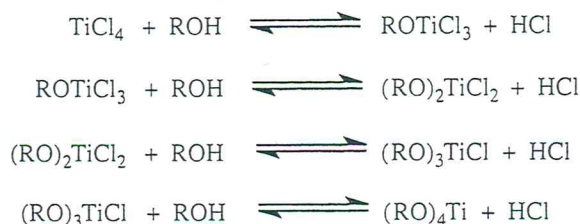


Arkles, B., Applications of Metal-Organic Titanium Compounds, in "Metal-Organics for Materials, Polymers and Synthesis" (3rd edition), 321-323, 2011.

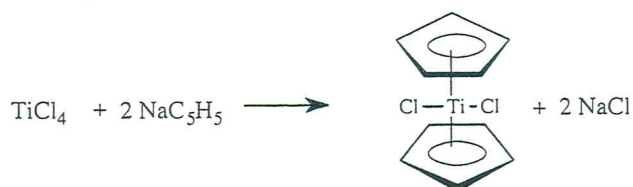
## Applications of Metal-Organic Titanium Compounds

Barry Arkles, Gelest Inc.

Metal-organic titanium compounds have a covalent bond directly between titanium and carbon or indirectly to carbon through another atom, most commonly oxygen. The most common metal-organic titanium compounds have 4 oxygen bridged bonds to carbon and are referred to titanate esters. The primary step in their production is the stepwise reaction of titanium tetrachloride with an alcohol.



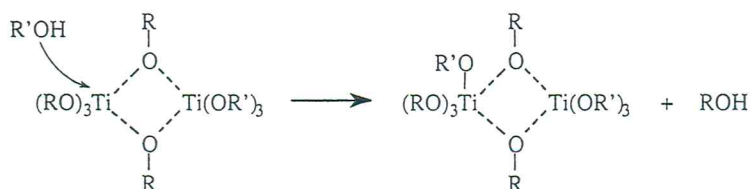
Titanate esters represent over 95% of the production of metal-organic titanium compounds. Titanate esters have a number of naming systems associated with them. Titanium methoxide, tetramethylorthotitanate and titanium tetramethoxide are all names for the simplest ester,  $\text{Ti}(\text{OCH}_3)_4$ . True organometallic titanium compounds having one or more titanium-carbon bonds are produced by the reaction with main-group organometallics such as organomagnesium, sodium or lithium reagents. Most titanium organometallics are relatively unstable, with the exception of bis(cyclopentadienyl)titanium dichloride (titanocene dichloride) and its analogs.



Metal-organic titanates have practical applications in catalysis including olefin polymerization, polyesterification and resin crosslinking and surface modification including formation of inorganic coatings for abrasion resistance and controlled refractive index, adhesion and inorganic particle dispersion. Comprehensive reviews of titanate ester chemistry<sup>1</sup> and organometallic titanium compounds<sup>2</sup> have been published. The purpose of this brief introduction is to provide a description of the chemistry associated with applications of the most common metal-organic titanium compounds, the titanate esters.

### Catalysis

*Alcohol Exchange.* The reaction of titanate esters with alcohols serves as a convenient model for the role of titanate esters in catalysis. The ability of titanium IV to reach a six-coordinate state provides a pathway for the rapid exchange of alkoxy groups. Departure of an alkoxy group and an accompanying proton is the first step in the exchange of all four alkoxy groups.



For preparative purposes the equilibrium may be shifted by using either an excess of the exchanging alcohol and/or by distilling a more volatile alcohol from the reaction mixture. The tendency of titanium to reach higher coordination states can have a strong influence, e.g. the exchange of methoxy groups for isopropoxy groups is strongly favored since the lack of steric constraints allows a coordinative association of titanium tetramethoxide that is not possible for titanium tetraisopropoxide.

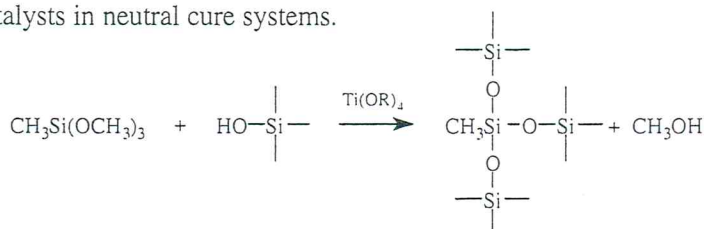
<sup>1</sup>D. Putzig, T. Del Pesco, "Titanium Compounds (Organic)" in Kirk-Othmer Encyclopedia of Chemical Technology, 24, 275

<sup>2</sup>D. Cardin, M. Lappert, C. Ralston "Chemistry of Organo-Zirconium and -Hafnium Compounds" Ellis Horwood-Wiley, 1986.

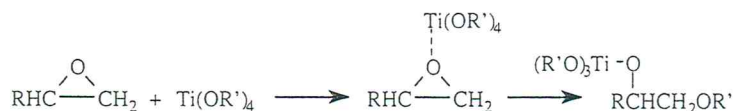
*Reaction with Esters.* Titanates catalyze ester exchange. In the reaction depicted an intermediate titanate ester is formed. Typically 1-3 mole% of the titanate ester is utilized.



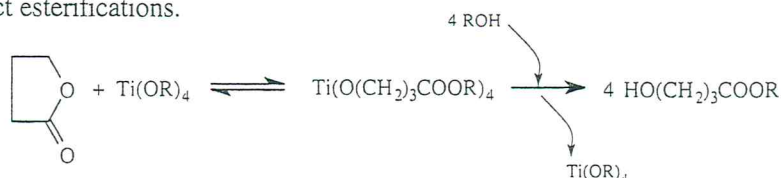
Polymers with pendant ester and hydroxyl functionalities can be crosslinked with titanates. High molecular weight linear polyester resins such as poly(ethylene terephthalate), PET, and poly(butylene terephthalate), PBT, can be produced by the transesterification of dimethylterephthalate with the appropriate diol. The catalysis is not limited to organic esters, but includes silicon esters as well. Condensation cure silicone RTVs use long chain alkyl titanate esters and mixed titanate ester chelates as catalysts in neutral cure systems.



*Reactions with Epoxides and Lactones.* Titanates facilitate ring opening reactions of epoxides and lactones. Titanates react with free hydroxyl groups in epoxy resins and with the epoxides themselves. Sufficient titanate concentration will harden an epoxide resin. At elevated temperatures some water-borne systems cure to form hybrid titanate-epoxide resins with low power factors.



Similarly, lactones undergo ring-opening reactions with titanates that can be used to form titanate esters or effect esterifications.

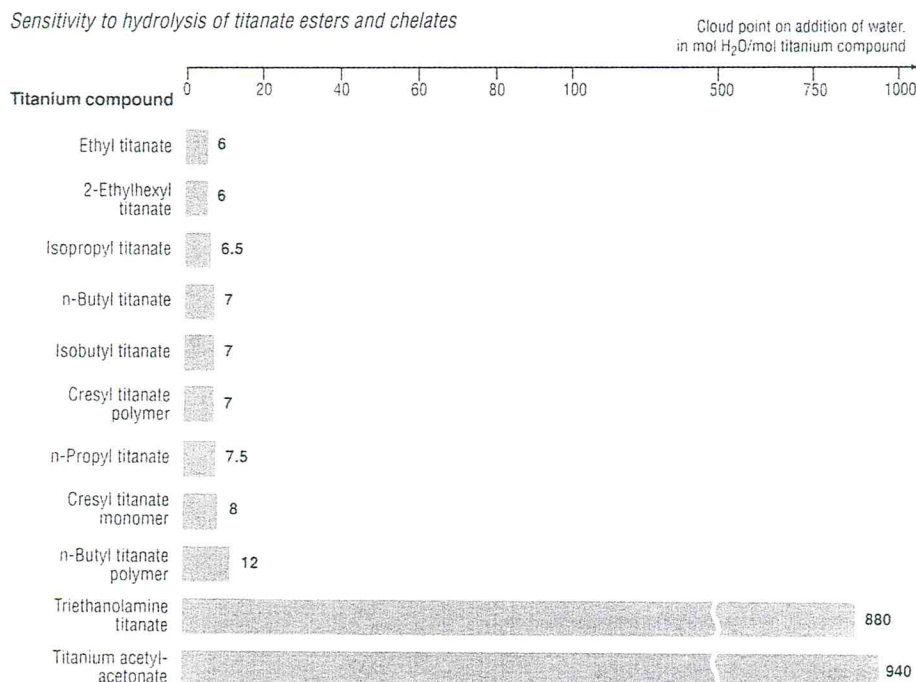


*Reactions with Isocyanates.* Isocyanates and polyisocyanate trimerization to isocyanurates and polyisocyanurates is catalyzed by titanates. Mixed chlorotitanium alkoxides ( $\text{Cl}_3\text{TiOR}$ ) initiate living polymerization of isocyanates.



### Surface Synthesis

*Hydrolysis.* Titanates are hydrolyzed by moist air or water initially forming condensation polymers and ultimately forming hydrous titanium oxides. The rate of hydrolysis is retarded by adding alcohol which is attributed primarily to coordinative solvation and secondarily to equilibrium effects. The rate of hydrolysis decreases as the size of the alkyl group increases. Chelation of the titanate catalyst with diketone or alkylacetoacetate groups effects a dramatic reduction in hydrolysis rate. Coatings obtained by hydrolytic deposition of  $\text{TiO}_2$  are used for antireflection coatings for optics, heads-up display screens, photochemically active surfaces for oxidation and, experimentally, in photovoltaics. Dielectric coatings for thin film capacitors and resistors can be deposited on metal and glass substrates.



**Thermolysis.** Titanate esters with simple hydrocarbon substitution are thermally stable to temperatures of 325°C. Thermolysis is used for the formation of titania films on glass and other surfaces. When a lower alkoxide such as tetraisopropyltitanate is vaporized in dry air and blown onto substrates at 500°C a thin abrasion resistant coating of titanium dioxide is formed. The films are believed to be bound to the surface by Ti-O-Si bonds. Most abrasion resistant coatings are <100nm. If the films are >150nm they form antireflection layers for visible light.

**Surface Modification**

**Adhesion and Dispersion** Solvent-borne titanates at 0.5-2.0% concentration are applied as primers for metals including steel, zinc, aluminum and copper to promote adhesion of coatings and inks. Fillers treated with organic titanates frequently wet out better in polymers, reducing viscosity or allowing higher loading levels. Magnetic and electrostatic media are prepared by surface treatment of magnetic particles such as strontium ferrite and carbon black with stearyl or dioctylphosphate substituted titanates.

**Thixotropy**

**Water-borne Coatings** Titanate esters and, in particular chelated titanate esters, are employed with associative thickeners in paint. Titanates are used to control properties such as brush drag, leveling, spatter and sag resistance. Acrylic emulsion coatings low viscosity during application due to the shear of a brush or roller, level and then thicken after a time delay. Associative thickeners such as hydroxyethyl cellulose and sodium carboxymethyl cellulose are thought to form shearable hydrogen bonds with hydrolyzed titanates such as titanium bis(triethanolamine)diisopropoxide and titanium diisopropoxide bis(pentanedionate).

