

whiTi project
Spinner Consortium
Department of Applied Chemistry and Materials Science
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“Whitening dental process
based on titanium
hydroperoxo nanocrystals”

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State of the art

- In the last decades tooth whitening is becoming more important in order to enhance the self consideration in the daily life about the social relationship with other people. The bleaching materials which characterize the market till now are all made by hydrogen peroxide and carbamide peroxide that decomposes when it's mixed with an specific activator

State of the art

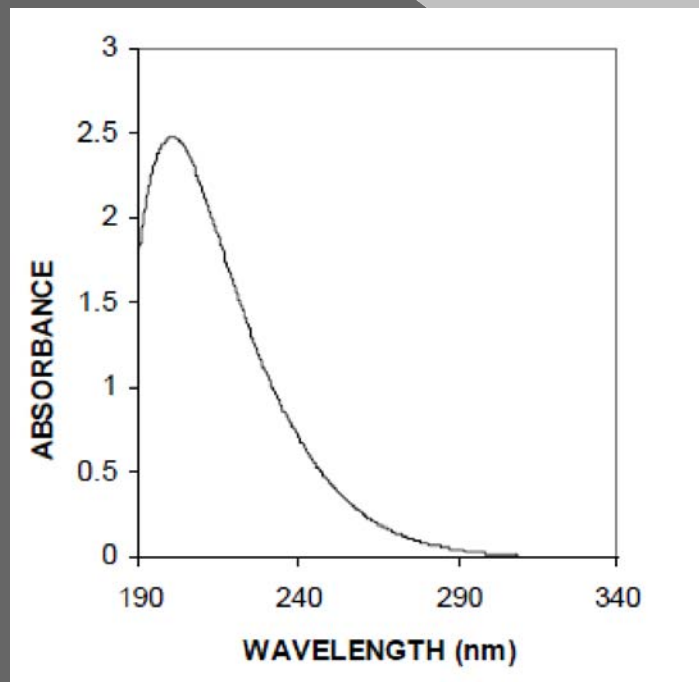
- The present invention is generally related to a innovative activator gel containing inorganic nanostructures which act under a specific light radiation to decompose faster the whitening gel based on peroxides
- Among the new materials under investigation, titanium dioxide is certainly the good candidate to set up a new scientific product that is able to have a strong beneficial effect in the whitening system due to its main characteristic to be a photocatalyst material

State of the art

- The oxygen molecules and the reactive radicals formed by the reaction go to oxidize the chromophores components situated in the interprismatic zone that are decomposed to a molecules characterized to be transparent towards the visible light
- Anatase is one of the polymorphic phase of titanium dioxide with rutile and brookite, and shows the best photocatalytic performances due to its favourite band gap energy (3.2 eV)

State of the art

- Hydrogen peroxide aqueous solution is characterized to show the following UV-Vis absorption spectrum:



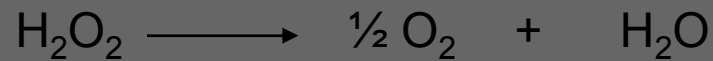
H₂O₂ UV-Vis Spectrum

State of the art

- Currently no whitening product is activated correctly through the absorption of the visible radiation by hydrogen peroxide
- The lamp efficiency is always actuated by increasing temperature of the bleaching gel

State of the art

- Hydrogen peroxide is dissociated following this reaction:



The decomposition reaction always occurs in aqueous solution as ionic dissociation



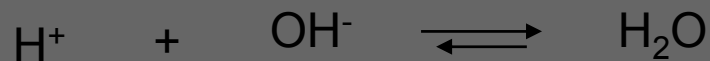
The ionic dissociation constant is very low and therefore the hydrogen peroxide is stable in the aqueous medium

State of the art

- The NaOH addition increases the pH and activates the OOH^- formation



There is also the visible radiation absorption which promotes other reactions:



The project

- The present project is generally related to an innovative activator gel containing inorganic nanostructures which act under a specific light radiation to decompose faster the whitening gel based on peroxides

The project

- This findings lead to a strong increasing of the peroxide rate decomposition inside the bleaching gel and allow forming hydroxyl radicals with oxygen molecules that are involved in the oxidation process of the cromophores in the interprismatic zone of the enamel

AcTivator

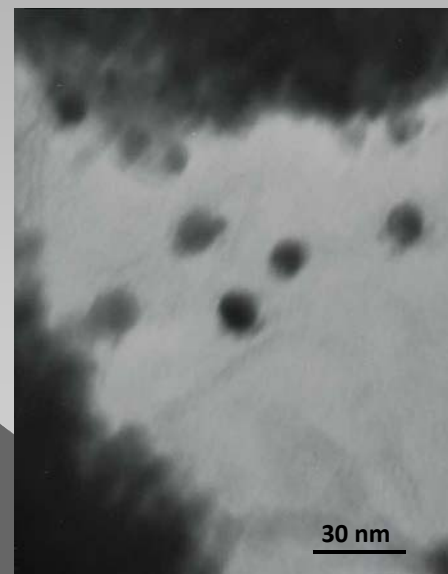
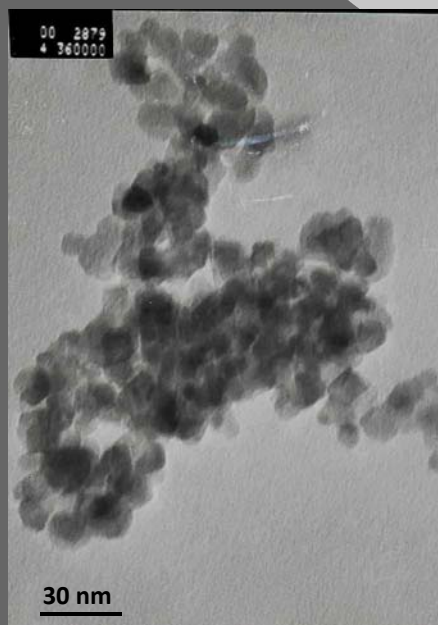
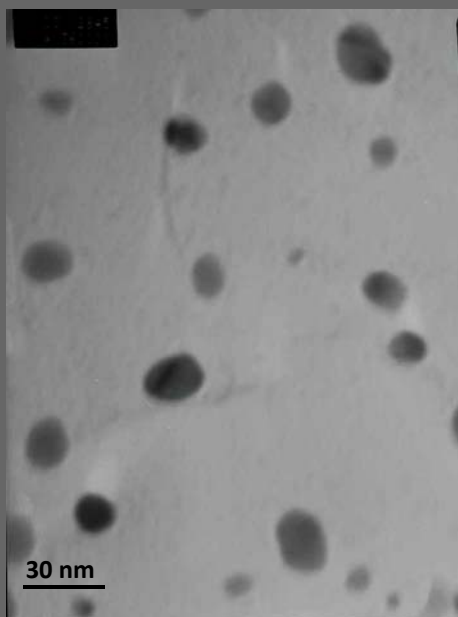
- TiO_2 shows many electronic vacancies on its surface which are involved in the absorption process of water for example producing acid and basic sites
- Neither TiO_2 nor H_2O_2 absorb the visible radiation but the UV radiation only below 380 nm, producing several radical reactive species

Activator

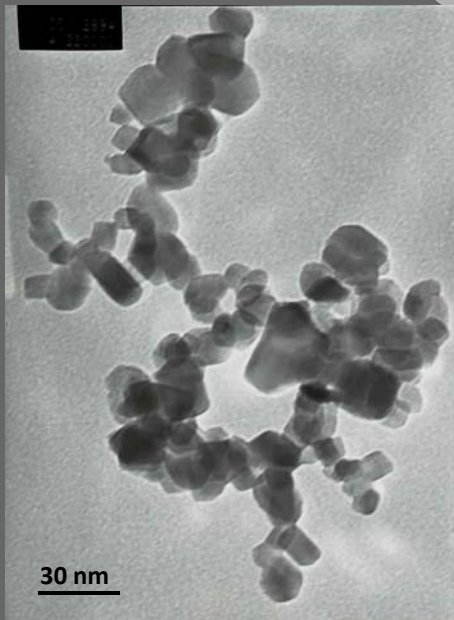
- Titanium dioxide nanocrystals have been synthesized in the anatase crystalline structure with a sol-gel procedure in the aqueous medium at room temperature following a calcination at 400 ° C
- TiO₂ crystals have been characterized by XRD, SEM, TEM and FT-IR ATR analyses

AcTivator – TiO₂

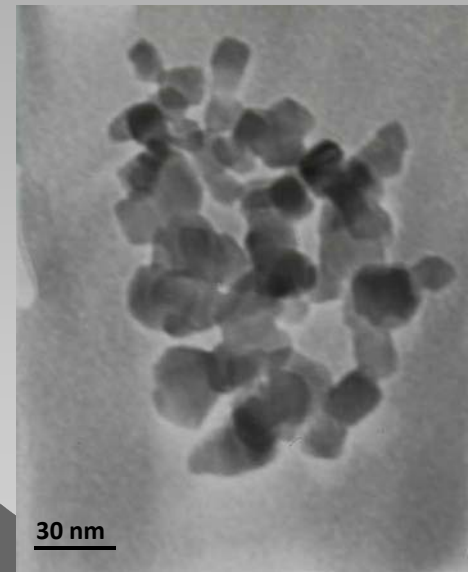
TEM images



AcTivator – TiO₂

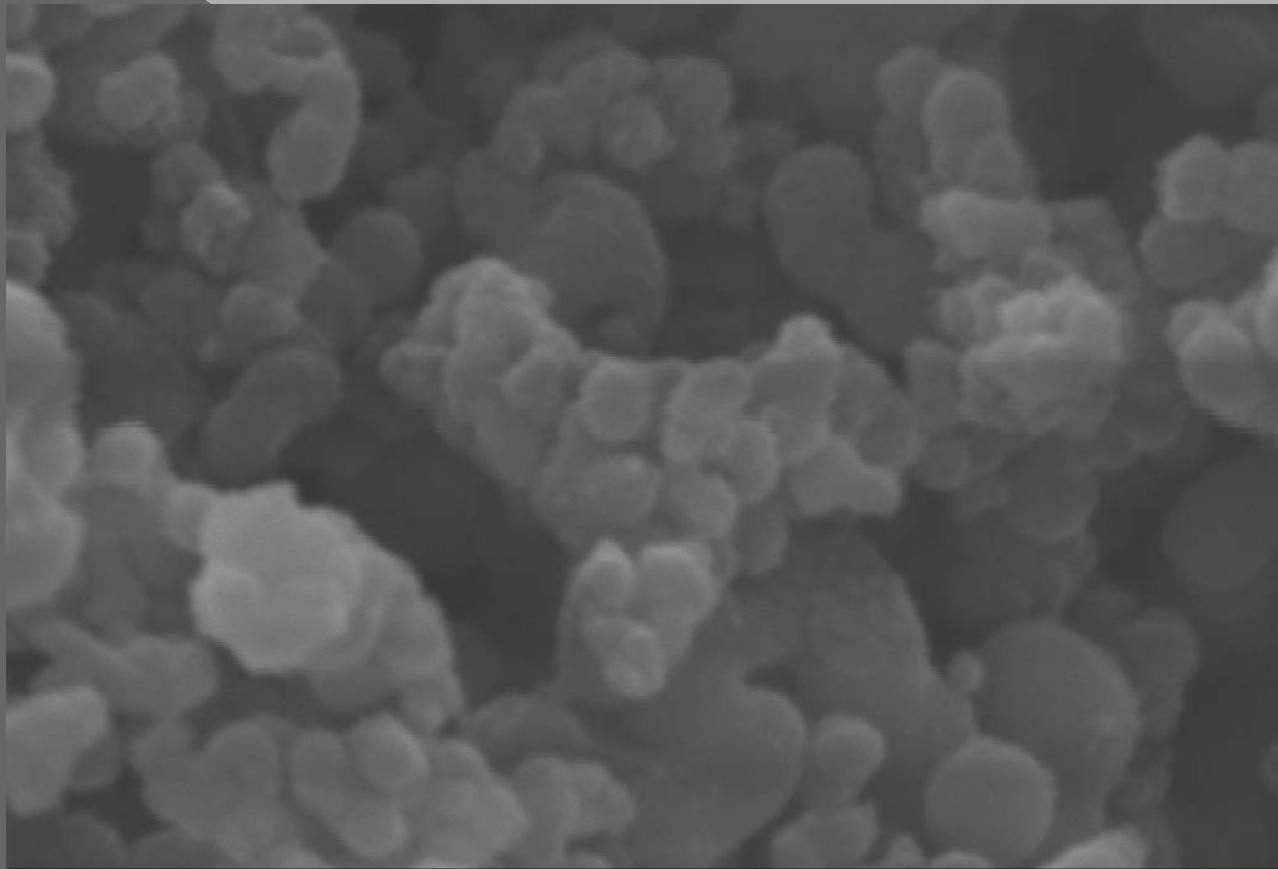


TEM images



AcTivator – TiO₂

SEM image



200nm


Mag = 100.00 K X

EHT = 25.00 kV

Signal A = SE1

Date :23 Sep 2009

WD = 7.0 mm

Photo No. = 4270

Time :15:16:29

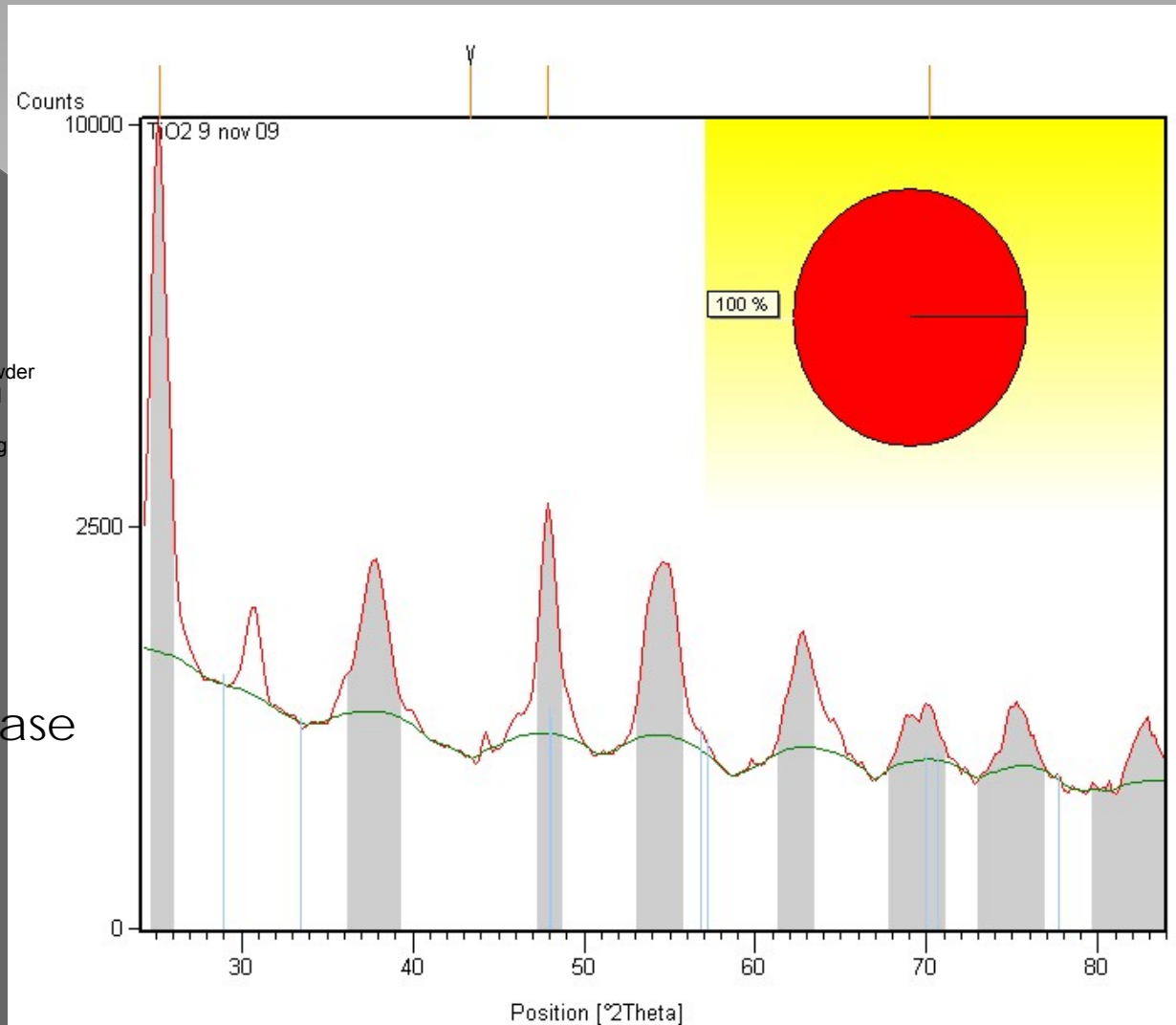


AcTivator – TiO₂

X Rays analysis

Analytical X'Pert Pro equipped with X'Celerator detector powder diffractometer using Cu K α radiation generated at 40 kV and 40 mA. The instrument was configured with a 1° divergence and 0.2mm receiving slits. The samples were prepared using the front loading of standard aluminium sample holders which are 1mm deep, 20mm high, and 15mm wide.

Crystalline structure = Anatase



AcTivator - Interaction

- Anatase crystals are characterized to react when they are mixed with a peroxide solution forming a new compound pale yellow on the surface of the semiconductor TiO_2
- The new innovative activator concerning this invention is based entirely on the formation of this material formed by a chemical-physical reaction between peroxides and the TiO_2 leading to a titanium hydroperoxide with specific properties

AcTivator - Interaction

- Titanium hydroperoxide is a chemical complex which shows the light absorption in the visible region till about 550 nm as reported in the UV-Vis solid-state spectra

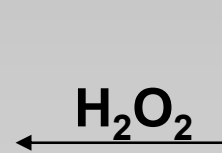
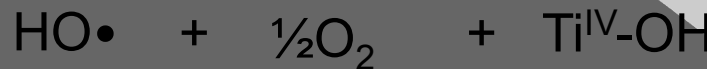
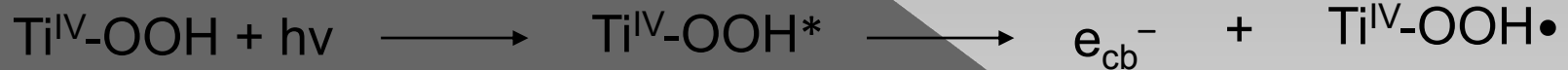
AcTivator - Interaction

- However, when it's irradiated by a cold light lamp with a wavelength peak included in the range from about 400 nm to about 460 nm, it absorbs the radiation and it's supposed to be involved in a surface electron transfer from the surface complex to the TiO_2 conduction band

AcTivator - Interaction

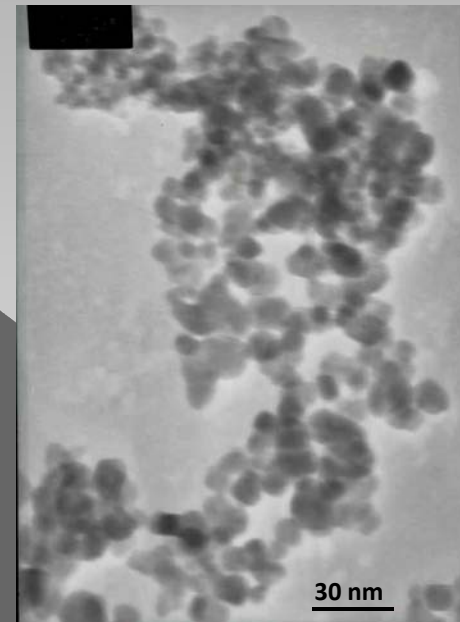
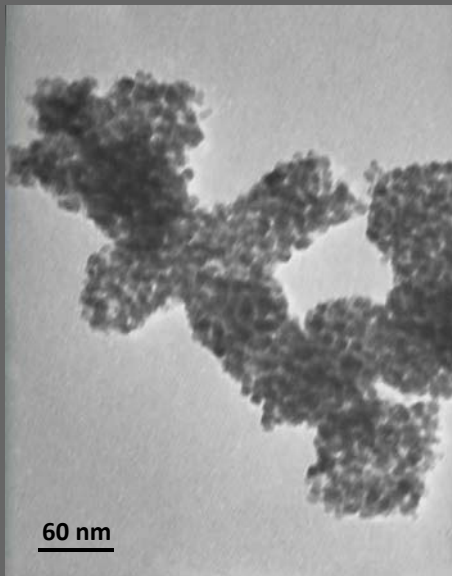


Compound which extends the TiO_2 absorption to the visible region



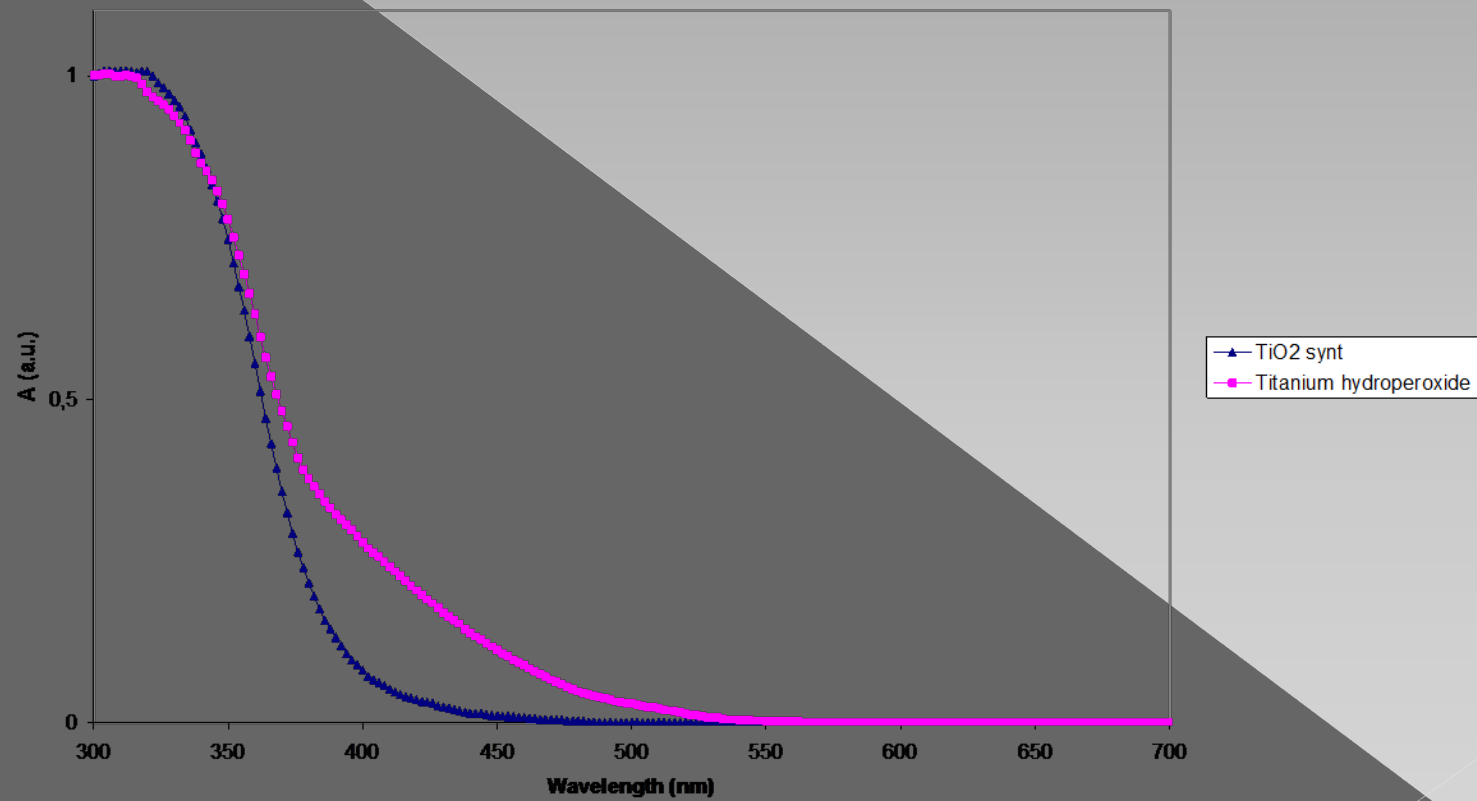
AcTivator

TEM images of Ti-OOH



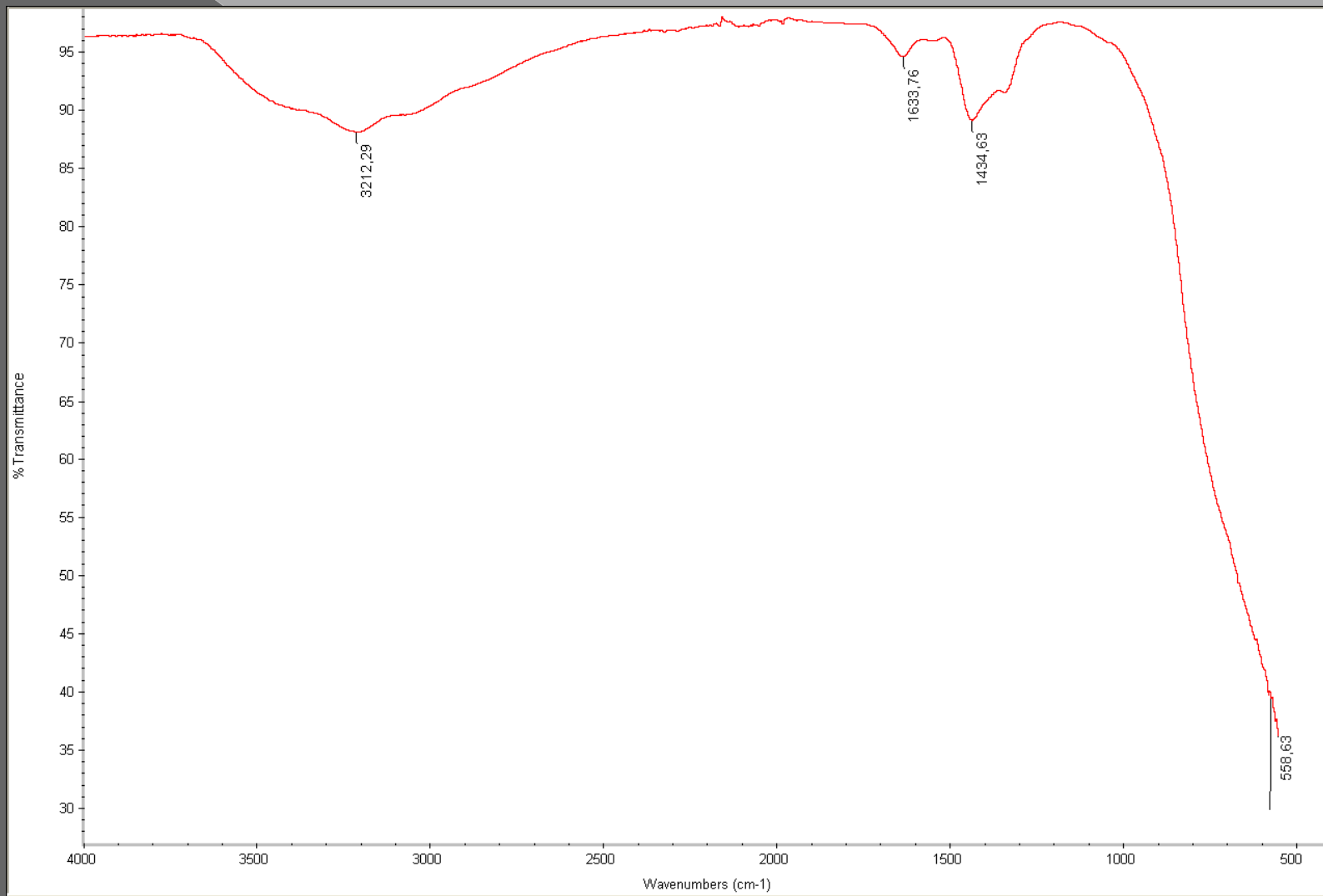
AcTivator

UV-Vis spectra



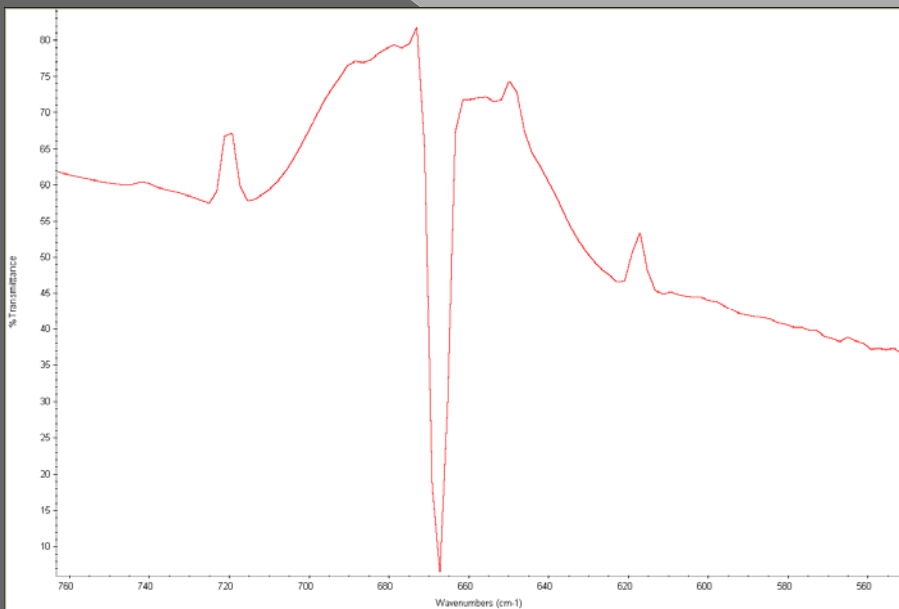
AcTivator

FT-IR ATR Spectrum TiOOH



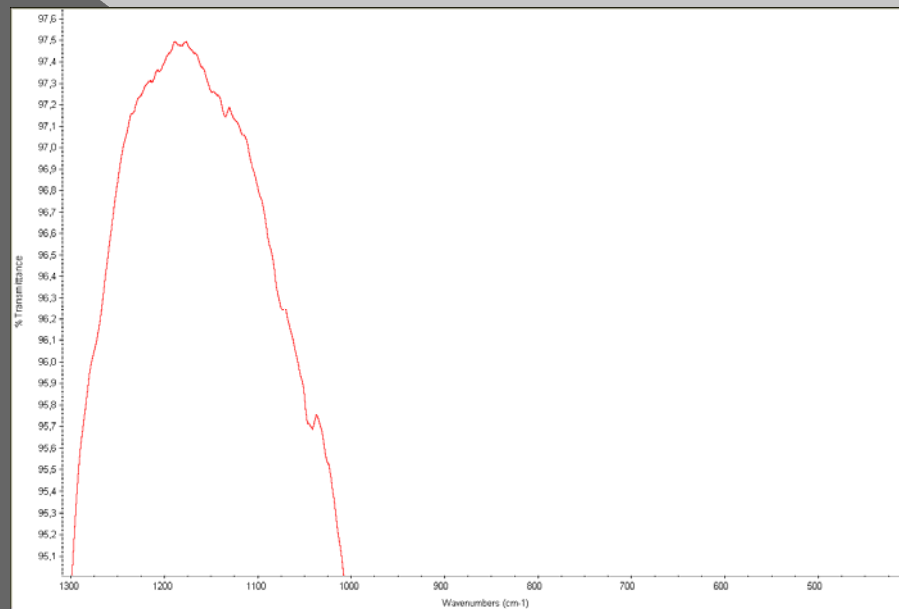
AcTivator

FT-IR ATR Spectrum TiOOH



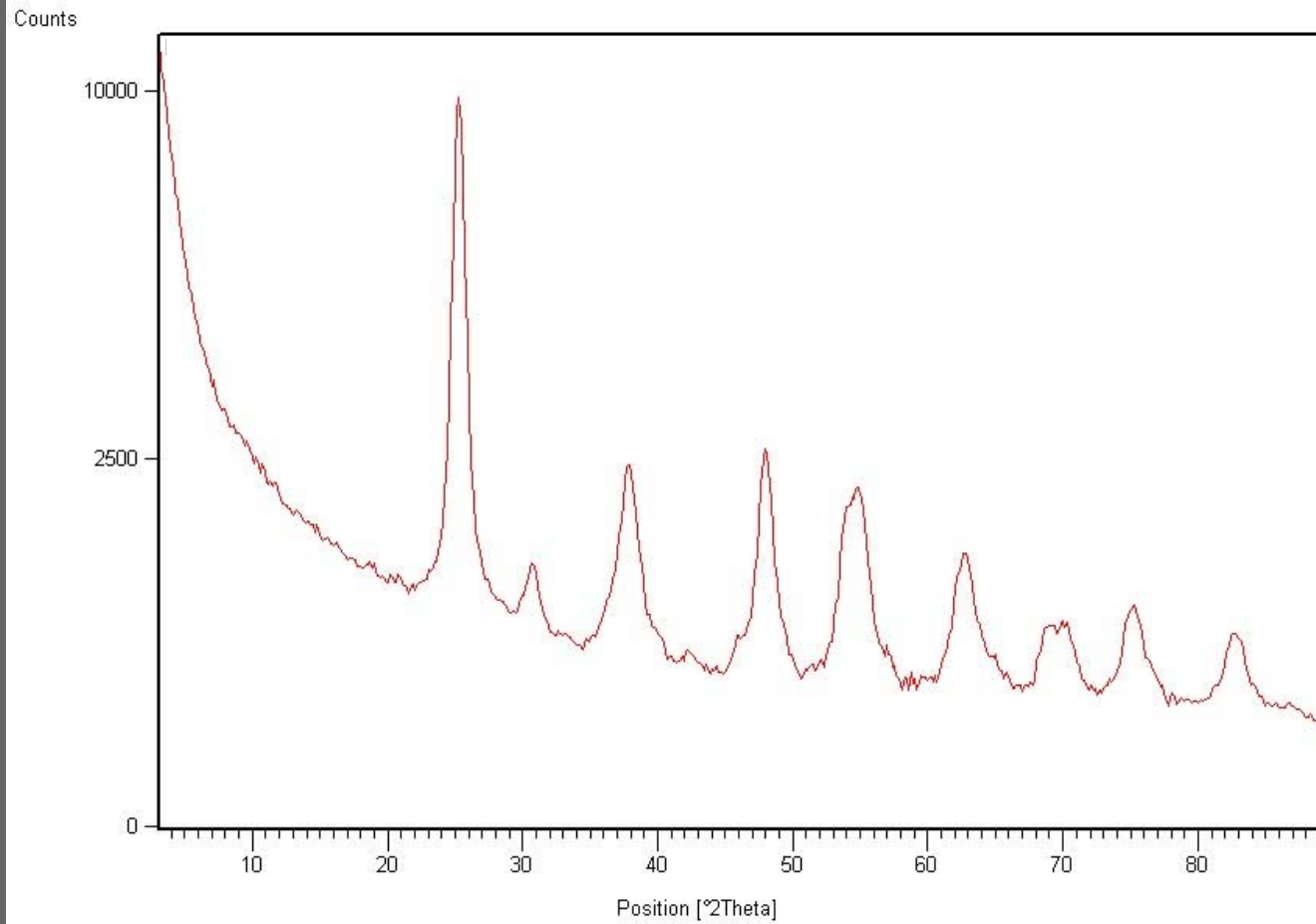
ν 668 cm⁻¹ Ti-O-O-Ti and Ti-O-OH

ν 1041 cm⁻¹ O-O of Ti μ -peroxidic stretching



AcTivator

XRD pattern of TiOOH



H₂O₂ activation

Determination of the hydrogen peroxide concentration with KMnO₄ titration in acid conditions after 20' interaction under lighting radiation

Starting solution H₂O₂ at 35 wt%

With general activator NaOH pH 12

After 20' H₂O₂ = 31 wt%

With TiO₂ acTivator

After 20' H₂O₂ = 21 wt%

H₂O₂ activation

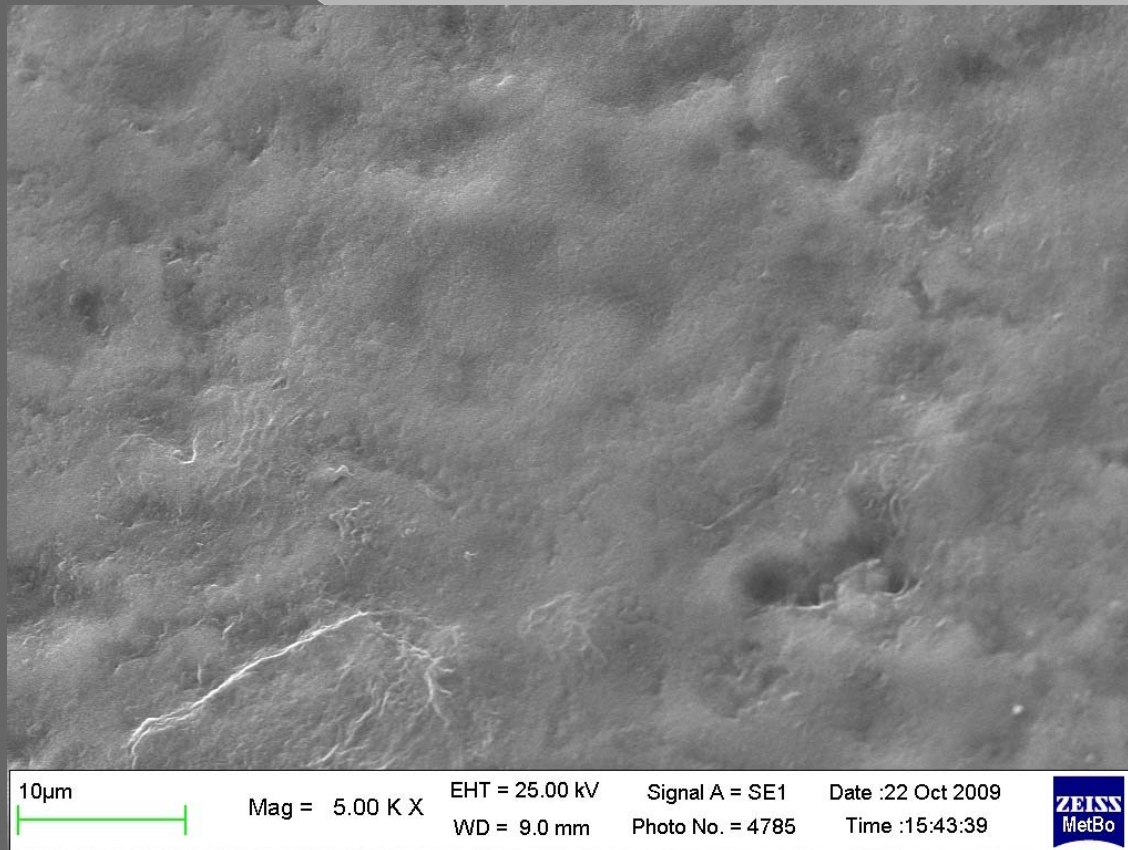
- Several interactions with TiO₂ based activator have been performed and it is occurred that the H₂O₂ decomposition rate is enhanced of **2,5** times factor than the most common commercial activators

Applied research

- The project development has shown in a clear and evident way that on the teeth surfaces were obtained significative whitening power results
- The fundamental parameters which have been considered during the teeth substrates examination are listed below:
 - *morphology*
 - *mineralization*
 - *whitening power*

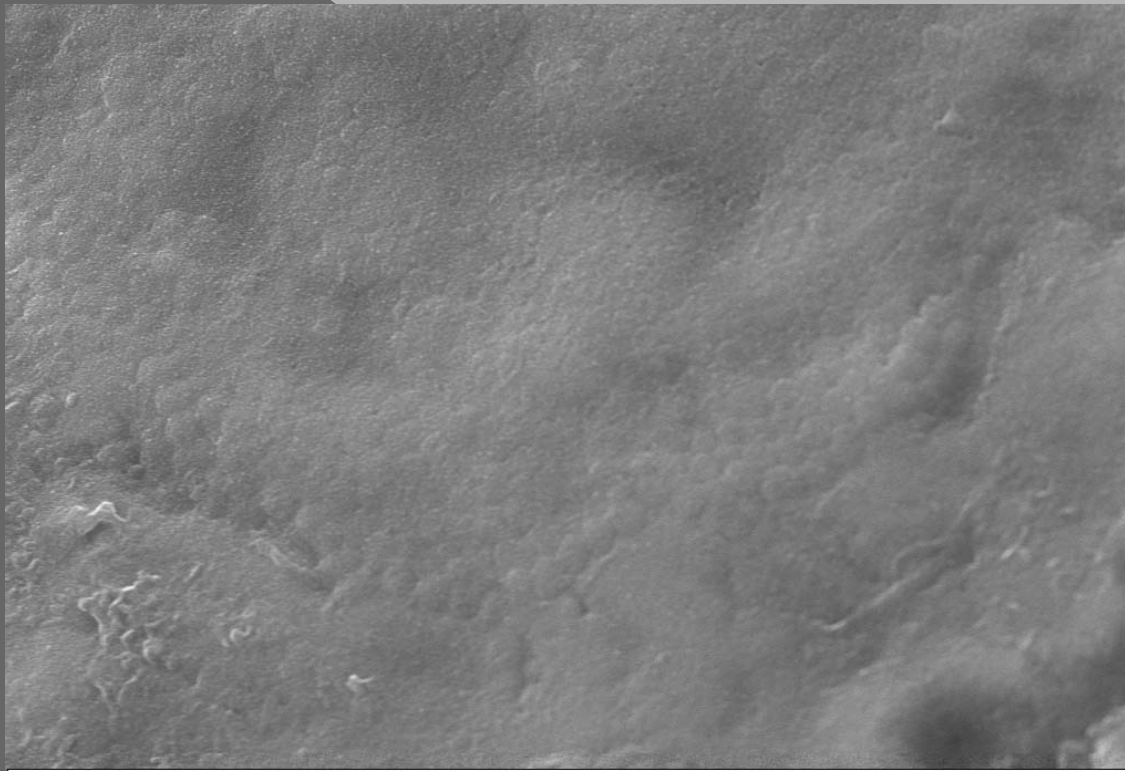
Enamel morphology

Untreated dental section
CONTROL



Enamel morphology

Untreated dental section
CONTROL



1 μ m
H

Mag = 10.00 K X

EHT = 25.00 kV
WD = 9.0 mm

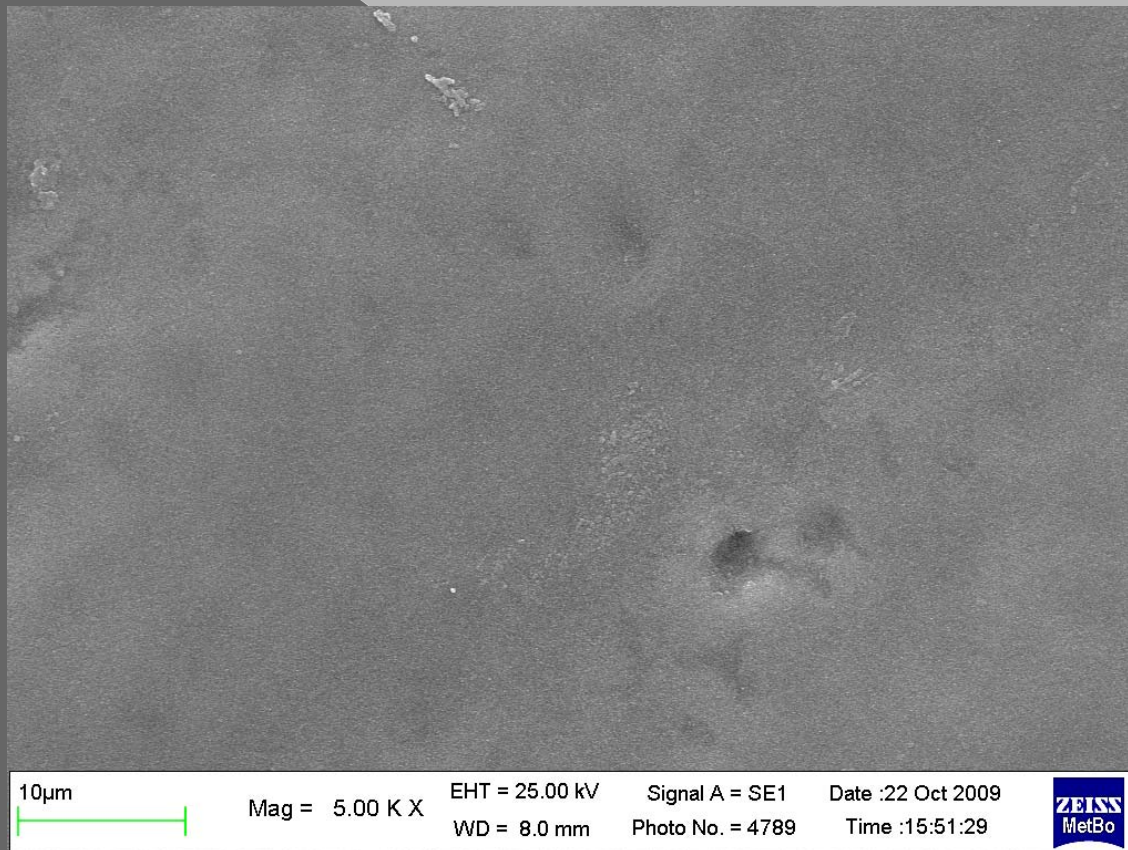
Signal A = SE1
Photo No. = 4786

Date :22 Oct 2009
Time :15:44:21



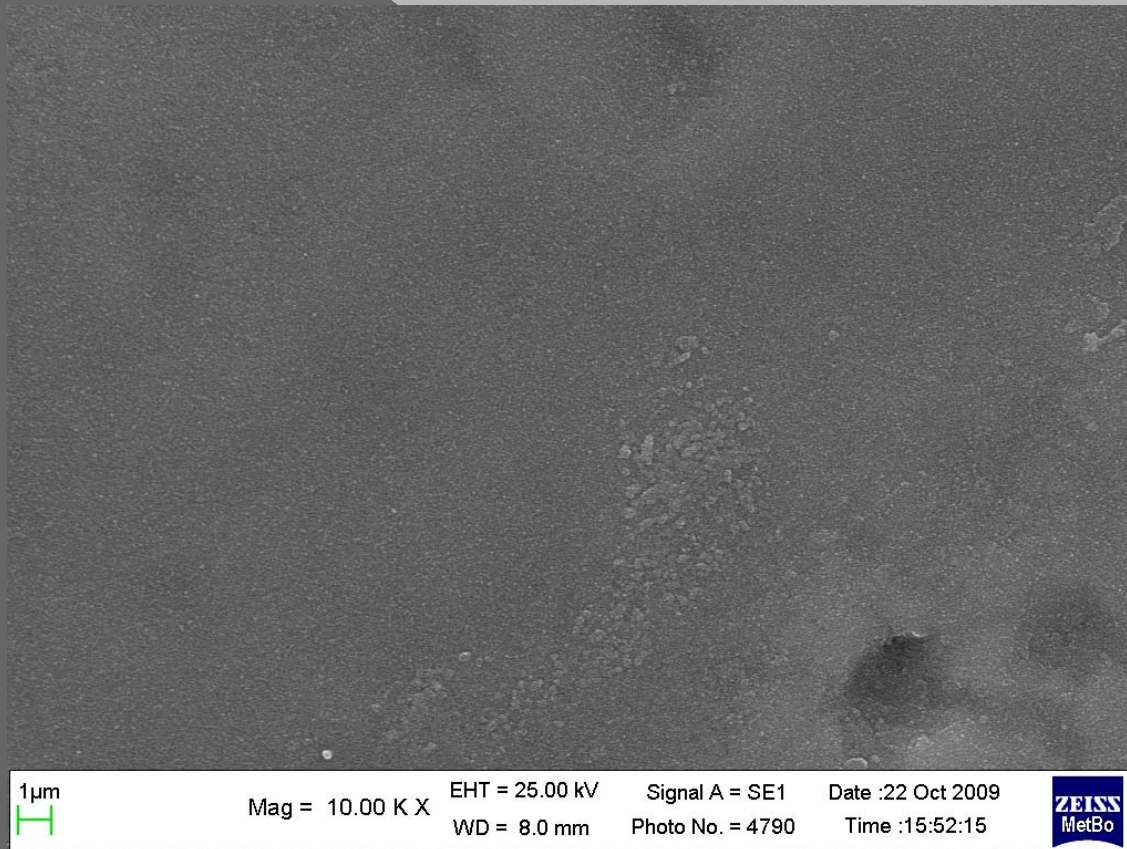
Enamel morphology

2 h whitening treatment on a human extracted dental surface with a led lamp and HP 35 wt% gel with TiO_2 acTivator + 24 h artificial saliva remineralization



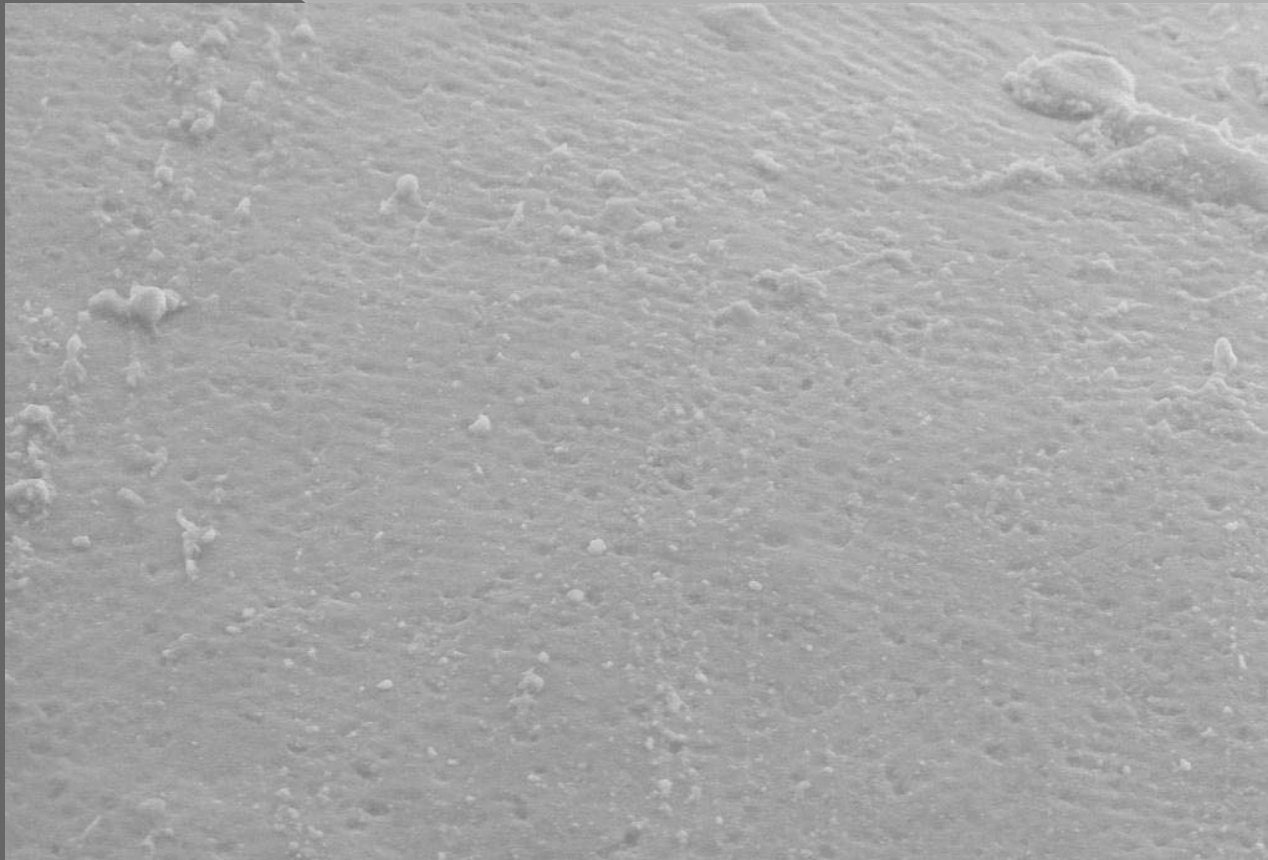
Enamel morphology

2 h whitening treatment on a human extracted dental surface with a led lamp and HP 35 wt% gel with TiO_2 acTivator + 24 h artificial saliva remineralization



Enamel morphology

HP 35 wt% acTivator LED 20' treatment
CONTROL



10 μ m



Mag = 1.00 K X

EHT = 20.00 kV

Signal A = VPSE

Date :1 Feb 2010

WD = 10.0 mm

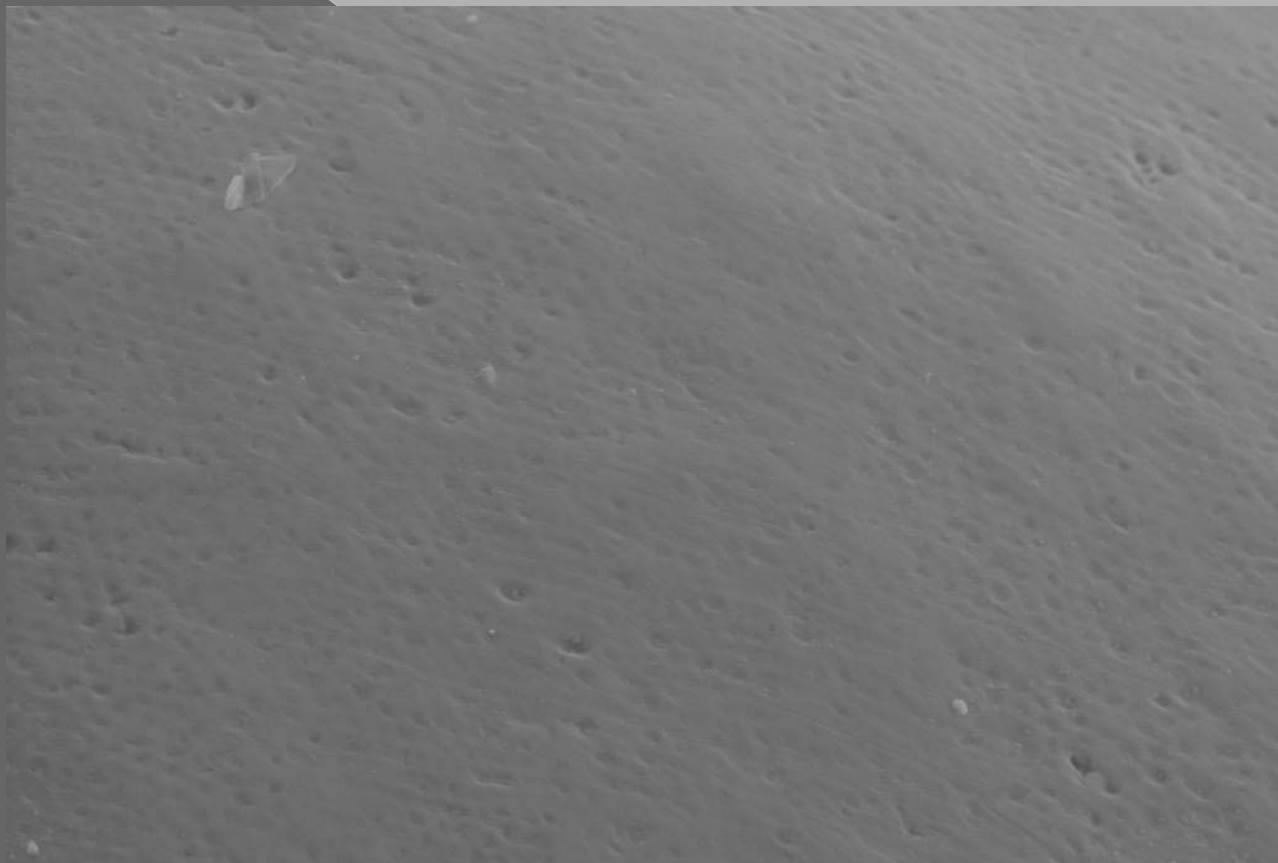
Photo No. = 6468

Time :15:36:36



Enamel morphology

HP 35 wt% acTivator LED 20' treatment
after bleaching



10 μ m



Mag = 1.00 K X

EHT = 20.00 kV

Signal A = VPSE

Date :23 Feb 2010

WD = 8.5 mm

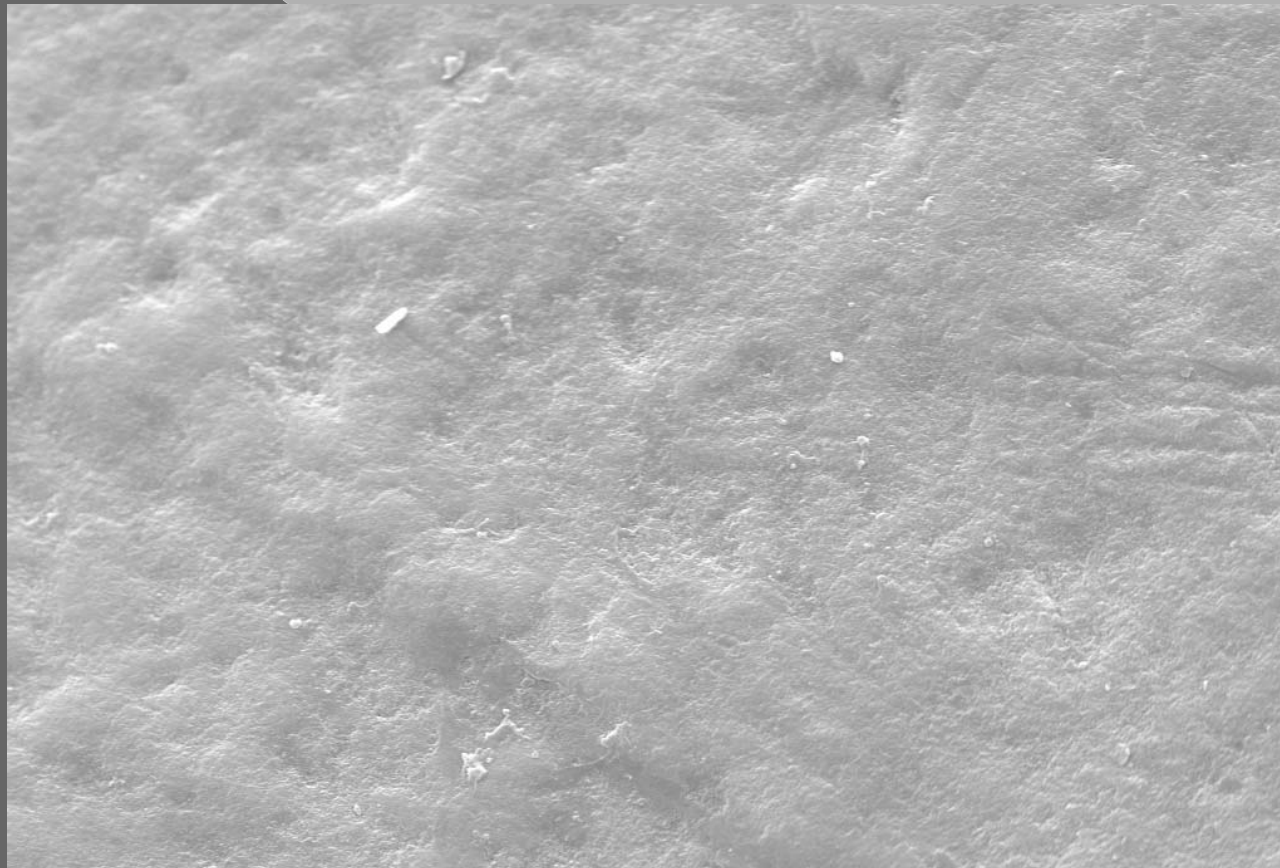
Photo No. = 7028

Time :17:37:46



Enamel morphology

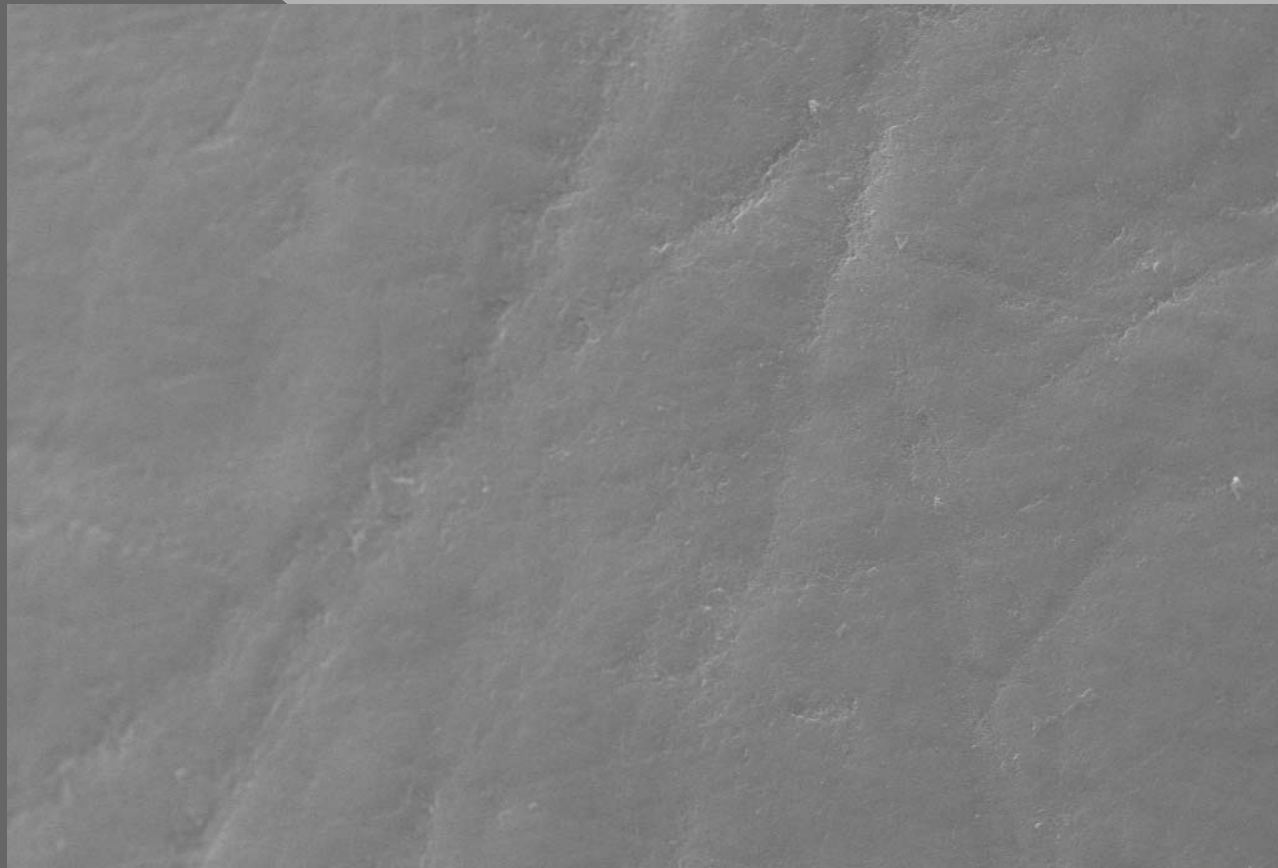
HP 35 wt% acTivator LED 20' treatment
CONTROL



10µm Mag = 5.00 K X EHT = 25.00 kV Signal A = SE1 Date :23 Sep 2009
WD = 5.5 mm Photo No. = 4252 Time :14:52:19 ZEISS MetBo

Enamel morphology

HP 35 wt% acTivator LED 20' treatment
after bleaching



10µm



Mag = 5.00 K X

EHT = 25.00 kV

Signal A = SE1

Date :23 Sep 2009

WD = 5.5 mm

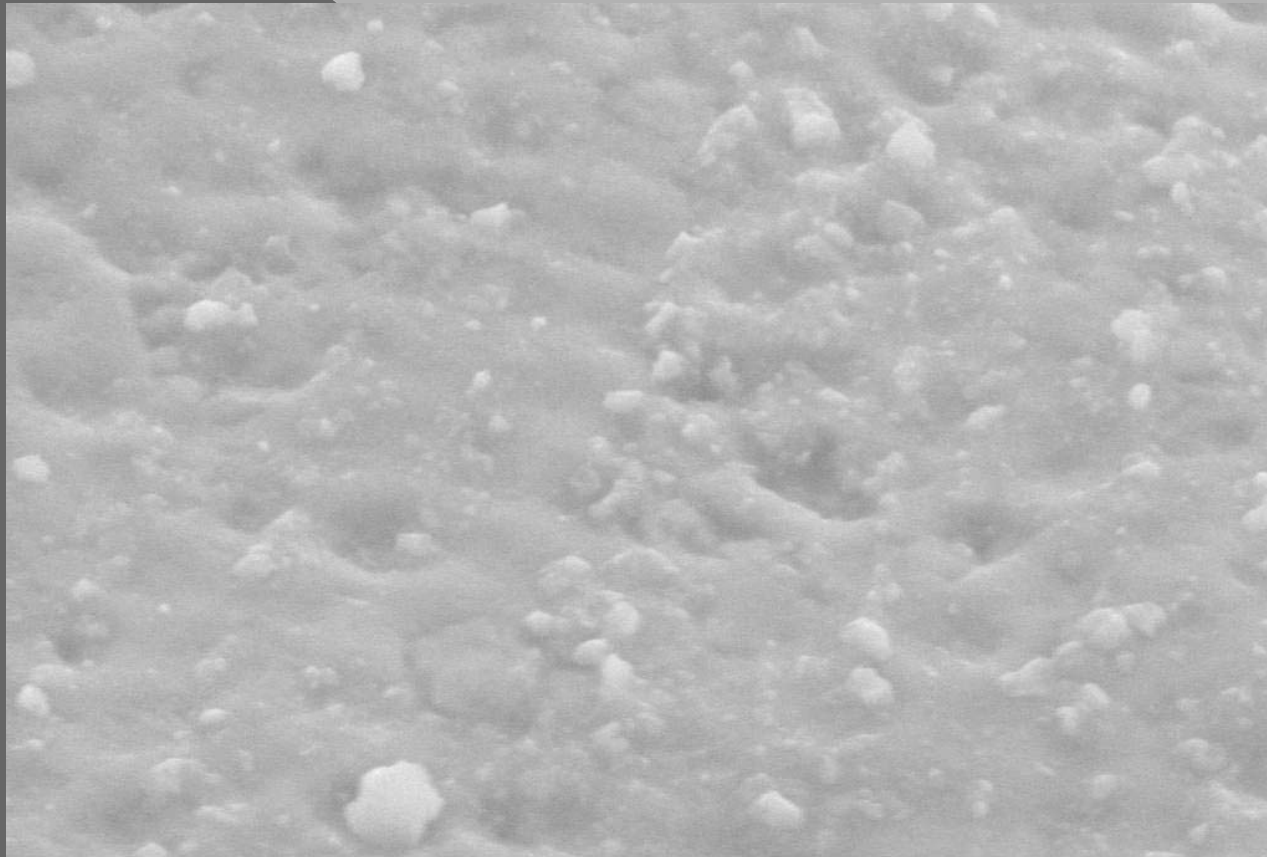
Photo No. = 4257

Time :15:02:06



Enamel morphology

HP 35 wt% acTivator LED 20' treatment
after bleaching



10 μ m



Mag = 5.00 K X

EHT = 20.00 kV

Signal A = VPSE

Date :1 Feb 2010

WD = 10.0 mm

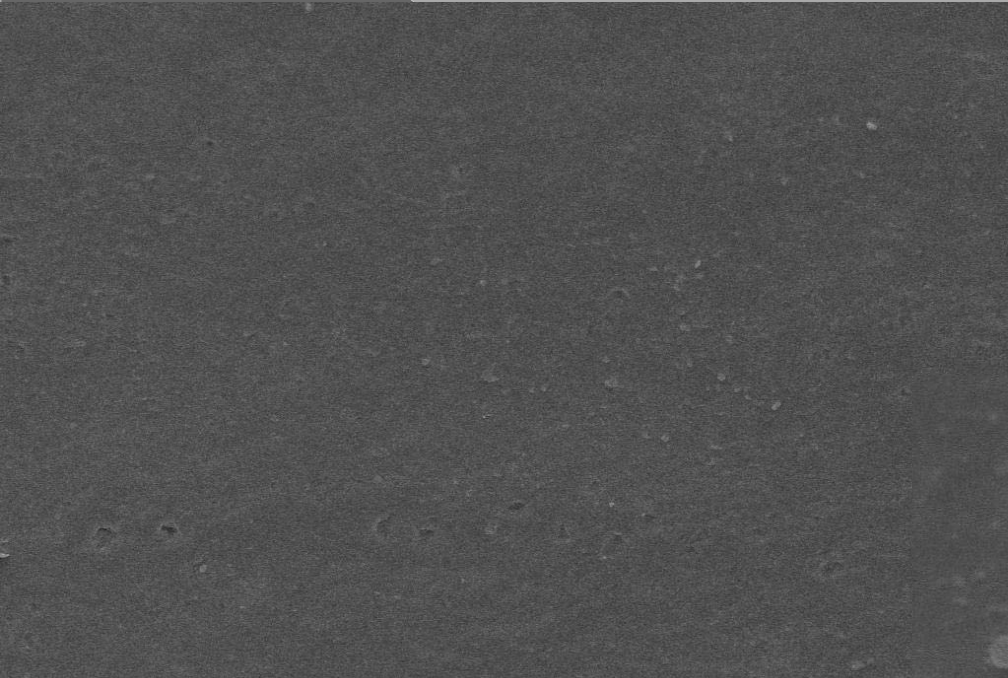
Photo No. = 6469

Time :15:37:40

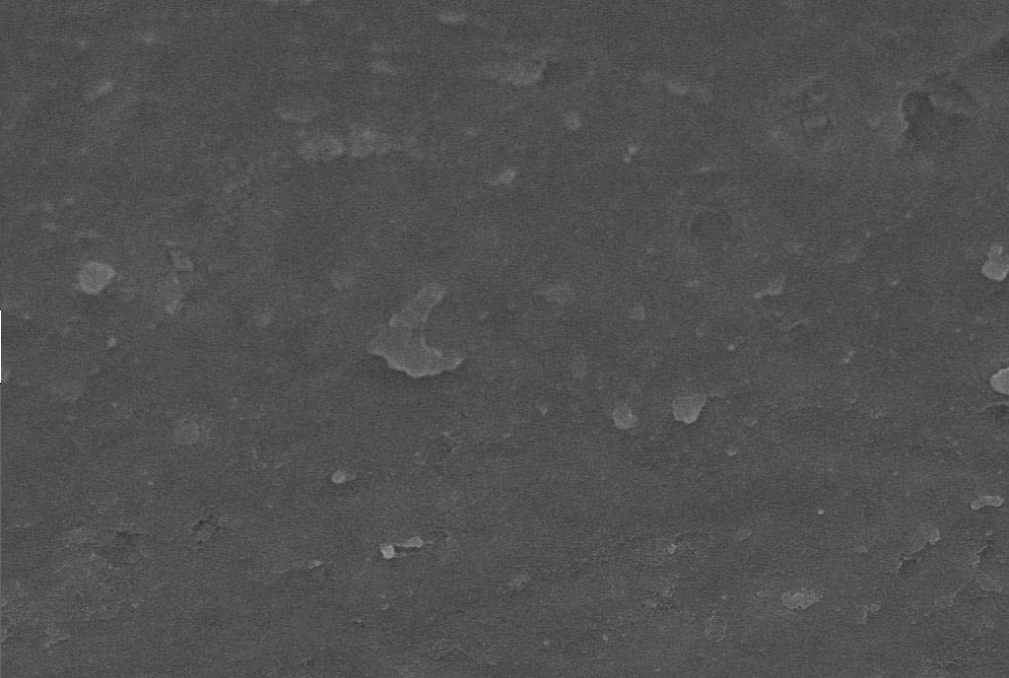


Comparative morphology

1 min coke treatment - CONTROL



10 μ m
Mag = 1.00 K X EHT = 15.00 kV Signal A = SE1 Date :18 Mar 2010
WD = 7.0 mm Photo No. = 7893 Time :17:59:13

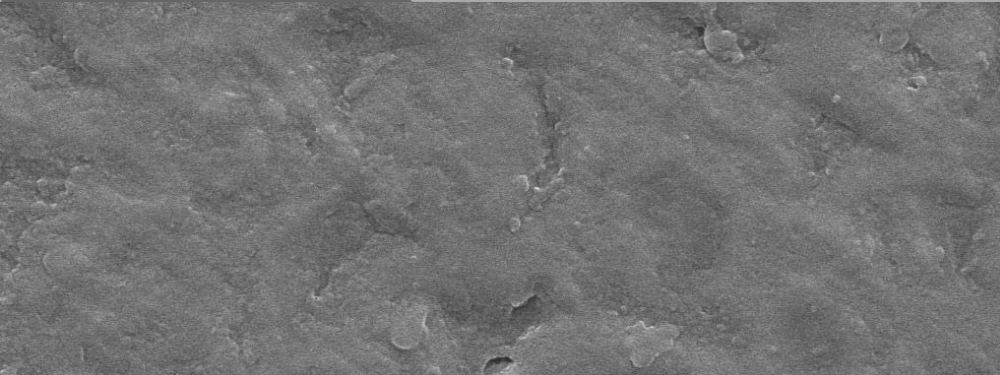


10 μ m
Mag = 5.00 K X EHT = 15.00 kV Signal A = SE1 Date :18 Mar 2010
WD = 7.0 mm Photo No. = 7894 Time :18:00:01

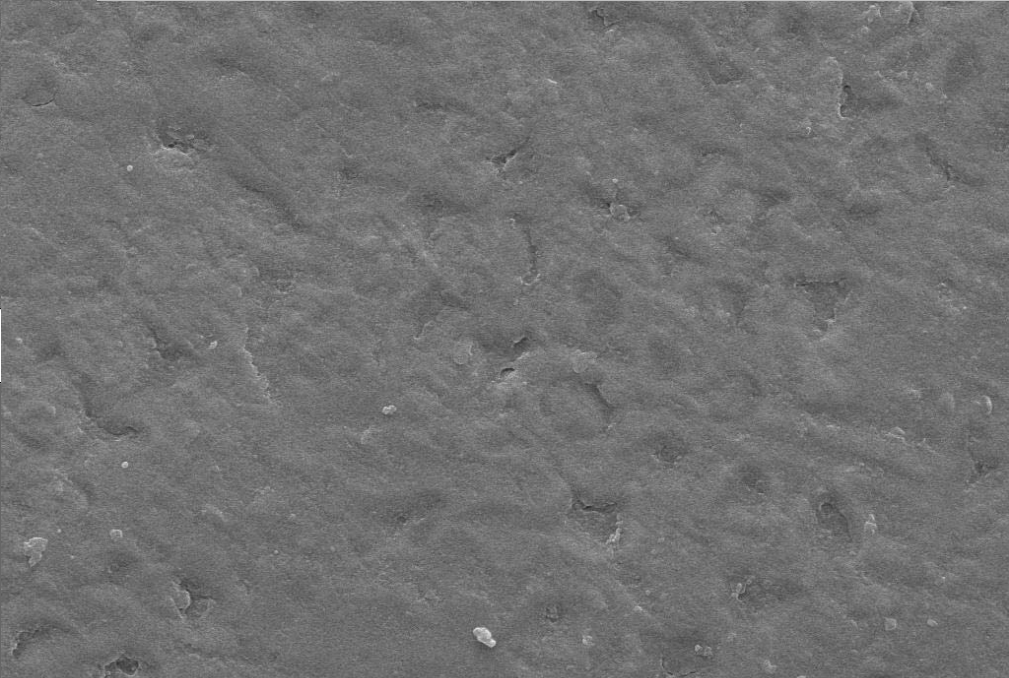


Comparative morphology

1 min coke treatment



2 μ m
Mag = 10.00 K X EHT = 15.00 kV Signal A = SE1 Date :18 Mar 2010
WD = 5.5 mm Photo No. = 7902 Time :18:11:40

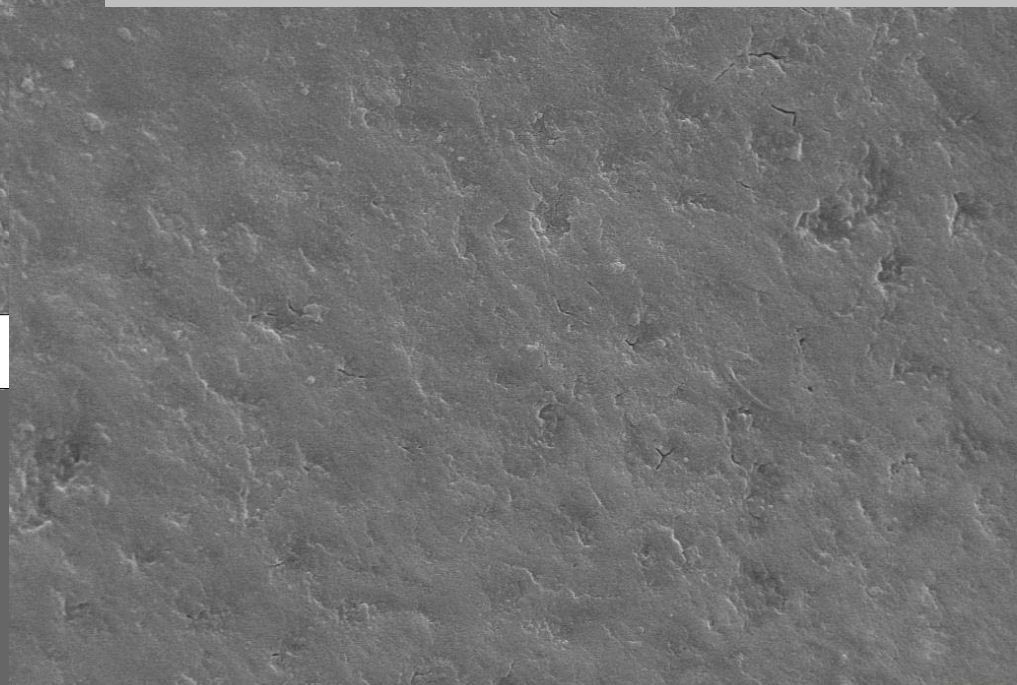
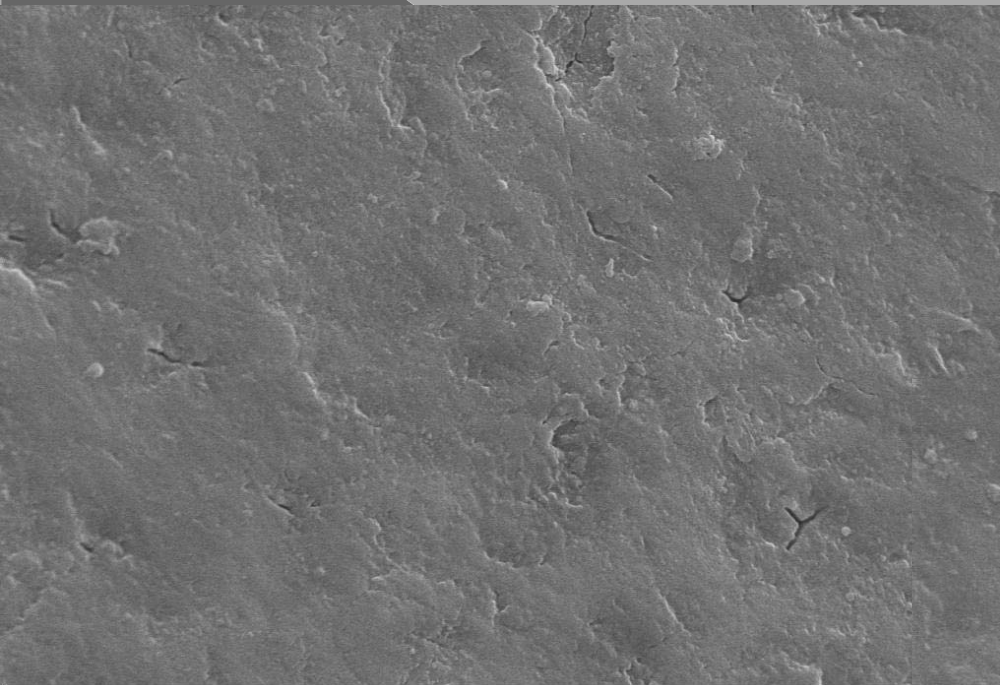


10 μ m
Mag = 5.00 K X EHT = 15.00 kV Signal A = SE1 Date :18 Mar 2010
WD = 5.5 mm Photo No. = 7903 Time :18:12:11



Comparative morphology

1 min coke treatment



1 μm | Mag = 10.00 K X | EHT = 15.00 kV | Signal A = SE1 | Date :18 Mar 2010
WD = 5.5 mm | Photo No. = 7900 | Time :18:07:42

10 μm | Mag = 5.00 K X | EHT = 15.00 kV | Signal A = SE1 | Date :18 Mar 2010
WD = 5.5 mm | Photo No. = 7899 | Time :18:07:04

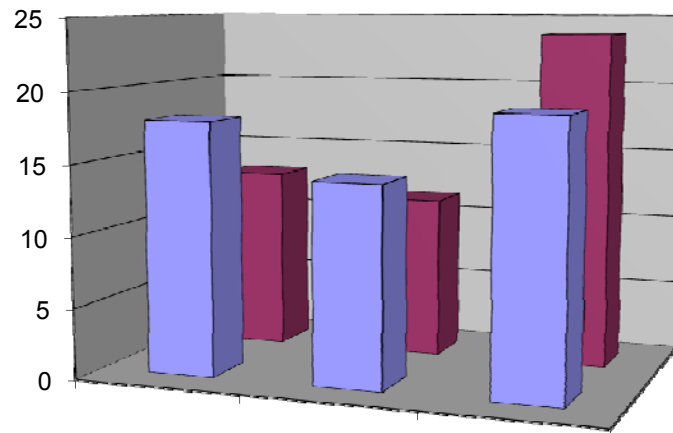


Mineralization

- Vickers microhardness analyses have been carried out on the teeth substrates to investigate which is the whitening power effect in respect to the untreated samples. The aim of the analysis was that to measure the enamel deminarization after "in office" treatment

Mineralization

Vickers Microhardness (VHN) office bleaching LED



■ HP35%+acTivator 20'

17,9

14,1

19

■ HP38%+acTivator 20'

13

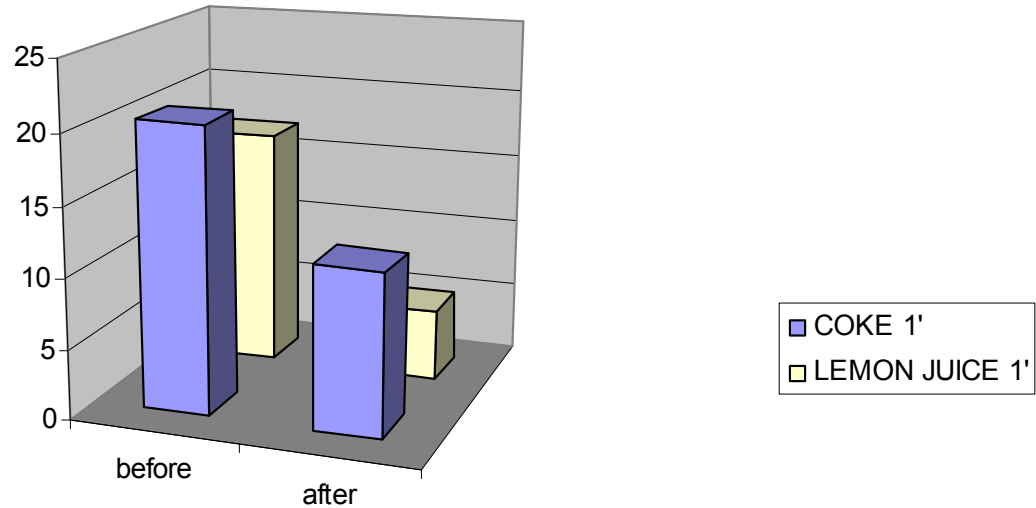
11,5

23,7

Mineralization

1 min acid beverages treatment

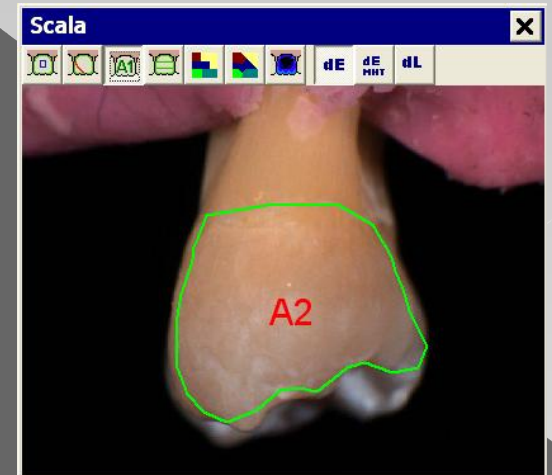
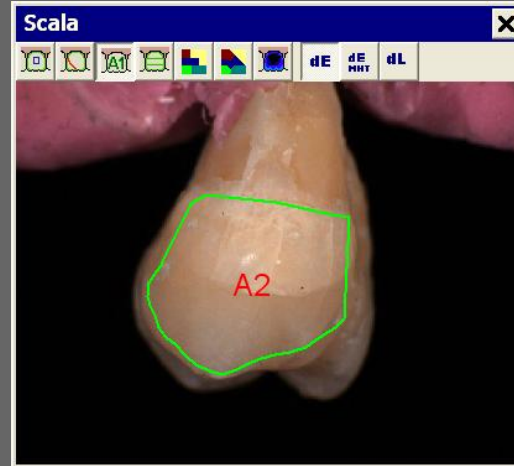
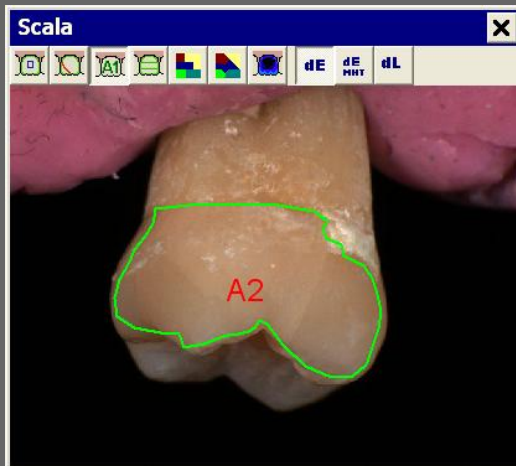
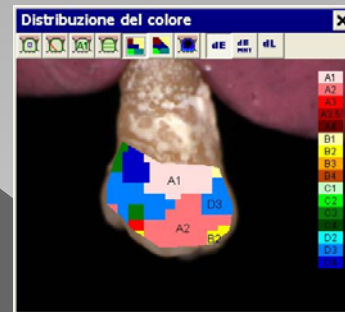
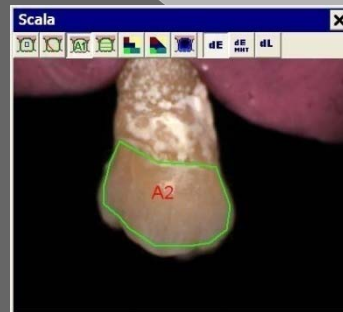
Vickers Microhardness (VHN) Acid Beverages



| | before | after |
|----------------|--------|-------|
| COKE 1' | 20,4 | 11,6 |
| LEMON JUICE 1' | 17,1 | 5,1 |

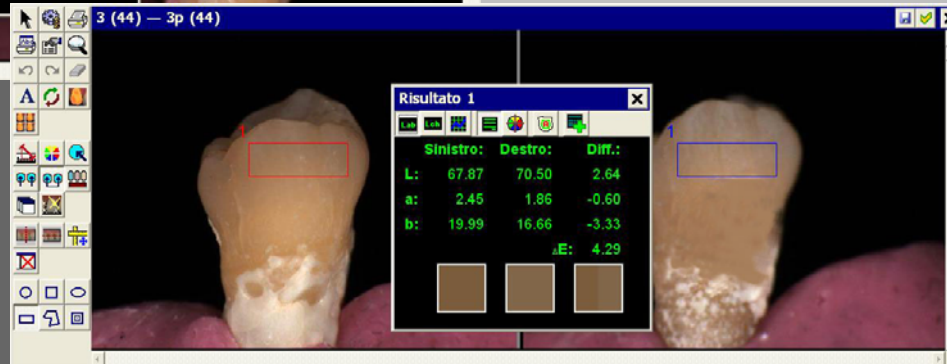
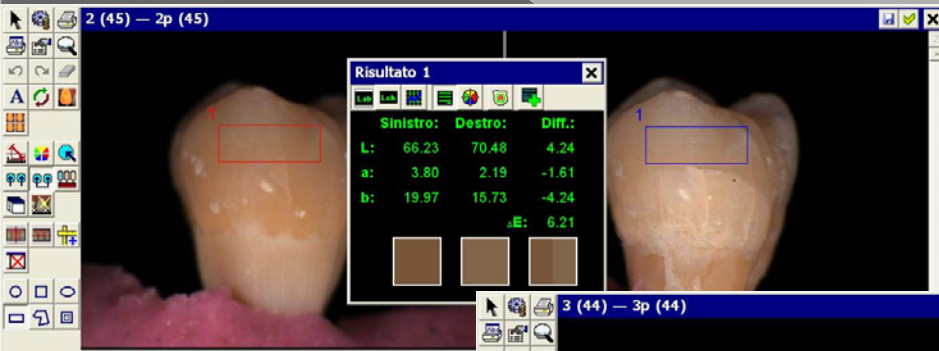
Whitening power – Spectroshade

HP 35 wt% acTivator LED 20' treatment
after bleaching



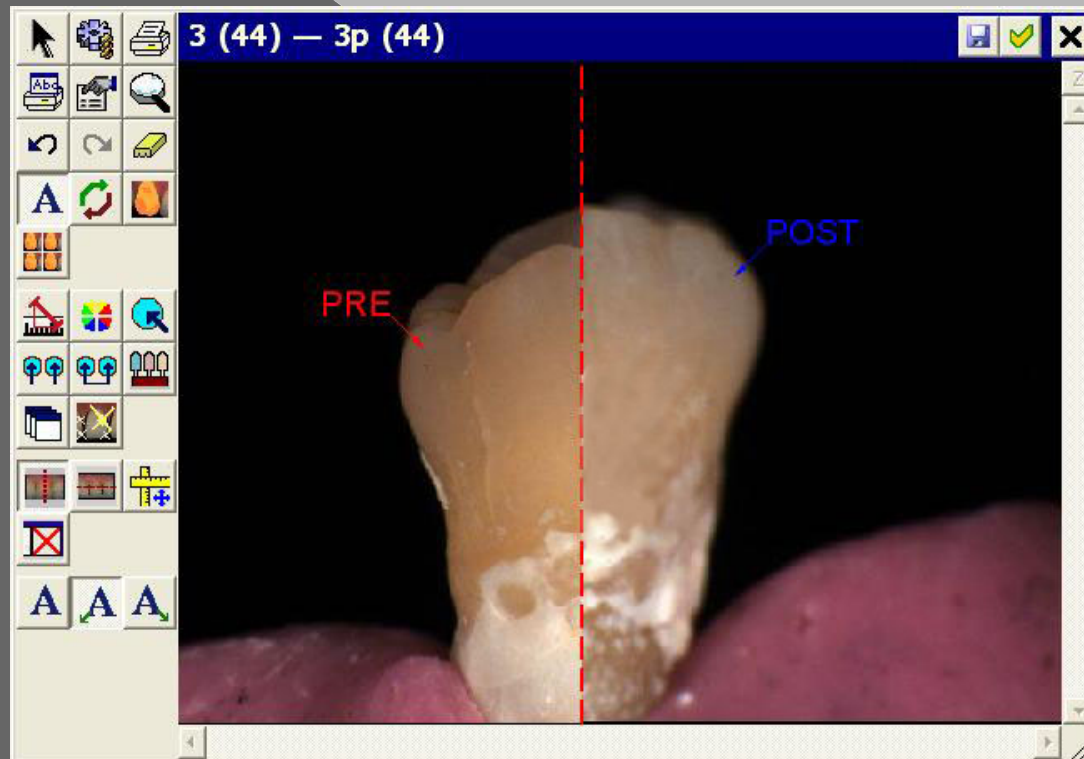
Whitening power – Spectroshade

HP 35 wt% acTivator LED 20' treatment
after bleaching



Whitening power – Spectroshade

HP 35 wt% acTivator LED 20' treatment
pre-post bleaching



Whitening power – Spectroshade

average value obtained from extracted teeth

| | |
|--|---|
| <i>BLEACHING PRODUCT</i> | HP 35% acTivator 20' + LED |
| <i>IN OFFICE BLEACHING</i> | X |
| <i>VITA SHADE average post BLEACHING</i> | A2 |
| ΔE | $\Delta E = 5,7$ |
| ΔSGU VITA SHADE GUIDE UNIT | $\Delta_{\text{average}} \approx 6$ |

References comparison

| Ref. | Deliperi et al., <i>J. Am. Dent. Assoc.</i> , 2004 , 35, 628-634 | Zekonis et al., <i>Operative Dentistry</i> , 2003 , 28-2, 114-121 | Sulieman et al., <i>Journal of Dentistry</i> , 2005 , 33, 33-40 | Gurgan et al., <i>Lasers Med Sci.</i> , 2009 , DOI 10.1007/s10103-009-0688-x |
|-------------------------------|---|--|--|---|
| BLEACHING PRODUCT | HP 35 wt% 30' (10' x 3 with new gel) + CP 10 wt% 60' X 3 gg | HP 35 wt% 1h (10' x 6 with new gel) + CP 10 wt% x 7 nights | HP 35 wt% 30' + Plasma (10' x 3 with new gel) | HP 35 wt% 60' (20' x 3 with new gel) + Plasma |
| IN OFFICE BLEACHING | X | X | X | X |
| HOME BLEACHING | X | X | | |
| ΔE | / | $\Delta E = 4.05$ | $\Delta E = 6,52$ | $\Delta E = 5,28$ |
| Δ SGU SHADE GUIDE UNIT | $\Delta = 6,4$ | $\Delta = 9,1$ | $\Delta = 5,2$ | $\Delta = 8,4$ |