

REGARDING

# PHOSPHATE, ALUMINA AND SILICA COATINGS ON COMMERCIAL TITANIA

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## **Surface Coatings on Nanoscale Test Materials are Non-Uniform**

Unless authors explicitly alert them, readers of toxicology papers are generally not aware of the coatings and residual process aids found on nanoscale TiO<sub>2</sub> test materials. Commercial manufacturers are similarly not aware of the extent to which dopants, processing aids and coatings influence toxicological test results. Certainly, information on these additives are not found in everyday product information sheets nor in product specifications, unless useful in industrial applications.

For titania, the immediate issues are: Al-species added to promote rutile formation, to reduce photoactivity and to aid in later dispersion steps; alumina and silica surface coatings to reduce surface free radical reactions; and phosphate to control particle sintering. Surprisingly, there is consistent information in the scientific literature that supports the following conclusions:

1. AlCl<sub>3</sub> and Al-salts in excess of doping requirements will appear as aluminum oxide surface species, without fully eliminating TiO<sub>2</sub> surface reactivity;
2. Coatings below 5% by weight, and possibly < 10%, should be viewed as non-uniform (present as islands or patches) and therefore leaving some titania surface sites accessible for chemical reactions;
3. Silica forms a more complete, uniform surface layer than does alumina;
4. Phosphate added to control particle size in precipitated TiO<sub>2</sub> milling and calcination affects catalysis; and
5. There are several simple laboratory tests methods for evaluating coating composition and uniformity: zeta potential titrations, XPS, FTIR, differential dissolution and photo-oxidation of organics, e.g., propan-2-ol.

## **Pyrogenic pigment-grade titania (chloride process)**

Professor Gayle E. Morris and co-workers examined the surface chemistry of commercial, pigment grade titania (rutile) manufactured by the chloride process (a.k.a. pyrogenic). In Morris 1999, the commercial pigment grade rutile particle is explicitly termed Al:TiO<sub>2</sub> to account for AlCl<sub>3</sub> added to the flame. Other samples, all from the same unidentified commercial source, were Al:TiO<sub>2</sub> that had also undergone solution-coating at nominal weights of: ~3% alumina; ~4.5% alumina + silica; and ~1% silica. The materials were characterized by zeta potential titrations for i.e.p. values; XPS for surface composition; and rheological yield values as a function of pH. The results were:

Sample	pH at i.e.p.	pH at yield	% of surface Ti
Uncoated AL:TiO <sub>2</sub>	7.9	7.8	60%

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2% Alumina Coated Al:TiO <sub>2</sub>	8.1	8	34%
4.5 % Alumina + Silica Coated Al:TiO <sub>2</sub>	6.6	6.3	23%
1% Silica Coated Al:TiO <sub>2</sub>	1.5	3	33%

The comparable i.e.p. values for uncoated and alumina-coated Al:TiO<sub>2</sub> confirm that excess AlCl<sub>3</sub> dopant appears as a surface aluminum oxide species on otherwise “uncoated” TiO<sub>2</sub>. Morris *et alia* caution that the % Ti values overestimate surface Ti-levels. An alternative estimate of heterogeneity interpolates between the i.e.p. of rutile (4.9 for an independently sourced rutile used by Morris, but 6.0 is recommended by Kosmulski) and alumina (9.2). For uncoated Al:TiO<sub>2</sub>, this would be 30% Ti using the 4.9 i.e.p. of Morris *et alia* and 40% Ti using the recommended value of 6.0.

The comparable i.e.p. values for uncoated and alumina coated Al:TiO<sub>2</sub> also imply that the externally applied hydrous alumina coating forms preferentially on the already existing surface aluminum oxide species generated by adding AlCl<sub>3</sub> to the flame. There was no net increase in alumina surface coverage and no decrease in accessible surface TiO<sub>2</sub>, as demonstrated by the relatively similar values of 34, 23, 33% TiO<sub>2</sub> for the solution-coated samples.

Morris *et alia*'s studies were continued in Taylor 2001 where increasing doping levels of up to 1.2% in the flame, led to surface enrichment of hydrous alumina reaching a 12%. Once again, Morris *et alia* caution that calculated concentrations from XPS include sub-surface contributions and, using the 4.9 value for i.e.p., they estimated that 20% of the surface had accessible TiO<sub>2</sub> atoms. Using the Kosmulski recommended i.e.p. of 6.0 leads to a higher value of 30% TiO<sub>2</sub>.

In both studies, the surface layers were described as “heterogeneous patches.”

### **Sulphate-Process Pigment Grade Titania**

In the sulphate process, a hydrous TiO<sub>2</sub>.nH<sub>2</sub>O is precipitated, washed and then calcined (along with process aids, dopants and coating precursors) to yield the final pigment particle that may also be solution-coated. The value of “n” is approximately 0.7 (Gesenhues 1997). Gesenhues 1994 utilized differential dissolution and potentiometric titrations to conclude that 20-30% of the solution-coated pigment particle exhibited accessible TiO<sub>2</sub>-sites. Potentiometric experiments led to uncovered TiO<sub>2</sub> estimates ranging from 60 - 30% for short solution contact times and 10-30% for longer solution contact times; electrophoretic experiments led to values of 20-40%.

His interpretation of coated-TiO<sub>2</sub> dissolving in H<sub>2</sub>SO<sub>4</sub> was that the coating exhibited a porosity within “coat islands.” Little lateral growth in the coating's surface coverage was noted beyond the first islands that formed during the initial period of high solution supersaturation.

In his 1997 study, Gesenhues evaluated increasing additions of hydrous alumina prior to calcining the hydrous TiO<sub>2</sub>.nH<sub>2</sub>O. He concluded that the surface density of aluminum oxide species was close to that of a fully substituted rutile structure (Al<sup>+3</sup> displacing Ti<sup>+4</sup>), but also noted clustering phenomena in the isotherm.

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As an employee of a major sulphate process producer, Gesenhues's articles have great credibility, but we can assume that he has been circumspect with proprietary information as with the cursory discussion of phosphate. Grzmil has generated a series of papers on additives for calcining commercially obtained hydrated titanium dioxide. Grzmil 2007 is particularly pertinent, pointing out that phosphate acts to retard both crystal growth (stabilizes surface area; prevent coarsening) and the anatase-to-rutile phase transformation. Potassium and aluminum enhance the activity of phosphate. Dekany (Korosi 2006 and 2007) utilized laboratory preparations to examine the influence of additives on milling hydrated TiO<sub>2</sub>, and noted similar stabilization effects including a mild increase in catalytic activity at low phosphate levels, but decreasing at higher levels. As sulphate process manufacturers supply both anatase-based and rutile-based products using the same process steps (installed equipment), we can expect that there are preferred, economical combinations of additive amounts, recycling of rutile seed crystals, and control of temperature and residence time specific to each product grade.

### Other Titania from Precipitation or Sol Gel Processes

Several commercial manufacturers hydrolyze TiCl<sub>4</sub>, titanium propoxide or other Ti-precursors to form sol gel or hydrous TiO<sub>2</sub>. From the literature articles on TiO<sub>2</sub> precipitation, the presence of sulphate ions leads to anatase, while the other source materials tend to form rutile. Ishihara and Croda are believed to use TiCl<sub>4</sub> as a precursor, and their use of additives is likely. Tooley of Croda (Uniquema) has published a number of articles with Egerton.

Egerton and Tooley (2002) report on surface characterization of coated and uncoated TiO<sub>2</sub> particles supplied by Uniqema, known to utilize the hydrolysis of TiCl<sub>4</sub> followed by Iler's "dense silica" coating procedures. FTIR spectroscopy and photo-oxidation of propan-2-ol were used for surface characterization. Essential to the analysis was the IR absorption by N<sub>2</sub> molecules "adsorbed at coordinatively unsaturated surface sites," where the N<sub>2</sub> stretching frequency is normally IR-inactive. Egerton and Tooley found that sample calcination at 350 °C ensured OH-group removal from all surfaces (coated and uncoated), which allowed a strong signal from active Ti sites that had been blocked by OH-groups. For both alumina and silica coatings, the results indicated that it would require a 30% surface coating to eliminate the N<sub>2</sub> adsorption. The photo-oxidation studies with propan-2-ol yielded mirror results, but with negligible reactivity occurring around 8% coating weight and above 15% for alumina.

For both IR absorption and propan-2-ol photo-oxidation, silica coatings exhibited sharply reduced surface reactivity compared to alumina: 50% reduction in acetone production at 0.5% for silica but at 7.5% for alumina. The silica results were confirmed in Egerton and Mattinson (2007) using propan-2-ol and DPPH photo-oxidation studies. The authors noted an initial increase in reaction rates at silica loadings below 0.5-to-1.0% and a decrease thereafter. Refined estimates for zero Ti-surface reactivity for photo-oxidation and photo-graying were in the range of 12-16% for silica coatings.

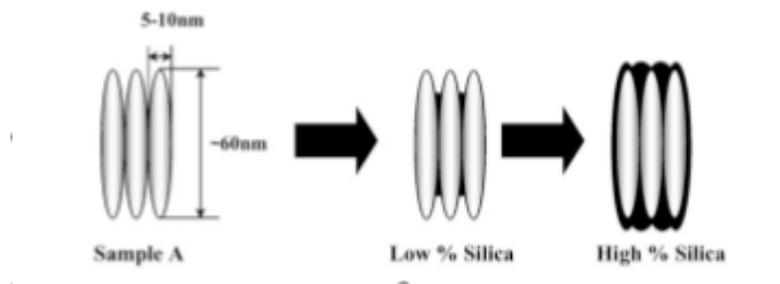
Overall, Egerton and co-workers proposed that the lenticular-shaped TiO<sub>2</sub> from hydrolysis of TiCl<sub>4</sub> did not have a uniform distribution of active Ti-sites, but rather a higher concentration near particle-to-particle contact points. At low silica coating levels, when chemisorbed silica clusters are isolated, there was in-

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creased reactivity. At higher coating levels, silica-to-silica interactions in the coating resulted in decreased reactivity. Complete elimination of Ti-activity took place when the total aggregate was encapsulated.



Egerton and Tooley did not offer an extensive discussion on the alumina coated titania, commenting that, “low levels of alumina, unlike silica, neither preferentially block sites for adsorption of IR-active nitrogen nor cap the pores.”

The catalytic reactivity of TiO<sub>2</sub> surfaces, the anatase-to-rutile transformation and the explanations behind using process additives for the milling and calcination steps appear to be connected. Criado 1989 demonstrated that adding phosphate to P25 (manufactured without additives) retarded the milling-induced phase transformation. They posit that phosphate ions chemisorb at surface defects to form bidentate ligands that block formation of a new phase. This explanation relies on evidence that the phase transition is initiated at the surface and propagates inwards. Sulphate is implied to act similarly, but is removed in washing steps prior to calcination leading to phosphate addition.

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Bidentate ligands retard the transformation and monodentate ones, such as chloride, do not. Dekany's work points to a combination of effects where the presence of phosphate retards the transition from amorphous to anatase as well as exhibiting effects on catalytic behavior. Combining these reports, we can assume that catalysis often occurs at an active Ti sites representing defects in the TiO<sub>2</sub>.nH<sub>2</sub>O surface. The energy gap for phase transformation is smaller at these sites, such that additives intended to control sintering and crystal size also influence catalytic activity. The inverse is true as well in the TiO<sub>2</sub> sol gel literature, where the presence of active sites aligns with anatase as the substrate representing an inhibited anatase-to-rutile transformation and not the underlying anatase crystal structure.

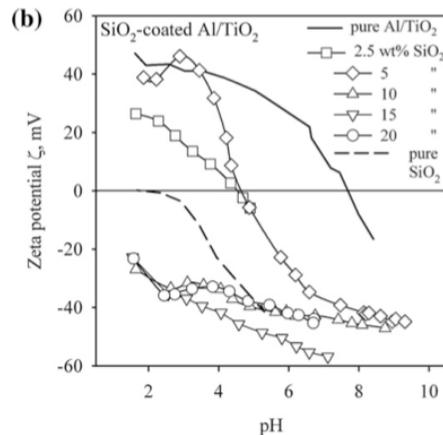
### **Other Pyrogenic Prepared Titania:**

Professor Pratsinis and colleagues have addressed the quality of silica surface coatings on TiO<sub>2</sub> (Teleki 2008). Laboratory prepared particles doped with 4% alumina were used with coatings, either applied by co-fuming (co-oxidizing) a silica source or by post-treating with an organosilane that was then oxidized. The latter post-particle-formation treatment consistently led to a more adherent silica film. In general, uniform coatings were confirmed by TEM, electrophoresis and chemisorption experiments when the silica coating exceeded 10%. Below 10% for co-oxidized silica coatings and below 5% for post-treatment coating, the data demonstrated the presence or influence of the underlying titania particle surface.

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These authors did not mention an aluminum oxide surface layer (they utilized 4% Al in the flame and obtained a very similar i.e.p. to Morris 1999); they did observe “patches” of SiO<sub>2</sub>; but they did not offer specific commentary on non-homogeneity or heterogenous coatings at low silica levels.

From Teleki 2008:

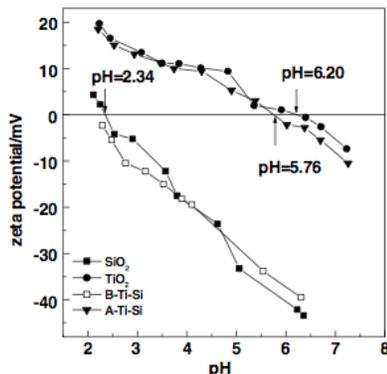


1) Break occurs between 5% and 10% SiO<sub>2</sub>

2) i.e.p. for Al/TiO<sub>2</sub> core particle is pH 7.7; Morris reported 7.8

Li and colleagues (Li 2005) utilize TEOS and ammonium hydroxide solutions to deposit silica coatings on AEROXIDE® P25. They observe that samples with 4.67% silica coating differ from those with 9.33% or higher levels. The differences were noted in TEM images, zeta potential measurements and photocatalytic activity. They comment on coating porosity being present for photocatalytic activity up to 25% silica.

From Li 2005:



1) A-Ti-Si is 4.67% SiO<sub>2</sub>

2) B-Ti-Si is 9.3% SiO<sub>2</sub>

3) i.e.p. for TiO<sub>2</sub> close to Kusmulski recommendation

Djerdjev *et alia* placed dense silica coatings on Al-doped rutile and also on anatase. They termed coating levels below 1% as “incomplete,” based on zeta potential measurements. These studies were done on acid washed commercial samples

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and point, in turn, to how processing aids and dopants may be the source of incomplete coatings found with commercial materials.

## **Conclusions:**

There is a broad acceptance that commercial silica and alumina surface coatings below 5% by weight  $\text{TiO}_2$ , and perhaps  $< 10\%$  weight, are non-uniform. Descriptions range from coating islands, coating porosity or unshielded titania surface reactions, but all involve chemical reactivity of Ti-surface species despite the nominal presence of a coating.

Investigators working with alumina doping are more likely to argue that  $\text{Al}^{+3}$  is uniformly distributed on the titania particle, but note that the reactivity of this  $\text{Al}^{+3}$  species differs from that on an  $\text{Al}_2\text{O}_3$  surface. This argument reflects underlying questions of how adsorbates, layers and coatings should be differentiated. The fact that industrial manufacturers do both, dope and apply external coatings, to stifle photocatalytic reactions on  $\text{TiO}_2$  points to the presence of a dynamic surface capable of rearrangement as one progresses from the wet (as precipitated) to the dry (as manufactured) and then returning to the wet (as dispersed) state.

From reviewing the literature, a number of commercial rutile and anatase sources utilize dopants, process aids and coatings. Adventitious carbon is also noted. No dopants, chemical processing aids or coatings are used with AEROXIDE® P25.

Industrial customers utilize specific processing steps when incorporating commercial  $\text{TiO}_2$  into the final end product. These steps presumably anticipate or even adjust for any effects of residual process additives. Academic colleagues utilizing “as is” material may observe artifacts, such as differing results over time or with “aged” samples, and should consider this during test study design.

## **Recommendations:**

- (1) Though the various coatings exhibit process-specific characteristics, it is reasonable to assume that coatings on titania below 10% should be evaluated for uniformity using zeta potential titrations, XPS, FTIR, differential or sequential dissolution and photo-oxidation techniques.
- (2) A standardized nomenclature or symbol system is desirable so that experimentalists and commercial supplier can explicitly communicate the presence of dopants, processing aids or coatings on nanoscale test samples.
- (3) Terminology refinements are needed to distinguish among coatings, layers, adsorbates, dopants and processing aids.

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