UNIVERSITY OF ILLINOIS

May 13, 1987

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED: The Synthesis of Monodisperse TiO₂ Particles by the Hydrolysis of Tetraethylorthotitanate in Ethanol.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF: Bachelor of Science / Chemical Engineering

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The Synthesis of Monodisperse TiO₂ Particles
by the
Hydrolysis of Tetraethylorthotitanate in Ethanol

By
Larry A. Winkless

Thesis
for the
Degree of Bachelor of Science
in
Chemical Engineering

College of Liberal Arts and Sciences
University of Illinois
Urbana, Illinois
1987
# Table of Contents

**Introduction**

**Survey of Literature**

**Experimental Procedure and Apparatus**

  - Concentration Range Experiments
  - Surfactant Experiments
  - Particle Growth Over Time and Reproducibility Tests
  - Induction Time Experiments
  - Solution pH Experiments

**Results and Discussion**

  - Concentration Range
  - Surfactants
  - Particle Growth Over Time
  - Reproducibility
  - Induction Time w/ and w/o HPC
  - Solution pH - TPT

**Conclusions**

**Recommendations**

**Acknowledgements**

**References**

**Appendix A - Solution Makeup Calculations**

**Appendix B - Surfactant Calculations**

**appendix C - Magnification Calculations**
Figure Table

1a - Jean & Ring Induction Time Experiments 3.
1b - Growth Rate Results for Both the PCS and TEM Methods 5.
1c & 1d - Particles Synthesized With and Without HPC by Jean & Ring 5.
2 & 3 - TEM Photographs of Samples from Concentration Range Experiments 13 & 14.
4 - Examples of generic Surfactants 16.
5 - Surfactant Performance 18.
8 - 16 - TEM Photographs of Particle Growth Over Time 22-31.
19 - Particle Size Distribution 32.
20 - Reproducibility Statistics 33.
21 & 22 - Absorbance vs Time for Particles Synthesized With and Without HPC 35 & 36.
24 - 26 - TEM Photographs of TiO₂ Particles Synthesized While Varying Reactant Water Acidity 40-42.
27 - Absorbance vs Time for Particles Synthesized While Varying Reactant Water Acidity 45.
Introduction

New generation high performance ceramic materials with enhanced electrical, optical, and structural properties can result through ultrastructural processing. Ultrastructural processing involves diminishing process related defects including powder raw material geometry and chemistry. Control stems back to the manipulation and control of surfaces and interfaces during the earliest stages of particle formation.

This thesis investigates the synthesis of monodisperse titanium dioxide particles by the hydrolysis of tetraethylorthotitanate in ethanol solution in order to verify existing results published by J. H. Jean and T. A. Ring (1)(2)(3) and to explore new areas where appropriate.

Experiments were performed using the hydrolysis of tetraethylorthotitanate in ethanol solution. The reaction proceeds by a stepwise hydrolysis.

\[
\text{Ti(OC}_2\text{H}_5)_4 + 4\text{H}_2\text{O} + 4\text{C}_2\text{H}_5\text{OH} \rightarrow \text{Ti(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH}
\]

To produce Ti(OH)_4. This undergoes condensation, eliminating water to give

\[
\text{Ti(OH)}_4 + (2-X)\text{H}_2\text{O} \rightarrow \text{TiO}_2\text{XH}_2\text{O(solid)} + (2-X)\text{H}_2\text{O}
\]
Survey of Literature

The most complete papers I have to compare my results to are three by J. H. Jean and T. A. Ring (1)(2)(3). Their papers discuss nucleation and growth in the generation of monodisperse titanium dioxide (TiO$_2$) particles by the hydrolysis of tetraethylorthotitanate [Ti(OC$_2$H$_5$)$_4$] in ethanol solution. Relevant experimental results by Jean & Ring include determination of induction time (the time in which the turbidity of the reacting solution increases rapidly), plotting of particle growth rates obtained from photon correlation spectroscopy (PCS), and noted effects of adding hydroxy-propyl cellulose (HPC) to the reactant solution. Hydroxy-propyl cellulose is a sterically hindering surfactant used to prevent flocculation in particle synthesis. In fact it wasn't until late in Jean & Ring's first paper, after all growth and induction data had been presented, that it becomes apparent that monodisperse TiO$_2$ particles hadn't been synthesized without the use of HPC.

Plots and correlations in the subsequent section are to present Jean & Ring's results and are taken from Jean & Ring's paper entitled "Nucleation and Growth of Monodisperse TiO$_2$ Powders from Alcohol Solution" (1).

The first thing Jean & Ring looked at relevant to this topic was induction time. The induction time for the reaction was measured at various reactant concentrations by using a Spectronic 21 at a wavelength of 690 nm. Reactants were dissolved in ethanol
first, then mixed by injecting into a tee mixing section and the optical cell of the Spectronic 21. A strip chart recorder monitored the optical density as a function of time. The time when the optical density increased abruptly was referred to as the induction time. Their curves for induction time experiments are presented below in Figure 1a.

Figure 1a. Turbidity vs reaction time, 0.125 M. TEOT
This data was fit to the equation:

\[ I = 0.33[\text{Ti(OC}_2\text{H}_5)_4]^{-2}[\text{H}_2\text{O}]^{-4} \]

thus showing that induction time increases with reactant water or titanate concentration with water having a 100 fold more effect.

Jean & Ring's second relevant topic was their study of growth rate using a Malvern photon correlation spectrometer (PCS) operating at an angle of 90° and a wavelength of 638 nm. Solutions were prepared in the same way and injected into the PCS unit. Size measurements were made every 30 seconds by sampling every 100 us for \(10^7\) us.

The growth data was confirmed by transmission electron microscopy (TEM) using a Philips Model 300C instrument. A sample aliquot of solution was diluted fourfold with propanol to stop growth, put into a tube containing a copper grid coated with a carbon film and centrifuged at 3000 RPM for 2 minutes. The grid was removed and dried rapidly on filter paper. It was shown that the time left in the diluted solution had no effect on the particle size for up to 15 minutes.

Figure 1b is the growth rate results for both the PCS and the TEM methods. The results using the TEM method are consistently lower than using the PCS method. Reasons cited for the differences in methods stemmed from the possibility of particle shrinkage using the dry TEM method rather than the in situ PCS method.
Figure 1b. Growth rate determined by the PCS and the TEM methods.

Figure 1c and 1d. Particles synthesized with and without HPC respectively.
More importantly though, the optical micrograph showed that the particles were not even monodispersed. Figures 1c and 1d on the previous page are optical micrographs of the product particles (by Jean & Ring) with and without HPC.

There is a marked difference. The particles synthesized without HPC cannot be considered monodispersed, and it is hard to determine how to weight results previous to this finding. Since this mention of product difference when synthesized with or without HPC at the end of their first paper, there is never a mention of TiO$_2$ particle synthesis without the use of HPC.

Subsequent work by Jean & Ring concentrated on polymer absorption and its effect on particle packing and fracture surfaces. This is beyond the scope of this project. This project primarily covers the types of experiments covered in this survey, with more focus on induction times and particle sizes with the use of HPC.

The papers by Jean & Ring were most closely followed when planning experimentation, but work by others is cited throughout when it pertains.
Experimental Procedure and Apparatus

The methods of Jean & Ring were followed except when their methods were not applicable. (eg. reactants may have been pipetted into an Erlenmeyer flask and shook rather than mixing by injection in an optical cell.) Reagent grade TEOT was purchased from Thomas Scientific and was kept refrigerated at 4°C. The TEOT was not distilled at first. The TEOT was found to be very sensitive to stray or atmospheric water. An open beaker of TEOT would form a white film on the edges. For this reason the TEOT was only pipetted from the reagent bottle under a flow of nitrogen. Even so, a white crust eventually formed on the ridges of the cap. Eventually it was found that the only way to extract the TEOT without contamination was by capping the reagent bottle with a rubber septum and extracting with a syringe.

Concentration Range Experiments

The first experiments looked at the range of reactant concentrations and their effect on achieving monodisperse particles. The range of water concentrations explored were from 0.125 M. to 1.0 M. The range of TEOT concentrations explored was from 0.025 M. to 0.2 M. These ranges are wider on the low side than those explored by Jean & Ring because severely flocculated particles were formed at higher concentrations.

Glassware was first washed with a 2% by volume hydrofluoric acid solution to remove particle residue. The glassware was then
rinsed with deionized water, rinsed with ethanol to remove water and allowed to dry overnight. Pipettes and reaction vessels were rinsed with ethanol immediately before use.

Calculated amounts of 18 megaohm water and TEOT were first added to solvent ethanol in separate beakers. The two were then combined in a 150 ml. Erlenmeyer flask equipped with a magnetic stir bar, capped, quickly shaken, and stirred at a moderate rate (just before a vortex was reached) for the length of the experiment. Sample calculations for the concentration range experiments solution makeup are in Appendix A.

Samples were taken by dipping a carbon coated copper grid in the solution and drying on filter paper. Transmission electron microscope (TEM) photographs were taken at 8000X.

**Surfactant Experiments**

Both electrostatically and sterically hindering surfactants were tried in the synthesis of titanium dioxide particles. The surfactants that were studied are listed below.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydroxy-propyl cellulose</td>
<td>steric</td>
</tr>
<tr>
<td>Dapral</td>
<td>steric</td>
</tr>
<tr>
<td>octyl phenoxl polyethoxyethanol</td>
<td>steric</td>
</tr>
<tr>
<td>sodium dodecyl sulfate</td>
<td>electrostatic</td>
</tr>
</tbody>
</table>
The powdered surfactants were dissolved in yet another separate volume of solvent ethanol and combined with the other portions containing the reactants water and TEOT simultaneously. Sample calculations for the surfactant experiments solution makeup are in Appendix B.

Samples were again taken using the carbon coated copper grids and analyzing under the electron microscope. The interest in surfactants was to prevent flocculation and promote the growth of monodisperse particles, rather than to examine their effect on growth mechanisms. Therefore, samples for the surfactant study were taken only after completion of the reaction, 24 hours assumed to be sufficient. The evaluation of the surfactants performance in preventing flocculation was based on magnified pictures of the particles from the grids.

Particle Growth Over Time and Reproducibility Tests

Relatively monodisperse particles were achieved at reactant concentrations of \([\text{TEOT}]=0.075 \text{ M.}, [\text{H}_2\text{O}]=0.3 \text{ M.}, [\text{HPC}]=1.17\times10^{-3}\) g/cc. Particle growth was monitored by taking sample grids every 15 minutes initially and every hour after growth had appeared to stop. Besides looking at growth versus time experiments, four sample grids were taken after 24 hours and compared to test the reproducibility of data taken from the grids and magnified pictures. The particle's mean size and standard deviation were measured for sample sizes of between 70 and 370 particles.
Induction Time Experiments

Induction time is the time in which a marked difference in turbidity is noticed due to the formation of particles on the order of the wavelength of visible light. Absorbance was measured as a function of time at 690 nm. on a Bausch & Lomb spectronic 1001 Spectrophotometer. Depending on the speed of the reaction, readings were taken by computer every 5 or 10 seconds and recorded on floppy disk.

Reactant solutions studied most carefully were [TEOT]=0.125 M., [H₂O]=0.5 M. with and without HPC and [TEOT]=0.125 M., [H₂O]=0.4 M. with the water used ranging from 1.0 M. HCl to pure. Sample grids were also taken and pictures were analyzed.

Changes in solution pH

Induction time experiments similar to those above were performed with tetraisopropyltitanate (TPT) substituted for TEOT and dilute acid or base ranging from 0.1 M. NaOH to 1.0 M. HCl substituted for 18 megaohm water. Induction time was plotted while varying acid concentration and sample grids were taken to compare resultant particles.
Results and Discussion

Concentration Range

Preliminary studies on the synthesis of monosized TiO$_2$ powders involved varying the concentrations of reactant water and TEOT. Tests were conducted as outlined in the procedure. The range of water concentrations explored was from 0.125 M. to 1.0 M. The range of TEOT concentrations explored was from 0.025 M. to 0.2 M.

At the lowest end of the concentration range, no visible reaction resulted after 5 hours. This means that if particles were formed, they were smaller than the wavelength of visible light, because they did not scatter it.

At all other concentrations ([H$_2$O]=0.225 and higher, [TEOT]=0.05 and higher) particles were synthesized, shown by a turbid solution. It was noticed (by visible inspection) that induction times do decrease with increasing concentrations of water and TEOT (as reported by Jean & Ring) with water having a more pronounced effect. It was also noticed that induction times at all concentrations explored were considerably shorter than those reported by Jean & Ring. It is estimated that the induction times were shorter by a factor of 10 to 15. This will be discussed in more detail in the section entitled "induction times".
At all concentrations, the pictures of the samples taken from the micrographs show that the particles are flocculated. At the higher end of the concentration range, flocculation is so severe that sediment can be seen on the walls and floor of the flask even after shaking.

The best particles in this concentration range were synthesized at \([\text{H}_2\text{O}]=0.225\ \text{M}\) and \([\text{TEOT}]=0.05\ \text{M}\). Lower concentrations showed no visible reaction. Only at these very low concentrations could induction time be stretched out to 5 minutes, or of the order that Jean & Ring were working with. But these concentrations are much lower than those explored by Jean & Ring. With the reaction slowed this much, the particles were still flocculated. Figures 2 and 3 on the next pages are sample micrographs of this best case and another sample of higher concentration reactants.

Before any micrographs had been analyzed, research had been directed towards examining temperature effects, stir rate effects, and atmospheric contamination effects of the monodisperse particle system. But monodisperse particles were never synthesized at any concentrations, and these effects on aggregated particles are not measurable. Research was then concentrated on just producing monodisperse particles, and thus led to the study of surfactants.
Figure 2. TiO₂ particles synthesized at 0.05 M TEOA, 0.225 M H₂O, no HPC
Surfactants

Electrostatically or sterically hindering surfactants can be dispersed in the ethanol solution to be incorporated in the TiO₂ particles. The purpose of the surfactant is to provide a sufficiently repulsive force to counter Brownian motion or sedimentation forces thus preventing agglomeration.

The theory describing the interactions between particles is called the DLVO theory and is described in "Processing Monosized Powders" by Barringer et al (5). Briefly, the general equation describing the particle interactions consists of attractive and repulsive terms.

\[ V_T = V_A(\text{van der Waals}) + V_R(\text{electrostatic}) + V_R(\text{others}) \]

The van der Waals attraction between two spherical particles of radius \(a\) and center to center distance \(r\) is given by

\[ V_A = -(A/6)[(2a^2/(r^2-4a^2)) + (2a^2/r^2) + \ln((r^2+4a^2)/r^2)] \]

where \(A\), the Hamacker constant, depends on the properties of the particles and the dispersion medium (\(A\) about \(10^{-12} - 10^{-13}\) ergs). The electrostatic repulsion arises from the interaction of the electrical double layers surrounding the dispersed particles and depends on the medium dielectric constant, the particle separation, and the Stern (diffuse layer) potential.
The rate of coagulation or flocculation of a dispersion depends on the sign and the magnitude of the interaction energies. Flocculation is retarded by the presence of repulsive interactions, as the maximum repulsive energy acts as an activation energy for the process. Generic examples of an electrostatic and steric surfactant are given below in Figure 4.

**Figure 4.** Generic examples of A.) a sterically hindering surfactant and B.) an electrostatically hindering surfactant
Several surfactants, including HPC (MW=60,000), have been used in synthesizing titanium dioxide by hydrolysis in ethanol. The surfactants are listed in Figure 5 and are classified as either sterically or electrostatically hindering. The surfactants are ranked by their performance for reducing flocculation and maintaining monodispersity. Their effectiveness was measured qualitatively from solution appearance and pictures from the electronmicroscope.

Sterically hindering surfactants performed better than electrostatic surfactants. In Jean & Ring's paper "Effect of In Situ Polymer Adsorption on the Synthesis of Monodisperse Particles" (2), they state that for the electrostatic surfactants to be effective, the pH of the reacting solution must be different from that of the isoelectric point of the precipitated powders. The ineffectiveness of electrostatic surfactants may be because solution pH range was not explored.

Based on the criterion above, particles synthesized with HPC were the best. Figure 6 and 7 are a comparison of particles synthesized with and without HPC. The most noticeable difference is the decreased amount of large flocculated particles. Also notice that particles synthesized with HPC are less defined and have a rougher contour. This is due to the hairlike polymeric fibers.

Based on these results, remaining induction time, growth rate and reproducibility experiments were conducted with 1.14x10^-3 g/cc HPC present in the solvent ethanol.
Figure 5

Surfactants Used in TiO₂ Synthesis

Surfactant

1.) hydroxy-propyl cellulose (s)
2.) Dapral (s)
3.) octyl phenoxy polyethoxystanol (s)
4.) sodium dodecyl sulfate (e)

\[ s = \text{sterically hindering surfactant} \]
\[ e = \text{electrostatically hindering surfactant} \]
Figure 7. TiC particles synthesized without HIC.
Particle Growth over Time

TiO\textsubscript{2} particles were synthesized with [TEOT]=0.075 M., [H\textsubscript{2}O]=0.3 M., and [HPC]=1.14\times10^{-3} g/cc and monitored by TEM photographs over time. Sample grids were taken every 15 minutes initially and every hour later. The last grid was taken at 24 hours. Figures 8 through 18 are photographs of these samples. Values of the mean and standard deviation particle size were calculated for samples ranging from 70 to 370 particles. Figure 19 is a table of these values. As was expected, the particles reached their maximum size within about 1 hour. The average particle size after 24 hours was determined to be 0.559 \textmu m from a sample size of 627 particles. After 1 hour and 1.5 hours the average particle sizes were 0.507 and 0.539 \textmu m respectively. Considering the standard deviation of the samples is about 0.1 \textmu m, no significant growth can be attributed to the time after 1 hour.

There is no reason to believe that further nucleation occurs after the maximum size is reached. White specks on the order of 0.007 \textmu m are noticed in the background of the particles, but these are not nucleated particles. These specks are only present in photographs of particles synthesized with HPC, and by comparing photographs with and without HPC, the specks must be due to the HPC.

The standard deviation increases as the particles grow. This is due to the fact that particles continue to nucleate and
Figure 8. TiO$_2$ particles synthesized at 0.075 M. TEOT, 0.3 M. H$_2$O, and 10$^{-3}$ M. HCl. 30 min at room temperature.
Figure 9. TiO$_2$ particles synthesized at 0.075 M. TEOT, 0.3 M. H$_2$O,
1.1 × 10$^{-3}$ M. HCl, 30 minutes.
Figure 10. TiO₂ particles synthesised at 0.075 M TEDT, 0.3 M H₂O, 1.14x10⁻³ g/cc HPC, t=45 minutes.
Figure 11. TiO$_2$ particles synthesized at 0.075 M TETT, 0.3 M H$_2$O, 1.14x10$^{-3}$ g/cc HPG, t=1 hour.
Figure 12. TiO$_2$ particles synthesised at 0.075 M. TEOT, 0.3 M. H$_2$O, $1.14 \times 10^{-3}$ g/cc HPO, t=1.5 hour.
Figure 13. TiO$_2$ particles synthesised at 0.075 M. TBOT, 0.3 M. H$_2$O, 1.14x10^{-3}$ g/cc HPC, t=3 hours.
Figure 14. TiO$_2$ particles synthesized at 0.075 M TEO, 0.3 M H$_2$O,
$1.14 \times 10^{-3}$ c/cc HFG, t=5 hours.
Figure 15. TiO$_2$ particles synthesized at 0.075 M TEOT, 0.3 M H$_2$O, 1.14x10$^{-3}$ g/cc HPC, t=24 hours.
Figure 16. TiO$_2$ particles synthesized at 0.075 M. TaOT, 0.3 M. H$_2$O, 1.14x10$^{-3}$ g/cc HPG, t=24 hours.
Figure 17. TiO₂ particles synthesized at 0.675 L, 3.0 V, 0.3 L N₂,
1.1×10⁻³ g/cc imp., t=24 hours.
Figure 19

Particle Growth - Mean and Standard Deviation Over Time

<table>
<thead>
<tr>
<th>Time</th>
<th>Mean (μm)</th>
<th>Standard Deviation</th>
<th>Sample Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min.</td>
<td>0.395</td>
<td>0.062</td>
<td>67</td>
</tr>
<tr>
<td>30 min.</td>
<td>0.414</td>
<td>0.073</td>
<td>122</td>
</tr>
<tr>
<td>45 min.</td>
<td>0.418</td>
<td>0.070</td>
<td>337</td>
</tr>
<tr>
<td>1 hour</td>
<td>0.507</td>
<td>0.075</td>
<td>103</td>
</tr>
<tr>
<td>1.5 hour</td>
<td>0.536</td>
<td>0.114</td>
<td>125</td>
</tr>
<tr>
<td>3 hour</td>
<td>0.533</td>
<td>0.110</td>
<td>270</td>
</tr>
<tr>
<td>5 hour</td>
<td>0.532</td>
<td>0.101</td>
<td>374</td>
</tr>
<tr>
<td>24 hour</td>
<td>0.559</td>
<td>0.093</td>
<td>627</td>
</tr>
</tbody>
</table>
grow in the early phases of the reaction, thus spreading the size range of the particles as a whole. The ratio of standard deviation to mean remains at a constant 17% for the entire reaction because the mean particle size also continues to increase as the reaction proceeds. A ratio of 17% indicates that the particles are not too monodisperse, and by examining the pictures one can see that there are disproportionately large and small particles. The particles are also not as spherical as desired, but this can be changed later with the addition of acid.

Reproducibility Tests

To confirm that the sizing of particles from 8x10 photographs is reliable and reproducible, 3 duplicate samples were taken of the growth vs time experiments after the assumed 24 hour completion time. Values for the mean and standard deviation particle size are listed below in Figure 20. The particle sizes were fairly reproducible and within the $z=0.05$ level of significance given in Miller & Freund's "Probability and Statistics - Inferences Concerning Means"(7).

**Figure 20**

Reaction Completion - Mean and Standard Deviation

<table>
<thead>
<tr>
<th>Time</th>
<th>Mean (um)</th>
<th>Standard Deviation</th>
<th>Sample Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 hour</td>
<td>0.867</td>
<td>0.009</td>
<td>236</td>
</tr>
<tr>
<td>24 hour</td>
<td>0.836</td>
<td>0.102</td>
<td>189</td>
</tr>
<tr>
<td>24 hour</td>
<td>0.870</td>
<td>0.088</td>
<td>202</td>
</tr>
</tbody>
</table>
Induction time is the time in which a marked difference in turbidity is noticed due to the formation of particles on the order of visible light. The induction time was measured for the reactant solutions consisting of \([\text{TEOT}]=0.125 \text{ M.}, [\text{H}_2\text{O}]=0.5 \text{ M.}\), with or without HPC. Experiments were carried out as described in the procedure.

Figures 21 and 22 are plots of absorbance vs time for the reactant solutions with and without HPC. Averages of the multiple trials show the induction time without HPC to be about 10 seconds and with HPC to be about 20 seconds. Data was fairly reproducible though differed from the published findings of Jean & Ring. At these concentrations, Jean & Ring report an induction time (without HPC) of 500 seconds.

The best explanation for the differences in induction time is that the reactant TEOT may be contaminated and thus already contain nucleated particle sites. The addition of reactant water pushes the reaction to be visibly noticeable. It has been shown that TEOT is sensitive to atmospheric water by forming a white powder when exposed to air for an extended period.

The contaminated TEOT was distilled at 27 in Hg and 250°C, and filtered through a 0.50 um cellulose nitrate membrane filter. The filtered reactant still showed no significant adjustment in induction times, perhaps because of a poor vacuum pump, or
Figure 21. Absorbance vs Time 0.125 M. TEGT, 0.5 M. H₂O in EtOH with HPC
Multiple Trials.
Figure 22. Absorbance vs Time 0.125 M. TBOT, 0.5 M. H₂O, in EtOH without HFC
Multiple Trials.
Figure 22. Absorbance vs Time 0.125 M TBTOT, 0.5 M H₂O, in EtOH without HPC
Multiple Trials.
perhaps because of improper handling when filtering. Because of
time constraints, it was decided to proceed with a new reactant,
tetraisopropyltitanate (TPT), rather than pursue TEOT further by
ordering more or distilling again. The TPT was stored in the
refrigerator at 4°C. and capped with a septum. TPT was only
removed with a syringe, thus keeping it from being exposed to the
atmosphere.
As mentioned before, to prevent flocculation, the TiO$_2$ particles require modification of their interparticle forces by controlling the surface chemistry such that a small repulsive interaction is achieved electrostatically or sterically.

E. Barringer, N. Jubb, B. Fegley, R. L. Pober, and H. K. Bowen (5) says that the electrostatic repulsions arising from the interaction of the electrical double layers surrounding the dispersed particles has the general form

$$V_R \propto \varepsilon_0 \Psi_d \exp(-KH)$$

with

$$1/\kappa = \left[ \frac{e^2 k_B T}{\varepsilon_0^2 k F} \right]^{1/2}$$

where $\varepsilon$ is the medium dielectric constant, $H$ the particle separation, $1/\kappa$ the Debye-Huckel length and $F$ is Faraday's constant.

The two solvent parameters we are interested in are the Stern (diffuse layer) potential, $\Psi_d$, and electrolyte concentration ($c_1$ through $K$). The term for Debye-Huckel length shows that to prevent particle agglomeration, the electrolyte concentration should be low.
is often approximated by the Zeta potential, which is a strong function of pH and electrolyte concentration. Figure 23 below is a plot of Zeta potential vs pH for an aqueous dispersion of TiO₂ in KCl.

![Zeta potential plot](image)

Figure 23. Zeta potential of the pure TiO₂ as a function of pH in aqueous KCl solutions (T=25°C.)

The isoelectric point (IEP) is defined as the pH at which the net charge is zero in the solid/liquid interface region. From the plot above, the IEP for the TiO₂ system is 5.5. To prevent particle agglomeration, the solution pH should be several pH units above or below the IEP.

Particles were synthesized at [TEOT]=0.125 M., [H₂O]=0.5 M. with 1.14x10⁻³ g/cc HPC while varying the acidity of the reactant water. Aqueous HCl from 0.0 to 1.0 M. was tried. Aqueous base was also tried, but with no success in synthesizing monodisperse particles. Figures 24 through 26 are photographs of the
Figure 24. $\text{TiO}_2$ particles synthesized at 0.125 M. TBOT, 0.5 M. $\text{H}_2\text{O}$, $1.14 \times 10^{-3}$ g/cc HPC, reactant water is pure.
Figure 25. TiO$_2$ particles synthesised at 0.125 M TEOT, 0.5 M H$_2$O, 1.14x10$^{-3}$ g/cc HPC, reactant water is 0.001 M HCl.
Figure 26. TiO$_2$ particles synthesized at 0.125 M. TEOT, 0.5 M. H$_2$O, 1.14x10^{-3} g/cc HPC, reactant water is 0.01 M. HCl.
particles synthesised while varying the acidity of the water.

Particles synthesised with aqueous acid in the place of reactant water were more spherical and smoother than those without. When synthesised with a moderate amount of acid (0.1 M HCl in the place of reactant water) the particles showed more dispersion in size and were more spherical. With higher acid concentration (1.0 M) the reaction was slowed and particles were so small, they could barely be seen at 100,000x magnification. There is more discussion of this in the next section "Varying pH and Induction Time".
Varying pH and Induction Time

Increasing the acidity of the reactant water increases the induction time of the reaction. Using reactant water of 1.0 M HCl, (1.0 M * 0.90 ml reactant water / 50. ml total solution ; or 0.018 M in solution), the reaction slows so much that turbidity doesn't occur even after 24 hours.

Figure 27 is a plot of absorbance vs time while varying the acidity of the reactant water. As shown, induction time increases with acidity. For comparison, a reactant solution made with 0.1 M HCl reaches a maximum absorbance of 0.346. It should be mentioned that some settling of the solutions occurred when left in the spectrophotometer for extended periods. Data were discarded when this settling was noticed.

Alan Bleier in his paper "Stability of Ceramic Suspensions"(4) mentions that agglomeration sometimes occurs because nucleation and growth stages are not sufficiently separated. It was thought that the slowing of the reaction with acid may aid in the synthesis of monodisperse particles. In the case of strong acid (1.0 M HCl replacing reactant water) the reaction was really slowed, to the point where reaction was not visibly noticeable. In the case of moderate acid (0.1 M HCl replacing reactant water) the reaction was again slowed. But the TEM photographs show more size dispersion when compared to other trials run without acid.
Figure 27. Absorbance vs Time -- Varying Reactant Water pH
Figure 27. Absorbance vs Time -- Varying Reactant Water pH

pure water  .001M HCl  .005M HCl  .01M HCl

Absorbance at 690 nm.

Time (Minutes)
Conclusions

1. TEOT is very difficult to work with because of its high reactivity with water.

2. Unagglomerated particles were not synthesized without the aid of HPC, a sterically hindering surfactant.

3. Reaction rate is increased with increasing concentration of either water or TEOT, with water having about a 100 fold more effect.

4. Of all the surfactants tried, steric or electrostatic, HPC gave the best unagglomerated particles.

5. Growth over time experiments showed the reaction to be over in about an hour. The mean particle size was about 0.5 μm with a standard deviation of about 0.1 μm.

6. The method of sizing the particles from 8x10 TEM photographs was shown to be fairly reliable.

7. Induction times were increased with the addition of HPC to the reactant mixture. Induction times were still much shorter than those reported by Jean & Ring by about a factor of 10. This led to the possibility that the TEOT may be contaminated.
8. Maintaining a low electrolyte concentration and a pH several units above the IEP for TiO₂ was shown theoretically to lead to unagglomerated particles. The addition of aqueous HCl actually slowed the reaction, and led to more spherical but more dispersed (in size) particles.
Recommendations

1. TEOC or TPT must be distilled just prior to use.

2. The results for induction time should be redone with the purest reactants possible and work should not proceed until the question of purity is reconciled. The induction time experiment may actually serve as a purity test.

3. Eventually, after the purity problem is solved and monodispersed particles can be reliably produced, concentration ranges should be explored and their effects on size, monodispersity, and flocculation tendencies noted.
Acknowledgements

I wish to thank C. F. Zuko, Leo Voegtli, Greg Bogush, and Jeanne Chang for their help and guidance throughout this project.
References


Appendix A

Sample calculation for solution make-up.

Assume a basis of a 50.0 ml total solution.

\[ 0.075 \text{ ml TEOT} \times \frac{288.15 \text{ g}}{\text{ mol}} \times \frac{\text{ ml}}{1.100 \text{ g}} \times 0.050 \text{ l} = 0.778 \text{ ml TEOT} \]

\[ 5 \times 0.075 \text{ ml H}_2\text{O} \times \frac{18.016 \text{ g}}{\text{ mol}} \times \frac{\text{ ml}}{1.00 \text{ g}} \times 0.050 \text{ l} = 0.338 \text{ ml H}_2\text{O} \]

Mix 0.778 ml TEOT in (50 - 0.778) ml EtOH.

Mix 0.338 ml H₂O in (25 - 0.338) ml EtOH.

Mix solution together & stir.
Appendix B

Sample calculation for surfactant study

See Appendix A for sample calculations of reactant water and TEOT. Substitute the soln below for the solvent EtOAc.

\[1.14 \times 10^3 \frac{g}{cc} \times 50cc = 5.7 \times 10^{-2} \frac{gm}{50ml}\]

multiply by the number of samples to be run, and make the solution all at once.
Appendix C

Conversion factor for converting photographs of particles (8x10) to actual size.

1 cm on film negative = 1.840 cm on 8x10
(taken from the IO box in the corner)

1 cm actual size = 7315.09 cm on film negative
(taken from 2160 lines/cm calibration grid)

\[
\frac{1 \text{ cm actual}}{7315.09 \text{ cm film neg}} \times \frac{1 \text{ cm film neg}}{1.840 \text{ cm 8x10}} \times \frac{1 \text{ m}}{100 \text{ cm}}
\]

Conversion factor is \(7.43 \times 10^{-7}\) m actual/cm measured on 8x10.