thin film on the enamels surfaces able to improve their abrasion resistance. The scratch resistance increase after treatment with nano ZrO_2 has been evaluated through pencil for Mhos scratch test.

Nanoparticles characterization

To obtain super-hydrophilic enamels a nano suspension of TiO_2 6% w/w in water was used. The particles have a spherical shape with dimension about 10 nm (fig 6, 7). In order to carry out an antibacterial coating, the enamels were treated with silver or zinc oxide nanosuspension: the first is a nano suspension of metallic Ag 4% in water, the second is of ZnO 1% in water. Both were characterized from a dimensional and morphological point of view (fig. 8, 9 and fig. 10, 11): silver nanoparticles turn out to be lower 10 nm, while zinc oxide nanoparticles. The morphological characterization has been carried out through FEG-STEM microscopy (Field Emission Gun-based Scanning Transmission Electron Microscope, model Supra40 by Zeiss), while the dimensional distribution has been obtained through DLS analysis (Dynamic Light Scattering, Nano-S model by Malvern).

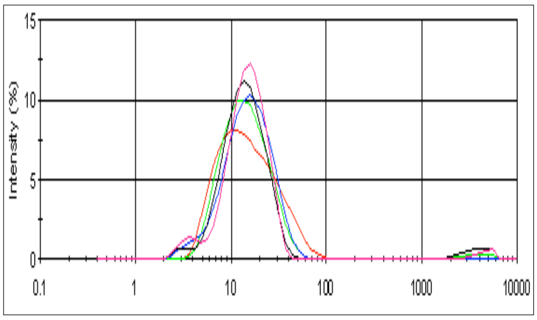


Fig. 6 nano TiO_2 DLS distribution

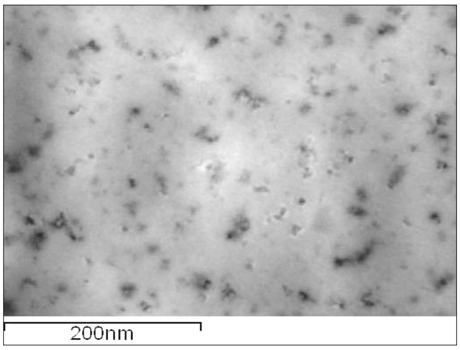


Fig. 7 nano TiO_2 suspension FEG- STEM image

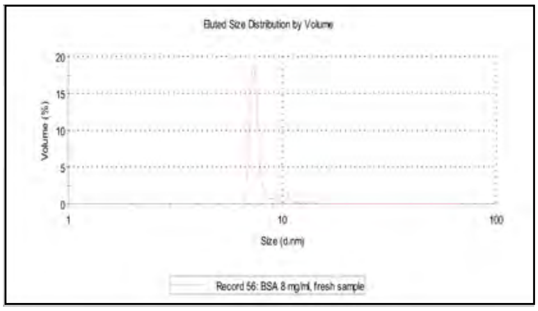


Fig. 8 nano Ag DLS distribution

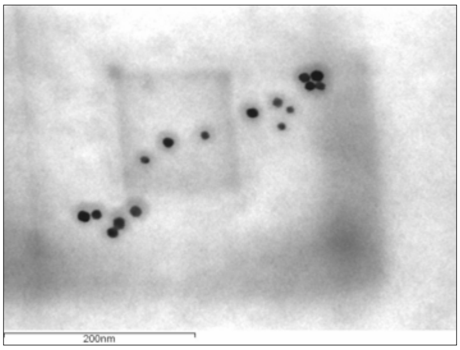


Fig 9: STEM image of Ag nanoparticles

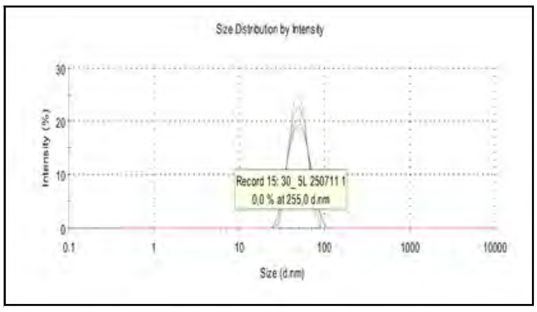


Fig 10: DLS analysis of zinc nanosuspension

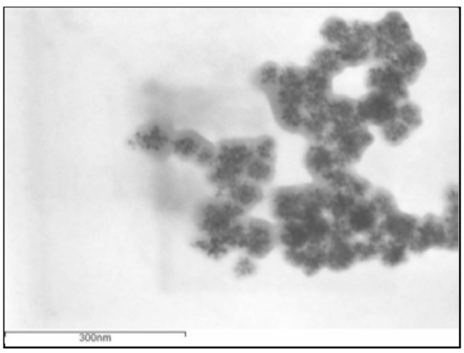


Fig 11: STEM image of zinc nanoparticles

Application

The nanotitania particles were applied through a spray-gun treatment. The spray-gun system was setted with nozzle dimension of 0.3 mm and air pressure of 3.5 bar. Samples were previously washed, heated at 90° C and treated. Then they were fired in an electric oven at 600°C for four minutes.
For zirconia coating, a sample of 20X20 cm was treated in half through spray-gun technique; the system was setted with the same characteristics used for titania application. The sample was earlier washed, heated at 90°C and treated with 30 coats. Then it was fired in an electric oven at 600°C for four minutes.
Screen printing application technique was used for silver and zinc oxide treatments. First, samples were cleaned with water and isopropilic alcohol and were heated at 100° C; then a net of 120 threads per cm^2 was employed to realize nanoparticles films. The coatings were fastened in oven at 520° C (cycle: 1 hour ramp and 1 hour plateau in electric oven).

Results

The treated and untreated with nano TiO_2 porcelain enamels were morphologically characterized through FEG-STEM microscopy. If the image of the sample treated with nano TiO_2 is compared with the image of the untreated sample, we can see the presence of a nanostructured texture with particles of about 50 nm. (fig. 12, 13). The variation of contact angle measure before and after activation through solar irradiation was assessed for 3 days (tab. 1). During this period, in order to have a irradiance value as reference (into a range 300-400 nm), the solar light irradiance was measured. The mean value was established as 26 W/m^2. In fig. 15 it can observe the absence of water drops on treated sample due to the presence of nanofilm. To evaluate the nano-coating resistance, the sample was submitted to repeated washability tests. Contact angle measures before and after irradiation was performed to evaluate the coating efficiency. The substrate life cycle was established with a soft sponge and a water-soap solution washing. In fig. 16 we can observe that the contact angle value on treated sample remains under 15°. This test proves that the coating is active after 7000 cleaning cycles yet.

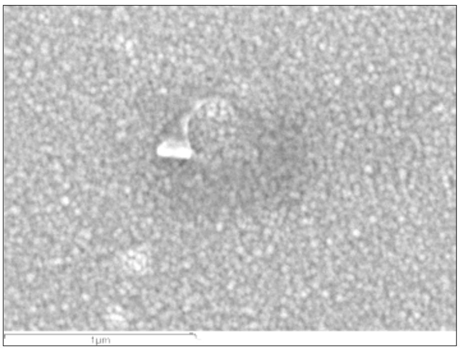


Fig. 12. FEG-STEM image of untreated sample 50000x

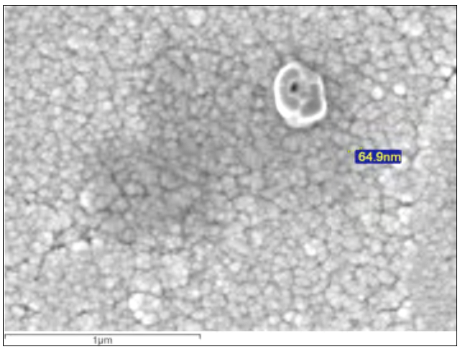


Fig. 13. FEG-STEM image of TiO_2 treated sample 50000x

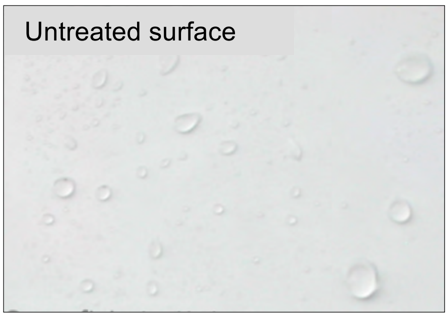


Fig. 14. Wet untreated sample

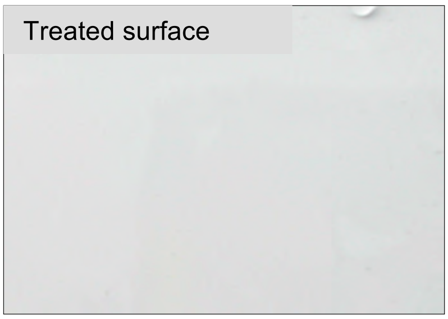


Fig. 15. Wet treated sample

SAMPLE	CONTACT ANGLE (°)	
	t=0 minutes	t=3 days
Untreated	19.57	44.18
TiO_2-Treated	43.38	7.70

Tab. 1. Contact angle values

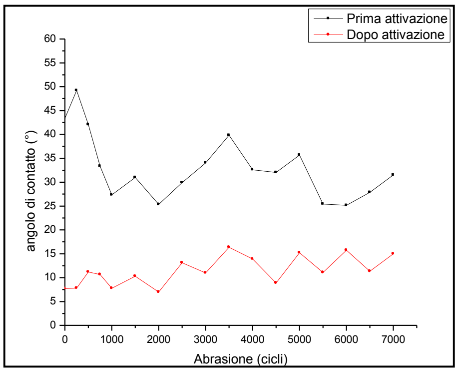
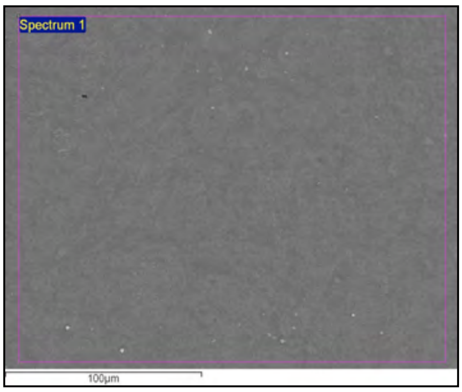


Fig. 16. Contact angle development vs cicles number

The antibacterial activity on surfaces treated with nano Ag and nano ZnO has been quantitatively evaluated using *Escherichia coli* as model (ATCC 8739 by modification of ISO 27447; 2009(E)). For the inoculum preparation, an overnight culture (TSB medium; 37°C for 24 hours) was diluted in order to obtain approximately 10^5 cell/ml. The culture absorbance at 546 nm was measured to control the actual cell density through spectrometer UV-Vis (model Lambda 800, by Perkin Elmer). This bacterial suspension was used to induce contamination of the enamel surfaces. The test was performed on 3 replicates for each treated sample and 3 other replicates for non treated. Each specimen has been placed in 90 mm petri plate containing a disk of absorbent paper with 3 ml of sterile water and inoculated with 0.4 ml of culture. On the score of this layout it can be reduced any sign of evaporation which could affect the bacterial suspension compromising results. Then it was determined the inoculum concentration at time 0, plating rate, appropriately diluted in Plate Count Agar and so it was proceeded with the incubation of samples at room temperature for 24 hours. The inoculum was recovered from each sample using 10 ml of the recovery solution, plating the opportunity dilution for inclusion on PCA and incubated at 37°C for the time necessary to develop well-distinguishable colonies (CFU = Colony Forming Units). The antimicrobial activity exerted by the samples was determined by reference to the behavior of non treated under the same conditions, in accordance with the following equation: $R = [\log(B/A) – \log(C/A)] = [\log(B/C)]$ where R is the value of antimicrobial activity, A is the average of the number of viable cells of bacteria immediately after inoculation on the untreated sample, B is the average of the number of viable cells of bacteria on the untreated sample after 24 h and C is the average of the number of viable cells of bacteria on the treated sample after 24 h. The R values for treated and untreated samples are shown in tables 2 and 3. FEG-STEM analysis was useful to display the nano ZnO coating (particles about 30 nm, fig. 17, 18) but it was not possible see the Ag coating, maybe because nano Ag melts into enamel.



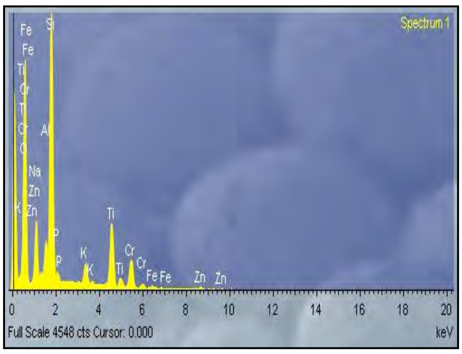


Fig. 17. FEG-STEM image of ZnO treated sample 500x and relative EDAX analysis

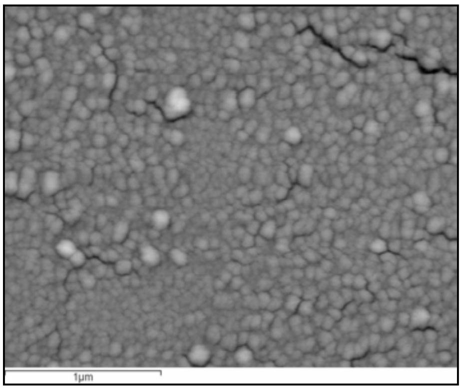


Fig. 18. FE
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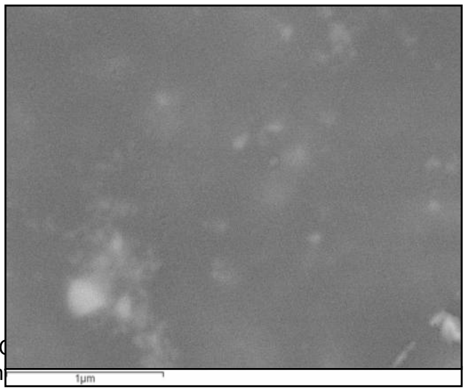

Fig. 19. FEG-STEM

SAMPLE	INOCULUM	RECOVERY 24h	R
Untreated	32 X 10^5	17.3 X 10^7	
Ag coating	32 X 10^5	29.6 X 10^6	**0.8**

Tab. 2. Antibacterial results of Ag coating

SAMPLE	INOCULUM	RECOVERY 24h	R
Untreated	23.5 X 10^5	17.1 X 10^7	
Zn coating	23.5 X 10^5	62.6 X 10^5	**1.4**

Tab.3. Antibacterial results on ZnO coating

Anti-scratch features were evaluated through pencil for Mohs scratch test on ZrO_2 treated (FEG-STEM image in fig.20) and untreated (FEG-STEM image in fig.21) samples. Pencil Mohs with 7, 7.5 and 8 hardness were able to mark out the untreated surfaces. The test was carried out scratching the samples on treated and untreated surfaces, applying the same strength. Because of the bright colour of enamel, the scrapes were highlighted with methylene blue solution (500 ppm) and photographed under optical microscope (fig. 22). On the left is shown the untreated part of sample where signs are evident, while on the right we can see how the treatment makes the surface more strong. Until 7.5 hardness value, there aren't any marks on treated side while with Mohs 8 signs begin to be evident, although this is not clearly visible from the photo below.

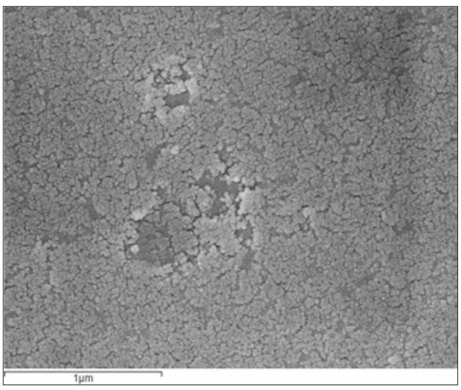

Fig. 20. FEG-STEM image of ZrO_2 treated sample 40000x

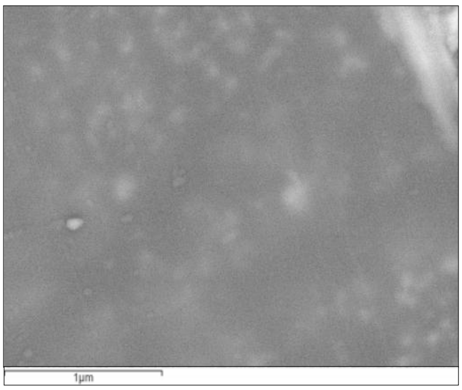

Fig. 21. FEG-STEM image of untreated sample 40000x

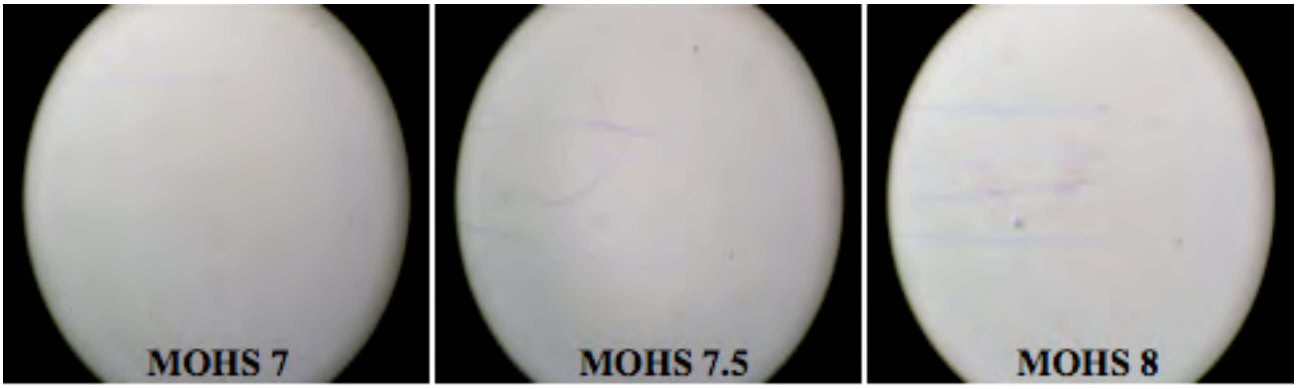

Fig. 22. Results of Mohs anti-scratch test resistance on zirconia treated samples

Conclusions

The treatments developed in Cericol laboratories gave the enamel surface new features: with nano TiO_2 coatings a super-hydrophilic surface can be obtained; the nano-texture appears very homogeneous and wear resistant. Antibacterial features emerge with nano ZnO and nano Ag coatings, a zinc oxide nanostructure is confirmed by SEM-FEG analysis while is not possible to evaluate the nano silver coating probably due to the metal melting during the firing cycle, anyway the Ag efficacy is confirmed by the microbiological results. The anti-scratch features have been evaluated through hardness Mohs test. The treated sample shows an increment of one point in the scale (8.0) respect to the untreated one (7.0).
Nanotechnology together with low cost applications can help to give new superficial features to porcelain enamels, in order to develop competitive products in the global market.

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