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# Hydrolysis of titanium alkoxide and effects of hydrolytic polycondensation parameters

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Titanium alkoxides hydrolyse vigorously with water producing polycondensates whose equivalent oxide content varies from ~70% to over 90%. This variation reflects the average molecular size and the nature of the terminal bonds. Hydrolysis conditions also affect the molecular and particle morphologies modifying the crystallization and sintering behaviour of oxide materials derived from polycondensates. It is also possible to form clear polymer solutions under excess water hydrolysis with the addition of certain acids. Investigations show that there is a window in the acid concentration which provides long-term solution stability. The gels formed from these clear solutions shrink in their liquor under certain conditions and the introduction of hydrogen peroxide into the liquor (surrounding the gel) causes vigorous gel shrinkage.

## 1. Introduction

The synthesis, chemistry and structure of metal alkoxides have been systematically investigated by chemists [1–4]. These compounds react vigorously with water, producing metal hydroxides or hydrated oxides. The reaction is often represented by the equation:

$$M(OR)_n + H_2O \rightarrow M(OH)_n + nR(OH) \quad (1)$$

In reality, hydrolysis of titanium alkoxides is very complex. These reactions produce polycondensates whose chemical compositions are a function of their physical size and polymeric morphology. This situation arises from the fact that, during the hydrolytic condensation, an inorganic network is formed by a chain of hydrolysis and polymerization reactions.

$$\equiv Ti{-}OR + H_2O \rightarrow \equiv Ti{-}OH + R(OH) \quad (2)$$

$$\equiv Ti{-}OH + RO{-}Ti\equiv \rightarrow \equiv Ti{-}O{-}Ti\equiv + R(OH) \quad (3)$$

The oxide network extends as far as the hydrolysis conditions permit. The terminating bonds of this otherwise expanding oxide polymer contain (OH) and (OR) groups, which make the overall composition of the resultant condensate dependent on the size and polymer morphology [5].

As was discussed in earlier work, [6, 7] certain parameters during the hydrolytic condensation determine the average molecular size and distribution. The polycondensed material from metal alkoxides can never be 100% oxide since this would require an infinite polymer with no terminal bonds. However, the concentration of (OH) and (OR) groups and their relative rations can be altered by the hydrolysis conditions. These conditions include water/alkoxide ratio, molecular separation by dilution, hydrolysis medium, catalyst, reaction temperature, and alkyl groups in the alkoxide [7]. By varying these parameters one can change the kinetics of the reactions that form the molecular structure. Modifications of molecular size and morphology in turn modify the behaviour and properties of oxide materials obtained by thermal degradation of these polycondensates, including crystallization and sintering [8]. For example, it has been observed that the monoclinic → tetragonal transformation of zirconia produced by hydrolytic condensation of zirconium alkoxides are affected by the nature of the alkyl group in the precursor alkoxide [9].

## 2. Hydrolytic polycondensation of $Ti(OR)_4$

### 2.1. Chemical makeup and oxide content of condensation

The equivalent oxide content of titanium oxide is given by the $TiO_2/Ti(OR)_4$ ratio. The molecular weights of the first three titanium alkoxides – $Ti(OC_2H_5)$, $Ti(OC_3H_7)_4$, and $Ti(OC_4H_9)_4$ – are 228, 284, and 340, respectively. Their oxide contents by weight are, therefore, ~35, 28.2 and 23.5%, respectively. If a complete hydrolysis to monomer tetrahydroxide, $Ti(OH)_4$, were to occur, the oxide content of this product would be $80/116 \simeq 70\%$ by weight.

Fig. 1 shows the variation in the oxide content of the hydrolytic condensates dried at 120° C as a function of hydrolysis water. As shown in the figure, when $Ti(OC_4H_9)_4$ was hydrolysed in secondary butyl alcohol with various amounts of water under a constant solution concentration of 5% wt equivalent $TiO_2$, the oxide content of the dried, partially hydrolysed material varies from less than 70 to more than 90%. When $Ti(OC_2H_5)_4$ is hydrolysed in ethanol, or when the higher titanium alkoxides are hydrolysed in lower alcohols, the curve shown in Fig. 1 flattens

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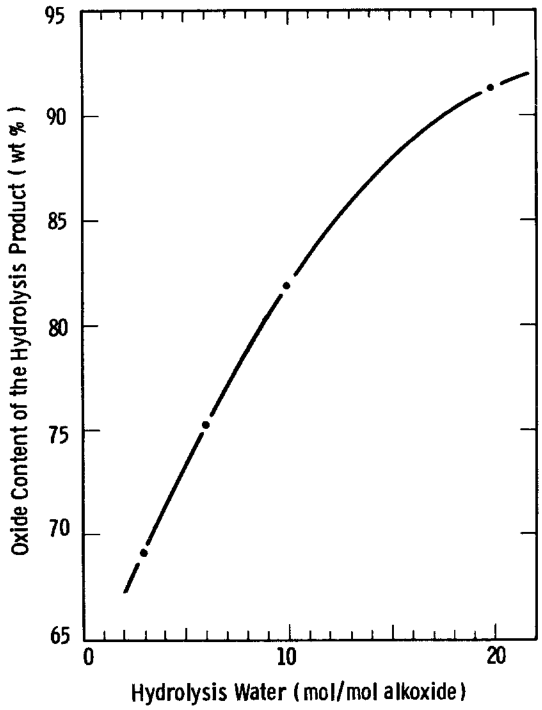

*Figure 1* Effect of the water/alkoxide ratio on the oxide content of hydrolytic polycondensation of $Ti(OC_4H_9)_4$ in butanol.

out considerably due to the reduced limitation by diffusion which controls the rate of polymerization.

The role of the water/alkoxide ratio during hydrolytic condensation goes beyond the chemical requirement: by affecting the statistical interactions of species, it becomes one of the parameters that determine the molecular size and polymer morphology.

A hydrolytic polycondensation equation which would take into account this variability of the oxide content and the polymeric nature of the condensates can be written:

$$n\mathrm{Ti(OR)_4} + (4n + x - y)\mathrm{H_2O} \rightarrow \mathrm{Ti}_n\mathrm{O}_{[2n-(x+y)/2]}(\mathrm{OH})_x(\mathrm{OR})_y + (4n - y)\mathrm{R(OH)} \quad (4)$$

where $n$ is the number of titanium ions polymerized in a given condensation, and $x$ and $y$ are the numbers of OH and OR groups in the molecule. The polymer size $n$ along with the nature of terminal bonds, $x$, and $y$, in $\mathrm{Ti}_n\mathrm{O}_{[2n-(x+y)/2]}(\mathrm{OH})_x(\mathrm{OR})_y$ determine the oxide content when this compound is decomposed to the oxide:

$$\mathrm{TiO}_{[2n-(x+y)/2]}(\mathrm{OH})_x(\mathrm{OR})_y \rightarrow n\,\mathrm{TiO_2} + x\,\mathrm{H_2O} + y\,\mathrm{R(OH)} \quad (5)$$

Analysis of the above equation shows an increase in the equivalent oxide content with increasing $n$. The initial increase in $n$ occurs rapidly, then it levels off. (For a detailed discussion of the relationship between $n$ and the oxide content of the polysiloxanes, see Reference [5].) The concentration of (OR) groups in the network structure decreases as the amount of water is increased in the hydrolysis medium. However, in the titania system, it was found that a certain concentration of OR groups always remains in the structure, regardless of the amount of water present. As the polycondensate is heated, a spontaneous burning of these residual organics takes place, often depositing carbon in the powder at around 185 to 190° C, when the polycondensate is produced from $Ti(OC_2H_5)_4$. Liberation of hydroxyl groups takes place more gradually, but the weight loss is almost complete at around 300° C for all practical purposes [10]. The contribution of the terminal bonds to the overall oxide content calculations decreases with the increasing polymer size, i.e., $n$.

## 2.2. Effect of hydrolysis conditions on oxide content and morphology

Various factors in addition to the water/alkoxide ratio also affect the kinetics of network forming reactions. Such factors include the type of alkyl groups in the alkoxide, the host medium, molecular separation of species, catalysts, and temperature. The alkoxides with higher alkyl groups are slower to hydrolyse and also slower to diffuse. Since polymerization requires partial hydrolysis and diffusion, higher alkoxides tend to produce smaller polymeric condensates; as a consequence the oxide component of their molecules is smaller. The host medium of the condensation process also affects the diffusion rates. The hydrolytic condensation of titanium alkoxides carried out in lower alcohols yields material with a higher equivalent oxide content, reflecting a greater degree of polymerization as well as reflecting the ester-exchange of heavier alkyls with lighter alkyls. For example, while dried hydrolytic condensate of $Ti(OC_2H_5)_4$ formed in ethanol has an equivalent oxide content of ~83 to 84% by weight, this figure drops to 73% when the hydrolysis is performed in butanol under the same conditions.

Table I gives the effect of some hydrolysis conditions on the oxide content of the condensate for $Ti(OC_2H_5)_4$ hydrolysed with water and with $H_2O_2$. In the first two experiments undiluted $Ti(OC_2H_5)_4$ was mixed with water at two temperatures. In the next two experiments the hydrolysis was performed at 25° C. In the fifth experiment 30% hydrogen peroxide was used. And finally, hydrolysis was performed by diluting 100 g of $Ti(OC_2H_5)_4$ with 1650 g of ethyl alcohol (thus the mixture contained 2% wt equivalent $TiO_2$) before hydrolysing with water. As shown in Table I, the oxide content of the condensates varied from ~75%

TABLE I Effect of hydrolysis conditions on the oxide content and sintering behaviour of hydrolytic condensates of $Ti(OC_2H_5)_4$

| Sample | Hydrolysis condition | Equivalent oxide[*] content (wt %) | % Linear[†] shrinkage at 1200° C |
|---|---|---|---|
| 1 | $H_2O$ at 25° C | 91.7 | 5 |
| 2 | $H_2O$ at 65° C | 93.7 | 20 |
| 3 | $H_2O + NH_4OH$ | 89.1 | 11 |
| 4 | $H_2O + HNO_3$ | 75.6 | 32 |
| 5 | $H_2O_2$ (30%) | 83.3 | 12 |
| 6[‡] | $H_2O$ (25° C) | 96.0 | 21 |

[*] Condensates dried at 120° C and calcined to 500° C to determine oxide content.

[†] 1 inch diameter samples pressed at 140 kg cm$^{-2}$ from thermally degraded $TiO_2$ powders, sintered at 1200° C for 1 h.

[‡] Only in this sample was $Ti(OC_2H_5)_4$ diluted with ethanol to 5 times its volume before reacting with water.

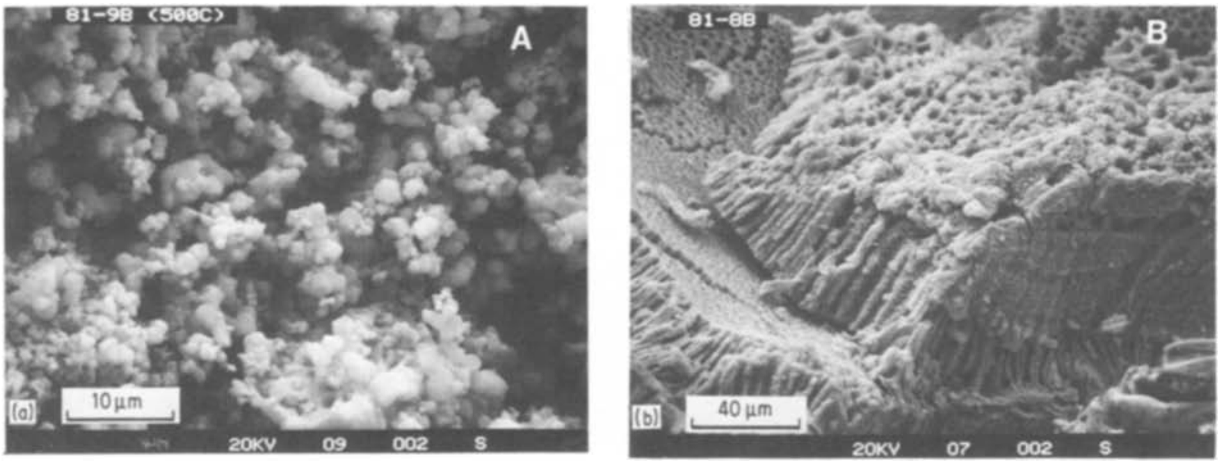

*Figure 2* Morphologies of titanium oxides produced via hydrolytic polycondensation of $Ti(OC_2H_5)_4$ (a) with acidic water (5% $HNO_3$); (b) with basic water (5% $NH_4OH$), condensates dried and heated to 500° C.

for acidic conditions to more than 90% for neutral water (specifically, 91.7% for water at 25° C and 93.7% for water at 65° C). Interestingly, dilute hydrolysis produced the condensate having the highest oxide content (~96%).

The resultant morphologies were also very interesting. Fig. 2 shows dramatic differences between the morphologies of titania samples formed via hydrolytic polycondensation of $Ti(OC_2H_5)_4$ under acidic and basic conditions (Samples 5 and 4 in Table I). The honeycomb morphology of the material formed under basic conditions with ammonia is rather unusual and contrasts with the particulate granular morphologies which result from neutral and acidic conditions. (Acids have other effects, as described in Section 4.)

The effect of $H_2O_2$ is also noteworthy. Hydrogen peroxide reacts vigorously with the condensation product, even when hydrolysis was completed earlier with water. Even more noteworthy is the fact that titania gels formed from clear solutions shrink rapidly without losing their shape when they are placed in $H_2O_2$ or when a small amount of $H_2O_2$ is introduced into their liquor. This phenomenon is thought to be caused by the removal and conversion of terminal alkyl groups possibly with a coordination change. Conversion of alkyl bonds to hydroxyl bonds by the action of $H_2O_2$ apparently initiates reaction between dangling bonds, creating bridging oxygens and causing the collapse of the previously open polymer network in a manner similar to the reaction shown in [3] or that shown by hydroxyl bonds.

The effect of hydrolysis conditions discussed here is not limited merely to the particle morphology of the material. Infrared spectroscopy shows molecular structural modifications in the oxide network, and these modifications are stable even at high temperatures (Fig. 3).

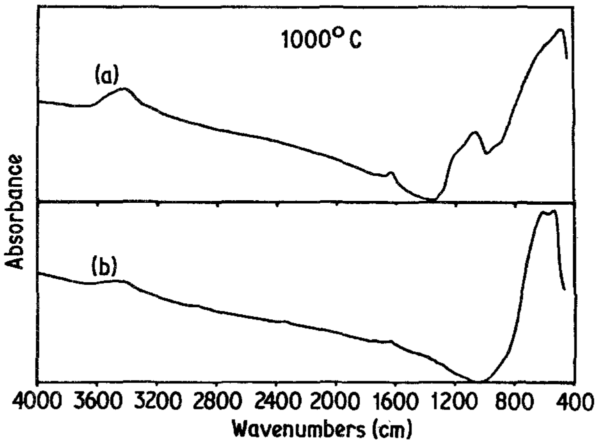

*Figure 3* Spectral absorption curves of oxide materials produced after heating to 1000° C via hydrolytic polycondensation of $Ti(OC_2H_5)_4$ (a) with 2 mol; (b) with 15 mol $H_2O$.

## 3. Effect of sintering and crystallization

Sintering of monodispersed alkoxide derived $TiO_2$ powders has been investigated by Barringer and Bowen [11]. The molecular and morphological variations discussed in Section 2 have an effect on sintering and crystallization behaviour. Table I shows the percentage shrinkage of the pressed $TiO_2$ pellets obtained by thermal degradation of hydrolytic

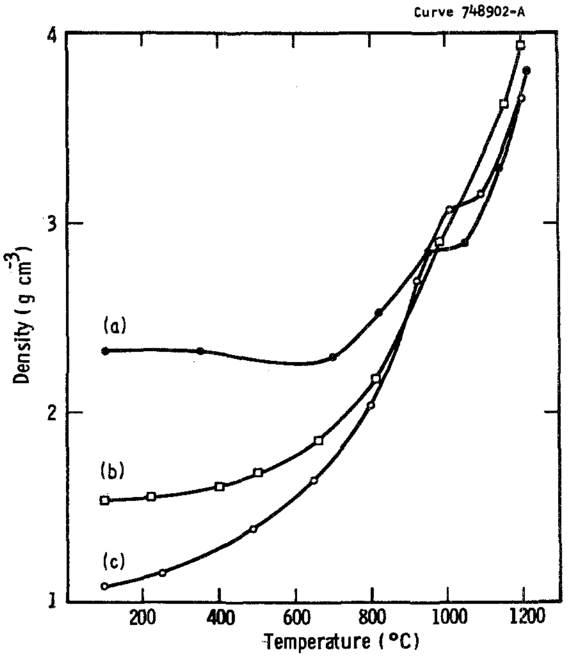

*Figure 4* Densification curves of oxide materials formed by hydrolytic polycondensation of $Ti(OC_2H_5)_4$ (a) with neutral water; (b) under basic conditions, $NH_4OH$; and (c) under acidic conditions, $HNO_3$. $TiO_2$ hot pressed at 140 kg cm$^{-2}$.

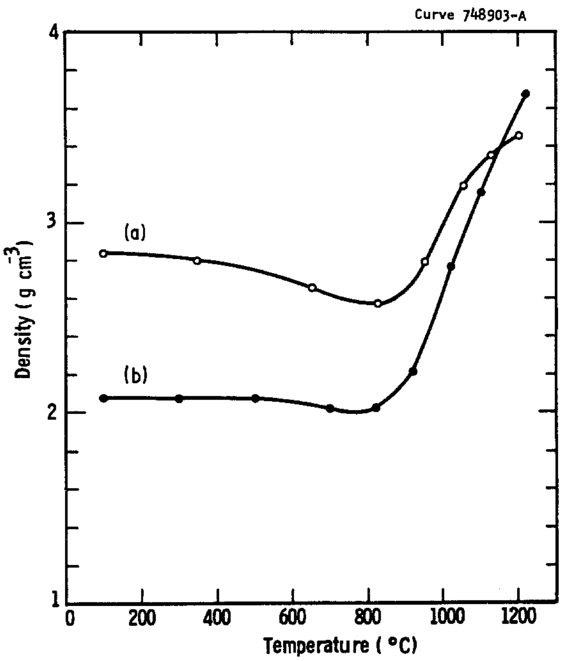

*Figure 5* Changing the molecular spacing, *ms*, of species during hydrolytic polycondensation of $Ti(OC_2H_5)_4$ affects the compaction and sintering behaviour of resultant titanias. (Separation of $Ti(OC_2H_5)_4$ molecules when diluted with ethanol is expressed relative to spacing of the molecules in undiluted $Ti(OC_2H_5)_4$ which is taken as unity). $TiO_2$ hot pressed at 140 kg cm$^{-2}$. (a) $ms = 1.0$, (b) $ms = 1.7$, $H_2O/Ti(OR)_4 = 2$.

condensates formed under various hydrolysis conditions. The condensation product of $Ti(OC_2H_5)_4$ were calcined at 500° C, pressed into pellets, and sintered at 1200° C for 1 h. Initial particle morphologies were considered part of the process and were not altered by grinding, etc. As shown in Table I, a 5% shrinkage of the cold water hydrolysed sample was improved to 20% when the water temperature was raised to 65° C and improved even further when acid was introduced into the liquor. Although these dimensional shrinkages do not necessarily reflect differences in densities between samples, they do give an indication of the morphological effects on densification behaviour.

Fig. 4 shows the densification under hot pressing of three $TiO_2$ samples similarly prepared by hydrolytic condensation of $Ti(OC_2H_5)_4$ under neutral, basic, and acidic conditions. Again it is clear that the initial compaction densities as well as the densification rates vary significantly for these three samples.

One other parameter – the molecular separation of species during the hydrolytic polycondensation by dilution – was found to affect the densification rate as well as the crystallization of $TiO_2$ samples. The effect of molecular separation of alkoxide species during the hydrolytic polycondensation is a complex one and is presented separately for a silica system [12]; Fig. 5 shows this effect on the sintering behaviour of two titania samples. One of these samples were formed by hydrolysis of undiluted $Ti(OC_2H_5)_4$ (a molecular separation of unity) with two moles of water; in the other case, $Ti(OC_2H_5)_4$ was diluted by ethanol to five times the volume where the molecular spacing is 1.7 times that in the undiluted form, before the hydrolysis. Hot pressing tends to obviate the differences between the materials at high temperatures. When the same samples were fired in air, the density of the sample prepared via hydrolysis of undiluted $Ti(OC_2H_5)_4$ (molecular spacing, $ms = 1$) changed only 0.04 g cm$^{-3}$ (from 2.58 to 2.62 g cm$^{-3}$) between 800 and 1200° C; however, the density of the $TiO_2$ samples obtained via hydrolysis of diluted $Ti(OC_2H_5)_4$ ($ms = 1.7$) changed by 0.9 g cm$^{-3}$ (from 2.08 to 2.98 g cm$^{-3}$) between the same temperatures. Molecular separation also affected crystallization. The hydrolytic polycondensation products of titanium alkoxides, even those of 96% oxide, were initially amorphous. Temperature stability of the initial amorphous phase depended on which titanium alkoxide it was produced from. The amorphous phase produced from $Ti(OC_2H_5)_4$ tended to crystallize to the anastase structure at temperatures as low as 150 to 190° C. (This temperature may correspond to the release of residual organics at 185° C.) This crystalline phase later converted to rutile. This conversion temperature was also affected by the molecular spacing during the hydrolytic polycondensation. Fig. 6 shows that, when the molecular spacing was 1, no rutile phase formed at 500° C. However, when the molecular spacing was 3, traces of rutile began to appear at 500° C.

## 4. Formation of clear polymer solutions

The hydrolytic polycondensation of titanium alkoxides under normal conditions leads to the formation and precipitation of particulate materials. Such precipitate formation and self-condensation can be prevented by careful control of molecular interactions during the hydrolysis, such that certain amounts of (OR) groups are left in the molecular structure. This is done first by controlling the amount of water and dilution of the system, and second, by the presence of a critical amount of certain acids [13]. These solutions are useful in depositing optical titania coatings on precise thickness as well as forming titania-based glass and ceramic materials [10, 13, 14].

In these solutions condensation of particulates is avoided by introducing at least 0.014 mol of either $HNO_3$ or HCl acid. If the acid is introduced into the water–alcohol solution before mixing with the alkoxide, no cloudiness ever occurs; therefore, this is the preferred method of introducing the acid. Acid can be added any time after the mixing occurs and will cause the cloudy slurry to turn into a clear solution. However, if more than 0.3 mol of acid are used per mole of alkoxide, the stability of the solution is reduced and it will turn cloudy after several days to several months, depending on the acid concentration (see Fig. 7). So far, no organic acids have been found which work, and the only inorganic mineral acids which have been found to work are hydrochloric acid and nitric acid, although not all acids have been tried.

One must also consider the concentration and water/alkoxide ratio criteria in these clear solutions. If the water/alkoxide ratio is less than 1.7, the solution does not deposit clear continuous films. If the water/alkoxide ratio is much above 2, the solution tends to gel to a clear single phase within hours or days, depending on the concentration. For example, if the

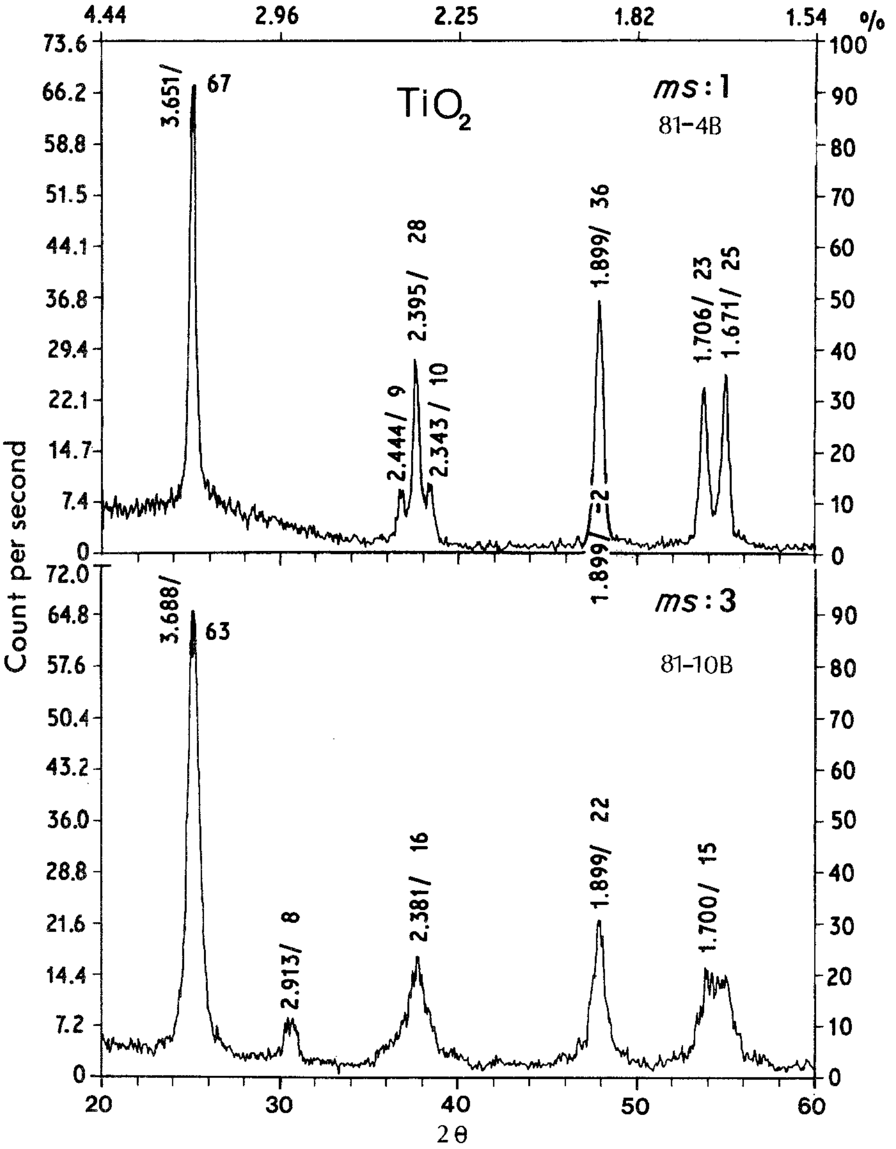

*Figure 6* Molecular separation of alkoxide species during the hydrolysis also affects the crystallization behaviour of the resultant oxides. Titanium oxide obtained via hydrolytic polycondensation of undiluted $Ti(OC_2H_5)_4$ (*ms* = 1) shows only the anastase phase (top), whereas that produced via highly diluted alkoxide (*ms* = 3) shows some rutile phase as well (bottom) at 500° C.

equivalent $TiO_2$ concentration of the solution is 5% by weight, 5 mol $H_2O$ per mole of alkoxide will cause gelling in about an hour. At higher water/alkoxide ratios, gelling occurs immediately at this concentration. Solutions with a concentration of 2% will gel in 24 h, while 1% concentrations will not gel at all.

These titania gels will shrink in their liquor (see Fig. 8). The shrinkage occurs as a result of the formation of bridging oxygens by the reaction of dangling bonds with each other

$$\equiv Ti{-}OH + RO{-}Ti\equiv \rightarrow \equiv Ti{-}O{-}Ti\equiv + R(OH) \qquad (6)$$

$$\equiv Ti{-}OH + OH{-}Ti\equiv \rightarrow \equiv Ti{-}O{-}Ti\equiv + H_2O \qquad (7)$$

which collapses the gel network. Reaction 6 appears to be the dominant one, since addition of water in the liquor accelerates the shrinkage, presumably by creating more hydroxyl bonds which can then react with neighbouring alkoxy bonds. Slight heating also accelerates the shrinkage. Creation of more bridging oxygens during the shrinkage is confirmed by chemical analysis. Gels initially containing 70 to 82% equivalent oxide, contained as much as 96% equivalent

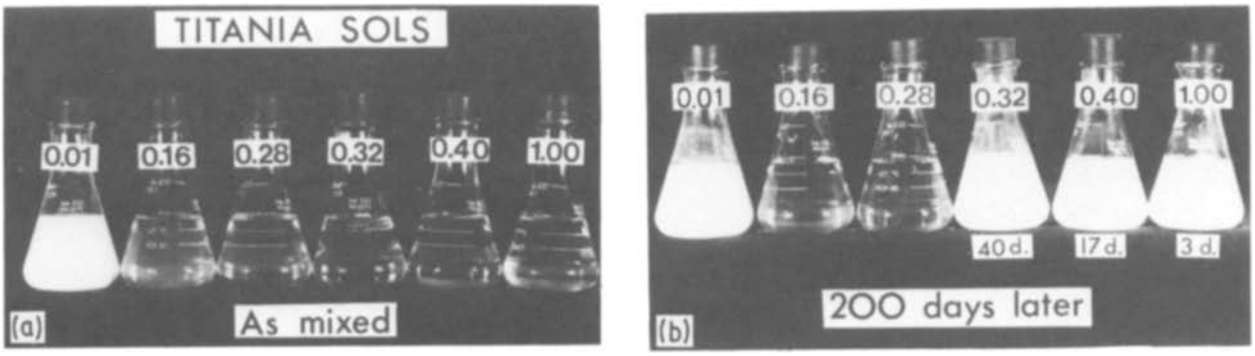

*Figure 7* (a) Clear polymer solutions are produced via two mole water hydrolysis of $Ti(OC_2H_5)_4$ in ethanol when more than ~0.15 mol of $HNO_3$ acid per mole of alkoxide are introduced. However, solutions with acid/alkoxide ratios 0.32, 0.40, and 1.00 turn cloudy in 40, 17 and 3 days, respectively. (b) The solutions with acid/alkoxide ratios 0.16 and 0.28 were still clear after 200 days.

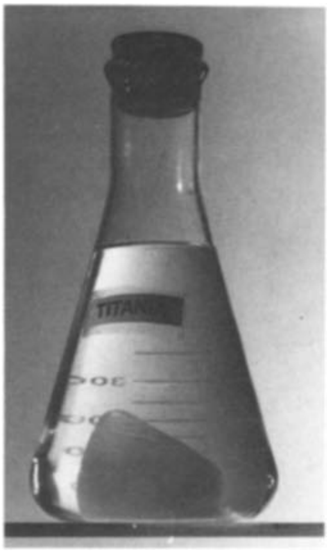

*Figure 8* Titania gel from a clear solution shrinks in its liquor to a fraction of its original size. This shrinkage is accelerated by introduction of a small amount of $H_2O$ or $H_2O_2$ into the liquor and slight heating. (The original volume of the gel was where the liquor level is now. The gel was tipped over later.)

oxide after shrinkage ceased in their liquor. This could only happen by elimination of (OR) and (OH) groups through the reactions shown in Equations 6 and 7 from the molecular structure. (The oxide content of the gels is measured by removing a portion of the gel at various stages, drying it at 120° C, and thermally degrading it to the oxide form at 500° C.)

Introduction of $H_2O_2$ into the liquor of the gel causes vigorous gel shrinkage as previously mentioned.

## 5. Summary

The parameters that affect the molecular makeup and structural morphology of the titanias obtained by hydrolytic condensation of titanium alkoxides were investigated. The effect of these structural and morphological modifications extends to the sintering and crystallization behaviour of the oxide materials.

The formation of clear solutions in titania systems requires the presence of certain acids. The stability of these clear solutions is a function of the acid/alkoxide ratio, and there is a window for the most stable solutions at 0.15 and 0.30 mol of acid per mole of alkoxide. Gelling time of these solutions is a function of solution concentration and water/alkoxide ratio.

The clear titania gels formed from clear polymer solutions shrink in their liquor by reaction of the dangling bonds of the molecules, forming bridging oxygens. The oxide content of these gels increases as they shrink. The shrinkage is accelerated by introducing water into the liquor and by heating.

Vigorous shrinkage of the gels occurs when hydrogen peroxide is introduced into the liquor surrounding the gels.

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