

# Nanoparticle Characterization and Analysis of Airborne Titanium Dioxide in Powdered Cosmetics

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## ABSTRACT

Screening of cosmetics and personal care products for detection and characterization of nanoparticles is an important step in the overall assessment of risk. In this study, several powdered cosmetic products were purchased and evaluated for the presence of TiO<sub>2</sub> nanoparticles first by automated particle sizing using scanning electron microscopy (SEM) with chemical typing by energy dispersive spectroscopy (EDS) and then by transmission electron microscopy (TEM). Our results show that automated particle sizing/chemical typing by SEM-EDS is a convenient screening tool for detection of nanoparticles (to 50 nm) and determination of elemental composition. This analysis may be followed up by TEM for a detailed investigation of morphology, and to assess the lower particle size limit and any association with other ingredients. Additionally, the results of a study on TiO<sub>2</sub> nanoparticle release in the breathing zone during cosmetic application will be presented.

**Keywords:** nanoparticles, titanium dioxide, cosmetics, SEM-EDS, TEM

## INTRODUCTION

The surge in consumer products containing nanomaterials continues to raise concern over potential exposure and the possible health risks associated with exposure is drawing the attention of manufacturers, consumers [1] and regulatory agencies [2,3]. Although not specifically disclosed in most cases, many cosmetics and personal care products available today contain nanoparticles. Titanium dioxide (TiO<sub>2</sub>) nanoparticles, in particular, are prevalent in these products for both their sunscreen and pigment properties and have been present in these functions since ancient times [4]. However, labeling is not currently required in the United States to indicate the presence of nanomaterials in cosmetics and personal care products with the exception of California. Proposition 65 in California requires products containing unbound TiO<sub>2</sub> that may become airborne and is of respirable size to carry a warning [5]. Therefore, screening of these cosmetics and personal care products for detection and characterization of

nanoparticles is an important step in the overall assessment of risk.

This study presents the microscopical examination results of two commercially available powdered cosmetic products for the presence of TiO<sub>2</sub> nanoparticles. Product A is a pressed powder with titanium dioxide listed in the ingredient list under the “may contain” section. Product B is a loose powder with titanium dioxide listed under the “may contain” section of the ingredient list and advertised on the container as the sunscreen present. Both powders were screened for TiO<sub>2</sub> content by automated SEM-EDS followed by a detailed TEM analysis to determine the smallest particle size and morphology. A nanoparticle release study was then conducted to evaluate exposure to airborne nanoparticles while applying Product A.

## METHODS

A subsample of each cosmetic powder was sonicated in DI H<sub>2</sub>O then filtered through a 0.1 μm pore size, 47 mm polycarbonate (PC) filter and allowed to dry. For automated SEM-EDS analyses, a section of the filter was excised, mounted onto an aluminum stub, and coated with carbon for enhanced conductivity. For TEM analyses, a Jaffe wick consisting of a stainless steel bridge covered with lens papers was set up in a petri dish. TEM grids (200 mesh) were placed on the Jaffe wick and covered with portions of the PC filter. A mixture consisting of 20% 1-2-diaminoethane and 80% 1-methyl-2-pyrrolidone solution was prepared and thoroughly mixed. The mixture was added to the petri dish with the solvent meniscus coming in contact with the bridge from below and allowed to set for 25 min. The stainless steel bridge was removed from the dish with forceps, placed in another dry petri dish and rinsed with DI H<sub>2</sub>O several times.

Automated SEM-EDS analyses were performed on a JEOL JSM-6500F field emission scanning electron microscope operating under the control of a Thermo Scientific Noran System SIX energy dispersive spectrometer at 15kV. The low energy cutoff was set to 380 eV to eliminate carbon from the analyses. Parameters were set to count all particles 0.0025 μm<sup>2</sup> and larger. Approximately 1000 particles were analyzed. Data were

analyzed in Microsoft Excel excluding all particles with Ti + O content <80 and other elements present in concentrations  $\geq 10$ . A particle size distribution was created by number of particles and mass of particles. The assumption has been made that all particles are of equal density and therefore the mass distribution is equal to the volume distribution.

Transmission electron microscopy was performed on a Philips CM 120 TEM operated at 100kV and equipped with an Oxford INCA energy dispersive spectrometer. Aggregates of and individual TiO<sub>2</sub> particles were measured using calibrated on screen divisions with over 250 particles measured per sample. Size data was imported into Microsoft Excel for particle size distribution and statistical analyses.

For the airborne study, the interior of a glove box was thoroughly cleaned and a mannequin head and cassette stand were placed inside. A stationary pump was calibrated to a flow rate of 2 L/min using a 0.1  $\mu\text{m}$  PC filter. A second 0.1  $\mu\text{m}$  PC filter was secured in the cassette stand and connected to the stationary pump. Product A was applied to the mannequin with a clean cosmetic sponge covering the face as a pressed powder would typically be applied. The air sample was collected over a period of 5 min including during (~3 min) and after (~2 min) application. The filter was prepared as previously described for TEM analysis.

## RESULTS AND DISCUSSION

### Product A

Automated SEM-EDS analysis of Product A detected 389 Ti + O-rich aggregates or individual particles. Of these 389 particles, 8.5% (33 particles) were in the 50-100 nm size range and all were below 2.0  $\mu\text{m}$  in diameter (Table 1). A distribution of particles by estimated mass is also presented in Table 1.

TEM analysis of pressed powder Product A revealed that the majority of TiO<sub>2</sub> present was in the form of aggregates (Figure 1). A few individual primary particles were also observed (Figure 2). Figure 3 presents a particle size distribution of TiO<sub>2</sub> aggregates and primary particles observed in Product A. The average particle size was  $490 \pm 232$  nm with 311 particles measured. The maximum particle size recorded was 1700 nm and the minimum particle size was 80 nm.

Analysis of the airborne exposure sample by TEM was performed on a detection only basis. Of 10 grid openings analyzed (0.1 mm<sup>2</sup>), two TiO<sub>2</sub> aggregates were observed. A representative aggregate is shown in Figure 4. The sizes of the two aggregates observed were 504 nm and 266 nm, respectively.

Product A		
Particle Size Range ( $\mu\text{m}$ )	Number %	Mass %
0.05 - <0.1	8.5	0.0
0.1 - <0.2	28.5	1.0
0.2 - <0.4	38.8	8.3
0.4 - <0.6	15.4	15.2
0.6 - <0.8	4.9	12.5
0.8 - <1.0	2.1	11.3
1.0 - <1.5	1.0	12.3
1.5 - <2.0	0.8	39.3
2.0 - <5.0	0.0	0.0
$\geq 5.0$	0.0	0.0

389

Table 1. Percentages of Particles in Various Diameter Ranges by Number and Mass of Particles – Product A.

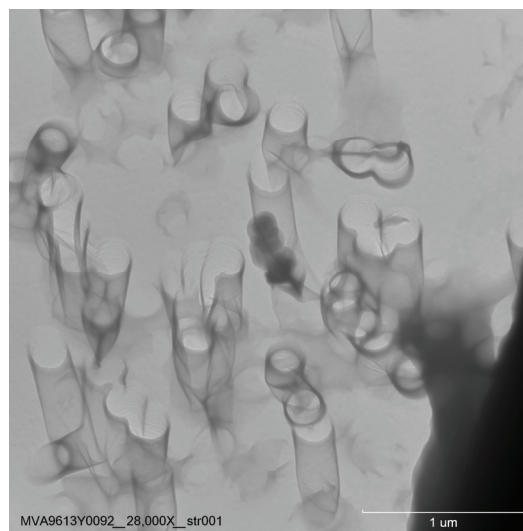


Figure 1. TEM image of TiO<sub>2</sub> aggregate in Product A.

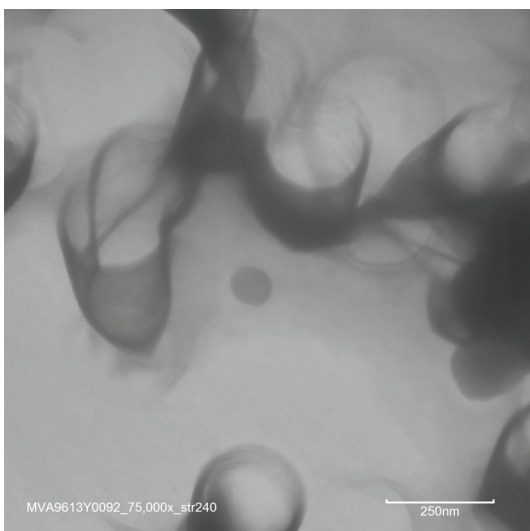


Figure 2. TEM image of TiO<sub>2</sub> primary particle in Product A.

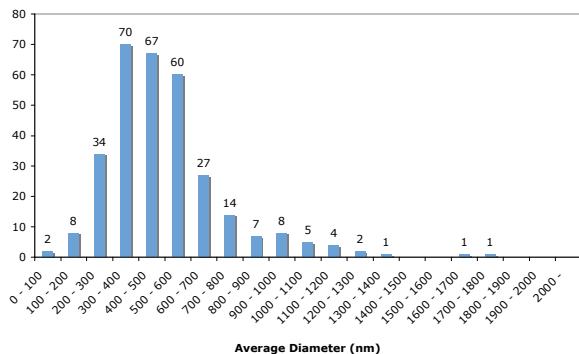


Figure 3. Particle size distribution of aggregates and primary particles in Product A.

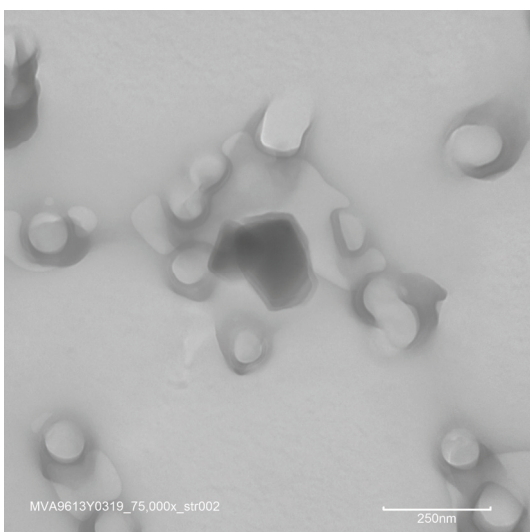


Figure 4. TEM image of TiO<sub>2</sub> aggregate observed on filter from airborne exposure study of Product A.

## Product B

Automated SEM-EDS analysis of Product B detected 485 Ti + O-rich aggregates or individual particles. Of these 485 particles, 8.5% (41 particles) were in the 50-100 nm size range and all were below 5.0  $\mu\text{m}$  in diameter (Table 2). A distribution of particles by estimated mass is also presented in Table 2.

TEM analysis of loose powder Product B revealed that the majority of TiO<sub>2</sub> present was in the form of aggregates (Figure 5). Several individual primary particles were also observed (Figure 6). Figure 7 presents a particle size distribution of TiO<sub>2</sub> aggregates and primary particles observed in Product B. The average particle size was  $269 \pm 148$  nm with 250 particles measured. The maximum particle size recorded was 1060 nm and the minimum particle size was 40 nm.

Product B		
Particle Size Range ( $\mu\text{m}$ )	Number %	Mass %
0.05 - <0.1	8.5	0.0
0.1 - <0.2	28.7	0.5
0.2 - <0.4	40.4	3.8
0.4 - <0.6	13.6	5.2
0.6 - <0.8	4.1	4.4
0.8 - <1.0	1.6	3.6
1.0 - <1.5	1.0	6.2
1.5 - <2.0	0.4	4.0
2.0 - <5.0	1.6	72.4
$\geq 5.0$	0.0	0.0

485

Table 2. Percentages of Particles in Various Diameter Ranges by Number of Particles – Product B.

## CONCLUSION

Automated SEM-EDS analysis of pressed powder Product A and loose powder Product B detected TiO<sub>2</sub> particles in the 50-100 nm size range. However, the technique does not allow for determination of whether these particles were aggregates or primary particles. Additionally, the instrument/method has a detection limit of 50 nm thus preventing determination of a minimum particle size if it is below this limit.

TEM analyses verified the presence of TiO<sub>2</sub> particles in both Product A and Product B that were below 100 nm in diameter. In both cases, primary particles were observed that fell in the  $\leq 100$  nm size range. In Product B, the minimum particle size observed was 40 nm, below the detection limit of the automated SEM-EDS method.

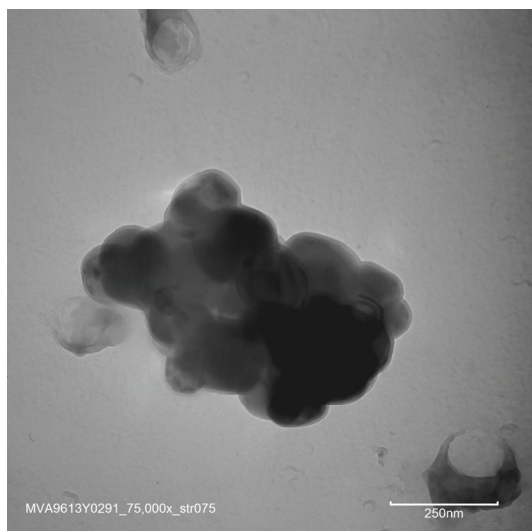


Figure 5. TEM image of TiO<sub>2</sub> aggregate in Product B.

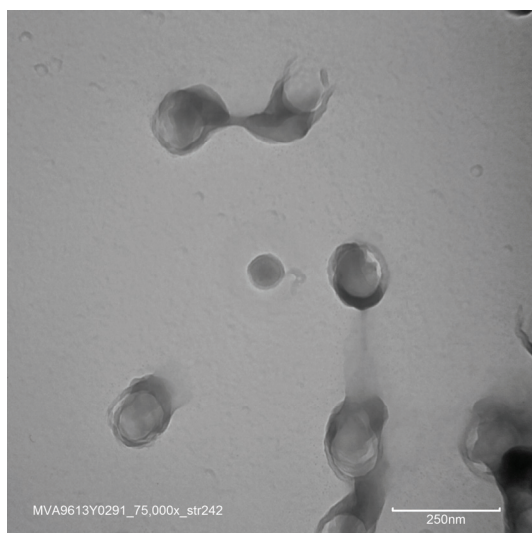


Figure 6. TEM image of TiO<sub>2</sub> primary particle in Product B.

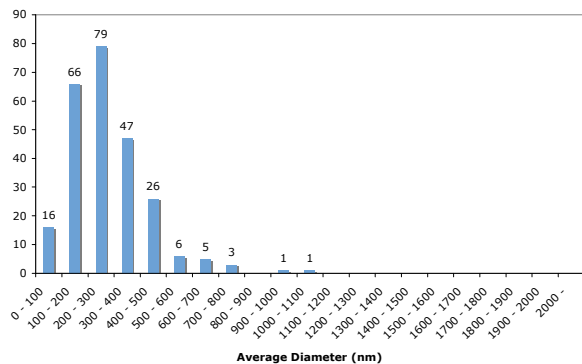


Figure 7. Particle size distribution of aggregates and primary particles in Product B.

Aggregates of TiO<sub>2</sub> were detected on the filter from the airborne exposure study. The presence of TiO<sub>2</sub> aggregates suggests that further studies are needed to assess potential airborne inhalation risk.

## ACKNOWLEDGEMENTS

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