



**UNIVERSITY OF ROME “LA SAPIENZA”  
NANOTECHNOLOGIES ENGINEERING**

# **SELECTED APPLICATIONS OF NANOPARTICLES**

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# **NANOPARTICLES IN COSMETICS**

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The nanoparticles used in cosmetics are materials that are not soluble in water and resistant to biological contamination.

Almost every cosmetic manufacturer uses nowadays nanoparticles in their products. EU estimates an average content of nanomaterials in cosmetic products being equal to 5%.

For cosmetic use, nanomaterials are:

- emulsions for skin care such as creams, lotions and detergents;
- sunscreen creams;
- pigmented make-up products.

## **APPLICATIONS**

Emulsions: tendency is to have smallest emulsions, in order to improve their appearance, stability and usability.  
Sunscreen creams: protection from UV rays and reduction of the negative effects given by skin oxidation by using zinc and titanium oxides coated by polymers.

In general, the nanoparticles are nanocomposites, build up by successive coatings, with higher and different functionalities.

Zinc on titanium oxide cores are used for make-up since they exhibit excellent optical properties, stickiness to the skin and persistence.

## **EMULSIONS**

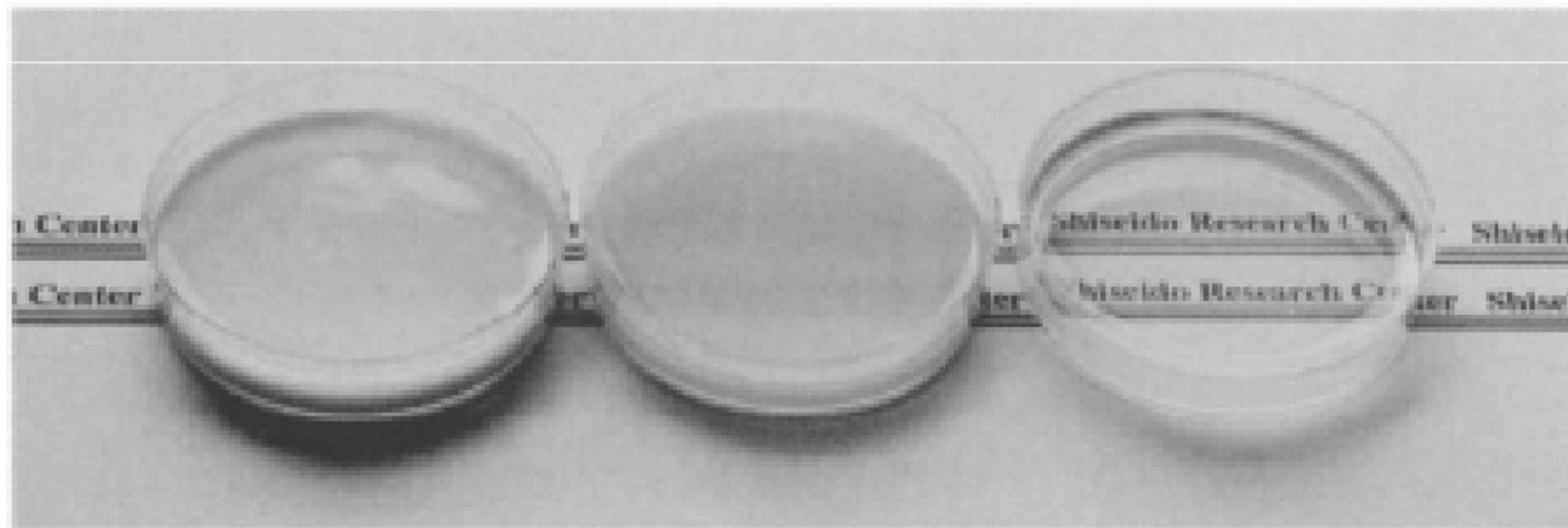
Changes in process sequence and/or pressure may give rise to water-oil emulsions at nanoscale.

Chemical method: solubilisation of surfactants at high temperatures, water and oil and quick quenching.

Mechanical methods: high velocity nozzles, homogeniser, emulsification assisted by ultrasound, etc.

## OIL – WATER EMULSION

	(a)	(b)	(c)
Emulsified particle diameter	1~10 $\mu\text{m}$	120 nm	30 nm(0.03 $\mu\text{m}$ )
Viscosity	1020 mPa · s	18 mPa · s	10 mPa · s
Preparation condition	Homogenizing mixer	High pressure homogenizer	High pressure homogenizer



(a)

(b)

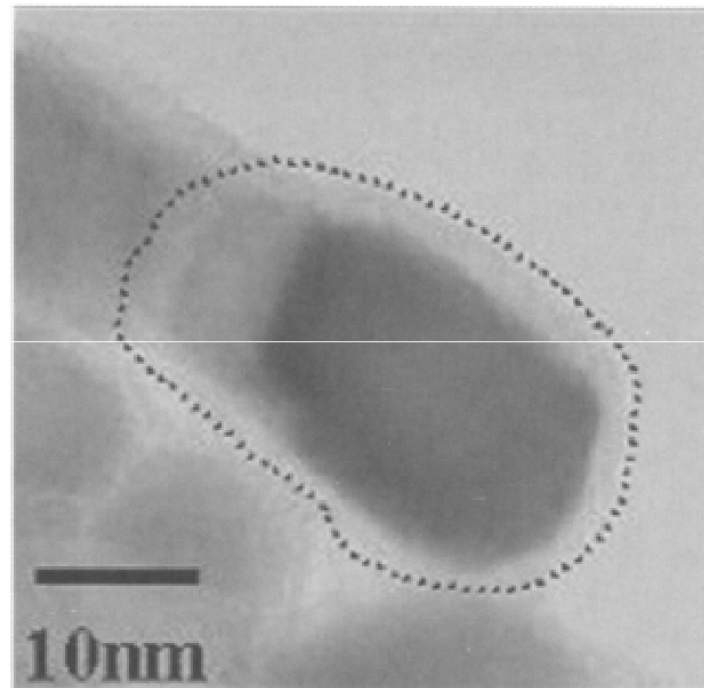
(c)

## **SKIN CARE**

These particles are capable to adsorb and deactivate enzymes on the skin that leads to dryness. Composite nanoparticles of zinc oxide on a silicon oxide core of 30nm are generally used.

These particles have an much higher efficiency if compared to the single components, where the silicon oxide promotes the adsorption and the zinc oxide the deactivation of the enzyme.

zinc oxide on a silicon oxide core





## PROBLEMS AND ISSUES

The high attention of the consumers pushes the industry to high attention and care using nanoparticles.

Nanoparticles may become dangerous around 20-30nm. In case of sunscreen creams, at this size titania exhibits highest efficiency. In order to prevent the penetration of these particles in the derma (and other interactions on the skin surface) therefore the use of particles of such a size are generally coated by polymers.

Test of several years are necessary to put new products on the market. This avoids the appearance of secondary effects to the consumer which may rely on safe products.

## REACH

(Restrictions and Authorization of Chemical compounds)

A particular legislation on the use of nanoparticles was introduced in the last years (REACH). Security on all the used materials at the specific size and composition must be demonstrated.

EU is performing a database collection on the used materials nowadays, taking data directly from the producer's experience and reports. The target is to make white and blacklists in the next future.

Moreover, even using recognized compounds in the product on the market, a 6 month long pre-alert must be given to EU before introduction.

On the ingredients list, now it is obligatory to add "nano" to those compounds at nanoscale.

## Nanoparticles for sunscreen creams

- **Ultraviolet (UV) radiation** from the sun **is harmful to the humankind** and excessive exposure causes sunburn, stain, and an increased risk for skin cancers. These effects are mainly attributed to the UV in the wave **length range of 280–320 nm**, which is referred to as **UVB** (**UVA's** wave range is 320-400 nm).
- Ultra-fine inorganic particles are very useful in sunscreen formulas owing to high safety and stability. The most widely used inorganic particles are titanium dioxide (**TiO<sub>2</sub>**) for UVB-protection.
- The optimum size for spherical **titanium dioxide** particles is considered to vary uniformly from **50 nanometer** for 0.3 micrometer UV radiation to **120 nanometer** for 0.4 micrometer radiation (Stamatakis, 2004)
- In cosmetic industries, the **sun protection factor (SPF)** is often used **to evaluate the UV absorption ability**.

## MAIN AIMS OF THE WORK

- **To produce  $\text{TiO}_2$**  in the **optimal size range** and in a **stable suspension** to be used for sunscreens.
- **To compare** the performances of two sunscreens formulated by using, respectively, a commercial  **$\text{TiO}_2$  powder** and the homemade **titania suspension**.

The UV absorption ability was evaluated on the basis of the sun protection factor (SPF).

# TITANIA PRODUCTION PROCESS

- Precipitation-reaction (hydrolysis + polycondensation):

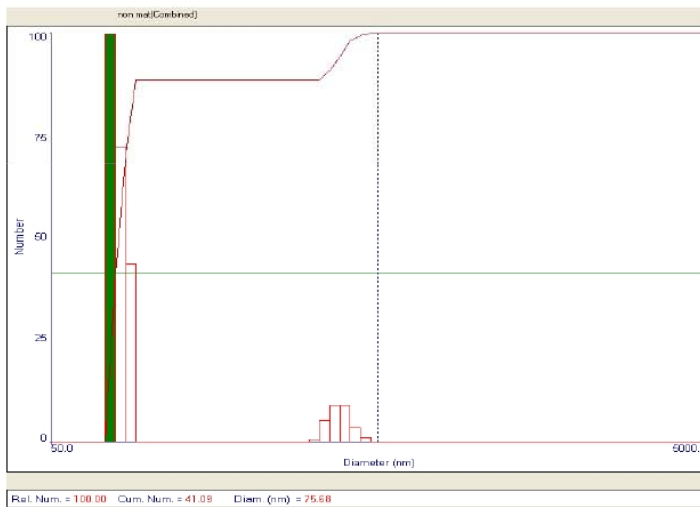


- Operating conditions:  
addition of citric acid,  $T = 80^\circ \text{C}$ ,  $t = 8 \text{ h}$
- Suspension evaporation to have a final concentration of  $\text{TiO}_2$  equal to 13 %
- $\text{pH } 3,0 \rightarrow 4,7$

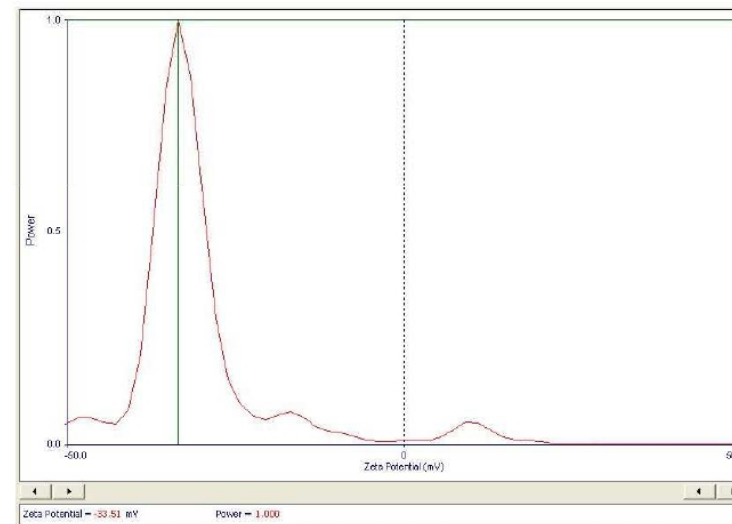


# PROPERTIES OF THE $\text{TiO}_2$ SUSPENSION

- By using a dynamic light scattering instrument supplied by Brookhaven, both the crystal size distribution and the Z potential were measured:



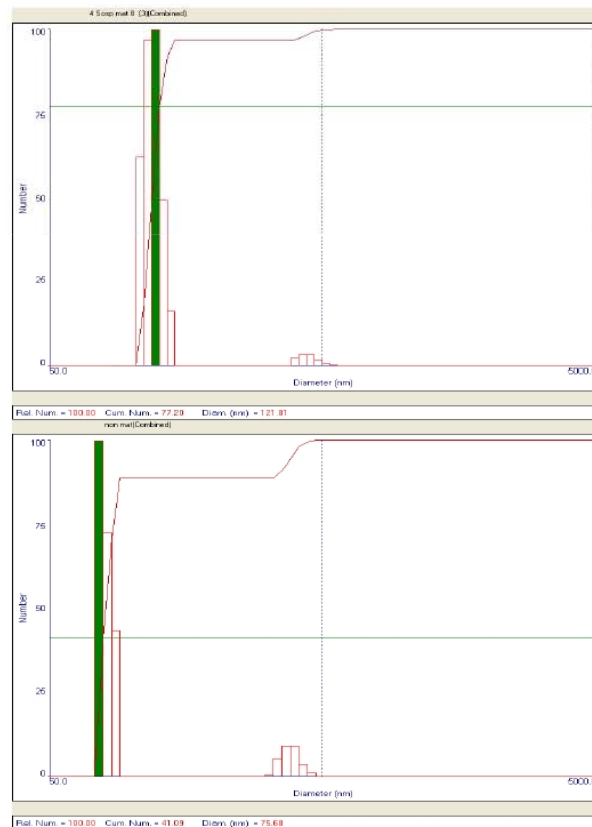
Diameter 75 nm



Z potential = -33,1 → suspension stability

# AGEING BY HYDROTHERMAL TREATMENT

- The ageing operated at 200 ° C in a reactor may change the CSD, due to the ripening phenomenon, leading to a narrower size range



After 8 h,  $D = 122$

Initial suspension,  $D = 75$

# THE PRODUCED SUNSCREEN EMULSION

- **Emulsion with commercial TiO<sub>2</sub> powder:**  
It contains 1% of titanium dioxide powder (Eusolex T-AVO by Merck) and was enriched with chitin nanofibrils. The titanium dioxide is an amphiphilic rutile type and it is mixed with a special coated silica.
- **Emulsion with the produced TiO<sub>2</sub> suspension:**  
It contains 7,7% of pre-dispersed titanium dioxide at 13% and was enriched with chitin nanofibrils. The pre-dispersed titanium dioxide was added at 60-65 ° C, with high shearing, at the end of the emulsion process during the cooling time, at temperature < 40° C.



# SKIN REACTIONS TO EXTERNAL STRESS

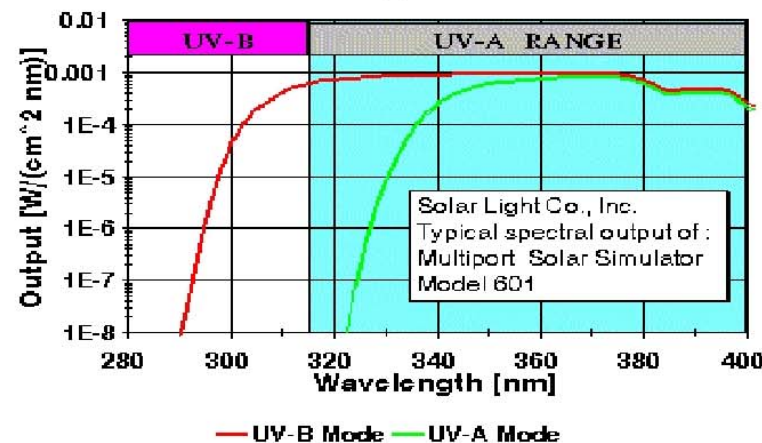
- Erythema is the most common cutaneous phenomenon resulting from irritant stress. It can be experimentally evoked by several types of stimuli.
- UV radiation is particularly effective in inducing erythematous reactions varying in extension and intensity.
- Erythema can be quantified with great precision by instruments (colorimeters) that measure the redness of skin surface
- Cosmetological applications of UV induced reactions :
  - ☐ Skin sensitivity to UV radiation
  - ☐ Assessment of sun protection factor (COLIPA)
  - ☐ Ability of antioxidant agents to prevent photo-damage
  - ☐ Effectiveness of anti-inflammatory ingredients

# INSTRUMENTS TO QUANTIFY UV-INDUCED ERYTHEMA

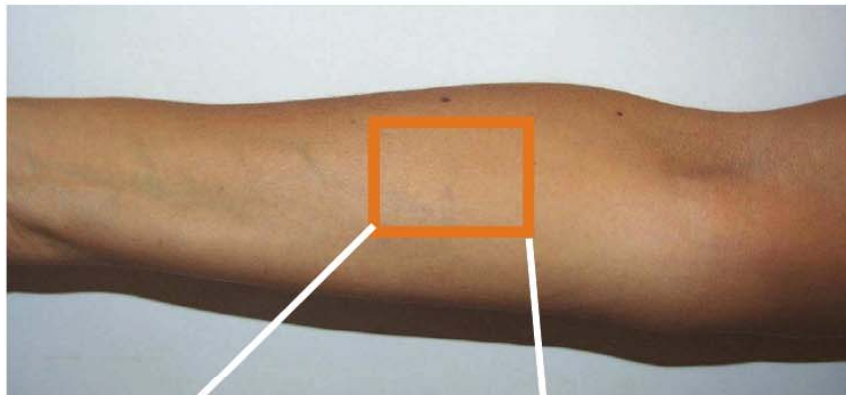
- **Solar Simulator:** The Multiport 601 is a 6 output simulator of solar UV radiation in a region of 290 to 400 nm. It produces radiation 15 to 20 times stronger than that of mid-latitude sun.



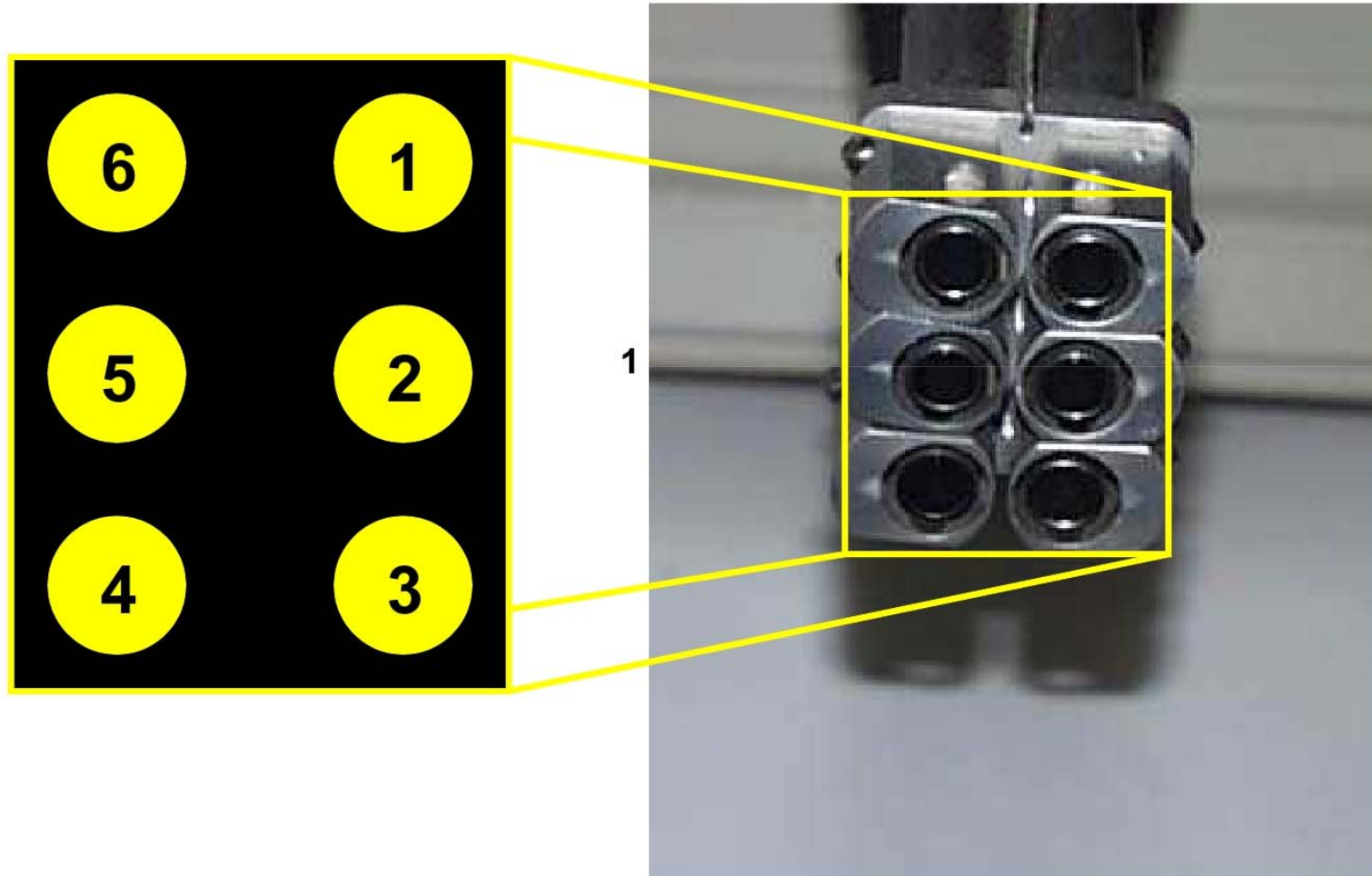
The light source is a 150 Watt xenon lamp, whose spectral output follows the distribution of sunlight from 290 to 400 nm.



The **Solar Simulator** is equipped with six optical fiber collectors that deliver the ultraviolet light directly to the skin.



The window of each collector can be regulated to produce a series of increasing UV output levels.



# ERYTHEMA INTENSITY EVALUATION

- A body area is irradiated for 120 sec.
- The erythema intensity evaluation is based on an intensity named Minimal Erythema Dose (MED).





# ERYTHEMA INTENSITY MEASUREMENT

Erythema can be easily quantified by means of colorimetric measurement.



**Minolta CR 200 Chroma** Meter contains a xenon lamp as a light source, photodetectors, a microcomputer, and coloured filters which closely match the CIE colorimetric Standard Observer curves.

The measuring head of *Chroma Meter* must be placed orthogonally to the cutaneous surface, without compressing the skin



# SPF ASSESSMENT

- The study has been carried out on 2 preparations, respectively containing
  - **commercial powdered TiO<sub>2</sub>**
  - **home-made pre-dispersed TiO<sub>2</sub>**

where the concentration of the active ingredient (TiO<sub>2</sub>) was supposed to provide an SPF value of about 7-8 for both the considered products

- The investigation has been performed according to the technique of European Cosmetic Toiletry and Perfumery Association (COLIPA)<sup>(1)</sup> aligned with other techniques.  
**1. COLIPA. Sun Protection Factor Test Method. COLIPA Publication 94/289 (1994): October 1994.**



## ADOPTED PROCEDURE

- **Population study**
  - 10 subjects
  - Age 20-42 years
  - Phototypes: I-III (Selected according to sun history and skin color evaluation)
- **Determination of MEDu** : Skin areas corresponding to the section of UV-output (cm 2 x 3) were delimited. For each subject, one of the selected sites was exposed to UV, in order to determine the ***MEDu (minimal erythematol dose of unprotected skin)***
- **Determination of MEDp** : After determining the value of MEDu, two other areas of the same subject have been treated with the products under study (2 mg/cm<sup>2</sup>) and irradiated with doses 7 times higher than those used for MEDu

## SPF ASSESSMENT OF PRODUCT WITH TiO<sub>2</sub> POWDER

Subject	Phototype	Pigmentation	SPF
1	III	intermediate	7,2
2	III	intermediate	10,2
3	I	fair	8
4	III	intermediate	6,5
5	I	fair	5,7
6	II	fair	5
7	III	intermediate	6,4
8	II	fair	5,4
9	II	fair	8,8
10	III	intermediate	5,1
SPF = 6,8		SD=1,72	

## SPF ASSESSMENT OF PRODUCT WITH PRE-DISPERSED TiO<sub>2</sub>

Subject	Phototype	Pigmentation	SPF
1	III	intermediate	5,8
2	III	intermediate	9,5
3	I	fair	7,2
4	III	intermediate	6,7
5	I	fair	5,1
6	II	fair	4,5
7	III	intermediate	6,2
8	II	fair	5,1
9	II	fair	7,2
10	III	intermediate	6,2
SPF=6.3		SD=1,42	

## CONCLUSIONS

- The **TiO<sub>2</sub> suspension** produced with addition of citric acid at 80 ° C was **stable** and exhibited ceramic **nanoparticles in the required size range**.
- It is possible to suitably change the CSD of titania nanoparticles by means of a hydrothermal process.
- The determination of **Sun Protection Factor** on the two examined products respectively containing powdered and pre-dispersed TiO<sub>2</sub> showed very close values. Therefore, **both the ingredients are able to play a protective action towards the UV**.