TITANIUM COMPOUNDS, ORGANIC

1. Introduction

Organic titanium compounds are materials having a covalent bond between titanium and another atom that is also bonded to a carbon-based group. Titanium tetrachloride [7550-45-0], $TiCl_4$, the basic raw material from which organic titanate compounds are made (see TITANIUM COMPOUNDS, INORGANIC), is readily converted to tetraisopropyl titanate, TYZOR TPT [546-68-9], by the Nelles process. This ester can be converted by alkoxy exchange (transesterification) to a wide variety of tetraalkyl titanates, sold commercially worldwide. The tetraalkyl titanates react with other ligands and chelating agents (qv), eg, glycols (qv), β-diketones and ketoesters, α-hydroxycarboxylic acids, and alkanolamines (qv), to give complexes having properties significantly different from the starting materials. These complexes are also important items of commerce.

True organometallic compounds having a titanium–carbon bond are prepared from $TiCl_4$ by reaction with main-group organometallics, such as organomagnesium, sodium, or lithium reagents. Most simple C–Ti bonds are very unstable. The predominant exceptions are bis(cyclopentadienyl)titanium dichloride [1271-19-8] and its analogues. Many organometallics and complexes of trivalent titanium are stable at room temperature, but most are attacked by oxygen and moisture. Organic derivatives of divalent titanium are much less common. Titanium(II) and titanium(0) are potent reducing agents.

Titanium alkoxides (titanate esters) are superb catalysts for esterification, transesterification, and cross-linking of ester-containing resins and epoxides (see ALKOXIDES, METAL; CAYTALYSIS). Water-soluble titanium chelates are widely used in cross-linking (gelling) of dilute polysaccharide solutions, which are used in oil-field fracturing fluid applications. Titanium's great affinity for oxygen atoms is reflected in its bonding to oxide surfaces, such as glass (qv) and plastic, to yield a scratch-resistant oxide coating (see COATING). Titanates are also used to cross-link silicone resins and as curing agents for wire coatings. Titanates disperse pigments (qv) and often help bond resins to fillers and reinforcement agents, eg, fiber glass.

2. Alkoxides

The standard manufacturing method for tetraalkyl titanates, eg, TYZOR TPT, or tetra- n-butyl titanate, TYZOR TnBT [5593-70-4], involves the addition of $TiCl_4$ to an alcohol. In a series of reversible displacement reactions, the alkoxy substitution products and hydrochloric acid form as follows:

$$\begin{aligned} TiCl_4 + ROH &\rightleftharpoons ROTiCl_3 + HCl \\ ROTiCl_3 + ROH &\rightleftharpoons (RO)_2TiCl_2 + HCl \\ (RO)_2TiCl_2 + ROH &\rightleftharpoons (RO)_3TiCl + HCl \\ (RO)_3TiCl + ROH &\rightleftharpoons (RO)_4Ti + HCl \end{aligned}$$

The reaction can be driven to the tetraalkoxide stage by addition of an amine or ammonia to scavenge the liberated hydrochloric acid. The amine or ammonium hydrochloride that forms can be filtered from the reaction mass and the tetraalkyl titanate purified by distillation. If the reaction is run in the starting alcohol as solvent, the chloride salts formed are in a finely divided state and difficult to filter. When the reaction is run in the presence of an inert hydrocarbon solvent, such as heptane or toluene, a much more readily filterable salt is obtained. The solution of crude tetraalkyl titanate can be distilled to remove solvent and give a pure product (1,2).

TYZOR TPT and the tetraethyl titanate, TYZOR ET [3087-36-3], have also been prepared by direct electrochemical synthesis. The reaction involves anode dissolution of titanium in the presence of the appropriate alcohol and a conductive admixture (3).

High purity tetraalkyl titanates can be obtained by a process whereby the liquid organic titanate esters are subjected to partial hydrolysis to form a solid that can be separated from the reaction mass. The remaining liquid is distilled to give a high purity product (4). For example, tetraisopropyl titanate purified in this manner contains:

Element, ppm	Starting titanate	Purified titanate
Fe	880	2
Si	370	1
Na	480	3
V	110	2
U	1	<0.001

The partially alkoxylated chlorotitanates, $(RO)_{4-n}TiCl_n$, can be prepared in high purity by reaction of $TiCl_4$ with an organosilane ester, $Si(OR)_4$ (see SILICON COMPOUNDS: ANTHROPOGENIC SILICAS AND SILICATES). The degree of esterification of the titanium can be controlled by the amount of silane ester used. When $n = 3$ or 4, the addition of the appropriate alcohol and an amine receptor is required (5).

Higher alkoxides, such as tetra(2-ethylhexyl) titanate, TYZOR TOT [1070-10-6], can be prepared by alcohol interchange (transesterification) in a solvent, eg, benzene or cyclohexane, to form a volatile azeotrope with the displaced alcohol, or by a solvent-free process involving vacuum removal of the more volatile displaced alcohol. The affinity of an alcohol for titanium decreases in the order: primary > secondary > tertiary, and unbranched > branched. Exchange processes are more convenient than direct synthesis of tetraalkoxide from $TiCl_4$, an alcohol, and a base because a metal chloride need not be handled. However, in general, traces of impurities of mixed tetraalkyl titanates can result.

$$(i\text{−}C_3H_7O)_4Ti + 4\ ROH \longrightarrow (RO)_4Ti + 4\ i\text{−}C_3H_7OH$$

Phenols react readily with tetraalkoxides to give highly colored (yellow to orange) titanium tetraphenoxides (6). A bis(cresyl titanate) [83897-99-8] derived from tetra-*n*- butyl titanate and the tetracresyl titanate [28503-70-0] are available commercially.

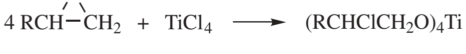
Mixed esters can be prepared from $Cl_nTi(OR)_{4-n}$ and a second alcohol in the presence of a base or by mixing a tetraalkoxide and the second alcohol in the desired proportions and flash-evaporating the mixed alcohols. Mixing of two pure tetraalkoxides of titanium also leads, via a rapid ester interchange reaction, to a mixture of all possible combinations of tetraalkyl titanates.

A rarely used preparation involves the reaction of tetraamido titanates, eg, tetradimethylamino titanate [3275-24-9], with an alcohol. This reaction goes to completion because of the greater affinity of titanium for oxygen over nitrogen.

$$((CH_3)_2N)_4Ti + 4\ ROH \longrightarrow (RO)_4Ti + 4\ NH(CH_3)_2$$

2.1. Fluoroalkyl-Substituted Titanates. Tetrahexafluoroisopropyl titanate [21416-30-8] can be prepared by the reaction of $TiCl_4$ and hexafluoroisopropyl alcohol [920-66-1], in a process similar to that used for TYZOR TPT (7). Alternatively, it can be prepared by the reaction of sodium hexafluoroisopropoxide and $TiCl_4$ in excess hexafluoroisopropyl alcohol (8). The fluoroalkyl material is much more volatile than its hydrocarbon counterpart, TYZOR TPT, and is used to deposit titanium dioxide on surfaces by chemical vapor-phase deposition (CVD).

2.2. β-Chloroalkoxy Titanates. The reaction of $TiCl_4$ with epoxides, eg, ethylene or propylene oxide (qv), gives β- chloroalkyl titanates (8,9). One example is $Ti(OCH_2CH_2Cl)_4$ [19600-95-5]. The β- chloroalkoxy titanates can be used to bind refractory powders and in admixture with diethanolamine to impart thixotropy to emulsion paints (10).



$$4\ RCH\overset{O}{-}CH_2 + TiCl_4 \longrightarrow (RCHClCH_2O)_4Ti$$

2.3. Titanium Complexes of Unsaturated Alcohols. Tetraallyl titanate can be prepared by reaction of TYZOR TPT with allyl alcohol, followed by removal of the by-product isopropyl alcohol. Ebullioscopic molecular weight determinations support its being the dimeric product, octaalloxydititanium. A vinyloxy titanate derivative can be formed by reaction of TYZOR TPT with vinyl alcohol formed by enolization of acetaldehyde (11):

$$4\ CH_3CH{=}O \longrightarrow 4\ CH_2{=}CHOH + Ti(OR)_4 \longrightarrow Ti(OCH{=}CH_2)_4 + 4\ ROH$$

2.4. Properties and Reactions. *Associations.* Organic titanates tend to associate (12). Although a titanium (IV) atom strives to achieve a coordination number of 6 by sharing electron pairs from nearby ester molecules, this tendency may be opposed by stearic crowding. X-ray diffraction (xrd) experiments performed on tetramethyl and tetraethyl titanate single crystals show that, in the solid state, these are tetramers (13). In benzene solution, however, cryoscopic measurements (14) and electrospray mass spectroscopy (15) suggest that tetraethyl and tetra-*n*-butyl titanate are trimeric; tetraisopropyl titanate is monomeric in nature. Titanium nuclear magnetic resonance (nmr) experiments support a monomeric structure for tetraisopropyl and tetra-*tert*-butyl titanate [3087-39-6] (16). These conclusions are supported by more recent X-ray absorption studies [xanes– extended X-ray absorption spectroscopy (exafs)], which indicate only one kind of Ti–O bond distance (1.8 nm) for tetra-*tert*-amyl and tetraisopropyl titanate, whereas there are bond distances of 18.0 and 20.5 nm for tetraethyl and tetra-*n*-butyl titanate. These latter have been attributed to terminal and bridging groups on trimeric oligomers, in which each titanium atom is five coordinate (Fig. 1).

Increased molecular association increases viscosity. Tetra-*tert*-butyl titanate and tetraisopropyl titanate are mobile liquids at room temperature; tetra-*n*-butyl titanate and tetra-*n*-propyl titanate, TYZOR NPT [3087-37-4], are thick and syrupy. The boiling points of these materials also reflect association (Table 1).

Hydrolysis and Condensation. The rate of hydrolysis of the tetraalkyl titanates is governed by the nature of the alkoxy groups. The lower titanium alkoxides, with the exception of tetramethyl titanate [992-92-7], are rapidly hydrolyzed by moist air or water, giving a series of condensed titanoxanes, $(Ti{-}O{-}Ti{-}O{-})_x$ (18). As the chain length of the alkyl group increases, the

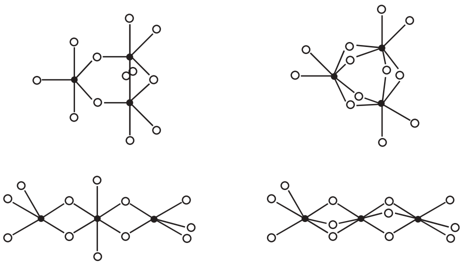


Fig. 1. Proposed structures for Ti $(OC_2H_5)_4$, where ● and ○ represent titanium and the ethoxy group, respectively.

Table 1. **Titanium(IV) Tetraalkoxides and Tetraaryloxides**

Titanate	CAS Registry Number	Formula	Mp, °C	Bp,[a] °C	Other properties
		Alkoxides			
titanium tetramethoxide	[992-92-7]	$Ti(OCH_3)_4$	210	$170_{1.33}$ sublimes	dipole moment 5.37×10^{-30} C·m[b]
titanium tetraethoxide	[3087-36-3]	$Ti(OC_2H_5)_4$		103_{13}	$n^{35}{}_D$ 1.5051, $d^{35}{}_4$ 1.107 g/cm^3, η_{25} 44.45 mPa·s(=cP)
titanium tetra-allyloxide	[5128-21-2]	$Ti(OCH_2CH{=}CH_2)_4$		$141{-}142_{133}$	$n^{35}{}_D$ 1.5381
titanium tetra-*n*-propoxide	[3087-37-4]	$Ti(OCH_2CH_2CH_3)_4$		124_{133}	$d^{35}{}_4$ 0.9970 g/cm^3, $n^{35}{}_D$ 1.4803, η_{25} 161.35 mPa·s(=cP)
titanium tetra-isopropoxide	[546-68-9]	$Ti(OCH(CH_3)_2)_4$	18.5	49_{133}	$n^{35}{}_D$ 1.4568, η_{25} 4.5 mPa·s(=cP), $d^{20}{}_4$ 0.9711 g/cm^3
titanium tetra-*n*-butoxide	[5593-70-4]	$Ti(OC_4H_9)_4$	ca. −50	142_{133}	$d^{35}{}_4$ 0.9927 g/cm^3, $n^{35}{}_D$ 1.4863, η_{25} 67 mPa·s(=cP), dipole moment 3.84×10^{-30}C·m
titanium tetra-isobutoxide	[7425-80-1]	$Ti(OCH_2CH(CH_3)_2)_4$		141_{133}	$n^{54}{}_D$ 1.4749, $d^{50}{}_4$ 0.9601 g/cm^3, η_{25} 97.40 mPa·s(=cP)
titanium tetra-*s*-butoxide	[3374-12-7]	$Ti(OCH_3CHC_2H_5)_4$	ca. −25	81_{133}	$n^{35}{}_D$ 1.4550, $d^{35}{}_4$ 0.9196 g/cm^3
titanium tetra-*tert*-butoxide	[3087-39-6]	$Ti(OC(CH_3)_3)_4$	107	$62{-}63_{133}$	$n^{20}{}_D$ 1.4436, $d^{20}{}_4$ 0.8893 g/cm^3
titanium tetra-*n*-pentoxide	[10585-24-7]	$Ti(OC_5H_{11})_4$		158_{133}	η_{25} 79.24 mPa·s(=cP), $d^{25}{}_4$ 0.9735 g/cm^3, $n^{35}{}_D$ 1.4813
titanium tetra-cyclopentyloxide	[1517-19-7]	$Ti(OC_5H_9)_4$	45	$200{-}201_{667}$	

Table 1. (*continued*)

Titanate	CAS Registry Number	Formula	Mp, °C	Bp,[a] °C	Other properties
titanium tetra-*n*-hexyloxide	[7360-52-3]	$Ti(OC_6H_{13})_4$		176_{133}	η_{25} 64.90 mPa·s(=cP), $d^{25}{}_4$ 0.9499 g/cm^3, $n^{20}{}_D$ 1.4830, dipole moment 5.54×10^{-30}C·m
titanium tetra-cyclohexyloxide	[6426-39-7]	$Ti(OC_6H_{11})_4$		$190.5{-}192_{133}$	$d^{25}{}_4$ 1.0589 g/cm^3, $n^{35}{}_D$ 1.5155
titanium tetra-benzyloxide	[103-50-4]	$Ti(OCH_2C_6H_5)_4$		250_{267} dec	
titanium tetra-*n*-octyloxide	[3061-42-5]	$Ti(OC_8H_{17})_4$		214_{133}	$n^{20}{}_D$ 1.4810, $d^{20}{}_4$ 0.9339 g/cm^3, dipole moment 5.68×10^{-30} cm
titanium tetra-2-ethylhexyloxide	[1070-10-6]	$Ti(OCH_2C_2H_5CHC_4{-}H_9)_4$	<-25	$248{-}249_{1467}$	$n^{35}{}_D$ 1.4750
titanium tetra-nonyloxide	[6167-42-6]	$Ti(OC_9H_{19})_4$		$264{-}265_{200}$	$n^{20}{}_D$ 1.4785, $d^{20}{}_0$ 0.9241 g/cm^3, dipole moment 5.60×10^{-30} C·m
titanium tetra-*n*-decyloxide		$Ti(OC_{10}H_{21})_4$	68	265_{27}	$d^{25}{}_4$ 0.87 g/cm^3, η_{25} 76.0 mPa·s(=cP)
titanium tetra-isooctyloxide		$Ti(OC_8H_{17})_4$		235_{13}	$d^{25}{}_4$ 0.940
		Aryloxides			
titanium tetra-isobornyloxide	[84215-64-5]	$Ti(OC_{10}H_{17})_4$			
titanium tetra-benzhydryloxide	[84215-65-6]	$Ti(OCH(C_6H_5)_2)_4$	57–59		

titanium tetra-oleyloxide	[26291-85-0]	$Ti(OC_{18}H_{35})_4$		288_{13}	$d^{20}{}_4$ 0.87 g/cm^3
titanium tetraphenoxide	[2892-89-9]	$Ti(OC_6H_5)_4$	153–154	267_{40}	orange-red solid
titanium tetra-*o*-chlorophenoxide	[22922-75-4]	$Ti(OC_6H_4Cl)_4$	145.5–147		red solid
titanium tetra-*p*-chlorophenoxide	[13438-75-0]	$Ti(OC_6H_4Cl)_4$	84–86		
titanium tetra-*o*-nitrophenoxide	[55535-59-6]	$Ti(OC_6H_4NO_2)_4$	154–158		shiny black solid
titanium tetra-*p*-nitrophenoxide	[22922-76-5]	$Ti(OC_6H_4NO_2)_4$	97		grayish black solid
titanium tetra-*o*-methylphenoxide	[22922-73-2]	$Ti(OC_6H_4CH_3)_4$	48–51		
titanium tetra-*m*-methylphenoxide	[22949-88-0]	$Ti(OC_6H_4CH_3)_4$		$323–325_{40}$	red crystalline solid
titanium tetra-1-naphthyloxide	[84215-66-7]	$Ti(OC_{10}H_7)_4$		[c]	
titanium tetra-2-naphthyloxide	[36452-22-9]	$Ti(OC_{10}H_7)_4$	60–64	[c]	
titanium tetra-resorcinyloxide	[34075-40-6]	$Ti(O_2C_6H_4)_2$			black solid
titanium tetra-stearyloxide		$Ti(OC_{18}H_{37})_4$			
titanium tetra-2,4,6-trinitrophenoxide	[84215-67-8]	$Ti(OC_6H_2(NO_2)_3)_4$			dark-brown solid

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[a] Subscripted values are pressure in Pa. To convert Pa to mm Hg, divide by 133.

[b] To convert C·m to D, divide by 3.336×10^{-30}.

[c] Does not distill.

rate of hydrolysis decreases. Titanium methoxides, aryloxides, and C-10 and higher alkyl titanates are hydrolyzed much more slowly.

In a limited amount of water, the first product of hydrolysis is the monohydroxy ester, which cannot be isolated because it immediately reacts with another alkyl titanate to give a μ-oxo dimer:

$$(RO)_3Ti\text{–}OR + H_2O \longrightarrow (RO)_3Ti\text{–}OH$$
$$(RO)_3Ti\text{–}OH + (RO)_4Ti \longrightarrow (RO)_3Ti\text{–}O\text{–}Ti(OR)_3 + ROH$$

Further addition of water leads to the stepwise formation of a whole range of condensation polymers. Initially, condensation most likely occurs at the less-hindered terminal ends forming linear oligomers. For example, TYZOR BTP [9022-96-2] is believed to be a linear C-8 oligomer. It is a viscous liquid soluble in hydrocarbon and alcohol solvents (19–21). Further condensation most likely leads to branching and the products become insoluble. Ultimately, hydrous titanium oxides are formed, although complete hydrolysis to TiO_2 is difficult to achieve without heating the reaction mixture.

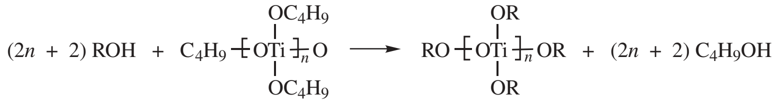
The less branched, more associated tetraalkyl titanates are more slowly hydrolyzed because titanium is more fully coordinated. The hydrolysis of tetraethyl titanate has also been considered in terms of its trimeric form:

$$2\,Ti_3(OC_2H_5)_{12} + 4\,H_2O \longrightarrow Ti_3(OC_2H_5)_8(O)_4Ti_3(OC_2H_5)_{11}$$

Several excellent reviews discussing the hydrolysis of tetraalkyl titanates are available (20,22–25).

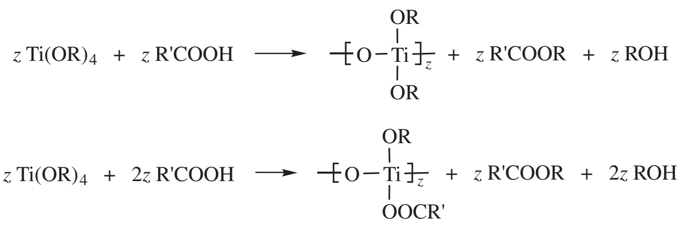
Complexing ligands have been shown to act as inhibitors to hydrolysis of tetraalkyl titanates due to chelate bond formation and stertic effects (26). Complexes of stronger ligands, eg, acetylacetone, are more hydrolytically stable than those of weaker ligands, eg, ethylacetoacetate (27).

Higher aliphatic alcohol and phenolic group-containing polytitanates may be prepared by transesterification of TYZOR BTP (28).



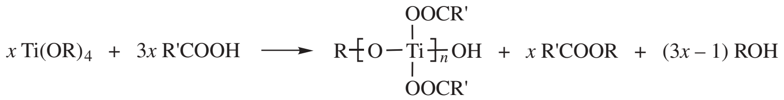
$$(2n + 2)\,ROH + C_4H_9\text{-}\Big[O\underset{OC_4H_9}{\overset{OC_4H_9}{Ti}}\Big]_nO \longrightarrow RO\text{-}\Big[O\underset{OR}{\overset{OR}{Ti}}\Big]_nOR + (2n + 2)\,C_4H_9OH$$

Titanoxanes can also be prepared by reaction of a tetraalkyl titanate and carboxylic acids (29). If the ratio of carboxylic acid to tetraalkyl titanate is 1:1, a simple polymeric titanate ester is formed. If two or more moles of acid are used per mole of tetraalkyl titanate, the resulting polymeric titanate ester contains ester carboxylate groups.



$$z\,Ti(OR)_4 + z\,R'COOH \longrightarrow \Big[O\text{–}\underset{OR}{\overset{OR}{Ti}}\Big]_z + z\,R'COOR + z\,ROH$$

$$z\,Ti(OR)_4 + 2z\,R'COOH \longrightarrow \Big[O\text{–}\underset{OOCR'}{\overset{OR}{Ti}}\Big]_z + z\,R'COOR + 2z\,ROH$$



$$x\,\mathrm{Ti(OR)_4} + 3x\,\mathrm{R'COOH} \longrightarrow \mathrm{R}\left[\mathrm{O}-\underset{\mathrm{OOCR'}}{\overset{\mathrm{OOCR'}}{\mathrm{Ti}}}\right]_n\mathrm{OH} + x\,\mathrm{R'COOR} + (3x-1)\,\mathrm{ROH}$$

Similar ester carboxylate group containing polymeric titanate esters are obtained by the reaction of titanoxanes with carboxylic acids (30), by reaction of a tetraalkyl titanate with a carboxylic acid and 1–2 mol of water (31), or by reacting a polymeric titanium acylate with a higher boiling carboxylic acid and removing the lower boiling carboxylic acid by distillation (32).

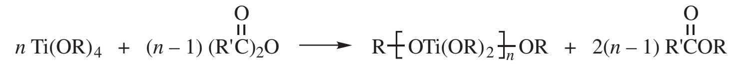
Titanoxanes can also be prepared by pyrolysis of tetraalkyl titanates at 200–250°C. Higher temperatures, however, can lead to thermal decomposition.

$$2(n\mathrm{-C_4H_9O})_4\mathrm{Ti} \longrightarrow (n\mathrm{-C_4H_9O})_3\mathrm{TiOTi(O}n\mathrm{C_4H_9)_3}+n\mathrm{-C_4H_9OH} + \mathrm{C_4H_8}$$

Oxidation of Ti(III) alkoxides also gives pure dimers (33):

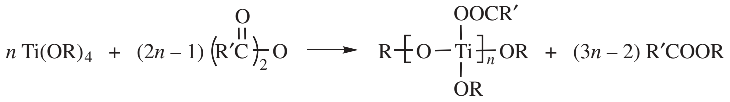
$$4\ (\mathrm{RO})_3\mathrm{Ti} + \mathrm{O_2} \longrightarrow 2\ (\mathrm{RO})_3\mathrm{TiOTi(OR)_3}$$

Alternatively, titanoxanes can be prepared by reaction of tetraalkyl titanates with carboxylic acid anhydrides (34):



$$n\,\mathrm{Ti(OR)_4} + (n-1)\,(\mathrm{R'}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}})_2\mathrm{O} \longrightarrow \mathrm{R}\left[\mathrm{OTi(OR)_2}\right]_n\mathrm{OR} + 2(n-1)\,\mathrm{R'}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR}$$

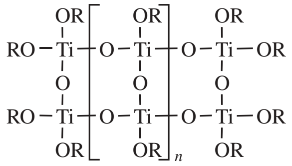
If more than one acid anhydride group per mole of tetraalkyl titanate is used, a polytitanyl acylate is formed as follows:

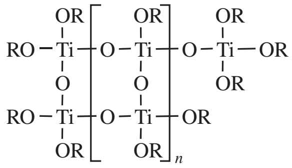


$$n\,\mathrm{Ti(OR)_4} + (2n-1)\left(\mathrm{R'}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\right)_2\mathrm{O} \longrightarrow \mathrm{R}\left[\mathrm{O}-\underset{\mathrm{OR}}{\overset{\mathrm{OOCR'}}{\mathrm{Ti}}}\right]_n\mathrm{OR} + (3n-2)\,\mathrm{R'COOR}$$

The polymeric acyl titanate esters are viscous liquids or waxes that are soluble in hydrocarbon solvents and can be used as $\mathrm{TiO_2}$-dispersing agents, water-repellent agents for textile fabrics, and rust inhibitors for steel.

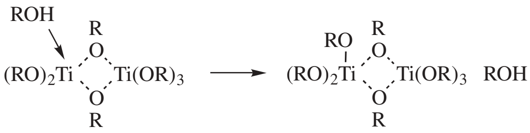
Organic solvent soluble, higher molecular weight polytitanoxanes, having a proposed rudder-shaped structure, can be prepared by careful addition of an alcohol solution of 1.0–1.7 mol of water per mole of tetraalkyl titanate, followed by distillation of the low boiling alcohol components. Polytitanoxanes having molecular weights up to 20,000 have been prepared by this method (35).





Substitution of some of the alkoxy groups on the polytitanoxanes with glycols, β- diketones, or β-ketoesters, fatty acids, diester phosphates or pyrophosphates, and sulfonic acids gives a group of products that are very effective surface-treating agents for carbon black, graphite, or fibers (36).

Reactions with Alcohols. The tendency of titanium(IV) to reach coordination number 6 accounts for the rapid exchange of alkoxy groups with alcohols. Departure of an alkoxy group with the proton is the first step in the ultimate exchange of all four alkoxyls. The four-coordinated monomer is expected to react



more rapidly than the dimer. The process is very fast, as evidenced by nmr studies at room temperature, which show no difference in chemical shift between free ROH and combined ROTi. At sufficiently lower temperatures, both kinds of alkoxyl can be seen (37).

For preparative purposes, the equilibrium must be shifted either by using an excess of the exchanging alcohol or by distilling away the more volatile lower alcohol. The TYZOR TPT is the preferred starting ester because of the low boiling point of isopropyl alcohol. Monohydric alcohols of varying complexity, diols and polyols, phenols, alkanolamines, and the enolic forms of β-diketones and β-ketoesters all react readily with TYZOR TPT. Often all four alkoxy groups can be interchanged.

Reactions with Esters. Ester interchange catalyzed by titanates is an important industrial reaction (38).

$$\mathrm{RCOOR' + R''OH \rightleftharpoons RCOOR'' + R'OH}$$

One commercial example is the formation of basic methacrylates from dialkylaminoethanols and methyl methacrylate:

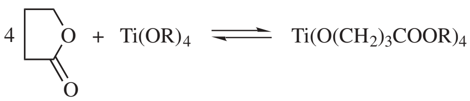
$$\mathrm{R_2NCH_2CH_2OH + CH_3OCOCCH_3{=}CH_2 \rightleftharpoons R_2NCH_2CH_2OCOCCH_3{=}CH_2 + CH_3OH}$$

The same reaction can be used to convert one alkoxide to another by distillation of a lower boiling ester:

$$\mathrm{Ti(OCH(CH_3)_2)_4 + 4\ CH_3COOC_4H_9 \rightleftharpoons Ti(OC_4H_9)_4 + 4\ CH_3COOCH(CH_3)_2}$$

Titanium-catalyzed ester interchange can be used to prepare polyesters from diester and diols as well as from diacids and diols at considerably higher temperatures. Polymer chains bearing pendant ester and hydroxy functions can be cross-linked with titanates.

Reaction with Lactones. Hydroxycarboxylic acid ester complexes of titanium are formed by reaction of a tetraalkyl titanate with a lactone, such as β-propiolactone, γ-butyrolactone, or valerolactone (39). For example,



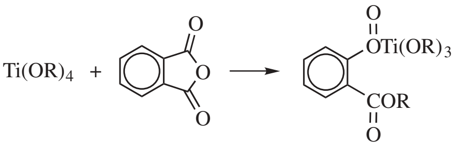
Reactions with Acids. Organic acids form acylates when heated with tetraalkyl titanates. Best results are obtained using only 1 or 2 mol of acid, as attempts to force the reaction with 3 or 4 mol of acid can yield polymers.

$$n\,\mathrm{RCOOH} + \mathrm{Ti(OR')_4} \longrightarrow \mathrm{(RCOO)}_n\mathrm{Ti(OR')}_{4-n} + n\,\mathrm{R'OH}$$

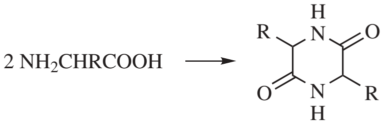
With acid anhydrides, the exothermic reaction yields similar products, subject to the limitation on n. For higher anhydride ratios, condensed acylates form. If $n = 3$, the result is $\mathrm{(R'OTi(OOCR)_2)_2O}$; if $n = 4$, then $\mathrm{((RCOO)_3Ti)_2O}$ forms.

$$n\,\mathrm{(RCO)_2O} + \mathrm{Ti(OR')_4} \longrightarrow \mathrm{(RCOO)}_n\mathrm{Ti(OR')}_{4-n} + n\,\mathrm{RCOOR'}$$

Phthalic anhydride does not give a cyclic product:



Reactions with α-Amino Acids. On heating 2 mol of an α-amino acid, eg, alanine, in the presence of a tetraalkyl titanate and an alcohol, reaction that gives a 2,5-piperazinedione and an oxytitanate occurs (40).



Reactions with Salicylaldehydes. Tetraalkyl titanates react in benzene with salicylaldehyde in a 1:1 or 1:2 molar ratio to give salicylaldehydotrialkoxy and dialkoxy products, which when heated at reflux seem to undergo a Meewein-Ponndorf reaction to give an aldehyde derived from the alcohol group on the titanate and a reduced titanate complex (41):

$$\mathrm{Ti(OR)_4} + n\,\mathrm{C_6H_4OHCHO} \longrightarrow \mathrm{(RO)}_{4-n}\mathrm{Ti(C_6H_4OCHO)}_n + n\,\mathrm{ROH} \longrightarrow$$
$$n\,\mathrm{R'CHO} + \mathrm{(RO)}_{4-2n}\mathrm{Ti(C_6H_4OCH_2O)}_n$$

Reactions with Isocyanates. TYZOR TPT catalyzes the trimerization of isocyanates and polyisocyanates to isocyanurates and polyisocyanurates (42).

Titanium alkoxides of the type Cl_3TiOR initiate the living polymerization of isocyanates. Polyisocyanates possessing controlled molecular weights and narrow polydispersities can be synthesized using these catalysts (43):

$$\mathrm{R{-}N{=}C{=}O} + \mathrm{Cl_3TiOR} \longrightarrow \left(\mathrm{C{=}ONR} \right)_n$$

Thermolysis. Lower tetraalkyl titanates are reasonably stable and can be distilled quickly at atmospheric pressure. Protracted heating forms condensation polymers plus, usually, alcohol and alkene. Longer or more branched chains are less stable. Thus, tetra-n-pentyl titanate [10585-24-7] can be distilled at 314°C and 101.3 kPa (1 atm), whereas tetra-n-hexyl titanate [7360-52-3] must be distilled at $<$18.7 kPa (140 mmHg) and tetra-n-hexadecyl titanate [34729-16-3] cannot be distilled even under high vacuum. Unsaturated groups, as in the allyloxide, also decrease thermal stability.

Thermolysis is used in the coating of glass and other surfaces with a film of titanium dioxide. When a lower alkoxide, eg, TYZOR TPT, vaporizes in a stream of dry air and is blown onto hot glass bottles above ~500°C, a thin, transparent protective coating of TiO_2 is deposited.

Production and Economic Aspects. The 2004 world production of organic titanates is estimated to be 15,000–16,000 metric tons, some of which is for captive use. Principal producers in the United States are DuPont and Kenrich Petrochemicals; in the United Kingdom, Johnson Matthey PLC; in Japan, Nippon Soda, Matsumoto Trading, and Mitsubishi Gas Chemicals; in India, Synthochem; and in China, Liantian.

The products offered commercially in the United States include a variety of tetraalkyl titanates, chelates thereof, and simple and complex acylates. Prices of some of these are listed in Table 2.

The alkoxides are manufactured by a modification of the classical Nelles process, in which $TiCl_4$ in an inert solvent, eg, heptane, is treated with a monohydric lower alcohol (44). If the hydrogen chloride by-product is expelled by heating or by sweeping with dry nitrogen, the product is the dialkoxydichlorotitanate (45,46). Expulsion of hydrogen chloride is facilitated by adding the required alcohol gradually with continuous sweep (47). An acid acceptor is required to obtain the tetraalkoxide; ammonia is preferred because of its low cost. In a variation, $TiCl_4$ in an inert solvent is converted to the ammine $TiCl_4 \cdot 8\,NH_3$. This ammine

Table 2. **Titanium Alkoxides and Chelates**

Products	CAS Registry Number
Alkoxides	
tetraisopropyl titanate	[546-68-9]
tetra-n-butyl titanate	[5593-70-4]
tetra-2-ethylhexyl titanate	[1070-10-6]
Chelates	
bis(triethanolamine) titanate	[36673-16-2]
diisopropoxy bis(acetylacetone)titanate	[17927-72-9]
bis(ethylacetoacetate) titanate	[27858-32-8]
bis(lactic acid) titanate	[65104-06-5]

reacts with almost any alcohol, yielding the tetraalkoxide. This operation can be performed in a continuous process (48,49). Higher alkoxides are readily prepared from TYZOR TPT or TYZOR TnBT by alcohol interchange (transesterification), with removal of the by-product isopropyl alcohol or *n*- butanol by distillation.

Chelated titanates are made simply by mixing the chelating agent with TYZOR TPT or another titanium alkoxide. The liberated alcohol is usually left in the product to maintain the product's fluidity. It may, however, be removed by distillation, if desirable. Organic titanates are normally shipped in 208-L drums, totes, cylinders, or tank trucks. Most titanates are moisture-sensitive and must be handled with care, preferably under dry nitrogen.

2.5. Alkoxy Halides. Titanium alkoxy halides have the formula $Ti(OR)_nX_{4-n}$, where R may be alkyl, alkenyl, or aryl, and X is F, Cl, or Br, but not I.

2.6. Properties. Alkoxytitanium fluorides and chlorides are colorless or pale-yellow solids or viscous liquids that darken on standing, especially in the light. Bromides are yellow crystalline solids. Aryloxytitanium halides are orange-to-red solids. The alkoxy halides are hygroscopic. Most dissolve in water without immediate decomposition, but hydrolyze slowly to hydrogen halide, alcohol, alkyl halide, and hydrous titanium dioxide. Using less than one mole of water, poly(alkoxytitanium) compounds can be prepared if the liberated hydrogen halide is neutralized by ammonia. Primary alkoxy halides are thermally stable, although they disproportionate on heating. Secondary and tertiary alkoxy halides decompose gradually on standing (more rapidly on heating) yielding alkyl halides, polymers, and titanium oxychloride. Physical properties of some alkoxytitanium halides are shown in Table 3.

2.7. Synthesis. Titanium alkoxy halides are intermediates in the preparation of alkoxides from a titanium tetrahalide (except the fluoride) and an alcohol or phenol. If $TiCl_4$ is heated with excess primary alcohol, only two chlorine atoms can be replaced and the product is dialkoxydichlorotitanium alcoholate, $(RO)_2TiCl_2 \cdot ROH$. The yields are poor, and some alcohols, eg, allyl, benzyl, and *tert*-butyl alcohols, are converted to chlorides (50). Using excess $TiCl_4$ at 0°C, the trichloride $ROTiCl_3$ is obtained nearly quantitatively, even from *sec*- and *tert*-alcohols (51,52).

For phenols, the number of chlorines replaced depends in part on the acidity of the phenol. Under mild conditions, phenol or *m*-nitrophenol displaces only one chlorine from $TiCl_4$, whereas *p*-chlorophenol, *o*-nitrophenol, *p*-nitrophenol, picric acid, or 2-naphthol gives $(ArO)_2TiCl_2$. If the mixtures are heated sufficiently, eg, in refluxing phenol, all four chlorines can be displaced(53–56).

Tetraalkoxides can be cleaved by hydrogen chloride or bromide in an inert solvent. Dialkoxytitanium dichloride is obtained as an alcoholate (57):

$$Ti(OR)_4 + 2\,HX \longrightarrow Ti(OR)_2X_2 \cdot ROH + ROH$$

The same products may be made from primary alkoxides by the violent reaction with elementary chlorine or bromine. A radical mechanism has been proposed to account for the oxidation of some of the alkoxy groups (58):

$$Ti(OCH_2R)_4 + X_2 \xrightarrow{[O]} Ti(OCH_2R)_2X_2 \cdot RCH_2OH + 0.5\,RCOOCH_2R$$

Table 3. **Titanium(IV) Alkoxyhalides and Aryloxyhalides**

Compound	CAS Registry Number	Formula	Mp, °C	Bp,[a] °C	Other properties
titanium ethoxytrifluoride	[1524-67-0]	$TiOC_2H_5F_3$	220		
titanium ethoxytrichloride	[3112-67-2]	$TiOC_2H_5Cl_3$	80–81 dec	185–186	
titanium ethoxytribromide	[2489-72-8]	$TiOC_2H_5Br_3$	indefinite		
titanium diethoxydifluoride	[650-27-1]	$Ti(OC_2H_5)_2F_2$	115		
titanium diethoxydichloride	[3582-00-1]	$Ti(OC_2H_5)_2Cl_2$	40–50	142_{240}	
titanium diethoxydibromide	[3981-88-2]	$Ti(OC_2H_5)_2Br_2$	47–50	$95–105_{67}$	red solid
titanium triethoxyfluoride	[1868-77-5]	$Ti(OC_2H_5)_3F$	75–78	$162–163_{27}$	
titanium triethoxychloride	[3712-48-9]	$Ti(OC_2H_5)_3Cl$		176_{240}	dipole moment, 9.57×10^{-30} C·m[b]
titanium propoxytrichloride	[7569-98-4]	$TiOC_3H_7Cl_3$	65–66	$83–85_{147}$	
titanium isopropoxytrichloride	[3981-83-7]	$TiOC_3H_7\text{-}i\text{-}Cl_3$	78–79	65_{13}	
titanium dipropoxydichloride	[1790-23-4]	$Ti(OC_3H_7)_2Cl_2$	53–57	159_{240}	
titanium diisopropoxydibromide	[37943-35-4]	$Ti(OC_3H_7\text{-}i)_2Br_2$		$100–102_{27}$	yellow solid

titanium triisopropoxyfluoride	[757-61-9]	$Ti(OC_3H_7\text{-}i)_3F$	83–85	$140–150_{80}$	
titanium tripropoxychloride	[24287-11-4]	$Ti(OC_3H_7)_3Cl$		168_{160}	$d^{25}{}_4$ 1.1348 g/cm^3
titanium butoxytrichloride	[3112-68-3]	$TiOC_4H_9Cl_3$	67.5–70	$124–127_{540–567}$	
titanium isobutoxytrichloride	[17754-61-9]	$TiOC_4H_9\text{-}i\text{-}Cl_3$	81–83	$92–94_{120}$	
titanium dibutoxydichloride	[1790-25-6]	$Ti(OC_4H_9)_2Cl_2$	52–53	$146–147_{133}$	
titanium diisobutoxydichloride	[14180-16-6]	$Ti(OC_4H_9\text{-}i)_2Cl_2$		184_{213}	
titanium tributoxyfluoride	[84215-68-9]	$Ti(OC_4H_9)_3F$	45–48	$175–180_{27}$	
titanium tributoxychloride	[4200-76-4]	$Ti(OC_4H_9)_3Cl$		$154–155_{27}$	$n^{20}{}_D$ 1.5169, $d^{20}{}_4$ 1.0985 g/cm^3
titanium triisobutoxychloride	[52027-15-3]	$Ti(OC_4H_9\text{-}i)Cl$		125_{27}	$n^{20}{}_D$ 1.5158, $d^{20}{}_4$ 1.1043 g/cm^3
titanium phenoxytrichloride	[4403-68-3]	$TiOC_6H_5Cl_3$			dark-red crystalline solid; dipole moment, 9.91×10^{-30} C·m[b]
titanium diphenoxydichloride	[2234-06-2]	$Ti(OC_6H_5)_2Cl_2$	116		reddish brown solid
titanium triphenoxychloride	[4401-43-8]	$Ti(OC_6H_5)_3Cl$		265_{53}	
titanium tri-*o*-xylenoxychloride	[84501-82-6]	$Ti((CH_3)_2C_6H_5O)_3Cl$		480_{27}	

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[a] Subscripted values are pressure in Pa. To convert Pa to mm Hg, divide by 133.

[b] To convert C·m to D, divide by 3.336×10^{-30}.

More useful than the preceding methods is cleavage of alkoxides by acetyl chloride or bromide. One, two, three, or four alkoxyls can be replaced by chloride or bromide. Benzoyl chloride gives poor yields, however. The tri- and tetrachlorides, which are stronger Lewis acids than mono- and dichlorides, coordinate with the alkyl acetate formed and yield distillable complexes (50,59,60).

$$\mathrm{Ti(OR)_4} + n\ \mathrm{CH_3COX} \longrightarrow \mathrm{Ti(OR)_{4-n}X_n} + n\ \mathrm{CH_3COOR}$$

A very useful method is the proportionation of alkoxides with a stoichiometric quantity of titanium tetrachloride or bromide, preferably in an inert hydrocarbon solvent (59,61), as follows, where n is 1, 2, or 3:

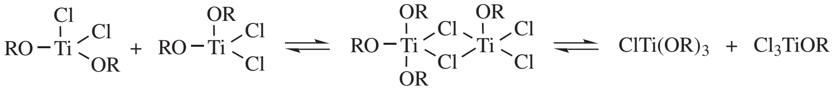
$$n\,\mathrm{Ti(OR)_4} + (4-n)\ \mathrm{TiCl_4} \longrightarrow 4\ \mathrm{Ti(OR)_nCl_{4-n}}$$

Alkoxy fluorides are prepared using acetyl fluoride. Alternatively, antimony trifluoride can be used to replace one alkoxyl by fluorine (62):

$$3\,\mathrm{Ti(OR)_4} + \mathrm{SbF_3} \longrightarrow 3\ \mathrm{Ti(OR)_3F} + \mathrm{Sb(OR)_3}$$

Titanium tetrafluoride reacts with $\mathrm{Ti(OR)_4}$ in a manner similar to $\mathrm{TiCl_4}$, especially if pyridine is present.

A principal use for the alkoxy halides is their reaction with organolithium or -magnesium compounds, R′M, in a Wurtz-type reaction to form compounds having carbon–titanium bonds. For this purpose, it is inconvenient that proportionation is reversible, and that the products $\mathrm{Cl_2Ti(OR)_2}$ and $\mathrm{ClTi(OR)_3}$ disproportionate on vacuum distillation. This occurs because the alkoxyhalides tend to satisfy their coordination needs through bridge structures, in which the halogen and alkoxyl readily interchange:



This can be prevented by supplying external electron pairs to satisfy the coordination needs of titanium. The strong base piperidine serves well, and a wide variety of compounds, $\mathrm{Ti(OR)_nCl_{4-n}\cdot C_5H_{10}NH}$, can be prepared (63). Alcohols and pyridine are also effective.

In a given $\mathrm{(RO)_nTiCl_{4-n}}$, the alkoxy group can be exchanged by a higher alcohol if the resulting lower alcohol is removed by distillation (64). In the intermediate, HOR departs much more easily than HCl.

3. Chelates

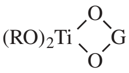
Titanium chelates are formed from tetraalkyl titanates or halides and bi- or polydentate ligands. One of the functional groups is usually alcoholic or enolic hydroxyl, which interchanges with an alkoxy group, RO, on titanium to liberate ROH. If the second function is hydroxyl or carboxyl, it may react similarly. Diols and polyols, α- hydroxycarboxylic acids and oxalic acid are all examples of this type. β-Keto esters, β- diketones, and alkanolamines are also excellent chelating ligands for titanium.

3.1. Glycol Titanates. Primary diols (HOGOH), eg, ethylene glycol and 1,3-propanediol, react by alkoxide interchange at both ends, yielding insoluble, white solids that are polymeric in nature(19,65–67):

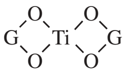
$$(RO)_4Ti + HOGOH \longrightarrow (RO)_3TiOGOTi(OR)_3 \longrightarrow (RO)_3TiOGOTi(OR)_2OGOTi(OR)_3$$
$$\longrightarrow (RO)_3TiOGO(RO)Ti\big(OGOTi(OR)_3\big)_2 \longrightarrow \text{etc}$$

The 1:1 molar addition products of a primary diol and a tetraalkyl titanate, $Ti(OGO)(OR)_2$ may react with water to give either $Ti(OGO)(OH)_2$ or condensed products $(Ti(OGO)O)_n$, which can be used as esterification catalysts (68). Single crystals of a $Ti(OCH_2CH_2O)_2$ titanium glycolate complex with a unique one-dimensional structure have been prepared by a hydrothermal method with careful control of pH (69). The structure is described as parallel chains built up from edge-sharing $Ti^{4+}O_6$ octahedra, where the oxygen atoms are associated with four ethylene glycol units and each ethylene glycol ligand bridges two titanium atoms with one of its oxygen atoms, the other being terminal.

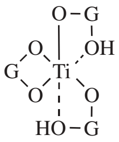
Where the glycol contains one or two secondary or tertiary hydroxyls, the products are more soluble and some are even monomeric cyclic chelates (70,71). Three compounds are obtained from 2-methylpentane-2,4-diol, depending on the mole ratio (72–75). Structure (**3**) represents an isolable but labile alcoholate of (**2**)(74).



(**1**)



(**2**)



(**3**)

The solvating glycol molecules can be driven off by heating. An alternative structure (**1**) has both hydroxyls of one HO−G−OH molecule involved in covalent bonds instead of one hydroxyl from each of two glycol molecules.

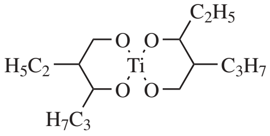
Soluble titanium glycolate complexes can also be prepared by reaction of either titanium dioxide or titanium orthoesters with glycol in the presence of alkali metal hydroxides (76). These complexes have been useful as polyesterification catalysts (77,78).

Solvent-soluble polymeric products of structures (**1**–**3**) can also be obtained upon reaction of tetraalkyl titanate, 2-methyl-*n*-pentane-2,4-diol, and water in a 2:4:1 molar ratio (79). The tetraprimary glycol titanate complexes have been used as catalysts for the production of polyisocyanurates and polyoxazolidones (80).

The complex Ti(2,4-dimethyl-2,4-pentanediolate)$_2$ has been shown by X-ray crystallography to be dimeric in nature in both the solid and gas phase (81).

Silanediols, eg, $(C_6H_5)_2Si(OH)_2$ and $HOSi(C_6H_5)_2OSi(C_6H_5)_2OH$, yield four- and six- membered rings with titanium alkoxides. Pinacols and 1,2-diols form chelates rather than polymers. The more branched the diol molecule, the more likely are its titanium derivatives to be soluble and even monomeric.

Reaction of 2,4-diorgano-1,3-diols, such as 2-ethylhexane-1,3-diol, with TYZOR TPT in a 2:1 molar ratio gives the solvent soluble titanate complex, TYZOR OGT [5575-43-9] (**4**) (82). If the reaction is conducted in an inert solvent, such as hexane, and the resultant slurry is treated with an excess of water, an oligomeric hydrolysis product, also solvent soluble, is obtained (83).

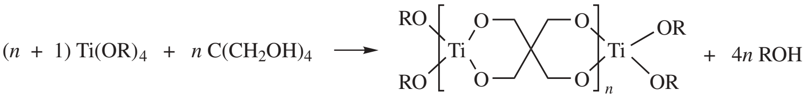


(**4**)

Products similar to (4) are obtained if one starts with $TiCl_4$ instead of a tetraalkyl titanate (84). These products are useful as adhesives (qv), as textile-treating agents to impart water repellency, and as coatings and sizes for treating paper.

The reaction products of TYZOR TPT with 2–4 mol of 1,3-diols having two to three alkyl substituents, eg, 2,2,4-trimethyl-1,3-pentanediol, gives complexes that could be used as cross-linking agents for hydroxy group containing powdered lacquer resins (85).

Highly cross-linked polyol polytitanates can be prepared by reaction of a tetraalkyl titanate with a polyol, such as pentaerythritol, followed by removal of the by-product alcohol (86). The isolated solids are high activity catalysts suitable for use in the preparation of plasticizers by esterification and/or transesterification reactions. The insoluble nature of these complexes facilitates their removal from the plasticizer resins.

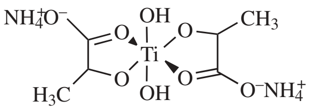


3.2. α-Hydroxycarboxylic Acid Complexes.

Water-soluble titanium lactate complexes can be prepared by reactions of an aqueous solution of a titanium salt, eg, $TiCl_4$, titanyl sulfate, or titanyl nitrate, with calcium, strontium, or barium lactate. The insoluble metal sulfate is filtered off and the filtrate neutralized using an alkaline metal hydroxide or carbonate, ammonium hydroxide, amine, or alkanolamine (87,88). Similar solutions of titanium lactate, malate, tartrate, and citrate can be produced by hydrolyzation of titanium salts, such as $TiCl_4$, in strongly (>pH 10) alkaline water, isolation of the titanium hydrate produced, followed by reaction of said hydride with an aqueous solution of the desired α-hydroxycarboxylic acid (89).

Solid, water-soluble α-hydroxycarboxylic acid and oxalic acid titanium complexes can be formed by reaction of the acid and a tetraalkyl titanate in an inert solvent, such as acetone or heptane. The precipitated complex is filtered, rinsed with solvent, and dried to give an amorphous white solid, which is water- and alcohol–water-soluble (90,91).

TYZOR LA [65104-06-5] (**5**), an aqueous solution of the ammonium salt of the titanium bis(lactate) complex, is prepared from 2 mol of lactic acid to one of TYZOR TPT. The by-product isopropyl alcohol is removed by distillation and the resultant solution is neutralized with ammonium hydroxide.



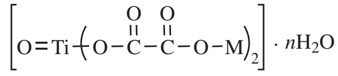
(**5**)

The structure of these products is uncertain and probably depends on pH and concentrations in solution. The hydroxyl or carboxyl or both are bonded to the titanium. It is likely that most, if not all, of these products are oligomeric in nature, containing Ti–O–Ti titanoxane bonds (90). Their aqueous solutions are stable at acidic or neutral pH. However, at pH ranges >9.0, the solutions readily hydrolyze to form insoluble hydrated oxides of titanium. The alkaline stability of these complexes can be improved by the addition of a polyol, such as glycerol or sorbitol (92). These solutions are useful in the textile, leather (qv), and cosmetics (qv) industries (see FIBERS).

Water-soluble, alkaline-stable ammonium or metal titanium malates and citrates can be formed by adding a tetraalkyl titanate to an aqueous solution of the ammonium or metal titanium malate or citrate (93). A typical formula is $M_xTiO(citrate)_x$, where M is NH_4, Na, K, Ca, or Ba.

The addition of an α-hydroxycarboxylic acid to a tetraethylene, propylene, diethylene, or hexylene glycol titanate gives water-soluble complexes suitable for gelling aqueous solutions of hydroxyl polymers, such as poly(vinyl alcohol) (PVA), or cellulose (qv) derivatives. These are useful as binding agents for glass fibers, clays (qv), and paper coatings (94).

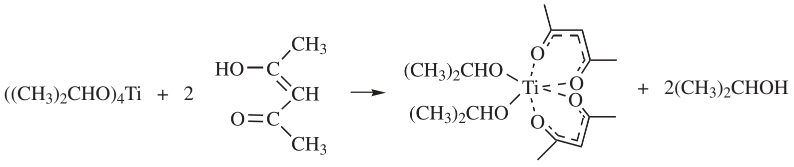
Oxalic acid behaves as an α-hydroxy acid, yielding crystalline ammonium or potassium salts from either aqueous titanium(IV) solutions or tetraalkyl titanates (95). These are written as:



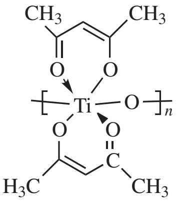
$$\left[O{=}Ti\left(O-\overset{O}{\overset{\parallel}{C}}-\overset{O}{\overset{\parallel}{C}}-O-M\right)_2\right]\cdot nH_2O$$

Dicarboxylic acids, eg, succinic or adipic, do not dissolve titanic acid. A phthalate has been prepared by adding acidic titanium sulfate solution to sodium phthalate solution.

3.3. β-Diketone Chelates. β-Diketones, reacting as enols, readily form chelates with titanium alkoxides, liberating in the process 1 mol of an alcohol. TYZOR AA [17927-72-9] (**6**) is the product mixture from TYZOR TPT and 2 mol of acetylacetone (acac) reacting in the enol form. The isopropyl alcohol is left in the product (96). The dotted bonds of structure 6 indicate electron delocalization. The chelate may be isolated by careful vacuum stripping of the residual isopropyl alcohol, but if the distillation is pushed, an oligomeric titanoxane (**7**) forms.



(**6**)



(**7**)

The six-coordinated titanium(IV) compounds, $Ti(acac)_2(X)_2$, where X is methoxy, ethoxy, isopropoxy, *n*-butoxy, or chloro and acac = acetylacetonat, all adopt the cis configuration. This is believed to result from the ligand-to-metal π-electron donation (97,98).

The orange-red titanium acetylacetone chelates are soluble in common solvents. These compounds are coordinately saturated (coordination number equals 6) and thus much more resistant to hydrolysis than the parent alkoxides (coordination number 4). The alkoxy groups are the moieties removed by hydrolysis. The initial product of hydrolysis is believed to be the bis(hydroxy) bis (acetylacetone) titanate, $(HO)_2Ti(acac)_2$, which oligomerizes to a polytitanaoxane,

$$HO(Ti(acac)_2\text{-}O\,)_n\,H$$

Hydrolysis is slowest at ~pH 4.5 (99,100).

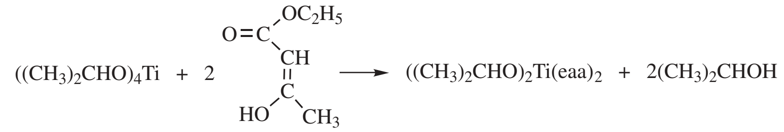
The addition of TYZOR AA to larger quantities of water results in precipitation of the polytitanaoxane as a yellow solid, which can be isolated and dried (101). The precipitation of this solid can be prevented by diluting the TYZOR AA with an equal volume of 10% aqueous acetic acid, and then 13 times the amount of a 1:1 mixture of isopropyl alcohol and water (102).

Alternatively, a water-stable bis(acetylacetone) titanate can be formed by replacing at least one of the alkoxy groups with an alkyloxyalkyleneoxy or alkyloxypolyalkyleneoxy group (103).

The TYZOR AA, which is a 75% isopropyl alcohol solution, is unstable in cold storage. The titanate complex precipitates from solution and causes handling difficulties. The addition of small amounts (0.05–0.15 mol water/mol titanate) of water gives a solution, TYZOR AA75, that is stable in cold-temperature storage (104).

The solvent-free mono-*n*-butyl, monoisopropyl bis(acetylacetone) titanate, TYZOR AA95 [9728-09-9], is a liquid at room temperature. By carefully controlling the mixture of alcohols used as solvent, a product, TYZOR GBA can be obtained, which is cold- storage-stable even in the presence of nucleating agents (105).

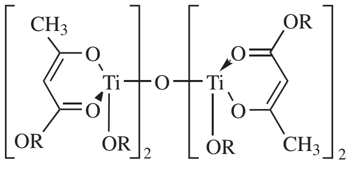
3.4. β-Ketoester Chelates. β-Ketoesters react in a fashion similar to the β-diketones. TYZOR DC [27858-32-8] is the light-yellow liquid that is produced by reacting TYZOR TPT and 2 mol of ethyl acetoacetate (eaa) followed by removal of the isopropyl alcohol. The bis(ethylacetoacetate) [20753-28-0] derived from the tetra-*n*-butyl titanate, and TYZOR IBAY [83877-91-2], the isobutoxy analogue, perform similarly to TYZOR DC in most applications. Both, however, have better cold-storage stability.



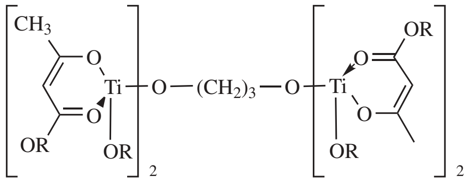
$$((CH_3)_2CHO)_4Ti + 2\ HOC(CH_3)=CHC(=O)OC_2H_5 \longrightarrow ((CH_3)_2CHO)_2Ti(eaa)_2 + 2(CH_3)_2CHOH$$

Beginning with a mixture of tetraalkyl titanates, the resultant bis(ethyl acetoacetate) contains a mixture of all possible combinations of alkoxy groups, resulting in a reduction in viscosity and improved cold-storage stability of the product (106).

Partial hydrolysis of TYZOR DC or the monoethylacetoacetate ester chelate, followed by removal of the isopropyl alcohol by-product, gives a dimeric μ-oxo chelate (**8**), which also has improved cold-temperature-storage stability (107).



(**8**)



(**9**)

Reaction of TYZOR DC and 1,3-propanediol gives titanium 1,3-propylenedioxide bis(ethyl acetoacetate) [36497-11-7], which can be used as a noncorrosive curing catalyst for room-temperature-vulcanizing silicone rubber compositions (108). Similar structures could be made, starting with titanium bis(acetylacetonates), such as that shown in structure (9).

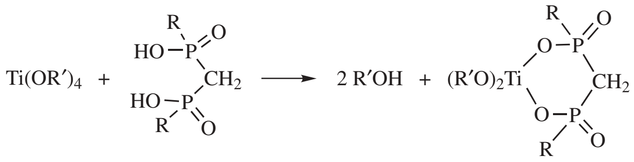
3.5. Titanium Phosphorous Containing Chelates. The reaction of a mixture of mono(alkyl)diacid orthophosphate, di(alkyl)monoacid orthophosphate, and $TiCl_4$ in a high boiling hydrocarbon solvent, such as heptane, with nitrogen-assisted evolution of liberated HCl, gives a mixture of titanium tetra (mixed alkylphosphate)esters, $(HO)(RO)O{=}PO)_nTi(OP{=}O(OR)_2)_{4-n}$ in heptane solution (109). A similar mixture can be prepared by the addition of 2 mol of P_2O_5 to 1 mol of $TiCl_4$ in the presence of 6 mol of alcohol:

$$2\,P_2O_5 + TiCl_4 + 6\,ROH \longrightarrow ((RO)_2P{=}OO)_2Ti(OP{=}O(OH)(OR))_2 + 4\,HCl$$

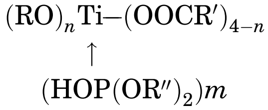
These mixed phosphate ester–titanium complexes or their amine salts are useful as fuel additives to help maintain cleanliness of carburetors and inhibit surface corrosion. Chloride-free mixed alcohol phosphate esters can be obtained if a tetraalkyl titanate is used (110).

Mixtures of mono- and diphosphoric acid react with tetraalkyl titanates, to form titanium phosphate complexes, which can be used as curing and adhesion promotion agents in printing inks. When reacted with potassium alkoxides via the sol–gel process, they can be used as precursors to potassium titanyl phosphate for use as ionic conductors, ion exchangers and in nonlinear optical applications (111–114).

Addition of 1 mol of *P,P′*-diphenylmethylenediphosphinic acid to tetraisopropyl titanate gives a chelated product, the solutions of which can be used as a primer coat for metals to enhance the adhesion of topcoats, eg, alkyds, polyalkyl acylates, and other polymeric surface coating products, and improve the corrosion resistance of the metal to salt water (115).



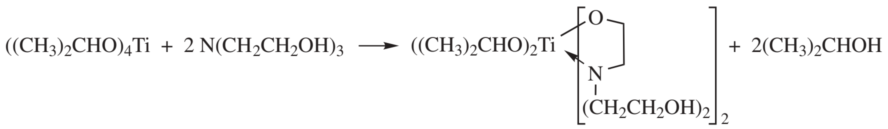
Alkoxy titanium acylate derivatives coordinated with a phosphite diester (phosphonate diester) can be prepared by reaction of a tetraalkyl titanate and an equal molar amount of a carboxylic acid, such as methacrylic acid or isostearic acid, and a phosphite or phosphonate diester, such as dibutyl hydrogen phosphite (116). These materials reduce the viscosity of a composite system, improve



$$\underset{(\mathrm{HOP(OR''})_2)m}{\overset{\uparrow}{(\mathrm{RO})_n\mathrm{Ti{-}(OOCR'})_{4-n}}}$$

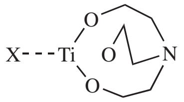
the dispersion of the filler in the composite system, and improve the mechanical properties of the cured composite system by modification of the surface of the filler.

3.6. Alkanolamine Chelates. Alkanolamine chelates, which are prepared by reaction of tetraalkyl titanates with one or more alkanolamines, are used primarily in cross-linking water-soluble polymers (qv) (117). The products are used in thixotropic paints, emulsion paints, in hydraulic fracturing and drilling of oil and gas wells, and in many other fields. The structure of



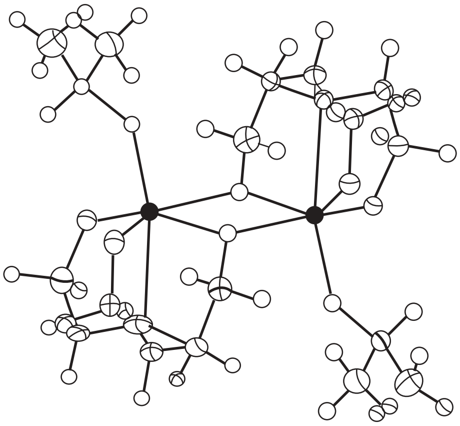
the product indicates that titanium has received electron pairs from both nitrogens to complete the coordination shell. No role is, however, ascribed to the four free hydroxyls. If the liberated isopropyl alcohol is left in place, the product is a mobile liquid; if the alcohol is removed, the product is a viscous, sticky, and doubtless oligomeric oil.

Titanatranes are titanium containing ring structures formed by reaction of an tetraalkyl- or chlorotitanate with an alkanolamine, such as triethanolamine (**10**).

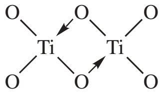


(**10**)

The 1-alkoxytitanatranes can be synthesized by the reaction of equimolar amounts of tetraalkyl titanates and triethanolamine (118). X-ray crystallographic analysis of the solid isolated from the reaction of 1 mol of triethanolamine and 1 mol of TYZOR TPT confirms the structure as a centrosymmetric dimer having a titanium/isopropoxy/nitrilotriethoxy ratio of 1:1:1. The titanium atoms have achieved a coordination number of 6 via a rather unsymmetrical titanium–oxygen bridge (119).

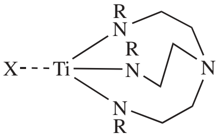


The structure of titanatranes has been shown by X-ray crystallography to be monomeric or dimeric dependent on the X group on the titanium (120,121). Each titanium atom in the dimer is bound by an O-bridge formed by sharing of electrons from an oxygen attached to the other titanium.



A variety of titanatranes can be formed by varying the X group from OR, OAr, OC=OR, $N(R)_2$, SR to cyclopentadienyl (122,123). Measurement of the ionization potential of the N–Ti bonding electrons indicates that the bonding interaction between N and Ti in titanatranes is weak (124). Flame spray pyrolysis of titanatranes or mixtures of titanatranes and aluminanes leads to formation of nano-TiO_2 (125) or nano alumina–titania mixtures (126).

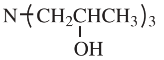
Azatitanatranes (11) can be synthesized in a similar fashion by reaction of a tetraalkyl titanate with N-substituted or unsubstituted tris-aminoalkylamines(14,127–129).



(**11**)

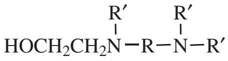
Mixtures of the monotriethanolamine titanate and polyols, eg, fructose and sorbitol, impart thixotropic properties to polymer-containing cement (130). A similar reaction of triethanolamine and tetraalkyl titanates previously treated with stearic acid gives the corresponding 1-acyloxytitatranes (131). Aqueous dispersions of these materials can be used to treat fabrics to impart a high degree of water repellency.

The diisopropoxy-bis(triethanolamine)titanate, TYZOR TE [36673-16-2], is an excellent cross-linker for aqueous solutions of hydroxyl-containing polymers. The reaction product of TYZOR TPT with a mixture of trialkanolamines and dialkanolamines or monoalkanolamines can be used to cure polyester-based powder coatings (132). Other ligands of this type include triisopropanolamine [122-20-3],



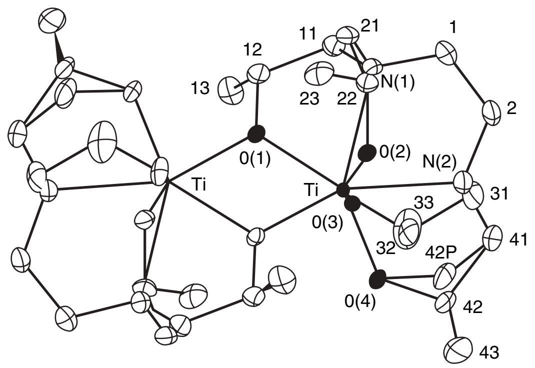
$$N\left(CH_2\underset{OH}{C}HCH_3\right)_3$$

and the general class



$$HOCH_2CH_2\overset{R'}{N}-R-\overset{R'}{N}-R'$$

where the R and R′ groups are alkyl, hydroxyalkyl, and aminoalkyl (133). The 1:1 molar addition product of TYZOR TPT and tetrakis[hydroxyisopropyl]-ethylenediamine, Quadrol [102-60-3] (12), has been isolated and shown by X-ray crystallography to consist of [(1,1′,1″,1‴-(ethylenedinitrilo)tetra-2-propoxy)titanium (IV)] dimers centered on crystallographic inversion centers. The titanium atom is seven coordinate, in which one oxygen from each triethanolamine chelate serves to bridge the titanium atoms (134).



(**12**)

The alkoxy titanate compounds formed by reaction of 1 mol of tetraalkyl titanate with 1 mol of a dialkanolamine are excellent esterification catalysts for the manufacture of phthalate-based plasticizers (135). If a 1:1 molar mixture of alkanolamine and water is used in place of the alkanolamine, oligomeric titanate complexes are formed, which have high catalyst activity and can be used as thixotropic additives in paints and other aqueous coating formulations (136).

The mono- and dialkanolamine titanates are water soluble and slowly hydrolyze at pH 9.0. Lowering the pH increases the rate of hydrolysis, which is shown by the development of turbidity. Turbidity also occurs above pH 11. The tetrahydroxyalkylethylenediamine titanate complexes form much more stable water solutions and can be used as dispersing agents for aqueous TiO_2 slurries (137).

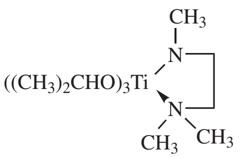
Addition of secondary chelating agents, polyols, eg, sorbitol or mannitol, and the strongly chelating α-hydroxycarboxylic acids, eg, citric or oxalic, prevents development of turbidity outside the pH range of 9–11 (138–140) .

These polyol-stabilized alkanolamine titanate solutions are used in a method to improve the wet strength of paper (138,141). The addition of 1–2 mol of a glycol ether, eg, methoxyethoxyethanol to TYZOR TE, gives either (monoalkoxy) (monoalkoxyalkylenoxy) bis(triethanolamine) titanates, or bis(alkoxyalkylenoxy) or bis-(triethanolamine) titanates, which also form stable aqueous solutions (142).

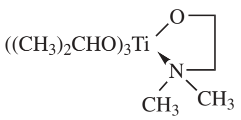
Similarly, the stability of aqueous solutions of monoacetylacetone or monotriethanolamine titanate complexes can be improved by the addition of glycol ethers (143). These solutions are useful in applications in which the catalytic cross-linking, or film-forming actions of titanates are desired to take place in aqueous systems.

The reactions of simpler alkanolamines with tetraalkyl titanates are not completely understood. Ethanolamine reacts with the lower tetraalkyl titanates to give insoluble white solids. *N*,*N*-Dialkylethanolamines, $R_2NCH_2CH_2OH$, react with TYZOR TPT and, depending on the mole ratio, yield all members of the family $[(CH_3)_2CHO]_{4-n}Ti(OCH_2CH_2NR_2)_n$, where $R = CH_3$ or C_2H_5 (144,145). When $R = CH_3$, all products are distillable (144); when $R = C_2H_5$, the products disproportionate on attempted distillation (145). All of these products are monomeric (ebullioscopy in benzene), which suggests that electron donation from nitrogen completes the coordination sphere of Ti. The compounds derived from $CH_3NHCH_2CH_2OH$ are dimeric crystalline solids.

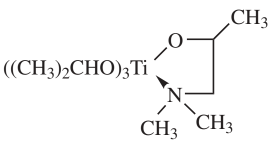
Products from aminoalcohols and TYZOR TPT were obtained by azeotroping the isopropyl alcohol with benzene (144,145). The reaction of trimethylethylenediamine, dimethylethanolamine, and dimethylisopropanolamine with TYZOR TPT, the orange (**13**), the yellow (**14**), and the pale-green (**15**) were obtained, respectively. The reaction of the lithium salt of the aforementioned ligands, prepared using C_4H_9Li, combined with $(RO)_3TiCl$ in hexane has also been described (146).



(**13**)



(**14**)



(**15**)

Compounds (13–15) are all five coordinated according to spectroscopic data (94,147).

3.7. Acylates.

Titanium acylates are prepared either from $TiCl_4$ or tetraalkyl titanates. Because it is difficult to obtain titanium tetraacylates, most compounds reported are either chloro- or alkoxyacylates. Under most conditions, $TiCl_4$ and acetic acid give dichlorotitanium diacetate [4644-35-3]. The best method involves passing preheated (136–170°C) $TiCl_4$ and acetic acid simultaneously into a heated chamber. The product separates as an HCl- free white powder (148):

$$TiCl_4 + 2\,HOOCCH_3 \longrightarrow Cl_2Ti(OOCCH_3)_2 + 2\,HCl$$

Alternatively, $TiCl_4$ reacts with a cold mixture of acetic acid and acetic anhydride to give a mixture of titanium chloroacetate complexes. If the mixture is heated, condensation occurs with elimination of acetyl chloride to yield hexaacetoxydititanoxane [4861-18-1] (149,150).

$$ClTi(OOCCH_3)_3 + Cl_2Ti(OOCCH_3)_2 \longrightarrow O(TiCl(OOCCH_3)_2) + CH_3COCl \xrightarrow{2(CH_3CO)_2O} O(Ti(OOCCH_3)_3)_2 + 2\,CH_3COCl$$

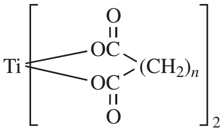
Trichlorotitanium monoacylates form, during thermal decomposition of $TiCl_4$, ester complexes (151):

$$TiCl_4{\cdot}RCOOR' \longrightarrow TiCl_3OOCR + R'Cl$$

Tetraacylates are prepared from titanium tetrabromide and excess carboxylic acid in an inert solvent. After solvent removal, the residue is heated to remove hydrogen bromide.

$$TiBr_4 + 4\,RCOOH \longrightarrow Ti(OOCR)_4 + 4\,HBr$$

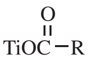
Tetraacylates have been prepared in this way from stearic, benzoic, cinnamic, and other acids, as well as from diacids, eg, succinic and adipic acids (16) (152). In some cases, $TiCl_4$ may also be used.

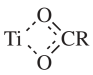


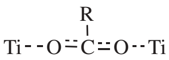
(16)

The usual products from alkoxides and acids are dialkoxytitanium diacylates (153,154). The third acyl group, but not the fourth, can often be introduced by azeotroping the lower alcohol with benzene (155). Using acetic anhydride, the same hexaacetoxydititanoxane is prepared from the chloride forms.

An acylate group is potentially a bidentate ligand. It may bond once or twice to one titanium, or bridge two titanium atoms as shown.



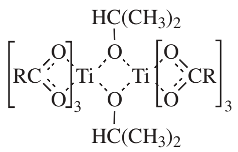




Dimeric (ebullioscopy in benzene)

$$(CH_3)_2CHOTi(O\overset{\overset{O}{\|}}{C}R)_3$$

has eight-coordinate Ti. If structure (**17**) is correct, isopropoxy is a better bridging ligand than acylate (155). This saturation of titanium coordination may explain the difficulty in preparing titanium tetraacylates by mild methods. Dimeric dichloro- and dibromotitanium diacylates exhibit three different carbonyl frequencies in the infrared (ir) region, ie, at 1650, 1540, and 1400 per cm, associated with three different types of bonding (156).



(**17**)

Heating of alkoxytitanium tris(2-ethylhexanoate) results in formation of oligomeric products and alkyl 2-ethylhexanoates(157)

$$Ti(R)(O_2CCH(Et)Bu)_3 \longrightarrow TiO(O_2CCH(Et)Bu)_2 + Bu(Et)COOR$$

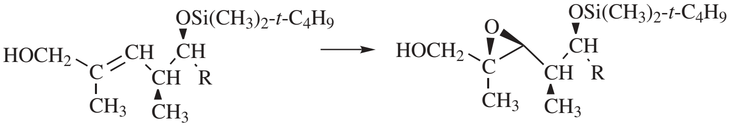
Water soluble titanate derivatives of carboxylic acids can be prepared by forming a mixture of a liquid or solid carboxylic acid in an inert solvent and reacting it with a tetraalkyl titanate, followed by precipitation the acyl titanate (158).

4. Titanium(IV) Complexes with Other Ligands

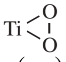
The d^0-titanium(IV) atom is hard, ie, not very polarizable, and can be expected to form its most stable complexes with hard ligands, eg, fluoride, chloride, oxygen, and nitrogen. Soft or relatively polarizable ligands containing second- and third-row elements or multiple bonds should give less stable complexes. The stability depends on the coordination number of titanium, on whether the ligand is mono- or polydentate, and on the method used to measure stability.

A partial list of ligands that bond to titanium(IV) includes sulfinates, $-OSOR$; sulfonates, $-OSO_2R$; peroxide, O_2^{2-}; superoxide, O_2; nitro groups, $-NO_2$; nitrites, $-ONO$; nitrates, $-ONO_2$; carbonate, CO_3^{2-}; phosphate, PO_4^{3-}; amide, $-NR_2$; acylamido, $-NRCOX$; Schiff base, $-N=CR_2$; N in a heterocyclic ring; azo, $-N=NR$; azido, $-N_3$; isocyanato, $-N=C=O$; isothiocyanato, $-N=C=S$; isoselenocyanato, $-N=C=Se$; alkanethio, $-SR$; arenethiol, $-SAr$; xanthato, $-SS=COR$; dialkyldithiocarbamato, $-SS=CNR_2$; tetrahydridoborato or borohydride, BH_4^-; trialkylsilyl, $-SiR_3$; and the corresponding Ge and Sn analogues. Phosphine, arsine, and stilbine ligands, as well as CO and hydride, associate only with lower valent titanium. Carbon ligands, eg, alkyl, aryl, dienyl, and cyclopentadienyl, give organometallic compounds. Early literature on many of these complexes has been reviewed (159).

4.1. Peroxide Titanate Complexes. Titanates may influence reactions of organic peroxides (see PEROXIDES AND PEROXIDES COMPOUNDS, ORGANIC PEROXIDES). For example, *tert*-butyl hydroperoxide epoxidizes olefins:



The ratio of syn-epoxide (shown above) to anti-epoxide is 10–25:1 with TYZOR TPT catalysis, whereas vanadylacetylacetonate is less selective and *m*-chloroperoxybenzoic acid gives the reverse 1:25 ratio. It is supposed that TYZOR TPT esterifies the free hydroxyl, then coordinates with the peroxide to favor syn-epoxidation (160). This procedure is related to that for enantioselective epoxidation of other allylic alcohols in 9–95% enantiomeric excess (ee) (160).

Titanates trigger peroxide-initiated curing of unsaturated polyesters to give products of superior color, compared to conventional cobalt -initiated curing (see INITIATORS, FREE–RADIAL) (161,162). Titanium coordinated to a porphyrin bonds hydrogen peroxides as  (163).

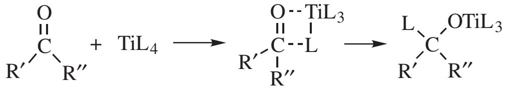
Hydrogen peroxide (qv) produces an intense yellow color with Ti(IV) in aqueous solution and has long been used as a qualitative test for Ti. Solid inorganic peroxides have been reported. The reaction of TYZOR TPT with a dilute solution of hydrogen peroxide and phosphoric acid generates a soluble titanate hydrolysis complex, which can be used to coat sheets of wood, paper, metal, glass, or plastics to form an hydrophilic surface (164). These hydrophilic sheets can be used in the formation of lithographic printing plates or color proofing elements.

4.2. Fluorocarbon Group Containing Titanium Complexes. Fluorocarbon groups containing carboxylic acids and alcohols, eg, perfluorooctanoic acid or 1*H*,1*H*,5*H*-octafluoropentanol, react with tetraalkyl titanates to give complexes that are useful either in the treatment of fabrics to render them water repellent (165,166), or as gasoline additives to minimize deposits and improve performance (167). Reaction of TYZOR TPT with a mixture of a fatty acid, eg, isovaleric acid, and a fluorinated carboxylic acid, eg, octafluoro-1*H*-pentanoic acid, produces a complex that is useful as a surface-treating agent for fillers used in polymeric composite applications (168).

Reaction of TYZOR TPT with polyperfluoroalkylene ethers containing a carbonyl group produces a complex that is an excellent surface-treating agent, imparting improved surface wettability and anticorrosion properties to metal surfaces (169). These complexes can be used by themselves, or as additives to perfluoropolyethers as vacuum pump oils, lubricant oils, or mold release agents.

The compound $C_8F_{17}CH_2CH_2O{\cdot}Ti(O\text{-}i\text{-}C_3H_7)_3$ is useful in car polishes to impart water repellency (170).

4.3. Chiral Titanium Complexes. Chiral titanium complexes are useful for the enantioselective addition of nucleophiles to carbonyl groups:

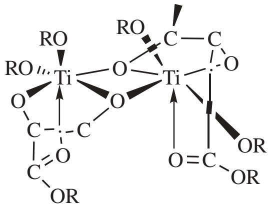


The advantages of titanium complexes over other metallic complexes is high selectivity, which can be readily adjusted by proper selection of ligands. Moreover, they are relative inert to redox processes. The most common synthesis of chiral titanium complexes involves displacement of chloride or alkoxide groups on titanium with a chiral ligand, L^*:

$$TiL_4 + L^* \longrightarrow TiL_3L^* + L$$

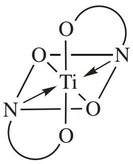
The chemistry of complexes having achiral ligands is based solely on the geometrical arrangement on titanium. Optically active alcohols are the most favored monodentate ligands. Cyclopentadienyl is also well suited for chiral modification of titanium complexes. Chiral titanium complexes of binaphthol (BINOL) and phenolic aromatic sulfonamides have been used to catalyze enantioselective alkylation of aldehydes with diethylzinc (171,172).

One of the most famous chiral titanium complexes is the Sharpless catalyst (**18**) (173,174), based on a diisopropyl tartarate complex. The nmr studies suggest that the complex is dimeric in nature (175,176). An excellent summary of chiral titanium complexes is available (177). More recent work suggests that an ion pair is involved in determining the stereoselectivity of the reaction (178). The yield and enantioselectivity of the epoxidation reaction can be improved by using polymer supported titanium complexes (179,180).

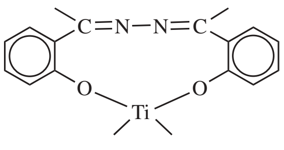


(**18**)

Other Complexes. The reaction of TYZOR TPT with 2 mol of a semicarbazone produces complex (**19**), the structure of which has been assigned the trans configuration (181):



(**19**)



(**20**)

Azines form an interesting class of nitrogen donor ligands, which can react in a 1:1 or 2:1 ratio with a tetraalkyl titanate to form complexes of stereochemical interest (**20**) (182).

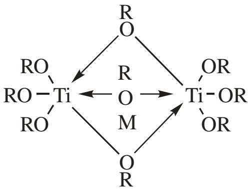
4.4. Composite Oxyalkoxides.

Composite oxyalkoxides can be prepared by reaction of tetraalkyl titanates and alkaline- earth metal hydroxides. These oxyalkoxides and their derivatives can be used as precursors to Ziegler-Natta catalysts (183) or hydrolyzed and thermally decomposed to give alkaline-earth metal titanates, eg, barium titanate (184).

$$\mathrm{M(OH)_2} + n\ \mathrm{Ti(OR)_4} \longrightarrow \left(\mathrm{MTiO_2(OR)_2}\right)_n + 2n\ \mathrm{ROH}$$

Barium titanate thin films can be deposited on various substances by treating with an aqueous solution containing barium salts and an alkanolamine-modified titanate, eg, TYZOR TE (185). In a similar fashion, reaction of a tetraalkyl titanate with an alkali metal hydroxide, eg, potassium hydroxide, gives oxyalkoxide derivatives $(\mathrm{KTi}_x\mathrm{O(OR)}_y)_n$, which can be further processed to give alkali metal titanate powders, films, and fibers (186–189). The fibers can be used as adsorbents for radioactive metals, eg, cesium, strontium, and uranium (190).

Addition of lithium or sodium alkoxide to TYZOR TPT gives a double alkoxide derivative, $\mathrm{MTi_2(OR)_9}$, the structure of which has been proposed (191) as follows, where M = Na or Li:

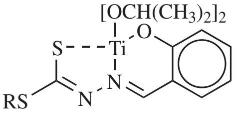


Hydrous metal oxide powders, eg, sodium titanate, $\mathrm{NaTi_2O_5H}$, can be prepared by treating TYZOR TPT with sodium hydroxide in methanol solvent to form a soluble intermediate, which is hydrolyzed in acetone–water to form an ion-exchange material useful in treating radioactive waste (192). Exchange of the sodium ion with an active metal, eg, Ni, Pt, or Pd, gives heterogeneous catalysts useful in olefin polymerization, coal liquification, and hydrotreating.

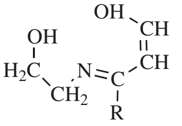
4.5. Titanium–Vanadium Mixed-Metal Alkoxides. Titanium–vanadium mixed-metal alkoxides, $\mathrm{VO(OTi(OR)_3)_2}$, are prepared by reaction of titanates, eg, TYZOR TnBT, with vanadium acetate in a high boiling hydrocarbon solvent. The by-product butyl acetate is distilled off to yield a product useful as a catalyst for polymerizing olefins, dienes, styrenics, vinyl chloride, acrylate esters, and epoxides (193,194).

4.6. Titanium Amides. The reaction of lithium amides, $\mathrm{LiNR_2}$, with $\mathrm{TiCl_4}$ gives tetrakisdialkylaminotitanates, $\mathrm{(R_2N)_4Ti}$, which can react with alcohols or other ligands to produce tetraalkyl titanates and chelated derivatives (195,196). The chlorotris(dialkylamino) titanates, $\mathrm{TiCl(NR_2)_3}$, are useful initiators for the polymerization of acrylic monomers to living polymers (197).

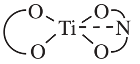
4.7. Schiff Bases. The nitrogen of a Schiff base unit in a polydentate ligand coordinates readily. Molecular mechanics calculations of titanium Shiff-base complexes having the general formula $\mathrm{Ti(Cl)_2(^-OC_6H_4\ {-}CH{=}N{-}\ (CH_2)_n{-}N{=}CH{-}C_6H_4O^-)_2}$, where $n = 2,3,4,5$, and 6 has predicted that when $n = 2$ and 3 the trans configuration is preferred and when n =4,5, and 6 the total energy difference between cis- and trans- configuration is too small to make a prediction (198). One example (**21**) involving a tridentate ONS ligand is salicylaldehyde dithiocarbazate, which is dimeric through double isopropoxy bridges (72). This compound is readily hydrolyzed. The related TiL_2, where L is salicylaldehyde dithiocarbazate, is monomeric and stable in hot water because the coordination number of Ti is 6. The related ONO ligands (**22**) derived from enol ketones or aldehydes, eg, acetylacetone or salicylaldehyde, and hydroxyamines react similarly with TYZOR TPT. Other products are analogous, pentacoordinate,



(**21**)



(**22**)



(**23**)

dimeric, 1:1 water-sensitive complexes and hexacoordinate, monomeric, 2:1 water-stable complexes. Both 1:1 complexes react with pyridine to become six coordinate, and react with 2-methylpentane-2,4-diol by displacing isopropoxy to form pentacoordinate chelates (**23**), which also add pyridine (199). Several similar ligands and their five- and six- coordinate complexes with Ti have been reported (200–202). Complexes with 8- hydroxyquinoline are well known (203,204).

4.8. Polymetallocarbosilanes. Polymetallocarbosilanes having a number-average molecular weight of 700−100,000 can be prepared by reaction of polycarbosilane,

$$-\!\!\left(\mathrm{Si(R)_2-CH_2}\right)_{\!x}\!\!-$$

where R = H, or lower alkyl, with a tetraalkyl titanate, to give a mono-, di-, tri-, or tetrafunctional polymer containing at least one Si−O−Ti bond. By firing polytitanocarbosilanes in a vacuum, an inert gas, or a nonoxidizing atmosphere, they can be converted to a molded article consisting mainly of SiC and TiC and having a higher mechanical strength and better oxidation resistance at higher temperatures than SiC itself (see Carbides, survey; Tool material) (205).

Polytitanosiloxane (PTS) polymers containing Si−O−Ti linkages have also been synthesized through hydrolysis−polycondensation or hydrolysis−polycondensation−pyrolysis reactions involving clear precursor sol solutions consisting of monomeric silanes, TYZOR TnBT, methanol, water, and hydrochloric acid (Fig. 2). These PTS polymers could be used to form excellent corrosion protection coatings on aluminum substrates (206).

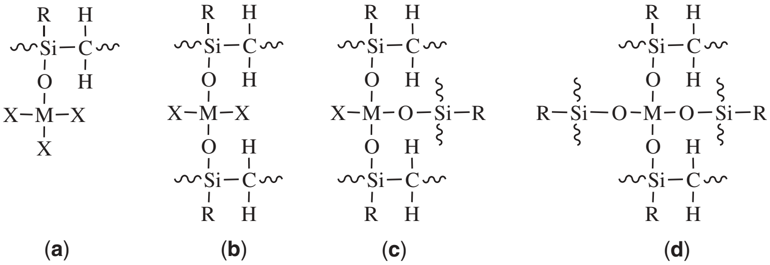


Fig. 2. Polytitanosiloxane polymers, where M = Ti/Zr and X = Cl. (**a**) Monofunctional, (**b**) difunctional, (**c**) trifunctional, and (**d**) tetrafunctional polymers.

5. Titanium Silicates

The synthesis of titanium silicate catalysts, such as TS-1, by controlled hydrolysis of a mixture of tetraethylorthosilicate (TEOS) and TYZOR TnBT was first reported in the mid-1980s (207,208). Since that time, several alternative methods of synthesis have been developed. The addition of sodium hydroxide during formation of the TS-1 precursor gel gives a titanium silicate having fewer acidic sites, which modifies its catalytic activity (209). The use of chelating agents, eg, acetylacetone, during the synthesis avoids formation of insoluble TiO_2 during gel–reaction mixture preparation before the formation of titanium silicate species (132,133,135–139,209). Prehydrolysis of the silicon precursor promotes homogeneous component mixing and minimizes formation of segregated silica and titania components (210). Titanium silicates are excellent catalysts for the selective oxidation of alkanes to alkenes (211) and for the hydroxylation of benzene and phenols (212,213). These have also found use as an ester-exchange catalyst in the formation of dimethyl carbonate from ethylene carbonate (214).

6. Lower Valent Titanates

Titanium(III) alkoxides can be produced by photoreduction of the tetraalkyl titanates in the presence of a base, eg, pyridine (215), and by reduction of tetraalkyl titanates by organosilicon compounds containing Si–H groups (216).

TYZOR ET is reduced by sodium and ethanol to a dark-blue compound (217). Use of potassium as the reducing agent in the alcohol permits the isolation and identification of $Ti(OC_3H_7)_3$ [22922-82-3] and $Ti(OC_4H_9)_3$ [5058-41-3] (218,219). The products precipitate as solid alcoholates, $(RO)_3Ti{\cdot}2ROH$, which can be dried to solvent-free material. Air oxidation in a radical reaction yields solvent-soluble materials formulated as $(C_3H_7O)_2Ti{=}O$ [20644-85-3], mp 100–113°C, and $(C_4H_9O)_2Ti{=}O$ [30860-71-0], mp 112–115°C, plus C_3H_7OH or C_4H_9OH and the corresponding aldehydes. These materials may be oligomers. With potassium in ether, triethoxytitanium [19726-75-1] can be prepared as a pink-lilac compound, which, on exposure to oxygen, yields $(C_2H_5O)_3TiO\text{-}Ti(OC_2H_5)_3$ [84215-71-4]. The ethoxy groups in the titanoxane exchange with C_3H_7OH without breaking the Ti–O–Ti bond. Table 4 contains a list of a few of the organotitanium compounds with a valency <4.

The family of Ti(III) derivatives roughly parallels those of Ti(IV). Titanium(III) chelates are known, eg, titanium trisacetylacetonate [14284-96-9] prepared in benzene from titanium trichloride, acetylacetone, and ammonia (220). This deep-blue compound is soluble in benzene but insoluble in water.

$$TiCl_4 + 3\ Hacac + 3\ NH_3 \longrightarrow Ti(acac)_3 + 3\ NH_4Cl$$

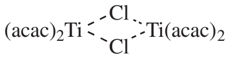
The compound is oxidized by air to orange-red crystals, which are possibly $O{=}Ti(acac)_2$ or an oligomer. If, however, the mixture is refluxed in the absence of ammonia, a red dimer is formed (mp 214°C), to which the doubly

Table 4. **Organotitanium Compounds of Lower Valence**

Compound	CAS Registry Number	Type[a]	Appearance	Mp, °C	Other properties
$Ti(CH_3)_3$	[32835-60-2]	Ti(III) trialkyl	not isolated; green in THF solution		solutions give positive Gilman test; decompose above −20°C
$(C_5H_5)_2TiCl$	[60955-54-6]	Ti(III) Cp_2 halide	green crystals	279–281	
$C_5H_5TiCl_2$	[31781-62-1]	Ti(III) Cp halide	violet	sublimes *in vacuo* at 150°C	insoluble in hydrocarbons; very sensitive to oxygen; blue solution in acetonitrile
$(CH_2{=}CH)_2TiCl$		Ti(III) (divinyl) halide	infusible powder		
$(C_9H_7)_2TiCl$	[12113-02-9]	Ti(III) (indenyl) halide	yellowish red		
$(C_5H_5)_2TiCH_2CHCH_2$	[12110-59-7]	Ti(III) Cp_2 allyl	purple-blue		monomeric; extremely air-sensitive
$(C_5H_5)_2TiOOCCH_3$	[12248-00-9] [56260-60-7]	Ti(III) Cp_2 carboxylate	blue	110	air-sensitive
$(C_5H_5)_2TiOOCC_9H_{19}$	[12248-77-0]		blue	ca. −5	air-sensitive
$(C_5H_5)_2TiBH_4$	[12772-20-2]	Ti(III) Cp_2 hydroborate	black-violet needles		solution very sensitive to air
$(C_5H_5)_2TiBF_4$	[83562-93-0]	Ti(III) fluoroborate	light blue		very sensitive to air; aqueous alkali → Ti_2O_3 (hydrate)
$(C_5H_5)_3Ti$	[39333-58-9]	Ti(III) Cp_3	green	sublimes at 125	extremely air-sensitive; gives $(C_5H_5)_2Ti(CO)_2$ with CO under pressure
$Ti(C_6H_5)_2$	[14724-88-0]	Ti(II) diphenyl	black solid		pyrophoric; gives phenylmercury chloride with $HgCl_2$
$C_5H_5TiC_6H_5$	[12109-06-7]	Ti(II) Cp_2 C_6H_5	black solid		sensitive to air and moisture; thermally stable to 170°C
$(C_5H_5)_2Ti$	[1271-29-0]	Ti(II) Cp_2	dark green	200	pyrophoric; catalyst for polymerization of olefins and acetylenes

[a] Cp = cyclopentadienyl.

bridged structure,



[61436-17-7], is assigned (221). Titanium(III), β-diketonates can also be prepared by reduction of the Ti(IV) chelates (222).

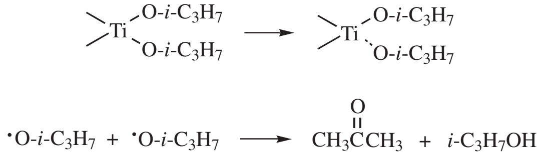
A titanous oxalate is prepared in water from $TiCl_3$ and oxalic acid, precipitating upon the addition of ethanol as a yellow solid (223). It forms double salts with metal oxalates, $MTi(C_2O_4)_2 \cdot 2\ H_2O$.

A group of violet titanium(III) acylates has been prepared from $TiCl_3$ and alkali carboxylates. All of the acylates are strong reducing agents similar to $TiCl_3$ (224). Studies of Ti(III) compounds include the reaction (225)

$$\mathrm{TiCl_3} + (\mathrm{RO})_3\ \mathrm{P{=}O} \longrightarrow \mathrm{TiCl_2OPO(OR)_2{+}RCl} \longrightarrow \mathrm{Ti\big(OPO(OR)_2\big)_3}$$

where R is either C_2H_5 [56170-51-5], C_3H_7 [56170-52-6], $CH_2CH{=}CH_2$ [56170-53-7], or C_4H_9 [56170-54-8].

The tris compounds are highly bridged three-dimensional (3D) polymers. Photoreduction of aqueous Ti(IV) complexes containing alcohols or glycols, but not ethylene glycol, yields Ti(III) and the aldehyde or ketone corresponding to the alcohol (226,227). A possible mechanism is



A broad selection of Ti(III) compounds coordinated to α-hydroxy acids, diboric acids, and 8-hydroxyquinoline has been prepared by the reaction

$$\mathrm{TiCl_3} + n\ \mathrm{HL} \xrightarrow[\mathrm{DMF}]{(\mathrm{C_2H_5})_3\mathrm{N}} \mathrm{TiCl}_{3-n}\mathrm{L}_n$$

where DMF = dimethylformamide

The electron spin resonance (esr) spectrum has been measured at 77 and 298 K. The compounds are dimers, but the Ti–Ti distances vary with the ligand (228,229).

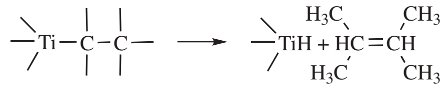
Exposure of $TiCl_4$ in ethyl, propyl, and butyl alcohols for 4 weeks results in the precipitation of green octahedral Ti(III) complexes. Similar products form on irradiating $Ti(OR)_4$ in ROH containing an equivalent of a lithium halide (227).

Among the applications of lower valent titanium, the McMurry reaction, which involves the reductive coupling of carbonyl compounds to produce alkenes, is the most well known. An excellent review of lower valent titanium reactions is available (230). Titanium(II)-based technology is less well known. A titanium(II)-based complex has been used to mediate a sterio- and regiospecific reduction of isolated conjugated triple bonds to the corresponding polyenes (231).

7. Organometallics

7.1. Titanium(IV) Organometallics.

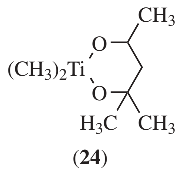
In classical organometallic chemistry, Grignard reagents (qv) or organolithium compounds react with halides of less active metals to form new carbon–metal bonds. This type of reaction with titanium halides invariably failed, until it was realized that many simple titanium alkyls are extraordinarily unstable thermally as well as to moisture and air. This thermal instability is derived from the presence of unfilled, low lying 3*d* orbitals. In titanium metal, the electron configuration is $3s^23p^63d^24s^2$; in simple tetralkyltitaniums, it is $3s^23p^63d\ ^64s^2$, and may also include hybrid $3d$–$4s$ orbitals. Supplying two extra electron pairs by coordination with, eg, pyridine, diamines, or strong donor ethers, gives stable molecules having a configuration of $3s^23p^63d^{10}4s^2$ (94,232,233). Another source of instability is the availability of facile decomposition mechanisms, eg, β-elimination:



This can be circumvented by choosing alkyl groups with no β-H, eg, methyl, neopentyl, trimethylsilylmethyl, phenyl and other aryl groups, and benzyl. The linear transition state for β-elimination can also be made sterically impossible. The most successful technique for stabilization combines both principles. The pentahaptocyclopentadienyl ring anion n^5- $C_5H_5^-$ (Cp) has six π-electrons available to share with titanium.

Biscyclopentadienyltitanium dichloride [1271-19-8] (titanocene dichloride), Cp_2TiCl_2, melts at 289°C, can be sublimed at 190°C at 267 Pa (2 mmHg), and can be recovered almost quantitatively from its solution in boiling dilute hydrochloric acid ($pH < 1$). The Cp ligand and its substitution derivatives, abbreviated as Cp′, can also stabilize the otherwise labile Ti–R compounds. Thus, $Cp_2Ti(C_6H_5)_2$ [1273-09-2] is unchanged for several days at room temperature.

Thermal stability is enhanced in chelates; thus dimethyl-2-methylpentane-2,4-dioltitanium [23916-35-0] (**24**) is much more stable than $(CH_3)_3Ti(OCH(CH_3)_2)_2$ (73). The structure of the former has been shown by X-ray diffraction to be dimeric and five coordinate through oxygen bridges. The more highly substituted the six-membered ring, the more thermally stable the compound.



(**24**)

Covalent Noncyclopentadienyl Compounds. The general synthesis of covalent non-Cp compounds, R_nTiX_{4-n}, where R = alkyl or aryl and X = halogen, logen, alkoxyl, or amido, involves the reaction of a lithium, sodium, or magnesium organometallic with a titanium–halogen compound in an inert atmosphere.

Solvents are usually either ethers, eg, $(C_2H_5)_2O$, tetrahydrofuran (THF), or glyme, or hydrocarbons, eg, hexane or benzene. In addition, a low temperature is required to compensate for the low thermal stability. Schlenk-tube techniques are commonly used. Grignard reagents and alkylaluminum compounds are reducing agents; organoalkalies generally give less reduction. The halides may be TiX_4 or a readily prepared alkoxytitanium halide $X_nTi(OR)_{4-n}$. Because the R–Ti bond is generally broken by protic reagents (HA), an alkoxyl cannot be introduced by alcoholysis after the R–Ti bond forms.

An unusual reaction leading to a Ti–C bond is unrelated to those just discussed.

Diphenylketene adds $Ti(OR)_4$ (234) as follows:

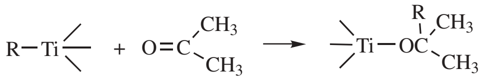
$$Ti(OR)_4 + n\ (C_6H_5)_2C{=}C{=}O \longrightarrow (RO)_{4-n}Ti\big(C(C_6H_5)_2COOR\big)_n$$

for $n = 1$, $R = C_2H_5$, [78319-02-5]; $n = 1$, $R = CH(CH_3)_2$, [78319-03-6]; $n = 2$, $R = C_2H_5$, [78319-05-8]; $n = 2$, $R{=}CH(CH_3)_2$, [78319-06-9]; and $n = 1$, $R = C_6H_5$, [78319-04-7].

Other heterocumulenes, eg, $C_6H_5N = C = O$, react similarly to yield carbamic esters (144,145).

The reaction of ketene itself with tetraalkyl titanates followed by a ketone $R^1R^2C = O$ gives β-hydroxyesters, $R\ ^1R^2COHCH_2CO_2R$. Polyinsertion of ketene and aldehyde into the Ti–O bond leads to di-, tri-, and tetraesters, eg, $HOCR^1R^2CH_2CO_2CR^1R^2CH_2CO_2R$ (235).

There are numerous alkyltitaniums, and many of their reactions resemble those of alkyllithiums and alkylmagnesium halides. They are protolyzed by water and alcohols, $R{-}Ti(R')_3 + HA \rightarrow RH + A\text{-}\ Ti(R')_3$; they insert oxygen, $R{-}TiR\,' + O\ _2 \rightarrow ROTiR\,'$; and they add to a carbonyl group:



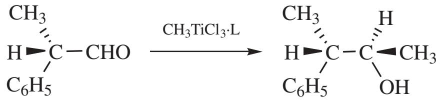
One reaction, disproportionation, has made it difficult to prepare di- and triaryltitanium alkoxides. It is easy to prepare phenyltitanium trialkoxide, $C_6H_5Ti(OR)_3$. However, the reaction

$$2\,C_6H_5Li + Cl_2TiOCH\,(CH_3)_2 \longrightarrow (C_6H_5)_2TiOCH(CH_3)_2$$

[762-99-2] [84215-72-5]

is followed by disproportionation, doubtless promoted by the intermolecular bridging of alkoxyl groups, which creates a molecule differing only slightly from a reasonable transition state for phenyl migration. Thermodynamics takes over and the products are $C_6H_5Ti(OR)_3$ and $(C_6H_5)_4Ti$.

The unstable CH_3TiCl_3 [12747-38-8] from $(CH_3)_2Zn + TiCl_4$ forms stable complexes with such donors as $(CH_3)_2NCH_2CH_2N(CH_3)_2$, THF, and sparteine, which methylate carbonyl groups stereoselectively. They give 80% of the isomer shown and 20% of the diastereomer; this is considerably more selective than the more active CH_3MgBr (236). Such complexes or $CH_3Ti(OC_3H_{7-i})_3$ methylate tertiary halides or ethers (237) as follows:



in which R_3CCl is methylated to R_3CCH_3; R_2CCl_2 to $R_2C(CH_3)_2$. Such reactions can even be performed with $(CH_3)_2Zn$ and catalytic amounts of $TiCl_4$ at −78°C. Gem dialkylation of a ketone has been achieved in a one-pot reaction (238,239).

Grignard reagents and lithium alkyls add to ester groups, but the CH_3Ti reagents do not. This selectivity has synthetic value (240). Titanium alkyls and aryls discriminate between aldehydes and ketones (241). Titanium alkyls minimize side reactions, eg, elimination, rearrangement, and enolization, which often occur with aluminum alkyls and other active organometallics (239). The solvent is important. Mesityllithium (MesLi) and $TiCl_4$ in THF yield $LiTiMes_4 \cdot 4THF$ [63916-94-1], but Mes_3Zn and $TiCl_4$ in hydrocarbon produces $MesTiCl_3$ [77801-18-4], which reacts with THF to yield $TiCl_3$ (242).

Other $RTiX_3$ (X = Hal or OR′) compounds are selective at −20°C. A chiral R′OH, eg, (*S*)(−)$C_2H_5CH_3CHCH_2OH$, permits asymmetric synthesis. A 98:2 or 99:1 selectivity for aldehyde over ketone has been reported (243–245). The activation energy difference is ~42 kJ/mol (10 kcal/mol) for RTi, and only 4 kJ/mol (1 kcal/mol) for RLi or RMgX. The kinetic reactivity of $RTi(OR')_3$ decreases in the order of n-$C_3H_7O > (CH_3)_3CHO > CH_3CH_2CHCH_3O > CH_3CH_2CH_3CHCH_2O$ for R′O; and $C_6H_5 > CH_3 > C_4H_9 >$ for R.

Titanium alkyls are prepared simply either as

$$TiCl_4 + 3\ TPT \longrightarrow ClTi\big(OCH(CH_3)_2\big)_3$$

where the product, [20717-86-6], is distillable, or as

$$CH_3COCl + TPT \longrightarrow ClTi\big(OCH(CH_3)_2\big)_3 + CH_3COOCH(CH_3)_2$$

followed by

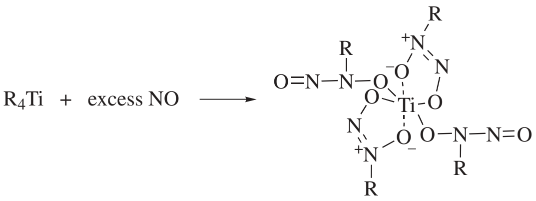
$$RLi + ClTi\big(OCH(CH_3)_2\big)_3 \longrightarrow RTi\big(OCH(CH_3)_2\big)_3 + LiCl$$

Titanium alkyls, known as tamed Grignard reagents, do not add to esters, nitriles, epoxides, or nitroalkanes at low temperatures. Rather, they add exclusively in a 1,2 fashion to unsaturated aldehydes (243–245).

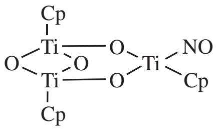
Tetraneopentyltitanium [36945-13-8], Np_4Ti, forms from the reaction of $TiCl_4$ and neopentyllithium in hexane at −80°C in modest yield only because of extensive reduction of Ti(IV). Tetranorbornyltitanium [36333-76-3] can be prepared similarly. When exposed to oxygen, $(NpO)_4Ti$ forms. If it is boiled in benzene, it liberates neopentane. When dissolved in monomers, eg, α-olefins or dienes, styrene, or methyl methacrylate, it initiates a slow polymerization (246,247). Results from copolymerization studies indicate a radical mechanism (247). Ultraviolet light (uv) increases the rate of dissociation to radicals. The titanocycle [79953-32-5],

is planar and may be an intermediate in some forms of olefin metathesis (248).

Tetraneopentyltitanium and $((CH_3)_3SiCH_2)_4Ti$ [33948-28-6] react with nitric oxide to yield compounds having R groups bonded in two different ways, as shown by nuclear magnetic resonance (nmr) (249). The reactions of NO with R_3TiCl and R_2TiCl_2 yield similar products that have Cl instead of the −ONRNO substituent. However, Cp_2TiR,

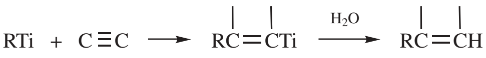


where R is C_6H_5 or $CH_2C_6H_5$ and Ti is paramagnetic Ti(III), reacts with NO, resulting in the loss of one Cp and one R group, to form the trinuclear, compound [76722-03-7] (**25**).



(**25**)

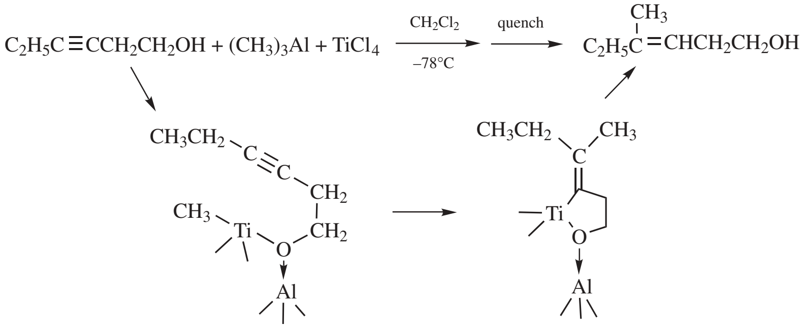
Carbometalation, an important reaction of RTi(IV) compounds in which RTi adds to a $C=C$ or $C=C$ multiple bond and results in a net R−H addition, is involved in Ziegler-Natta polymerization as follows:



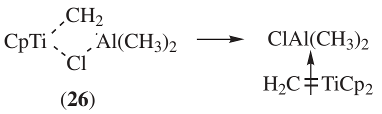
$$RTi + C{\equiv}C \longrightarrow \overset{|}{R}\overset{|}{C}{=}\overset{|}{C}Ti \xrightarrow{H_2O} R\overset{|}{C}{=}\overset{|}{C}H$$

Solutions of RC triple-bond C−Ti(O-*i*-$C_3H_7)_3$ can be prepared by treating acetylenic compounds, eg, phenylacetylene, with butyl lithium and then Cl−Ti(O-*i*-$C_3H_7)_3$. These materials can react with aldehydes and epoxides to give the expected addition products (250).

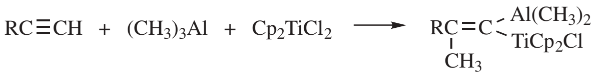
In the following cases, only those reactions in which there is no chain growth, or at most dimerization, are considered. Alkyltitanium halides can be prepared from alkylaluminum derivatives. The ring structure imparts regiospecificity to the ensuing carbometalation (251):



The metallocycle [67719-69-1] (26) undergoes an apparent β-elimination to a carbene- like reagent, which adds regiospecifically to terminal acetylenes (252).



(**26**)

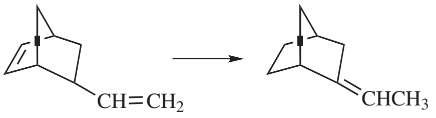


$RC{\equiv}CH + (CH_3)_3Al + Cp_2TiCl_2 \longrightarrow RC(CH_3){=}C(Al(CH_3)_2)(TiCp_2Cl)$

(**27**)

The intermediate (**27**) reacts with ketones (R'_2CO) to form cumulenes $RC(CH_3) = C = CR_2$. The indenyl derivative reacts similarly.

Olefin isomerization is often catalyzed by titanium. An example is the conversion of vinylnorbornene to the comonomer ethylidenenorbornene (166). The catalyst is a mixture of a sodium suspension, $AlCl_3$, and $(RO)_4Ti$ or Cp_2TiCl_2. Although isomerization is slow, the yield is high. The active reagent is doubtless a Ti(III) compound.



Complexes of titanium, eg, 2,6-$(RNCH_2)_2NC_5H_3TiCl_2$, prepared by reaction of $TiCl_4$ with 2,6-$((CH_3)_3Si)RNCH_2)_2NC_5H_3$, can react with various Grignard reagents to prepare conformationally rigid diamide mono- and dialkyl titanate complexes (253,254).

Cyclopentadienyltitanium Compounds. Properties. The structure of Cp_2TiCl_2 (Cp = cyclopentadienyl) has been shown by X-ray diffraction to be a distorted tetrahedron: Ti–Cl = 236.4pm, Ti-centroid = 205.8pm, and C–C = 133.9–141.9 pm (255,256). The compound has also been studied by electron diffraction (257). Changes in the structure are imposed by bridging the Cp rings with

$-(CH_2)_n-$ or other groups (258). In $Cp_2Ti(C_6H_5)_2$, the C−C bonds in the Cp rings have different lengths, as do those in the phenyl rings (259). Chemical ionization mass spectrometry of Cp_2TiCl_2 gives mainly $M^+(^-Cl)$ (260,261); ^{13}C-nmr results are available (262). The rings of Cp_2TiCl_2 spin rapidly, so the ^1H-nmr spectrum produces one peak. Bridging the rings prevents spinning and splitting can be detected (263,264). Electron spectroscopy for Cp_2TiX_2, where X is halogen, and other CpTi(IV) compounds has been reported (265–267). Infrared and Raman spectra are discussed elsewhere (268–271) and the photoelectron spectrum has been determined (272). Molecular orbital calculations have been reported for many Cp−Ti compounds (272–280). Vapor pressure equations for Cp_2TiCl_2 and TYZOR TnBT are available, as are other thermodynamic quantities (281,282). Selected titanium(IV) cyclopentadienyls and biscyclopentadienyls are given in Tables 5 and 6, respectively.

Titanium tetrachloride is a Lewis acid having many useful synthetic properties (283). Replacing Cl by OR weakens the acid. Acid−base complexes having dimethyl sulfoxide (DMSO), DMF, dimethylacetamide (DMAc), which are all oxygen bonded, as well as pyridine (py) and ethylenediamine (en), have been reported (284). The compound $CpTiCl_3$ forms stable, sublimable complexes having ditertiary amines or arsines, eg, $(CH_3)_2ECH_2CH_2E(CH_3)_2$, where E = N or As. The less-basic analogues, where E = O, S, or P, do not form stable complexes. The monodentates pyridine, $(CH_3)_2S$, $(CH_3)_3As$, and $(C_6H_5)_3P$ also do not form complexes. The bromide and iodide behave similarly (285). Bis(cyclopentadienyltitanium) dichloride is virtually devoid of Lewis acidity. The properties of ring-substituted Cp derivatives differ from those of the parent Cp derivatives in a manner predictable from the electronic properties of the substituent.

Synthesis. The discovery of stable cyclopentadienyltitanium compounds, in particular Cp_2TiCl_2, stimulated the synthesis and study of a host of related compounds. These include both $CpTiX_3$ and Cp_2TiX_2, where X = halogen.

The basic laboratory synthesis involves the reaction of a salt of cyclopentadiene, eg, lithium, sodium, potassium, or magnesium, and a titanium(IV) halide, usually in an ether solvent (286–288). However, this is probably too expensive for industrial use. Different Cp groups can be introduced in two separate steps (289). One patent shows that merely heating CpH and $TiCl_4$ in dioxane at 60−80°C in the presence of diethylamine yields Cp_2TiCl_2 (290). Titanium alkoxides react with CpMgBr to yield $CpTiBr(OR)_2$ or Cp_2TiBr_2, depending on the mole ratio (291). Another patent describes the reaction (292).

$$\text{CpH} + \text{Cl}_2\text{Ti(OR)}_2 + (\text{C}_2\text{H}_5)_3\text{N (or piperidine)} \longrightarrow \text{CpTi(OR)}_2\text{Cl}$$

The product forms in 80% yield and is distillable. However, no additional amine is necessary for the following reaction (196), where $n = 1$ or 2:

$$n\text{CpH} + \text{Ti(NR}_2)_4 \longrightarrow \text{CpnTi(NR}_2)_{4-n}$$

For laboratory use, cyclopentadienylthallium [34822-90-7] reacts cleanly with TiX bonds, where X is halogen (293–299). The cost and toxicity of thallium compounds are drawbacks to large-scale use. However, Cp_2Pb may, in certain cases, be useful (see LEAD COMPOUND; THALLIUM AND THALLIUM COMPOUNS) (300).

Table 5. **Organotitanium(IV) Compounds Cyclopentadienyls**

Compound	CAS Registry Number	X in $C_5H_5TiX_3$	Appearance	Mp,[a] °C	Bp,[a] °C	Other properties
$C_5H_5TiCl_3$	[1270-98-0]	halide	orange	140–142		on hydrolysis gives $(C_5H_5TiClO)_n$
$C_5H_5TiBr_3$	[12240-42-5]		orange	163–165		
$C_5H_5TiI_3$	[12240-43-6]		deep red	185–190		
$C_5H_5TiBrCl_2$	[70568-74-0]		orange	165–170		
$C_5H_5Ti(OCH_3)_3$		alkoxy		50–52	88_{200}	readily hydrolyzes; darkens on storage
$C_5H_5Ti(OC_2H_5)_3$	[1282-41-3]				$106–107_{400}$	very sensitive to moisture; monomeric in benzene
$C_5H_5Ti(OC_3H_7)_3$	[12242-59-0]				$106–107_{67}$	very sensitive to moisture; monomeric in benzene
$C_5H_5Ti(OC_4H_9)_3$	[84215-74-7]				$124.5–125.5_{67–133}$	n^{20}_{D} 1.5224
$C_5H_5Ti(OC(CH_3)_3)_3$	[12148-33-3]				102_{133}	n^{20}_{D} 1.5065
$C_5H_5Ti(OC_6H_{13})_3$	[12290-79-8]				$177–181_{133}$	n^{20}_{D} 1.5082
$C_5H_5TiOCH_3Cl_2$	[12192-52-8]	alkoxyhalide	yellow crystals	93–96		
$C_5H_5TiOC_2H_5Cl_2$	[1282-32-2]			49		
$C_5H_5TiOC_3H_7Cl_2$	[70046-23-0]		yellow-green		$159–161_{267}$ dec	
$C_5H_5Ti(OCH_3)_2Cl$	[84215-75-8]					
$C_5H_5Ti(OC_2H_5)_2Cl$	[1282-38-8]				$109–111_{133}$	n^{20}_{D} 1.5818
$C_5H_5Ti(OC_3H_7)_2Cl$	[84215-76-9]		yellow-green		$132–145_{133}$ dec	
$C_5H_5Ti(OC_4H_9)_2Cl$	[84215-77-0]				$145–150_{267–400}$	
$C_5H_5Ti(OC_4H_9)_2Br$	[84215-78-1]				$36–45_{107}$	
$C_5H_5Ti(OC_6H_5)Cl_2$	[12288-59-4]	aryloxyhalide				very sensitive to moisture
$C_5H_5Ti(OC_2H_5)_2OOCCH_3$	[84215-79-2]	alkoxyacetate			$106–108_{267}$	on heating $C_5H_5Ti(OC_2H_5)_3$ is formed

Table 5. (*Continued*)

Compound	CAS Registry Number	X in $C_5H_5TiX_3$	Appearance	Mp,[a] °C	Bp,[a] °C	Other properties
$C_5H_5Ti_5(OOCCH_3)_3$	[1282-42-4]	acetate		115–117		hydrolytically and thermally unstable
$C_5H_5Ti(SCH_3)_3$	[84215-80-5]	mercapto				
$C_5H_5Ti(SCH_3)_2Cl$	[84215-81-6]	mercaptohalide				
$C_5H_5Ti(OSi(CH_3)_3)_3$	[57665-25-5]	siloxy			$138–139_{133}$	$n^{20}{}_D$ 1.45824; $d^{20}{}_4$ 0.9436 g/cm^3
$CH_3C_5H_4TiCl_3$	[1282-31-1]	halide (substituted cyclopentadiene)		98–99		
$C_2H_5C_5H_4TiCl_3$	[1282-33-3]		orange solid	136_{133} sub		crystals liquefy in air
$(CH_3)_5C_4TiCl_3$	[12129-06-5]		red solid	225–227		
$CH_3C_5H_4TiOC_2H_5Cl_2$	[1282-39-9]	alkoxyhalide (sub-stituted cyclopentadiene)	green			viscous mass
$CH_3C_5H_4Ti(OC_2{-}H_5)_2Cl$	[1282-36-6]	alkoxy (substituted cyclopentadiene)			$143–145_{267}$	easily hydrolyzed in air; $n^{20}{}_D$ 1.5401, d^{20} 1.0780 g/cm^3
$CH_3C_5H_4Ti(OC_2{-}H_5)_3$	[1282-47-9]				$80–81_{133}$	easily hydrolyzed; darkens in storage even at −500C
$C_2H_5C_5H_4Ti(OC_2{-}H_5)_3$	[1292-46-8]				$101–102_{267}$	$n^{20}{}_D$ 1.5359; d^{20} 1.0717 g/cm^3

[a] Subscripted values are pressure in Pa. To convert Pa to mm Hg, divide by 133.

Table 6. **Organotitanium(IV) Compounds Biscyclopentadienyls**

Compound, $(C_5H_5)_2TiX_2$	CAS Registry Number	X	Appearance	Mp, °C	Other properties
$(C_5H_5)_2TiCl_2$	[1271-19-8]	halide	vivid-red crystals	289	slightly soluble in water; forms salts with acids
$(C_5H_5)_2TiBr_2$	[1293-73-8]		vivid-red crystals	314	diamagnetic, soluble in nonpolar solvents
$(C_5H_5)_2TiI_2$	[12152-92-0]		purple crystals	319	
$(C_5H_5)_2TiF_2$	[309-89-7]		yellow		
$(C_5H_5)_2Ti(OC_4H_9)_2$	[12303-65-0]	alkoxy			
$(C_5H_5)_2Ti(OC_6H_5)_2$	[12246-19-4]	aryloxy	yellow	142	thermally stable; hydrolyzed only when heating with concentrated NaOH
$(C_5H_5)_2Ti(o\text{-}ClC_6H_4O)_2$	[12309-06-7]		orange-yellow	145–147	thermally stable; hydrolyzed only when heating with concentrated NaOH
$(C_5H_5)_2Ti(o\text{-}CH_3C_6H_4O)_2$	[12309-37-4]		yellow	162	thermally stable; hydrolyzed only when heating with concentrated NaOH
$(C_5H_5)_2Ti(o\text{-}NO_2C_6H_4O)_2$	[12309-11-4]		red	122–124	thermally stable; hydrolyzed only when heating with concentrated NaOH
$(C_5H_5)_2Ti(p\text{-}ClC_6H_4O)_2$	[12309-07-8]		yellow	125–127	thermally stable; hydrolyzed only when heating with concentrated NaOH
$(C_5H_5)_2TiOC_2H_5Cl$	[12129-76-9]	alkoxyhalide		91–92	
$(C_5H_5)_2TiOC_3H_7Cl$	[12715-66-1]			57–58	
$(C_5H_5)_2TiOC_6H_5Cl$	[62652-01-1]	aryloxyhalide		71–73	
$(C_5H_5)_2Ti(SH)_2$	[12170-34-2]	mercapto		150–160 dec	stable to air and water

Table 6. (*Continued*)

Compound, $(C_5H_5)_2TiX_2$	CAS Registry Number	X	Appearance	Mp, °C	Other properties
$(C_5H_5)_2Ti(SCH_3)_2$	[12089-78-0]	alkylmercapto	deep red	193–197	
$(C_5H_5)_2Ti(SC_2H_5)_2$	[1291-79-8]			107–110	
$(C_5H_5)_2Ti(SC_3H_7)_2$	[1292-07-5]			88–93	
$(C_5H_5)_2Ti(SC_6H_5)_2$	[1292-72-4]	arylmercapto		199–201	
$(C_5H_5)_2Ti(SCH_2C_6H_5)_2$	[1292-61-1]			172–174	
$(C_5H_5)_2Ti(SCH_2CH_2C_6H_5)_2$	[1292-47-3]			92–94	
$(C_5H_5)_2Ti(OOCCH_3)_2$	[1282-51-5]	acyl	orange	126–128	
$(C_5H_5)_2Ti(OOCC_3H_7)_2$	[12290-20-9]		red-orange	114–116	readily hydrolyzed and thermally unstable
$(C_5H_5)_2Ti(OOCCH_2Cl)_2$	[1282-44-6]		red-orange	98–99	readily hydrolyzed and thermally unstable
$(C_5H_5)_2TiOOCCCl_3$	[12212-37-2]		red-orange	192–194	readily hydrolyzed and thermally unstable
$(C_5H_5)_2Ti(OOCCF_3)_2$	[1282-45-7]		orange	178–180	soluble in benzene, ethyl acetate, ethyl alcohol; moderately soluble in chloroform; thermally stable
$(C_5H_5)_2Ti(OOCC_6H_5)_2$	[51178-00-8]	benzoyl	yellow	188	reacts with aqueous alkali to give benzoic acid
$(C_5H_5)_2Ti(OSi(CH_3)_3)_2$	[12319-01-6]	siloxy			$n^{20}{}_D$ 1.4582, $d^{20}{}_4$ 0.9436 g/cm^3
$(C_5H_5)_2Ti(OSi(C_6H_5)_3)_2$	[12321-33-4]				stable in air but not in acidic or basic media
$(C_5H_5)_2TiOSi(CH_3)_3Cl$	[12319-01-6]	siloxyhalide	orange	137.5	

$(C_5H_5)_2TiOSi(C_6H_5)_3Cl$	[12320-99-9]			210–212	stable in air but not in acidic or basic media
$(C_5H_5)_2Ti(CO)_2$	[12129-51-0]	carbonyl	dark reddish-brown crystals	dec ~90	extremely air-sensitive
$(C_5H_5)_2Ti(CH_3)_2$	[1271-66-5]	alkyl	yellow-orange	dec ~100	
$(C_5H_5)_2TiCH_3Cl$	[1278-83-7]	alkylhalide	orange-red	168–170 dec	
$(C_5H_5)_2TiC_3H_7Cl$	[12715-66-1]		orange	160	
$(C_5H_5)_2Ti(C_6H_5)_2$	[1278-09-2]	aryl	orange-yellow	146–148 dec	
$(C_5H_5)_2Ti(m\text{-}CH_3C_6H_4)_2$	[12156-57-9]		red	137–139	
$(C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)_2$	[12156-58-0]		yellow-orange	133–134	
$(C_5H_5)_2Ti\text{-}p\text{-}((CH_3)_2NC_6\text{-}H_4)_2$	[12156-86-4]		maroon	137–139 dec	
$(C_5H_5)_2Ti(p\text{-}FC_6H_4)_2$	[12155-98-5]		orange	120 dec	
$(C_5H_5)_2Ti(p\text{-}ClC_6H_4)_2$	[12155-97-4]		orange	130 dec	
$(C_5H_5)_2Ti(p\text{-}BrC_6H_4)_2$	[12155-95-2]		orange	130 dec	
$(C_5H_5)_2Ti(m\text{-}CF_3C_6H_4)_2$	[12156-38-6]		orange-yellow	145–146	
$(C_5H_5)_2Ti(p\text{-}CF_3C_6H_4)_2$	[12156-39-7]			142–143	
$(C_5H_5)_2Ti(C{\equiv}CC_6H_5)_2$	[12303-93-4]		orange-brown crystals	141	
$(C_5H_5)_2Ti(C_6F_5)_2$	[12155-89-4]	fluorophenyl	orange needles	228–230	thermally stable *in vacuo* at 110°C
$(C_5H_5)_2TiClC_6F_5$	[50648-18-5]		pale-orange needles	201–203	
$(C_5H_5)_2TiOC_2H_5C_6F_5$	[84215-82-7]		yellow solid	117	stable in dry air; soluble in organic
$(C_5H_5)_2TiOHC_6F_5$	[84215-83-8]		yellow solid	183–185 dec	soluble in organic solvents
$(C_5H_5)_2TiC_6F_5F$	[84501-83-7]		yellow solid	240 dec	

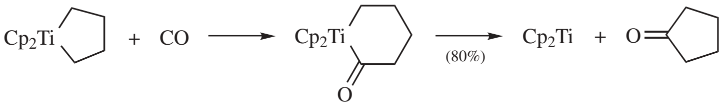
Monocyclopentadienyl compounds can be prepared by the above techniques with appropriate control of the stoichiometric proportion of reagents or by use of reagents, eg, $ClTi(OR)_3$ (301). Biscyclopentadienyltitanium dichloride can be carefully chlorinolyzed with Cl_2 or with SO_2Cl_2 in refluxing $SOCl_2$ (289,302). A wide variety of ring-substituted cyclopentadienes have been converted to $Cp'{-}Ti$ compounds. Methyl and other alkyl and aryl groups and $(CH_3)_3Si{-}$ are most common: Pentamethylcyclopentadiene is a popular, although expensive, ligand (303,304). Bridged bis(cyclopentadiene)s, eg, $Cp(CH_2)_nCp$ and $CpSi(CH_3)_2Cp$, have received much attention (263,305). The properties of derivatives with various length bridges have been compared (306,307). Indene and, to a very limited extent, fluorene function as ligands.

Titanium-containing polyethers have been prepared by the reaction of dicyclopentadienyltitanium dichloride with aromatic and aliphatic diols via an interfacial and/or aqueous solution polycondensation technique (308).

Cyclopentadienyltitanium Compounds with Other Carbon Titanium Links. Cyclopentadienyltitanium trichloride and, particularly, Cp_2TiCl_2 react with RLi or with RAl compounds to form one or more R–Ti bonds. As noted, the Cp groups stabilize the Ti–R bond considerably against thermal decomposition, although the sensitivity to air and moisture remains. Depending on the temperature, mole ratio, and structure of R, reduction of Ti(IV) may be a serious side reaction, which often has preparative value for $Cp_nTi(III)$ compounds (303,309,310).

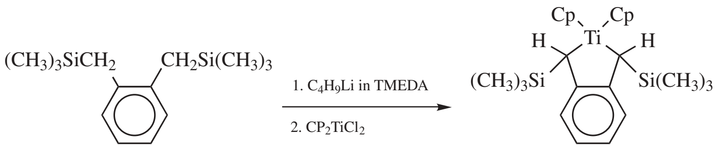
Methyl and aryl groups are most commonly used. Higher alkyltitaniums tend to decompose by β-elimination except when R is $CH_2Si(CH_3)_3$ or $CH_2C(CH_3)_3$ (311). Ring compounds or titanocycles, made from Cp_2TiCl_2 and 1,n-dilithioalkanes, $Li(CH_2)_nLi$, at $-78°C$, are quite thermolabile, though more stable than $Cp_2Ti(C_4H_9)_2$ [52124-69-3; 71297-31-9]. In the compound where n is 4, β-elimination is suppressed because the Ti–C–C–H dihedral angle is far from 0°. The compound inserts carbon monoxide to yield a titanoketone, which expels Ti at 25°C. These reactions do not occur when n is 5.

Other titanocene synthons may undergo similar reactions with CO (312–314). Both vinylic and ethynylic groups can be attached to the Cp_2Ti framework. These tend to be stable thermally and to air and moisture (315).



[*52124-67-1*] [*52124-68-2*]

A rather air-stable titanocycle [76933-94-3; 76933-97-6] has been prepared in meso form only (316):



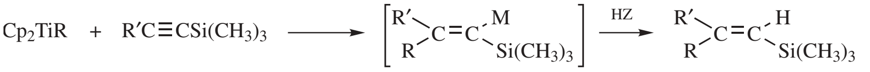
TMEDA = N,N,N',N'- tetramethylethylendiamine

Related examples of silicon-containing titanocycles have also been prepared (317). These compounds are air-stable and not decomposed by methanol. When CpCp′TiClOAr reacts with Grignard reagents, the aryloxy group is replaced by R, not by Cl (318). Compounds of the formula $(Cp_2TiR)_2O$ prepared from $(CP_2TiCl)_2O$ + RLi, where R is CH_3, C_2H_5, C_6H_5, *p*-tolyl, $C_6H_5C = C$, or $CH_2 = CH$, are thermally stable and quite stable to air (318,319).

Alkyl and aryl groups are cleaved by iodine, but Cp groups are not affected (320).

Carbometalation of olefins and acetylenes is a useful reaction. For example, in

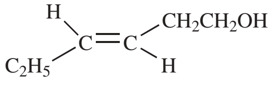
$$Cp_2TiCl_2 + R_nAlCl_{3-n} \longrightarrow Cp_2TiRCl{\cdot}AlR_{n-1}Cl_{4-n} \longrightarrow Cp_2TiR^+ + AlR_{n-1}Cl_{5-n}$$



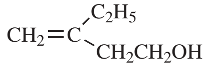
up to 90% trans-addition is obtained, where M is a complex of Ti and Al. The hydrogen in the product is acquired from the solvent or from elsewhere in the reaction mixture, because if the mixture is quenched with $(C_2H_5)_3N$ followed by D_2O, no deuterium occurs in the olefin. If R′ in the acetylene is phenyl or 1-cyclohexenyl, equal amounts of cis- and trans-products are obtained. If the unsilylated parent $R'C = CH$ is exposed to this catalyst system, it is cyclotrimerized to the 1,3,5-$C_6H_3R'_3$. However, this system does not polymerize propylene (321,322).

Other authors disagree with the results of this carbometalation sequence. They find that the initial product results strictly from cis-carbometalation; but with a trace of base, H is abstracted from the medium homolytically with loss of stereochemistry (323). They show that M in the above structure must be Ti, not Al. If the reaction mixture is quenched with D_2O containing NaOD, 95 mol% D is incorporated into the olefin.

Alkynols are ethylated by $(C_2H_5)_2AlCl$ catalyzed by Cp_2TiCl_2 (324). $(CH_3Cp)_2TiCl_2$ [1282-40-2] is sometimes preferred because it is more soluble in nonpolar solvents. Ten- to-fifty percent of the titanium compound is required, because many alkynols rapidly deactivate the titanium. In one example, when a prereacted mixture of $(C_2H_5)_2AlCl$ and $HOCH_2CH_2C = CH$ is treated with Cp_2TiCl_2, a 1:1 mixture of (28) and (29) forms in only 55% yield. Reducing the amount of Cp_2TiCl_2 to 10 mol% raises the yield to 80–90%. The corresponding olefin is also carbometalated by ethylaluminum–titanium combinations. There are marked differences among the titanate esters of the unsaturated alcohol



(28)



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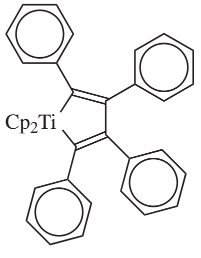
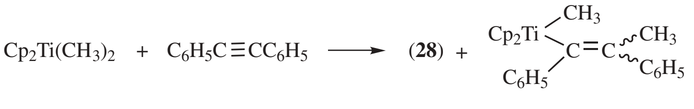


(30)

$HOCH_2CH_2CH{=}CH_2$ prepared with $TiCl_4$, $Cl_2Ti(acac)_2$, or Cp_2TiCl_2 (325). Olefin dimerization involves carbometalation. High selectivity (98%) for the ethylene-to-1-butane dimerization is achieved by adding 10 mol% of $Ti(OC_4H_9)_4$ and 0.5 mol% of Cp_2TiCl_2 to the $(C_2H_5)_3Al$ catalyst (326).

Photolysis has been intensively studied. For example, $Cp_2Ti(C_6H_5)_2$ yields a green polymer $(Cp_2TiH)_x$[11136-22-4]. At low temperature in benzene or THF, a dark-green transient Cp_2Ti−solvent species forms and quickly dimerizes. The phenyl groups appear as benzene and biphenyl. In the presence of CO or $C_6H_5C{=}CC_6H_5$, $Cp_2Ti(CO)_2$ [12159-51-0] or **30** [1317-21-1] forms, respectively (327,328).

Photolysis of Cp_2TiAr_2 in benzene solution yields titanocene and a variety of aryl products derived both intra- and intermolecularly (328–332). Dimethyltitanocene photolyzed in hydrocarbons yields methane, but the hydrogen is derived from the other methyl group and from the cyclopentadienyl rings, as demonstrated by deuteration. Photolysis in the presence of diphenylacetylene yields the dimeric titanocycle (30) and a titanomethylation product [65090-11-1].



The fluorinated titanocycle related to 30 is not obtained from $C_6H_5C{=}CC_6F_5$. Photolysis of Cp_2TiX_2 always gives first scission of a Cp−Ti bond. In a chlorinated solvent, the place vacated by Cp is assumed by Cl. In the absence of some donor, the radical dimerizes (333,334).

When $Cp_2Ti(CH_3)_2$ is photolyzed in toluene, 2 mol of CH_4 are produced; but in monomers, only 3 mol (1.08 mol in styrene, 0.90 mol in methyl methacrylate) of CH_4 is liberated as the monomers polymerize (335). The $Cp_2Ti(CD_3)_2$ [65554-67-8] photolyzed in $C_6D_5CD_3$ gives CD_3H, but not CD_4, thus ruling out free CD_3. In methyl methacrylate, $Cp_2Ti(^{14}CH_3)_2$ yields a polymer containing 0.8−1.1 ^{14}C per polymer chain, but no Ti. If tritiated $(Cp{-}T)_2Ti(CH_3)_2$ is used in methyl methacrylate, the polymer contains only traces of tritium. Clearly, the hydrogen for the methane comes from the Cp groups.

Pyrolysis of solid $Cp_2Ti(CD_3)_2$ yields CD_3H, but not CD_4. Pyrolysis of $(C_5D_5)_2Ti(CH_3)_2$ yields CH_3D. These results show that the radical attacks the Cp rings (336,337). Pyrolysis of $Cp_2Ti(C_6H_5)_2$ proceeds via a benzyne intermediate, as shown by trapping experiments involving cycloadditions (328,338–341).

The detailed mechanism of pyrolysis of Cp_2TiR_2 compounds has been studied (342–348). A useful titanocycle is formed from Cp_2TiCl_2 and trimethylaluminum; triethylaluminum gives a different product (349). The titanocycle adds to terminal olefins in the presence of 4-dimethylaminopyridine; the adduct expels olefin > above 0°C to yield a bis(titanocyclobutane) (350). The titanocycle can also behave like a Wittig reagent, reacting with aldehydes and ketones to give olefins (349,351).

Displacement Reactions. Cyclopentadienyltitanium halides undergo displacements with a wide variety of nucleophiles. Hydroxylic reagents cleave

Ti−R bonds (352,353):

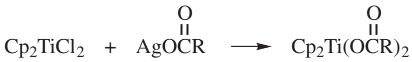
$$Cp_2TiCH_3Cl + H_2O \longrightarrow CH_4 + (Cp_2TiCl)_2O$$

Amides are formed with amines, often with strong base assistance (354,355). Occasionally Cp groups are lost (356–367):

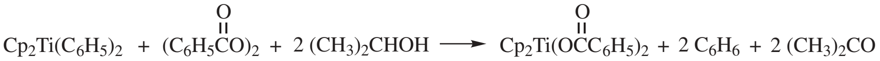
$$Cp_2TiCl_2 + NaNRAr \longrightarrow Cp_2TiClNRAr \longrightarrow Cp_2Ti(NRAr)_2$$

$$Cp_2TiCl_2 + LiN(CH_3)_2 \text{ (excess)} \longrightarrow CpTi(NCH_3)_3$$

In titanium acylates, the carboxylate ligands are unidentate, not bidentate, as shown by ir studies (368,369). The ligands are generally prepared from the halide and silver acylate (370). The benzoate is available also from a curious oxidative addition with benzoyl peroxide (370–373):



$$Cp_2TiCl_2 + AgO\overset{\overset{O}{\|}}{C}R \longrightarrow Cp_2Ti(O\overset{\overset{O}{\|}}{C}R)_2$$



$$Cp_2Ti(C_6H_5)_2 + (C_6H_5\overset{\overset{O}{\|}}{C}O)_2 + 2\,(CH_3)_2CHOH \longrightarrow Cp_2Ti(O\overset{\overset{O}{\|}}{C}C_6H_5)_2 + 2\,C_6H_6 + 2\,(CH_3)_2CO$$

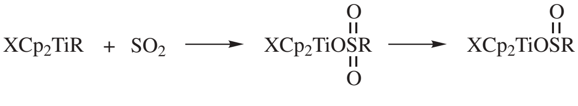
The acylates undergo facile hydrolysis or alcoholysis with loss of one or both Cp groups (370).

A silyl group can be attached to titanium by using $Al(Si(CH_3)_3)_3$ or $KSi(C_6H_5)_3$; $LiSi(CH_3)_3$ causes reduction (374,375). Germyl and stannyl groups can also be attached to titanium (376,377). Organometallic ligands can be attached to titanium by displacement reactions involving Cp_2TiCl_2. Both chlorines are displaceable (378–381). Unusual titanocycles are formed from sulfur and phosphorus reagents (276,277,297,382–387).

Reaction of cyclopentadienyltitanium halides and oxygen-bonding reagents is confusing. On the one hand, alcohols cleave one Cp group readily, and the second more slowly, from Cp_2TiCl_2. Sodium alkoxides or aryloxides in aprotic solvents give less cleavage (388–399). Silanols and ambident nitrite and nitrate do not cleave Cp groups (400,401). Several studies have attempted to explain the often facile cleavage by O-bonding reagents, which contrasts with normal displacement by N- or S-bonding reagents (385,402–423).

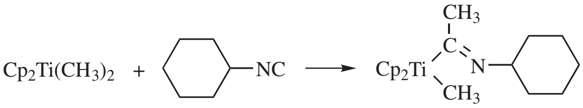
On the other hand, Cp_2TiCl_2 and CpTiCl dissolve in boiling dilute hydrochloric acid, yielding aqua cations that retain the Cp groups, eg, $(Cp_2TiOH{\cdot}H_2O)^+Cl^-$; [11216-84-6] and $(Cp_2Ti_3{\cdot}H_2O)^{3+}{\cdot}3Cl^-$; [1270-90-0]. These can be isolated as salts (296, 424–441).

Insertion into the CpTi−R Bond. Sulfur dioxide yields sulfones and ultimately sulfinates. The latter are available also from RSO_2Na, where $R = CH_3$, C_2H_5, C_4H_9, or C_6H_5, and $X = F$ or Cl.



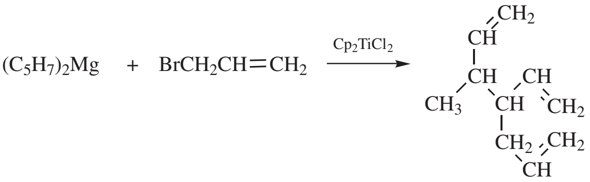
$$XCp_2TiR + SO_2 \longrightarrow XCp_2TiO\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}R \longrightarrow XCp_2TiO\overset{\overset{O}{\|}}{S}R$$

Such titanium sulfinates are reported to increase crop yields (442–449). Isocyanides insert to yield imines as follows (445,446):



Organic isocyanates and isothiocyanates as well as nitric oxide insert similarly (447). Carbon monoxide inserts to yield very stable acyltitaniums (447,448).

Miscellaneous Reactions of Cp_2Ti Derivatives. Coupling of fluxional pentadienide ion with allyl bromide is regiospecifically catalyzed by Cp_2TiCl_2 (449,450). In contrast, cuprous chloride gives the linear triene:



Reactions of titanium alkyls with aldehydes and ketones are generally more stereospecific and selective than the corresponding Grignard reactions (451).

Transition-metal-catalyzed polymerizations of β-propiolactone and $CH_2=CHOCH_2CH_2Cl$ are markedly accelerated by Cp_2TiCl_2 (452,453). Formation of dicyclopentadienylmagnesium is promoted by Cp_2TiCl_2, but not by $TiCl_4$ or $CpTiCl_3$ (454). In olefin metathesis, the potent WCl_6 and $WOCl_4$ catalysts are tamed sufficiently by $CpTiCl_2$ to permit metathesis with unsaturated esters (455).

8. Health and Safety Factors

Commercial titanates should be handled according to good industrial practice. The tetraalkyl titanates have a low acute oral toxicity, LD_{50}, of 7500–11,000 mg/kg in rats. Because of their rapid hydrolysis, these titanates can cause severe eye damage. They cause mild-to-moderate irritation of guinea pig skin, but are not skin sensitizers. The titanium chelates possess the added toxicity of the chelating agent. For example, the LD_{50} (rat, oral) of acetylacetonate is 5000 mg/kg. The chelates containing isopropyl alcohol have flash points of 12–27°C. The toxicology of titanium compounds has been reviewed (456).

9. Uses

Organic titanates perform three important functions for a variety of industrial applications. These are (*1*) catalysis, especially polyesterification and olefin polymerization; (*2*) polymer cross-linking to enhance performance properties; and (*3*) Surface modification for adhesion, lubricity, or pigment dispersion.

9.1. Glass–Surface Coating. A thin (<100 nm) film of $(TiO_2)_x$is virtually transparent. On glass, these films are bonded by Ti−O−Si bridges. After application of a lubricant, they impart considerable scratch resistance to glass and consequently greatly reduce its fragility (457,458). The lower alkoxides, particularly TYZOR TPT, are preferred for glass treatment. They can be applied undiluted, ie, in a hot process, or in a solvent, which may be hot or cold. Chelates, usually with TYZOR TE, may be used in water solution and applied hot or cold. Mixtures of TYZOR TPT and chelates, eg, TYZOR TE and TYZOR AA, are said to give more uniform coatings (44).

The $(TiO_2)_x$films are also applied to glass or vitreous enamel for decorative purposes. Thin films enhance brilliance; thicker films impart a silver-gray luster. Milk glass can be produced by mixing the titanate with a low melting enamel, which sinters when the coating is baked (459).

When the $(TiO_2)_x$ film is ~150-nm thick, ie, one-quarter wavelength of average visible light, it is antireflective toward visible light, yet reflective toward heat-producing ir radiation. Precisely coated window glass is used in hot countries to reduce solar heating of houses (460). Thicker coatings pass ir light for solar cells and are valuable as antireflective coatings for lightwave guides, photodiodes, or semiconductors (461–467). In some of these applications, mixtures of titanate with a silicate ester are valuable. These protective coatings have been used in liquid-crystal devices and electronic products and sometimes as mixtures with silicates or zirconates (464–467) (see LIQUID CRYSTALLINE MATERIALS). The coatings adhere to polytetrafluoroethylene (PTFE) (465). In an unusual application, titanoxane−siloxane mixtures, which may contain a borate, are applied to glass or glass particles that are then fired in an oxidizing atmosphere to yield a crystalline glass (pyroceram) of superior thermal properties (468) (see GLASS–CERAMICS).

The bonding properties of $(TiO_2)_x$have been used for size-reinforcing of glass fibers so that they adhere to asphalt or to a PTFE−polysulfide mixture to impart enhanced flex endurance (469–471). Poly(vinyl alcohol) solutions mixed with sucrose can be cross-linked with the lactic acid chelate and used generally for glass-fiber sizing (472).

9.2. Nonemulsion Paints. Heat-resistant paint (up to 500−600°C) can only yield films containing little or no organic residues because most C−C or C−H bonds are pyrolyzed below those temperatures. Pyrolysis of oligomeric titanates, obtained by controlled hydrolysis of TYZOR **TnBT**, furnishes adherent films of nearly inorganic $(TiO_2)_x$. These oligomers suspend pigments, particularly aluminum, alumina, and silica. Paints were formulated from these treated pigments, oligomers, ethylcellulose (to prevent pigment settling), and mineral-spirit solvent. Whereas encouraging results were reported for these paints on rocket launchers, smokestacks, motor exhaust systems, and fire doors (473,474), scant patent literature on such applications implies that the needs for heat-resistant paints are met by other formulations.

Titanates are valuable in other paint applications. Corrosion-resistant coatings have been described for tinplate, steel, and aluminum (475–479). Incorporation of phosphoric acid or polyphosphates enhances the corrosion resistance. Because titanates promote hardening of epoxy resins, they are often used in epoxy-based paint (480). Silicones (polysiloxanes) are often cured by titanates. Pigments, eg, TiO_2, SiO_2, Al_2O_3, and ZrO_2, are frequently pretreated with titanates before incorporation into paints (476,481). In these applications, the $Ti(OR)_4$ compounds are often mixed with $Si(OR)_4$, $Al(OR)_3$, $Zr(OR)_4$, and other metal alkoxides (12).

Titanates react with ester groups in paint vehicles, eg, linseed oil, tuna oil, and alkyds, and with hydroxy groups, eg, in caster oil and some alkyds, to prevent wrinkling of paint films (117,482).

9.3. Adhesives. Tetrafunctional titanates react with hydroxyl, ester, amide, imide, and other functions, and with oxide groups on metals and nonmetal oxides. Titanates bond such materials together (133). Titanates bond to polyethylene and fluorinated polymers (483). Packaging films, eg, Mylar polyester or aluminized films, are coated with a titanate, then warmed in moist air to hydrolyze and oligomerize the titanate and evaporate volatile organics (484). The resulting film is not tacky and can be rolled and stored. Subsequently, polyethylene is extruded onto the surface and bonded by calendering. Printing inks and decorations can also be bonded.

Titanates have been instrumental in the bonding of fluorinated resins to packaging films, poly(hydantoin)–polyester to polyester wire enamel, polysulfide sealant to polyurethane (a phosphated titanate is recommended), polyethylene to cellophane using a titanated polyethylenimine, and silicone rubber sealant to metal or plastic support using polysilane (Si–H) plus polysiloxane (Si–OR) and titanate as the adhesive ingredients (485–489). Polyester film coated first with a titanium alkoxide, then with a PVR–polyethylenimine blend, becomes impermeable to gases (490).

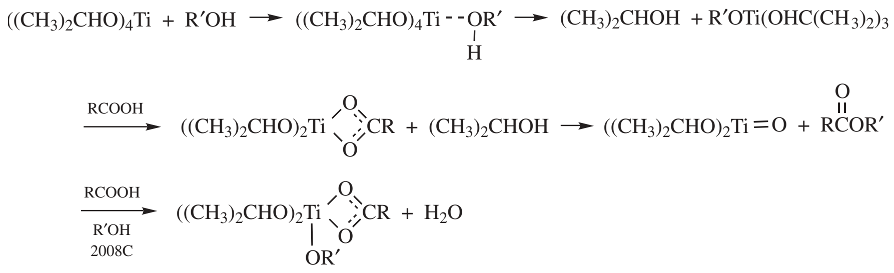
9.4. Water Repellents. Titanate–wax compositions have been used for the rewaterproofing of textiles that have been dry cleaned. Typically, a slowly hydrolyzable titanate ester from octylene glycol or 3,5,5-trimethyl-1-hexanol is dissolved in a dry cleaning solvent with wax and applied to the garment before the final drying stage. Hydrolysis and bonding to the cellulosic textile occur during steam pressing. In a variation of this process, a silicone is applied with the titanate; the former furnishes repellency, the latter bonds it for durability. A perchloroethylene solution of an epoxy-functional polysioloxane and a titanate orthoester can be used to improve the water repellency of polyester, polyester–cotton and polyamide textiles (491). Tetraalkyl titanates can also be used as extenders to improve the oil- and/or water repellency of fluoropolymer textile coatings (492). Leather waterproofed with silicones possesses improved properties when the resin is bonded with TYZOR TnBT (493) (see WATER, WATERPROOFING AND WATER/OIL REPELLENCY).

9.5. Catalysts. Titanates accelerate many organic reactions and frequently provide significant advantages in product purity and yield over conventional catalysts (see CATALYSIS). Their polyfunctionality permits assembling oxygen-containing reactants at one location in a geometrical, usually octahedral, arrangement, which permits facile shuffling of groups to yield products.

9.6. Olefin Polymerization. Titanates having a carbon–titanium bond are extensively involved in Ziegler-Natta and metallocene polymerization of olefins.

9.7. Esterification. Esterification of an acid and an alcohol can be catalyzed by small quantities of tetraalkyl titanates (see ESTERIFICATION). Although the water that forms can hydrolyze and inactivate the titanate, titanoxane oligomers are cleaved by carboxylic acids to bicoordinated monomeric acylates.

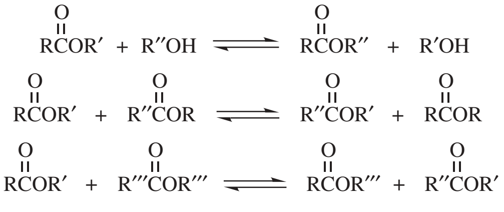
A simplified mechanism is illustrated:



In plasticizer manufacture, eg, of phthalates or sebacates, using sulfuric or *p*- toluenesulfonic acid catalysts, the temperature (140–150°C) required for rapid reaction and high conversion may dehydrate or oxidize the alcohol and may yield a dark or foul- smelling product. Neutral titanates do not cause such side reactions. Although a temperature of 200°C is required, esterifications can easily be forced to $>99\%$ conversion without the formation of odors or discoloration. Preparations include long- chain esters from neopentyl glycol, trimethylolpropane, and pentaerythritol for synthetic lubricants, and triglycerides from mixed long-chain acids for suppositories (494–496).

In polyester manufacture from dibasic acids and diols, color is particularly important for fiber and film products. Moreover, destruction of diol by strong acids upsets the stoichiometric balance required for high molecular weight and forms by-products, eg, diethylene glycol or toxic dioxane from ethylene glycol or THF from tetramethylene glycol. Titanate catalysts, eg, $MgTi(OR)_6$ and $(RO)_4Ti$, are devoid of these problems (497–500). Using hydroxyl-terminated prepolymers, chain extension by diisocyanates is also accelerated by titanates (497).

Ester Interchange. Ester interchange is exemplified by the following reactions, all of which are strongly promoted by titanates:



$$\mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR'} + \mathrm{R''OH} \rightleftharpoons \mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR''} + \mathrm{R'OH}$$

$$\mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR'} + \mathrm{R''}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR} \rightleftharpoons \mathrm{R''}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR'} + \mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR}$$

$$\mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR'} + \mathrm{R'''}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR'''} \rightleftharpoons \mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR'''} + \mathrm{R''}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR'}$$

The first is the most common synthetically, whereas the third is important in cross-linking polyesters. Classical catalysts, ie, sulfuric acid and NaOR, react with other functional groups to lower yield and product purity (501). In transesterification, the methyl ester of sebacic or other acid is heated with an equivalent amount of a long-chain alcohol and titanate (0.1–2.0 mol % of TYZOR TPT) at atmospheric or reduced pressure to distill methanol and drive the reaction to completion. A solvent, eg, benzene or cyclohexane, which forms a low boiling azeotrope with methanol, may be added. Esters prepared from methyl esters include diaryl carbonates from phenols, long-chain carbamates (urethanes), and diethylaminoethyl methacrylate (502–505). In the first example, the catalyst is the solid prepared by calcining the precipitate from cohydrolysis of $TiCl_4$ and $SiCl_4$. The third and forth examples are typical of the preparation of a host of methacrylate or acrylate esters from low cost methyl methacrylate (MMA) or ethyl acrylate (EAA) and other alcohols under nonpolymerizing conditions. The product methacrylate is often pure enough for subsequent polymerization. To remove the titanate catalyst, if required, 2 mol of water should be added to each mole of titanate and the $Ti(OCH(CH_3)_2O$ [66593-86-0] should be removed by filtration through diatomaceous earth. Alternatively, a solid titanate catalyst can be used, which is removed by filtration at the end of the transesterifcation reaction (506). Tetraalkyl titanates can also catalyze the transesterifcation of tetramethyl- and tetraethyl orthosilicates (507).

Polyesterification. High molecular weight linear polyester resins, eg, poly(ethylene terephthalate) (PET), poly(propylene terephthalate) (PPT), and poly(butylene terephthalate) (PBT), can be produced by either transesterification of dimethyl terephthalate (DMT) with an excess of the corresponding diol or by direct esterification of terephthalic acid (TPA). Tetraalkyl titanates, eg, TYZOR TPT or -TYZOR TnBT, have been found to be excellent catalysts for either of these reactions.

Complexes of titanium alkoxides with acetic acid also work well (508–511), as have mixed metal complexes formed by reaction of titanium alkoxides with alkali or alkaline earth metals (512–515). Inorganic titania and titania/silica or titania–zirconia heterogeneous catalysts prepared by hydrolysis of titanium alkoxides or mixtures of alkoxides of titanium and silica or titanium and zirconium have also been shown to be good polyesterification catalysts (516–519). However, in the case of PET, the residual titanate catalyst reacts with trace quantities of aldehydic impurities produced in the polymerization process to generate a yellow discoloration of the polymer (520,521).

The organic titanate catalysts are typically used at the 50–300 ppm Ti concentration range based on DMT or TPA. Higher concentrations, which give a higher polymerization rate, also lead to greater yellow discoloration in the final product. A variety of methods have been developed to reduce the yellow discoloration found in PET when titanates are used as a catalyst. Most aproaches involve forming complexes of titanium, which have been shown to minimize color delevopment. Complexes formed by the reaction of titanium alkoxides (522,523), alpha-hydroxycarboxylic acid complexes of titanium (524–527) or aromatic carboxylic acid complexes of titanium (528) with an organic or inorganic phosphorus compound are believed to prevent titanium from entering into color-forming reactions. The use of oxalic acid complexes of titanium (529–532) are believed to function in a similar fashion. However, the use of phosphorus compounds and other strong ligands invariably slow down the rate of catalysis so that their use must be carefully regulated (533–535). The use of toners based on cobalt complexes of phosphorous (522,536,537) have been shown to mask the yellow discoloration.

Generation of color is related to Ti concentration in the polymer. The concentration of Ti used in the polymerization reaction can be reduced by using mixtures of Ti and other metals (538–543). Concentration of Ti required can also be reduced by depositing titanium alkoxides on high surface area, inorganic supports (544–546). The addition of tetraalkylammonium hydroxides to mixtures of tetraalkyl titanates and zirconates has been shown to provide more active catalysts that yield polyester with less color than the individual titanates or zirconates or mixtures thereof (547).

The addition of an alkanolamine, eg, diethanolamine, to TYZOR TnBT, as well as the use of a less moisture-sensitive alkanolamine titanate complex, eg, TYZOR TE, has been reported to prolong catalyst life and minimize haze formation in the polymer (548,549). Several excellent papers are available that discuss the kinetics and mechanism of titanate-catalyzed esterification and polycondensation reactions (550–557).

Mixtures of titanium complexes of alpha-hydroxycarboxylic acids and phosphorous compounds have also been used to produce 5-sulfoisophthalate bis(glycolate) ester metal salt precursors to cationic dyeable polyester (558). The water resistance of aqueous-based printing inks that use sulfonated polyester resins can be improved by using TYZOR TE (559).

In the case of PPT and PBT, where the color of polymer is not as critical, organic titanates are the catalyst of choice because of their greater reactivity than antimony or tin (560–562). Numerous processing variations have been described in the literature to minimize formation of THF in the PBT process (563,564). Mixtures of tetraalkyl titanates and/or zirconates with various phosphorous compounds have also been used to catalyze the reaction of terephthalic acid (565) or dimethyl terephthalate (566) with 1,4-butanediol in the manufacture of PBT. The use of alkali metal salts of hypophosphorous acid avoids catalyst deactivation and still provides an improvement in polymer color and minimizes THF by-product formation (567).

Recently, macrocyclic oligoesters have been developed as precursors to polyesters. Macrocyclic oligoesters exhibit low melt viscosity, which allows them to melt and polymerize at temperatures well below the polymers. In the presence of hindered phenol and polyol complexes of titanium, these oligoesters often can be converted under isothermal conditions to linear polyesters of high crystallinity and solvent resistance (568–573).

Biodegradable polylactide polymers are finding increasing use in packaging films, diapers, medical implant devices, and as timed-release coatings. The ring-opening polymerization of cyclic esters, eg, lactide and caprolatone, can be polymerized by tetraalkyl titanates or titanatranes prepared from them (574,575).

Polyester resin-based powder coatings can be cured with alkanolamine titanate (576,577), titanium–zirconium (578,579) and titanium–aluminum (580) complexes. These powder coatings can be used to coat insulated elecrical conductors and provide highly durable and decorative systems for steel and aluminum. The use of mixed-metal systems has been shown to yield better yellowing and solvent resistance and curing rate.

Alkyd Resins. Polyesters bearing pendant ester groups react with such groups on adjacent chains, resulting in alkyd resin formation. These reactions are catalyzed by titanates. Acrylic polymers are cross-linked with glycols or to hydroxyl-containing alkyds (581,582) (see ALKYD RESINS).

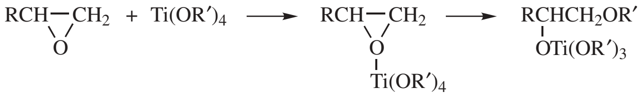
Polycarbonate Resins. Polycarbonate molding resins can be prepared by the titanate-catalyzed transesterification of diphenylcarbonate with a dihydroxy compound, eg, bisphenol A. Polycarbonates can be blended with other polyesters, eg, polybutylene terephthalate (PBT), to give molding resins having improved toughness and ductility. Under the high temperatures required for blending, ester–carbonate interchange reactions can occur, which result in reduced strength and increased mold cycle times. The use of complexes of tetraalkyl titanates with phosphorus compounds, such as phenylphosphinic acid or dialkyl- or diarylphosphites, minimizes this interchange reaction (583).

Methyl Esters. The addition product of 2 mol of TYZOR TPT and 1 mol of ethylene glycol, GLY-TI, can be used as a transesterification catalyst for the preparation of methyl esters. The low solubility of tetramethyl titanate has prevented the use of them as a catalyst for methyl ester preparation (584).

$$2\,\mathrm{Ti(OC_2H_5)_4} + \mathrm{HO(CH_2)_2OH} \longrightarrow \mathrm{(C_2H_5O)_3TiO(CH_2)_2OTi(OC_2H_5)_3} + 2\,\mathrm{C_2H_5OH}$$

Unsaturated Polyester Resins. Unsaturated polyester resins are widely used as fiber-reinforced plastics, coating materials, tire cords, films, and casting or molding resins. Organic titanates, eg, TYZOR TPT, TYZOR TnBT, or TYZOR TOT, can be used to catalyze the preparation of the resins, which involves the polyesterification of a mixture of α- and β-unsaturated polybasic acids, such as maleic or fumaric acid, and alicyclic polybasic acids, eg, adipic or isophthalic acid with polyhydroxyalcohols (585).

Epoxy Resins. Titanates react with free hydroxy groups in epoxy resins or with the epoxy group itself:



$$\mathrm{RCH{-}CH_2\ (epoxide)} + \mathrm{Ti(OR')_4} \longrightarrow \mathrm{RCH{-}CH_2\ (O{\rightarrow}Ti(OR')_4)} \longrightarrow \mathrm{RCH(OTi(OR')_3)CH_2OR'}$$

Sufficient titanate leads to a fully hardened polymer. Using only enough titanate to react with free hydroxyls, the resin may subsequently be cured at lower cost with conventional cross-linking agents. The titanated epoxy resin has a low power factor, which is important in electrical applications, eg, potting components and insulation (see Embedding). Titanates improve adhesion of metals to epoxies.

Epoxy cross-linking is catalyzed by TYZOR TPT and TYZOR TnBT, alone or with piperidine, and by TYZOR TE. The solid condensation product from 3 TPT:4 TEA (triethanolamine) has also been applied to epoxy curing (586). Titanate curing is accelerated by selected phenolic ethers and esters at 150°C; the mixtures have a long pot life at 50°C (587) (see Epoxy resins).

Copper powder suspended in titanate-cured epoxy resin shields electronic apparatus against electromagnetic interference (588). Magnetic particles, eg, iron, iron oxides, and magnetic alloys, suspended in resin containing a titanate yield a superior recording tape (589,590). Titanates are very effective in dispersing and suspending particles. Such compositions can be formed into larger magnets (591). Other titanate-curable resins useful for these purposes include silicones, polyesters, phenolics, polyurethanes, polyamides, and acrylics (591). The combination $\mathrm{(C_4H_9O)_4Ti}$ and $\mathrm{(C_4H_9O)_3B}$ provides a fast-curing system suitable for metal coating (548).

9.8. Thixotropic Paints. Water-based latex emulsion paints may be made thixotropic or nondrip by the addition of alkanolamine-based titanium chelates. Thixotropic paints are very viscous, yet thin out enough when applied to a surface. They remain thin long enough to allow leveling to occur. Such easy applicability is the result of shear forces.

It is believed that the thixotropic structure in these systems is produced by hydrogen bonding between the hydroxyl groups on the cellulose ether colloids present in the paint and the hydroxyl end groups formed by partial hydrolysis of the chelated titanates. This association is reversible and may take place repeatedly. However, if the alkoxy groups on the titanate undergo chemical reaction with the hydroxyl groups present in the colloid polymer, an irreversible covalent bond is formed, which in the case of PVA polymers can lead to the formation of rubber-like gels. With cellulose ethers this chemical reaction is somewhat slow and the physical hydrogen-bonded structure predominates, leading to the observed thixotropy. As a rule, the more reactive chelates, eg, diethanolamine titanates, give rapid buildup in gel strength. Trialkanolamine titanates, eg, TYZOR TE, and chelates based on use of an alkanolamine in combination with other chelating ligands and/or glycols, are less reactive, giving paints that have excellent thixotropic structure (592). The stability of the titanium chelates is dependent on the ratio of the total number of moles of glycol, alkanolamine, and other ligands to the number of moles of titanium metal. The lower this ratio, the stronger the gelling effect on the aqueous emulsion paints (593,594).

Incorporation of an α-hydroxycarboxylic acid in the formulation slows the rate of metal gelation of the paint, making it possible to fill more containers during the packing operation before the paint becomes too viscous to flow, and improves the ability to blend the chelated titanate into the paint without localized areas of gelation (595,596). These paints are also less likely to lose potential gel strength resulting from excessive shearing during the manufacturing process.

Metal complexes prepared by reacting a titanium alkoxide with < 1 mol of an alkanolamine and an excess of a polyhydric alcohol, eg, polyethylene glycol 200-400 or glycerol, reportedly impart a greater degree of thixotropy to systems containing protective organic colloids (597).

9.9. Printing Inks. Organic titanates are useful for reducing the drying time of flexographic and gravure printing inks. In the case of uv-curable printing inks, tetraalkyl titanates, eg, TYZOR TPT or TYZOR TnBT are believed to catalyze the polymerization of vinyl monomers, such as styrene, with unsaturated polyesters comprising the ink vehicle to form a hard surface in a matter of seconds (598) (see Lnks).

For ink vehicles based on hydroxyl group containing binders, eg, nitrocellulose and cellulose acetate, the tetraalkyl titanates cross-link the binder prematurely, limiting the storage stability of the printing ink. Chelated organic titanates, eg, TYZOR AA and TYZOR TE, are preferred for use in these cases because they only initiate cross-linking when the ink is heated to temperatures $>80°C$ (599).

The chelated organic titanates also function as adhesion promoters of the ink binder to printed substrates, eg, plastic films, paper, and aluminum foil (600). The acetylacetone complexes of titanium are the preferred products for promoting adhesion of printing inks to polypropylene films.

The intense reddish-brown color of the acetylacetone titanium complexes impart a yellow discoloration to white inks. This discoloration is accentuated when the inks are used to print substrates that contain phenol-based antioxidants. The phenolic compounds react with the organic titanate to form a highly colored titanium phenolate. Replacement of 0.25–0.75 mol of acetylacetone with a malonic acid dialkyl ester, eg, diethyl malonate, gives a titanium complex that maintains the performance advantages of the acetyl acetone titanium complexes, but which is only slightly yellow in color (601). These complexes still form highly colored titanium phenolates.

Mixtures of a titanium complex of saturated diols, eg, TYZOR OGT, and a titanium acylate, eg, bis-*n*-butyl-bis(caproic) acid titanate, do not have a yellowing or discoloring effect on white inks used to print polyolefin surfaces (602). The complexes formed by the reaction of 1 or 2 mol of diethyl citrate with TYZOR TPT have an insignificant color on their own and do not generate color with phenol-based antioxidants (603). The complexes formed by the addition of a mixture of mono- and dialkyl phosphate esters to TYZOR TnBT are also low color-generating, adhesion-promoting additives for use in printing polyolefin films (604).

The addition of 1 mol of a diol, eg, ethylene glycol, 1,2-propanediol, or 1,4-butanediol, to bis(acetylacetone) titanate complexes gives a complex that is stable on dilution with water and that can be used in aqueous printing inks (605). An excellent review of the use of organic titanates in printing inks is available (606).

Other Inks. The alkanolamine titanates, eg, TYZOR TE, when mixed with a coloring agent used to print fibrous materials, eg, cotton, wool, or silk, promote adhesion of the dye molecule to the fiber, thus minimizing bleeding of the printed design (607).

The titanium triethanolamine chelates, eg, TYZOR TE, are excellent adhesion promoters for use in water-based laminating inks typically used to bond two similar or dissimilar plastic films together (608). The use of α-hydroxycarboxylic acid titanates, such as TYZOR LA, in nonaqueous or aqueous ink-jet printing ink minimizes premature destruction of bubble-jet printer nozzles by forming a protective coating on the printing head (609). To improve the deinking capability of sheet- and web-fed lithographic printing ink systems, tetralinoleic alcohol titanate drying oils may be incorporated in the alkyd-resin-based inks (610). Tetraalkylene titanates of unsaturated alcohols, eg, 3- methyl-2-buten-1-ol, are excellent adhesion promoters for uv or electron beam (EB) cured printing inks (611).

9.10. Polysiloxane Resin Coatings. Various organopolysiloxane waterproofing compositions have been proposed, which use organic titanates as catalysts, curing agents, and adhesion-promoting materials. Solutions of TYZOR TPT or TYZOR TnBT and a polysiloxane resin in hydrocarbon solvents have been used to impart water repellency to leather goods (612) and cotton, wool, and synthetic fabrics (613). Water-compatible, chelated organic titanates, eg, TYZOR TE, TYZOR AA, or TYZOR LA can be used in aqueous formulations to impart water repellency to fibrous organic materials (614). These aqueous emulsions can also be used to size paper for improving its water repellency and antiadhesion properties (615). An increased level of organic titanate can be used to ensure the rapid curing ($\leq$5s) for fast-paced paper or fiber curing operations (616).

9.11. Room-Temperature Vulcanizable Silicone Rubber. Organic titanates are incorporated into room-temperature vulcanizable (RTV) silicone rubber formulations to provide a one-component system that is stable in the absence of moisture, but that also cures spontaneously at room temperature on exposure to moisture (617,618). Chelated titanates, eg, TYZOR AA or TYZOR DC, can be used to prevent the composition from curing prematurely and to increase the adhesion of the resulting elastomer (619,620). To avoid thickening during initial mixing of the ingredients and to provide a more fluid system, glycol complexes of TYZOR AA or TYZOR DC can be used (621,622). Use of citric acid in combination with the glycol complexes of Tyzor DC (623), or use of titanate complexes of a mixture of mono- and dialkyl phosphate esters (624) have been used to reduce the tendency of titanates to discolor the silicone sealant. Primers comprising a mixture of γ-glycidoxypropyltrimethoxysilane, tetraethyl ortho silicate and/or disiloxanes and TYZOR TPT (625) or TyzorTnBT (626) can be used to promote adhesion of these silicone elastomers to metal (aluminum) and PVC surfaces.

9.12. Coupling Agents for Polymer Composites. Organic titanate esters and their chelates or functionalized derivatives are finding increasing utility as coupling agents for reinforcing fillers in polymeric resin composites. The main function of a coupling agent is to serve as a molecular bridge at the interface of two dissimilar surfaces, thereby promoting adhesion of the fillers to the polymer matrix. Fillers treated appropriately with organic titanates should wet out better and disperse more readily in the polymer matrix, thereby reducing viscosity and improving flow characteristics of the mix. Reduced water sensitivity at the filler polymer interface aids in maintenance of a composite's flexural and tensile strength.

Titanate coupling agents may be applied to an inorganic filler as a pretreatment, or added to the polymer resin, where they migrate to the interface of the two substances during mixing and compounding. They may be applied in a liquid or vapor state, or as a solution in a hydrocarbon- or alcohol-based solvent. Amounts required vary between 0.1 and 5% based on the weight of filler.

The mechanism of titanate coupling is dependent on the type of titanate, substrate, solvent–plasticizer, and binder used. It falls into one or more of the following categories: alcoholysis (solvolysis), surface chelation; coordination exchange, coordination to salt formation, polymer ligand exchange catalysis, and organic ligand interaction (627).

Recommended for use as coupling agents are monoalkoxytriacyl titanates, eg, isopropoxytriisostearyl titanate, Ken-React KR TTS, or TYZOR ISTT [61417-49-0], which are useful in mineral-filled polyolefin resins (628); chelated titanates, eg, di(dioctyl)pyrophosphatooxoethylene titanate, Ken-React KR 138S, or di(dioctyl)pyrophosphatoethylene titanate, Ken-React KR 238S, which maintain high activity even when applied to fillers containing free water (629); organophosphite- coordinated titanates, eg, tetraiisopropyl di(dioctyl)phosphito titanate, Ken-React KR 41B, which are useful in PVC resins because they exhibit minimal interaction with the polyester-based plasticizers, and that also exhibit significant viscosity reduction with epoxy resin formulations without accelerating cure rates (630); quaternized titanate coupling agents, eg, Ken-React KR 238T, the triethylamine adduct of KR 238S, which are water soluble and useful in controlling the viscosity, flow, and conductivity of many filled resin systems

(631); neoalkoxytitanates, such as neopentyl(diallyl)oxy, tri(dioctyl)pyrophosphato titanate, LICA 38, which have improved thermal and/or solvolytic stability compared to their isopropoxy group containing counterparts and can therefore be used in polymeric systems requiring higher extrusion temperatures (632); cycloheteroatom type titanates, eg, dicylo(dioctyl)pyrophosphato titanate, Ken-React KR OPP2, which have been developed for ultrahigh thermal and specialty applications; and organic titanates, eg, TYZOR TnBT, which may be used in combination with silane coupling agents containing ethylenically unsaturated groups, eg, γ- methacryloxypropyl, trimethoxysilane to reduce the viscosity of an acrylic ester-based resin formulation containing finely dispersed inorganic fillers (633).

9.13. Precursors to Ultrafine and Nanoparticle TiO_2 and Mixed-Metal Oxides.

Tetraalkyl titanates are versatile precursors for the synthesis of titanium dioxide and its mixed metal oxides in a variety of shapes and sizes. Solution, Aerosol and vapor phase techniques are being employed to make TiO_2 from titanium alkoxides and various complexes thereof.

One of the most frequently used solution techniques is known as the sol–gel process (634). The sol–gel process involves conversion of a metal alkoxide or mixture of metal alkoxides, dissolved in an organic solvent (generally the parent alcohol) into a hydroxooxyalkoxide sol, followed by gelation and sintering to give the desired ceramic material. Sol–gel chemistry is based on hydroxylation and condensation of the tetraalkyl titanates (635). By controlling the molar ratio of water to titanium alkoxide, the hydroxysis reaction can be stopped at any given point to form titanium oxoalkoxide oligomers having the following structure:

$$(n+1)\mathrm{Ti(OR)_4} + n\mathrm{H_2O} \rightarrow \mathrm{(RO)_3Ti} - [\mathrm{O} - \mathrm{Ti(OR)_2}]_{(n-1)} - \mathrm{O} - \mathrm{Ti(OR)_3} + 2n\mathrm{ROH}$$

An excellent review of metal oxoalkoxides has been published (636). The overall chemical reaction to fully hydrolyzed titanium hydroxide can be written as:

$$\mathrm{Ti(OR)_4} + 4\,\mathrm{H_2O} \longrightarrow \mathrm{Ti(OH)_4} + 4\,\mathrm{ROH}$$

Once formed, the Ti–OH groups can undergo three competing reactions to generate Ti–O– Ti bridges:

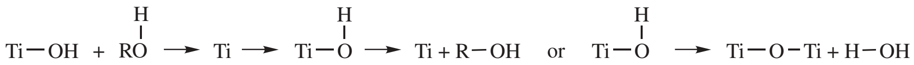
Alkoxolation:

$$\mathrm{Ti - OH + Ti - OR \longrightarrow Ti - O - Ti + R - OH}$$

Oxalation:

$$\mathrm{Ti - OH + Ti - OH \longrightarrow Ti - O - Ti + H - OH}$$

Olation:



$$\mathrm{Ti{-}OH} + \mathrm{R}\overset{\mathrm{H}}{\mathrm{O}} \rightarrow \mathrm{Ti} \rightarrow \mathrm{Ti{-}}\overset{\mathrm{H}}{\mathrm{O}} \rightarrow \mathrm{Ti + R{-}OH} \text{ or } \mathrm{Ti{-}}\overset{\mathrm{H}}{\mathrm{O}} \rightarrow \mathrm{Ti{-}O{-}Ti + H{-}OH}$$

The control of phase (anatase or rutile), size distribution, shape, surface area, and pore structure of the TiO_2 can be affected by water concentration, pH, temperature of the reaction and the use of surfactants (637), and additives that form complexes with the titanium alkoxides (638–643). Microreactors equipped with axel duel pipes have been used to produce monomodal spherical particles of TiO_2 (644). High temperature hydrothermal and vapor-phase processes have been used to make fine particle (645) and nano-size crystals of TiO_2 (646–649). Nano particles of TiO_2 have also been sysnthesized via hydrolysis in solvents, eg, liquid CO_2 (650), hydrocarbon (651,652), and polyol solvents (653,654).

One of the major drawbacks of tetraalkyl titanates in the sol−gel reaction is the difficulty in controlling the hydrolysis reaction. Chemical modification of the alkoxides can be used to control their reactivity by impacting the hydrolysis and condensation steps of the reaction (634,655,656).

Thin films of TiO_2 can be deposited on various surfaces by sol−gel techniques using tetraalkyl titanates (657–659). Hydroxylamine (660), carboxylic acid (661), 2- hydroxycarboxylic acid (662,663) and β-diketone complexes of titanium can be used as well (664). These films can impart antimicrobial (659,665), uv screening (667) and photocatalytic (663,664) effects to the treated surface.

The sol−gel technique has been used to produce photocatalytic, nanoparticulate TiO_2 (668–670). A titanium bis(ammonium lactate) complex, TYZOR LA, has been used to coat molybdenum oxide particles to generate a nanoparticle size core-shell material, the photo adsorption of which, is shifted more toward the visible region of the spectrum (671). Nitrogen (672) and rare earth (673) doping of sol−gel derived nanoparticles have also been used to shift absorption wavelength. sol−gel derived, photocatalytic, nanoparticle TiO_2has been used in waste water (674,675) and air purification (676,677) as well as to produce self-cleaning surfaces (678).

Nanoparticle TiO_2 has also been produced by an aerosol or aero−sol−gel technique, where a fine mist of tetraalkyl titanate droplets are put into contact with water vapor at an elevated temperature (679–683). Laser induced vapor-phase synthesis has also been employed (684,685). Other methods of producing nanoparticle TiO_2 from tetraalkyl titanates include ultrasonic spray pyrolysis (686) and flame pyrolysis . Electrospray techniques have been used to produce hollow, nanosize fibers of TiO_2 (690,691).

By using mixtures of titanium and other metal alkoxides, mixed-metal oxide particles of titanium and aluminum (692), titanium and strontium (693), and titanium and silicon (694–696) have been produced.

Spherical, monodisperse, fine-particle titanium dioxide that has no agglomeration can be manufactured by carrying out a gas-phase reaction between a tetraalkyl titanate vapor and methanol vapor in a carrier gas to form an initial fine particle, which can then be hydrolyzed with water or steam (697).

Hollow fibers of titanium dioxide can also be manufactured by preparing a solution of a tetraalkyl titanate, an acid, eg, HCl, and an alcohol, eg, isopropyl alcohol, followed by spinning and drying the resultant fiber (698).

Colloidal dispersions of TiO_2(699,700), TiO_2/ZrO_2(701), or TiO_2/SiO_2(702) can be formed by similar sol−gel or aerosol procedures.

Metal-organic chemical vapor deposition (MOCVD) can also be used to deposit TiO_2 thin films by flash evaporation of thermally stable complexes of titanium, eg, titanium (*n*- alkoxy-β-ketoiminate)$_2$ (703) and titanium-diisopropoxy, di-2,2,6,6- tetramethylheptanedionate (704).

9.14. Other Uses. *Cross-Linking of Polyols.* Polyols, eg, natural polysaccharides, eg, cellulose, starch, guar gum, and their derivatives, and PVA and its derivatives can be cross-linked by organic titanates.

Gelled Explosives. Aqueous solutions of water-dispersible, nonionic, natural hydroxylated polymers, eg, galactomannans and their derivatives, can be cross-linked with organic titanates, eg, TYZOR TE, TYZOR AA, and TYZOR LA to give water-bearing gels, which can be used to form gelled explosives (705–707).

Incorporation of a conductive salt into similar cross-linked gels can be used in preparing a device to measure and transmit electrical signals (708).

Cellulose. Cellulose or starch xanthate cross-linked by titanates can adsorb uranium from seawater (709). Carboxymethylcellulose cross-linked with TYZOR ISTT is the bonding agent for clay, talc, wax, and pigments to make colored pencil leads of unusual strength (710).

Wood Protection. Stabilization and photoprotection of wood surfaces with chromic acid is well known, however, chrome generates discoloration of the wood surface and it is coming under increasing regulatory pressure. Tetraalkyl titanates or their chelates, eg, TYZOR LA or TYZOR TE, have been shown to increase the tensile strength of wood veneers (711) and prevent discoloration caused by bleeding of wood components (712).

Paper Sizing. Various materials are added to paper to improve its wet strength and ink acceptance, to make possible clay coating, etc. Titanic acid precipitation of paper fibers can be controlled (144). Aqueous TYZOR TE, when neutralized, rapidly deposits titanic acid. Addition of a monosaccharide or derivative delays precipitation for several hours or months, depending on the stereochemistry of the sugar. Glucose, lacking *cis*-hydroxyl pairs, is less effective than mannose (2,3-*cis*-diol) and also lactose. Yet fructose is better than mannose, which indicates that the hemiketal structure, ie, the furanose ring, furnishes a cis-diol structure. Alditols are better than the corresponding aldose, and mannitol surpasses sorbitol. Handsheets prepared from semibleached kraft pulp treated with sugar-stabilized TYZOR TE solutions exhibit a considerably higher wet strength than those from untitanated pulp.

Poly(Vinyl Alcohol). Poly(vinyl alcohol) is used extensively as a paper size, alone or in combination with dyes or pigments; it is rendered insoluble by cross-linking with titanates. A rayon- based paper has been made resistant to boiling water (713,714). A size of PVA and hydroxyethyl starch cross-linked with titanium citrate or lactate prevents liming in the sizing press (715). A mixed chelate (diol and hydroxyacid) has been recommended (716). A mixture of PVA and a silicone with TYZOR TE provides a release treatment for papers, though silicones alone or with an epoxyamine also provide release coatings or waterproofed paper (503,716–720). The patent literature includes many other examples of titanate-cross-linked PVA. A smokeable sausage casing has been prepared from PVA, hydrolyzed ethylene–vinyl acetate copolymer, and glycerol on paper (721). Poly(vinyl alcohol) and poly(oxyethylene)sorbitan laurate suspend kaolin in cosmetic mud packs (722). Cross-linked PVA is foamed and then dried to give porous material for an unspecified medicinal use (723). Cotton textiles sized with cross-linked PVA are wrinkle resistant (724). Clay or humus soils are stabilized with PVA–titanate products (725,726). Poly(vinyl alcohol) titanates are used as capsule walls for microencapsulated dyes for copy paper (727). A PVA solution reinforced with lignin has been recommended as a temporary plug for leaks in equipment containing $TiCl_4$ (728).

Oilfield Hydraulic Fracturing Fluids. Hydraulic fracturing can be used to stimulate production of oil and gas from subterranean formations. In a typical fracturing operation, a thickened fluid is pumped down the well- bore under sufficient pressure to produce a fracture in the rock formation. The fluid is required to maintain sufficient viscosity to carry a propping agent, typically sand, into the fracture, where it is deposited once the fluid breaks down and loses viscosity. A typical fluid consists of an aqueous liquid that contains a polysaccharide gelling agent, a borate, an organic titanate, or a zirconate cross-linking agent; pH buffers; thermal stabilizers (sodium thiosulfate); and, if necessary, an enzyme or peroxygen gel breaker (729). Water-compatible chelated titanates, eg, TYZOR TE, TYZOR LA, and TYZOR AA, are excellent cross-linking agents (729). However, they also develop viscosity at too great a rate to allow pumping into the formation before they are shear degraded. A delay in cross-linking rate can be achieved by the addition of a retarding agent, such as a polyol, an α-hydroxycarboxylic acid or an alkanolamine to the aqueous polymer solution prior to addition of the cross-linker (730–735) or TYZOR TE can be reacted with glycerol and water to form a delayed cross-linker (736,737). The reaction of a combination of an α-hydroxycarboxylic acid and a polyol sugar with $TiCl_4$, followed by neutralization with a base, eg, sodium hydroxide, gives a water-soluble titanium complex, which shows a delayed rate of cross-linking (738,739).

Tetraalkyl titanates react with organic borates, $B(OR')_3$, to give complexes of the general formula $Ti(OR)_4{:}B(OR')_3$, which are useful as catalysts and cross-linking agents (740). Mixtures of chelated organic titanates, eg, TYZOR TE and TYZOR LA with alkali metal borates, eg, borax or boric acid, can be used to produce shear-stable fracturing fluids (741,742).

A more complete discussion of the rheology and molecular structure of HP Guar gels used in fracturing fluids has been published (743–745).

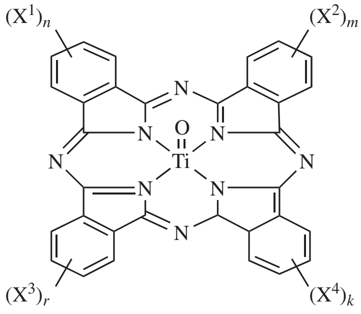
Oilfield Drilling Fluids. A fluid-loss reduction agent for oil-based drilling fluids has been prepared by reacting an organic titanate, eg, TYZOR TPT, TYZOR TnBT, TYZOR AA, or TYZOR TE, with a fatty acid, eg, oleic or stearic acid and a metal oxide (746). The reaction product of an organic titanate, eg, TYZOR TOT, TYZOR AA, or TYZOR TE, with an anionic emulsifying agent, eg, calcium dodecylbenzene sulfonate, can be used to stabilize oil-based drilling fluids against inorganic salt contamination (747).

Enhanced Oil Recovery. A hydrocarbon solution of TYZOR TPT, TYZOR TnBT, or TYZOR TOT can be pumped into the porous zones of an oil-bearing formation; upon contact with water, an amorphous, gelatinous TiO_2 plug is formed, which allows water to be diverted to less porous zones (748).

The use of a strong chelating ligand, eg, bis(hydroxyethyl glycine), gives a titanate complex, which has an extremely slow cross-linking rate. This can therefore be used at high temperatures or high pH and still effect cross-linking at acceptable rates (749).

Anticorrosion Coatings. Chromated or phosphated zinc or zinc-coated metal parts, eg, nuts, bolts, and fasteners used in automobiles and trucks can be protected from corrosion by application of a dip coating comprising a binder combination in a solvent of a tetraalkyl titanate and an organofunctional polysiloxane in a solvent or a binder comprising a tetraalkyl titanate, a chelate thereof and an organofunctional polysiloxane in a solvent (750). Baking of the resultant coating forms a protective titania/silica layer on the surface of the metal part. Chrome-free anticorrosion coatings comprising a silicate and organic titanate binder and a zinc or aluminum flake corrosion inhibitor in an organic solvent have also been developed (751). The preferred binder composition is a mixture of 30–45% mono- or polysilicate esters and 55–70% of mono- or condensed tetraalkyl titanates (TYZOR PBT) or chelated (TYZOR TE, TYZOR AA) titanates.

Electrophotographic Photoconductor. Titanyloxyphthalocyanine (31) can be prepared by either reacting a quinoline solution of phthalonitrile with $TiCl_4$ (752,753),



(**31**)

or a chloronaphthalene solution of 1,3-diiminoisoindoline with a tetraalkyl titanate, eg, TYZOR TnBT (754).

The crude titanyloxyphthalocyanine can be recrystallized by a varity of methods to give a material that can be used as an electrophotographic photoconductor in devices, eg, printers and copying machines (755–757).

The surface of the titanyloxyphthalonitrile can be charged by subjecting it to corona discharge in the dark. An electrostatic latent image is produced by exposing the charged surface to light. The latent image is visualized by use of toners that adhere to the charged surface. The developed image is transferred to paper or other surfaces and the photoreceptor discharged and cleaned for reuse.

Polyurethane Applications. Polyisocyanate Binders. Organopolyisocyanates can be used as binders for lignosulfonate materials used in the manufacture of sheets or molded articles, such as waferboard, chipboard, fiberboard, or plywood. Titanium carboxylates, alkoxides, and chelated complexes can be added to the polyisocyanates to improve curing rates and release of the article from the mold (758). Ethylacetoacetate complexes of titanium, eg, TYZOR DC, are particularly effective (759). Use of excess ethylacetoacetate improves the storage stability of the polyisocyanate composition (760).

Polyurethane Foams. Polyurethane foams are widely used in automotive, housing, and other industries. The foams are generated by reaction of a polyisocycanate with a polyol in the presence of a blowing agent and gelling catalyst. Chlorofluorocarbons (CFCs) are particularly effective blowing agents, however, they have been regulated out of use because of their effect on ozone depletion. It has been found that titanium or zirconium alkoxides and their chelates are effective gelling agents and blowing agents when polyisocyanates are reacted with polyols in the presence of water (761). The water reacts with isocyanates to generate CO_2, which acts as the blowing agent.

Coatings, Adhesives, Sealants and Elastomers (CASE). Amines and mercury and tin compounds have typically been used as catalysts in curing of polyurethane resins used in CASE applications. Recent environmental concerns about these materials has led to the development of novel titanium-based catalysts, the reactivity of which is controlled by proper selection of chelating ligands, eg, acetyl acetone (762), hydroxy Shiff-bases and oximes (763), diketones and ketoesters (764,765), and hydroxycarboxylic acids (766).

Rubber Additives. Sulfur-containing organic titanates have been shown to improve the interaction of silica fillers with rubber formulations containing olefin unsaturation (767,768).

Epoxidation Catalysts. Titanium silsequioxane complexes $[Ti(L)R_{7}Si_{7}O_{12}]$ have been shown to be highly active and selective catalysts for liquid-phase alkene epoxidation reactions (769,770). Because of their difficulty in preparation, much simpler catalysts, prepared by reaction of a tert- alkyl trihydroxysilane with TYZOR TPT have also been used (771). Grafting titanium–calixarene complexes onto silica supports have proven to be 20 times more active and far more selective than solution- phase compounds in olefin epoxidation reactions using organic hydrogen peroxides as oxidizing agents (772). The bulky structure of the calixarene ligand is believed to keep the metal centers isolated from one another during the reaction with alkenes, preventing oligomerization, which would form unreactive Ti– O–Ti compositions.

9.15. Analytical Chemistry.

The use of organic titanates in analytical chemistry has been reviewed (424,773–793).

BIBLIOGRAPHY

"Titanium Compounds" in *ECT* 1st ed., Vol. 14, pp. 213–241, by L. R. Blair, H. H. Beacham, and W. K. Nelson, National Lead Co.; "Titanium Compounds (Organic)" in *ECT* 2nd ed., Vol. 20, pp. 424–503, by R. H. Stanley, Titanium Intermediates, Ltd.; in *ECT* 3rd ed., Vol. 23, pp. 176–245, by C. S. Rondestvedt, Jr., E. I. du Pont de Nemours & Co., Inc.; in *ECT* 4th ed., Vol. 24, pp. 275–349, by D. E. Putzig and T. W. Del Pesco, E. I. du Pont de Nemours & Company, Inc.; "Titanium Compounds, Organic" in *ECT* (online), posting date: December 4, 2000, by D. E. Putzig and T. W. Del Pesco, E. I. du Pont de Nemours & Company, Inc.

CITED PUBLICATIONS

1. U.S. Pat. 3,119,852 (Jan. 28, 1961), R. T. Gilsdorf (to E. I. du Pont de Nemours & Co., Inc.).
2. U.S. Pat. 4,789,752 (Dec. 5, 1988), H. J. Kotzch, H. G. Srenby, and H. J. Vehlensieck (to Huels Troisdorf AG).
3. V. A. Shreider and co-workers, *Inorg. Chim. Acta* **53**(2), 73 (1981).
4. U.S. Pat. 4,650,895 (Mar. 17, 1987), H. Kadokura, H. Umezaki, and Y. Higuchi (to Sumitomo Chemical Co.).
5. U.S. Pat. 4,824,979 (Apr. 25, 1989), H. J. Kotzch, H. G. Srenby, and H. J. Vehlensieck (to Huels Troisdorf AG).
6. B. D. Jain and R. Kumar, *Proc. Indian Acad. Sci. Sect.* **A60**, 265 (1964); *Indian J. Chem.* **1**, 317 (1963); V. Patrovsky, *Coll. Czech. Chem. Commun.* **27**, 1824 (1962).
7. P. N. Kapoor, R. N. Kapoor, and R. C. Mehrotra, *Chem. Ind.* **39**, 1314 (1968).
8. K. S. Mazdujasni, B. J. Schaper, and L. M. Burr, *Inorg. Chem.* **10**(5), 889 (1971).
9. U.S. Pat. 2,709,174 (May 24, 1955), J. B. Rust and L. Spialter (to Montclair Research and Ellis-Foster Co.); U.S. Pat. 2,883,238 (Apr. 21, 1959), A. Pechucas (to Columbia Southern Chemical Co.).
10. H. G. Emblem and S. E. Maskery, *J. Appl. Chem.* **20**, 183 (1970).
11. P. N. Kapoor, S. K. Mehrotra, and R. C. Mehrotra, *Inorg. Chim. Acta* **12**(3), 273 (1975).
12. D. C. Bradley, R. C. Mehrotra, and D. P. Gaur, *Metal Alkoxides*, Academic Press, New York, 1978.
13. J. A. Ibers, *Nature (London)* **197**, 686 (1963).
14. D. C. Bradley and C. E. Holloway, *J. Chem. Soc.* **A2**, 1316 (1968).
15. T. Lover and co-workers, *J. Mater. Chem.* **7**(8), 1553 (1997).
16. N. Hao and co-workers, *J. Magn. Reson.* **50**, 50 (1982).
17. F. Babonneau and co-workers, *Inorg. Chem.* **27**, 3166 (1988).
18. U.S. Pat. 2,689,858 (Sept. 21, 1954), T. Boyd (to Monsanto Chemical Co.).
19. I. Kraitzer, F. K. McTaggart, and G. Winter, *J. Counc. Sci. Ind. Res.* **21**, 328 (1948).
20. T. Boyd, *J. Polym. Sci.* **7**, 591 (1951).
21. T. Ishino and S. Minami, *Tech. Rep. Osaka Univ.* **3**, 357 (1953).
22. D. C. Bradley, R. Gaze, and W. Wardlaw, *J. Chem. Soc.* **1**, 468 (1957).
23. D. C. Bradley, R. Gaze, and W. Wardlaw, *J. Chem. Soc.* **1**, 721 (1955).
24. D. C. Bradley, R. Gaze, and W. Wardlaw, *J. Chem. Soc.* **4**, 3973 (1955).
25. J. Blanchard, M. B. Schaudel, and C. Sanchez, *Eur. J. Inorg. Chem.* 1115 (1998).
26. J. Blanchard, S. Barboux-Doeuff, J. Marquet and C. Sanchez, *New J. Chem.* **19**, 929–941 (1995).
27. D. Hoebbel, S. Reinhart, and H. Schmidt, *J. Sol Gel Sci.* **10**, 115–126 (1997).
28. U.S. Pat. 2,614,112 (Oct. 14, 1952), T. Boyd (to Monsanto Chemical Co.).
29. U.S. Pat. 2,621,193 (Dec. 9, 1952), C. Langkammerer (to E. I. du Pont de Nemours & Co., Inc.).
30. U.S. Pat. 2,666,772 (Jan. 19, 1954), T. Boyd (to Monsanto Chemical Co.).
31. U.S. Pat. 2,621,195 (Dec. 9, 1952), J. H. Haslam (to E. I. du Pont de Nemours & Co., Inc.).
32. U.S. Pat. 2,708,203 (May 10, 1955), J. Haslam (to E. I. du Pont de Nemours & Co., Inc.).
33. A. N. Nesmeyanov, O. V. Nogina, and R. K. Freidlina, *Bull. Acad. Sci. USSR Div. Chem. Sci.*, 355 (1956).
34. U.S. Pat. 2,980,719 (Apr. 18, 1961), J. Haslam (to E. I. du Pont de Nemours & Co., Inc.).
35. Jpn. Pat. 1 129,032 (May 22, 1989), A. Mori and co-workers (to Nippon Soda Co. Ltd.).

36. Jpn. Pat. 1 129,031 (May 22, 1989), A. Mori and co-workers (to Nippon Soda Co. Ltd.).
37. Ref. 12, p. 27ff.
38. D. Seebach and co-workers, *Synthesis* 138 (1982).
39. U.S. Pat. 3,006,941 (Oct. 31, 1961), A. Murdrak and L. Stevick (to Harshaw Chemical Co.).
40. N. Yoshino and T. Yoshino, *Bull. Chem. Soc. Jpn.* **46**(9), 2899 (1973).
41. R. C. Mehrotra, V. D. Gupta, and P. C. Bharara, *Indian J. Chem.* **11**, 814–816 (1973).
42. U.S. Pat. 4,568,703 (Feb. 4, 1986), K. Ashida (to B.P. Chemicals).
43. B. M. Novak, S. M. Hoff, and Y. He, *Polym. Prep. Am. Chem. Soc. (Div. Poly. Chem.)* **34**(11), 258 (1993).
44. Brit. Pat. 1,510,587 (May 10, 1978) (to St. Gobain Industries).
45. Ger. Pat. 934,352 (Oct. 20, 1955), D. F. Herman (to Titangesellschaft).
46. U.S. Pats. 3,091,625 (May 28, 1963) and 3,119,852 (Jan. 28, 1964), R. T. Gilsdorf (to E. I. du Pont de Nemours & Co., Inc.).
47. Brit. Pat. 997,892 (July 14, 1965), L. J. Lawrence (to British Titan).
48. U.S. Pat. 2,684,972 (July 27, 1954), J. H. Haslam (to E. I. du Pont de Nemours & Co., Inc.).
49. Brit. Pat. 787,180 (Dec. 4, 1957), J. H. Haslam (to E. I. du Pont de Nemours & Co., Inc.).
50. J. S. Jennings, W. Wardlaw, and W. J. Way, *J. Chem. Soc.* **1**, 637 (1936).
51. A. N. Nesmeyanov and co-workers, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk* 1037 (1952).
52. G. A. Razuvaev and co-workers, *Dokl. Akad. Nauk SSSR* **122**, 618 (1958).
53. S. Prasad and J. B. Tripathi, *J. Indian Chem. Soc.* **35**, 177 (1958).
54. G. P. Luchinskii, *Zh. Obshch. Khim.* **7**, 2044 (1937).
55. O. C. Dermer and W. C. Fernelius, *Z. Anorg. Allg. Chem.* **221**, 83 (1934).
56. H. Funk and E. Rogler, *Z. Anorg. Allg. Chem.* **252**, 323 (1944).
57. R. C. Mehrotra, *J. Indian Chem. Soc.* **30**, 731 (1953).
58. A. N. Nesmeyanov, O. V. Nogina, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk.* 518 (1951).
59. D. C. Bradley, D. C. Hancock, and W. Wardlaw, *J. Chem. Soc.* **3**, 2773 (1952).
60. I. D. Verma and R. C. Mehrotra, *J. Less Common Met.* **1**, 263 (1959).
61. A. N. Nesmeyanov, E. M. Brainina, and R. K. Freidlina, *Dokl. Akad. Nauk. SSSR* **94**, 249 (1954).
62. A. B. Bruker, R. I. Frenkel, and L. Z. Soborovskii, *Zh. Obshch. Khim.* **28**, 2413 (1958).
63. A. N. Nesmeyanov, E. M. Brainina, and R. K. Freidlina, *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk.* 987 (1954).
64. O. V. Nogina, R. K. Freidlina, and A. N. Nesmeyanov, *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk.* 74 (1952).
65. D. M. Puri and R. C. Mehrotra, *Indian J. Chem.* **5**, 448 (1967); R. C. Mehrotra and R. K. Mehrotra, *J. Indian Chem. Soc.* **39**, 635 (1962).
66. R. E. Reeves and L. W. Mazzeno, *J. Am. Chem. Soc.* **76**, 2533 (1954).
67. U.S. Pat. 2,920,089 (Jan. 5, 1980), C. M. Samoui (to Kendall Co.).
68. Brit. Pat. 1,586,671 (Mar. 25, 1981), M. S. Howarth and B. W. H. Terry (to Imperial Chemical Industries).
69. D. Wang, R. Wu, N. Kumada, and N. Kinomura, *Chem. Mater.* **11**, 2008 (1999).
70. N. Baggett, D. S. P. Poolton, and W. B. Jennings, *J. Chem. Soc. Dalton Trans.* **6**, 1128 (1979); *J. Chem. Soc. Chem. Commun.* **7**, 239 (1975).

71. R. C. Fay and A. F. Lindmark, *J. Am. Chem. Soc.* **97**, 5928 (1975); P. Finocchiaro, *J. Am. Chem. Soc.* **97**, 4443 (1975).
72. R. V. Singh, R. V. Sharma, and J. P. Tandon, *Synth. React. Inorg. Met. Org. Chem.* **11**, 139 (1981).
73. H. Sugahara and Y. Shuto, *J. Organomet. Chem.* **24**, 709 (1970).
74. A. Yamamoto and S. Kambara, *J. Am. Chem. Soc.* **81**, 2663 (1959).
75. A. Yamamoto and S. Kambara, *J. Am. Chem. Soc.* **79**, 4344 (1957).
76. G. J. Gainsford, T. Kemmitt, C. Lensink and N. B. Milestone, *Inorg. Chem.* **33**, 746 (1995).
77. Jap. Pat. 95-207010 (Aug. 8, 1995), H. Heiwa (to Mitsubishi Chemical Corp.).
78. World Pat. 2004/065452 (Aug. 5, 2004), J. Siddiqui (to Saudi Basic Industries Corp.).
79. Brit. Pat. 975,452 (Nov. 18, 1964), R. Feld (to Laporte Titanium Co.).
80. U.S. Pat. 4,568,703 (Feb. 4, 1986), K. Ashida (to B.P. Chemicals Ltd.).
81. S. M. Damo, K. Lam, A. Rheingold, and M. A. Walters, *Inorg. Chem.* **39**, 1635–1638 (2000).
82. U.S. Pat. 2,628,171 (Feb. 10, 1953), L. Q. Green (to E. I. du Pont de Nemours & Co., Inc.).
83. U.S. Pat. 2,643,262 (June 23, 1953), C. O. Bostwick (to E. I. du Pont de Nemours & Co., Inc.).
84. U.S. Pat. 3,091,625 (May 28, 1963), R. T. Gilsdorf (to E. I. du Pont de Nemours & Co., Inc.).
85. U.S. Pat. 4,148,989 (Apr. 10, 1979), G. Tews, H. Wilff, and G. Shade (to Dynamit Nobel AG).
86. U.S. Pat. 4,705,714 (Oct. 11, 1987), S. Matsumoto (to Research and Development Corp. of Japan).
87. U.S. Pat. 2,926,183 (Feb. 23, 1960), C. A. Russell (to National Lead Co.).
88. Brit. Pat. 811,425 (Apr. 8, 1959) and Brit. Pat. 811,426 (Apr. 8, 1959) (to National Lead Co.).
89. Jpn. Pat. 81 46,835 (Apr. 28, 1981), I. Kishima and co-workers (to Matsumoto Pharmaceutical Co.).
90. Brit. Pat. 757,190 (Sept. 12, 1956) (to E. I. du Pont de Nemours & Co., Inc.).
91. U.S. Pat. 5,260,466 (Nov. 9, 1993), G. McGibbon (to Tioxide Specialties Ltd.).
92. U.S. Pat. 2,898,356 (Aug. 4, 1959), C. A. Russell (to National Lead Co.).
93. Brit. Pat. 1,191,480 (May 13, 1970), R. H. Stanley, D. W. Brock, and L. J. Lawrence (to British Titan Products Co. Ltd.).
94. R. J. H. Clark and A. J. McAlees, *J. Chem. Soc.* **A2**, 2026 (1970).
95. U.S. Pat. 3,699,137 (Oct. 17, 1972), E. Termin and O. Bleh (to Dynamit-Nobel A.G.); V. Zatka and O. Hoffman, *Analyst (London)* **95**, 200 (1970).
96. U.S. Pat. 3,682,688 (Aug. 8, 1972), C. T. Hughes and D. A. Paulsen (to E. I. du Pont de Nemours & Co., Inc.).
97. D. C. Bradley and C. E. Holloway, *J. Chem. Soc.* **A1**, 282 (1969).
98. N. Serpone and R. C. Fay, *Inorg. Chem.* **6**(10), 1835 (1967).
99. S. Minami, H. Takano, and T. Ishino, *J. Chem. Soc. Jpn.* **60**, 1406 (1957).
100. A. Yamamoto and S. Kambara, *J. Am. Chem. Soc.* **79**, 4344 (1957).
101. Eur. Pat. 122,312 (Oct. 24, 1984), G. J. Rummo (to Kay-Fries Inc.).
102. U.S. Pat. 3,017,282 (Jan. 16, 1962), H. C. Brill (to E. I. du Pont de Nemours & Co., Inc.).
103. U.S. Pat. 4,647,680 (Mar. 3, 1987), D. Barfurth and H. Nestler (to Dynamit Nobel AG).
104. U.S. Pat. 4,313,851 (Feb. 2, 1982), D. Barfurth and H. Nestler (to Dynamit Nobel AG).
105. U.S. Pat. 4,551,544 (Nov. 5, 1985), G. B. Robbins (to E. I. du Pont de Nemours & Co., Inc.).

106. U.S. Pat. 4,478,755 (Oct. 23, 1984), G. B. Robbins (to E. I. du Pont de Nemours & Co., Inc.).
107. U.S. Pat. 4,924,016 (May 8, 1990), D. Barfurth and H. Nestler (to Huels Troisdorf AG).
108. Ger. Offen. 2,200,347 (Oct. 25, 1973), S. D. Smith and S. B. Hamilton, Jr. (to General Electric Co.).
109. U.S. Pat. 3,338,935 (Aug. 26, 1967), P. M. Kerschner and F. G. Hess (to Cities Service Oil Co.).
110. U.S. Pat. 3,422,126 (Jan. 14, 1969), C. R. Bauer (to E. I. du Pont de Nemours & Co., Inc.).
111. C. Schmutz, E. Bassett, P. Barboux, and J. Maquet, *Mater. Chem.* **3**(4), 393 (1993).
112. S. Hirano and co-workers, *J. Am. Ceram. Soc.* **78**(11), 2956 (1995).
113. K. Noda and co-workers, *Chem. Mater.* **9**, 2174 (1997).
114. K. Noda, W. Sakamoto, T. Yogo, and S. Hiram, *J. Am. Ceram. Soc.* **80**(9), 2437 (1997).
115. U.S. Pat. 3,415,762 (Dec. 10, 1968), B. P. Block and G. H. Dahl (to Pennwalt Chemicals).
116. U.S. Pat. 4,999,442 (Mar. 12, 1991), M. Sato and co-workers (to Nippon Soda Co. Ltd.).
117. Brit. Pat. 755,728 (Aug. 27, 1956) (to National Lead Co.).
118. M. G. Voronkov and V. P. Baryshok, *J. Organomet. Chem.* **239**, 228 (1982).
119. R. L. Harlow, *Acta Chrystal. Sect. C. Cryst. Struct. Commun.* **C39**(10), 1344 (1983).
120. A. A. Naini, W. M. P. B. Menge, and J. G. Verkade, *Inorg. Chem.* **30**(26), 5009 (1991).
121. W. M. P. B. Menge and J. G. Verkade, *Inorg. Chem.* **30**(24), 4628 (1991).
122. Y. Kim and co-workers, *Organometallics* **21**(6), 1127 (2002).
123. Y. Kim and Y. Do, *Macromolecular Rapid Comm.* **21**(16), 1148 (2000).
124. Z. Sun, S. Zheng, L. Meng and D. Wang, *Hauxue Xuebac* **59**(12), 2080 (2001).
125. C. Bickmore and co-workers, *J. Eur. Ceram. Soc.* **18**(4), 287 (1998).
126. S. Kim and co-workers, *Chem. Mater.* **16**(12), 2236 (2004).
127. F. Rioux, M. W. Schmidt, and M. S. Gordon, *Organometallics* **16**(2), 158 (1997).
128. Z. Daun and J. G. Verkade, *Inorg. Chem.* **34**(17), 4311 (1995).
129. M. Schubert and co-workers, *Inorg. Chem.* **33**(18), 3893 (1994).
130. U.S. Pat. 4,618,435 (Oct. 21, 1986), D. E. Putzig (to E. I. du Pont de Nemours & Co., Inc.).
131. U.S. Pat. 2,845,445 (July 29, 1958), C. A. Russell (to National Lead Co.).
132. Brit. Pat. 2,290,795 (Oct. 1, 1996), J. Ridland (to Tioxide Specialties Ltd.).
133. U.S. Pat. 2,935,522 (May 3, 1960), C. M. Samour (to Kendall Co.); Brit. Pat. 786,388 (Nov. 20, 1957) (to National Lead Co.).
134. Technical data, R. L. Harlow (to E. I. du Pont de Nemours & Co., Inc.).
135. U.S. Pat. 4,526,725 (July 2, 1985), D. L. Deardorff.
136. U.S. Pat. 4,788,172 (Nov. 29, 1988), D. L. Deardorff.
137. U.S. Pat. 2,524,115 (Feb. 18, 1958), H. H. Beacham and D. F. Herman (to National Lead Co.).
138. P. Lagally and H. Lagally, *TAPPI* **39**, 747 (1956).
139. U.S. Pat. 2,894,966 (July 14, 1959), C. A. Russell (to National Lead Co.).
140. U.S. Pat. 2,950,174 (Aug. 23, 1960), P. Lagally.
141. U.S. Pat. 3,028,297 (Apr. 3, 1962), P. Lagally (to Linden Laboratories Inc.).
142. U.S. Pat. 4,621,148 (Nov. 4, 1986), D. Barfurth and H. Nestler (to Dynamit Nobel AG).
143. U.S. Pat. 4,609,746 (Sept. 2, 1986), D. Barfurth and H. Nestler (to Dynamit Nobel AG).
144. P. C. Bharara, V. D. Gupta, and R. C. Mehrotra, *Z. Anorg. Allg. Chem.* **403**, 337 (1974).

145. P. C. Bharara, V. D. Gupta, and R. C. Mehrotra, *J. Indian Chem. Soc.* **51**, 859 (1974).
146. E. C. Alyea and P. H. Merrell, *Inorg. Nucl. Chem. Lett.* **9**, 69 (1973).
147. D. A. Baldwin and G. H. Leigh, *J. Chem. Soc.* **A2**, 1432 (1968).
148. U.S. Pat. 2,670,363 (Feb. 23, 1954), J. P. Wadington (to National Lead Co.).
149. K. C. Pande and R. C. Mehrotra, *J. Prakt. Chem.* **5**, 101 (1957).
150. K. C. Pande and R. C. Mehrotra, *Chem. Ind.* 114 (1957).
151. Y. A. Lysenko and O. A. Osipov, *Zh. Obshch. Khim.* **28**, 1724 (1958).
152. S. Prasad and R. C. Srivastava, *J. Indian Chem. Soc.* **39**, 9 (1962).
153. Brit. Pat. 787,180 (Dec. 4, 1957), J. H. Haslam (to E. I. du Pont de Nemours & Co., Inc.).
154. I. D. Varma and R. C. Mehrotra, *J. Prakt. Chem.* **8**, 235 (1959).
155. A. N. Solanki, K. R. Nahar, and A. M. Bhandari, *Synth. React. Inorg. Met. Org. Chem.* **8**, 335 (1978).
156. J. Amaudrut, *Bull. Soc. Chim. Fr.* **7–8**(1), 624 (1977); J. Amaudrut, B. Viard, and R. Mercier, *J. Chem. Res. Synop.* **4**, 138 (1979).
157. T. V. Rogova and co-workers, *Russ. J. Gen. Chem.* **67**(7), 1134 (1997).
158. U.S. Pat. 5,260,466 (Nov. 9, 1993), G. McGibbon (to Tioxide Specialties Ltd.).
159. R. Feld and P. L. Cowe, *The Organic Chemistry of Titanium*, Butterworths, London, 1965.
160. M. Isobe and co-workers, *Tetrahedron Lett.* **23**, 221 (1982); B. E. Rossiter, T. Katsuki, and K. B. Sharpless, *J. Am. Chem. Soc.* **102**, 5976 (1980); **103**, 464 (1981).
161. Rus. Pat. 771,056 (Oct. 15, 1980), V. K. Skubin and co-workers.
162. Brit. Pat. 2,051,093 (Jan. 14, 1981) and Ger. Offen. 3,017,887 (May 9, 1979), H. Kamio, Y. Ogina, and K. Nakamura (to Nippon Mining Co.).
163. J. M. Latour, B. Galland, and J. C. Marchon, *J. Chem. Soc. Chem. Commun.* **13**, 570 (1979).
164. U.S. Pat. 3,694,251 (Sept. 26, 1972), J. F. Houle and G. R. VanNorman (to Eastman Kodak Co.).
165. Brit. Pat. 2,085,491 (Oct. 16, 1980), P. S. Collishaw and D. Bird (to Caligen Foam Ltd.).
166. U.S. Pat. 2,628,170 (Feb. 10, 1953), L. Q. Green (to E. I. du Pont de Nemours & Co., Inc.).
167. U.S. Pat. 3,478,088 (Nov. 11, 1969), A. Revukas (to Cities Service Oil Co.).
168. Jpn. Pat. 62 89,690 (Apr. 24, 1987), M. Sato, N. Kobayashi, and M. Aizawa (to Nippon Soda Co. Ltd.).
169. U.S. Pat. 4,978,389 (Dec. 18, 1990), M. Sato, A. Mori, and M. Aizawa (to Nippon Soda Co. Ltd.).
170. Jpn. Pat. 5 163,482 (June 29, 1993), A. Mori and H. Kobayashi (to Nippon Soda Co. Ltd.).
171. M. Mori and T. Nakai, *Tetrahedron Lett.* **38**(35), 6233 (1997).
172. J. Qiu, C. Guo, and X. Zhang, *J. Org. Chem.* **62**, 2665 (1997).
173. U.S. Pat. 4,900,847 (Feb. 13, 1990), R. M. Hanson, S. Y. Ko, and K. B. Sharpless (to Massichusetts Institute of Technology).
174. P. R. Carlier and K. B. Sharpless, *J. Org. Chem.* **54**, 4016 (1989).
175. M. G. Finn and K. B. Sharpless, *Assy. Synthesis* **5**, 247 (1985).
176. I. D. Williams, S. F. Pedersen, K. B. Sharpless, and S. J. Lippard, *J. Am. Chem. Soc.* **106**, 6430 (1984).
177. R. O. Duthaler and A. Hafner, *Chem. Rev.* **92**, 807 (1992).
178. E. J. Corey, *J. Org. Chem.* **55**(6), 1693 (1990).
179. J. K. Karjalainen, O. E. O. Hormi, and D. C. Sharrington, *Tetrahedron: Asymmetry* **9**, 2019 (1998).
180. J. K. Karjalainen, O. E. O. Hormi, and D. C. Sharrington, *Tetrahedron: Asymmetry* **9**, 3895 (1998).

181. R. K. Sharma, R. V. Singh, and J. P. Tandon, *J. Pract. Chem.* **322**(3), 508 (1980).
182. R. K. Sharma and J. P. Tandon, *J. Pract. Chem.* **322**(1), 161 (1980).
183. U.S. Pat. 4,529,552 (July 16, 1985), I. Kato and co-workers (to Nippon Soda Co. Ltd.).
184. U.S. Pat. 6,294,682 (Sept. 25, 2001), H. Rauleder and co-workers (to E.I.DuPont de Nemours & Co. Inc.).
185. U.S. Pat. 5,328,718 (Sept. 27, 1996), Y. Abe, Y. Hamaji, and Y. Saakabe (to Myrata Manufacturing Co.).
186. Jpn. Pat. 58-77,889 (May 11, 1983), I. Kato and A. T. Sakamura (to Nippon Soda Co. Ltd.).
187. Jpn. Pat. 58-81,618 (May 17, 1983), S. Trukamura and I. Kato (to Nippon Soda Co. Ltd.).
188. Jpn. Pat. 58-217,429 (Dec. 17, 1983), S. Trukamura and I. Kato (to Nippon Soda Co. Ltd.).
189. Jpn. Pat. 58-172,395 (Nov. 11, 1983), I. Kato and S. Trukamura (to Nippon Soda Co. Ltd.).
190. Jpn. Pat. 58-156,347 (Sept. 17, 1983), S. Trukamura and I. Kato (to Nippon Soda Co. Ltd.).
191. R. C. Mehrotra and A. Mehrotra, *Inorg. Chem. Acta Rev.* **5**, 127 (1971).
192. U.S. Pat. Appl. 515,844 (Sept. 14, 1984), to R. G. Dosch, H. P. Stepens, and F. V. Stohl.
193. U.S. Pat. 4,324,736 (Apr. 13, 1982), W. Josten and H. J. Vehlensieck (to Dynamit Nobel AG).
194. U.S. Pat. 4,387,199 (June 7, 1983), W. Josten and H. J. Vehlensieck (to Dynamit Nobel AG).
195. D. C. Bradley and I. M. Thomas, *J. Chem. Soc.* **3**, 3854 (1960).
196. G. Chandra and M. F. Lappert, *Inorg. Nucl. Chem. Lett.* **1**(2), 83 (1965); *J. Chem. Soc.* **A2**, 1940 (1968).
197. U.S. Pat. 4,728,706 (Mar. 1, 1988), W. Farnham (to E. I. du Pont de Nemours & Co., Inc.).
198. R. Rajan, V. Subramanian, B. U. Nair, and T. Ramasami, *Bull. Chem. Soc. Jap.* **71**, 1293 (1998).
199. R. K. Sharma, R. V. Singh, and J. P. Tandon, *Synth. React. Inorg. Met. Org. Chem.* **9**, 519 (1979).
200. E. C. Alyea, A. Malek, and P. H. Merrell, *Trans. Met. Chem.* **4**, 172 (1979).
201. E. C. Alyea and A. Malek, *Inorg. Nucl. Chem. Lett.* **13**, 587 (1977).
202. E. C. Alyea, A. Malek, and P. H. Merrell, *J. Coord. Chem.* **4**, 55 (1974).
203. I. R. Unny, S. Gopinathan, and C. Gopinathan, *Indian J. Chem.* **19A**, 598 (1980).
204. J. F. Harrod and K. R. Taylor, *Inorg. Chem.* **14**, 1541 (1975).
205. U.S. Pat. 4,359,559 (Nov. 16, 1992), S. Yajima and co-workers (to UBE Industries Ltd.).
206. T. Sugama, J. R. Fair, and A. P. Reed, *J. Coating Tech.* **65**(826), 27 (1993).
207. U.S. Pat. 4,401,501 (Oct. 18, 1983), M. Taramasso, G. Perego, and B. Notari (to SNAM Progetti SpA).
208. U.S. Pat. 4,547,557 (Oct. 15, 1985), M. McDaniel (to Phillips Petroleum Co.).
209. J. Weitkamp and co-workers, eds., *Zeolite and Related Microprous Materials, State of the Art 1994, Studies in Surface Science and Catalysis*, Vol. 84, Elsevier Science Publishing Co., Inc., New York, 1994, pp. 653–659.
210. J. B. Miller, S. T. Johnston, and E. I. Ko, *J. Catal.* **150**, 310 (1994).
211. C. B. Khouw and co-workers, *J. Catal.* **149**, 195 (1995).
212. S. Vetter and co-workers, *Chem. Eng. Tech.* **17**, 348 (1994).
213. T. Tatsumi, K. Yuasa, and H. Tominaga, *J. Chem. Soc. Chem. Commun.* **19**, 1446 (1992).

214. T. Tatsumi, Y. Watanabe, and K. A. Koyano, *J. Chem. Soc. Chem. Commun.* **19**, 2281 (1996).
215. Jpn. Kokai Tokkyo Koho 80 139,392 (Oct. 31, 1980), I. Kijama.
216. E. Albizatti and co-workers, *Inorg. Chem. Acta* **120**(2), 197 (1986).
217. D. W. MacCorquodale and H. Adkins, *J. Am. Chem. Soc.* **50**, 1938 (1928).
218. A. N. Nesmeyanov, O. V. Nogina, and R. K. Freidlina, *Dokl. Akad. Nauk. SSSR* **95**, 813 (1954).
219. A. N. Nesmeyanov and co-workers, *Bull. Acad. Sci. USSR Div. Chem. Sci.* 1117 (1960).
220. B. N. Chakravarti, *Naturwissenschaften* **45**, 286 (1958).
221. A. Pflugmacher and co-workers, *Naturwissenschaften* **45**, 490 (1958).
222. Ger. Pat. 1,091,105 (Oct. 20, 1960), A. Gumboldt and W. Herwig (to Hoechst).
223. A. Stahler and H. Wirthwein, *Chem. Ber.* **38**, 2619 (1905).
224. A. Monnier, *Ann. Chim. Anal.* **20**, 1 (1915).
225. C. M. Mikulski and co-workers, *J. Inorg. Nucl. Chem.* **41**, 1671 (1979).
226. F. E. McFarlane and G. W. Tindall, *Inorg. Nucl. Chem. Lett.* **9**, 907 (1973).
227. M. R. Hunt and G. Winter, *Inorg. Nucl. Chem. Lett.* **6**, 529 (1970).
228. T. D. Smith, T. Lund, and J. R. Pilbrow, *J. Chem. Soc.* **A2**, 2786 (1971).
229. A. N. Glebov, P. A. Vasil'ev, and Y. I. Sal'nikov, *Russ. J. Inorg. Chem.* **26**, 140 (1981).
230. A. Furstner and B. Bogdanovic, *Angew. Chem. Int. Ed. Engl.* **35**, 2442 (1996).
231. N. L. Hungerford and W. Kitching, *J. Chem. Soc. Chem. Commun.* **14**, 1697 (1996).
232. R. J. H. Clark and A. J. McAlees, *Inorg. Chem.* **11**, 342 (1972).
233. R. J. H. Clark and A. J. McAlees, *J. Chem. Soc. Dalton Trans.* **5**, 640 (1972).
234. C. Blandy and D. Gervais, *Inorg. Chim. Acta* **47**, 197 (1981).
235. R. Hofer, D. Evard, and A. Jacot-Guillarmod, *Helv. Chim. Acta* **68**(4), 969 (1985).
236. M. T. Reetz and J. Westermann, *Synth. Commun.* **11**, 647 (1981).
237. M. T. Reetz, R. Steinbach, and B. Wenderoth, *Synth. Commun.* **11**, 261 (1981).
238. M. T. Reetz, J. Westermann, and R. Steinbach, *Angew. Chem. Int. Ed. Engl.* **19**, 900 (1980).
239. M. T. Reetz, J. Westermann, and R. Steinbach, *J. Chem. Soc. Chem. Commun.* **5**, 237 (1981).
240. M. T. Reetz, J. Westermann, and R. Steinbach, *Angew. Chem. Int. Ed. Engl.* **19**, 901 (1980).
241. M. T. Reetz and co-workers, *Angew. Chem. Int. Ed. Engl.* **19**, 1011 (1980).
242. W. Seidel and E. Riesenberg, *Z. Chem.* **20**, 450 (1980).
243. B. Weidmann and co-workers, *Helv. Chim. Acta* **64**, 357 (1981).
244. A. G. Olivero, B. Weidmann, and D. Seebach, *Helv. Chim. Acta* **64**, 2485 (1981).
245. B. Weidmann and D. Seebach, *Helv. Chim. Acta* **63**, 2451 (1980).
246. P. J. Davidson, M. F. Lappert, and R. Pearce, *J. Organomet. Chem.* **57**, 269 (1973).
247. J. C. W. Chien, J. Wu, and M. D. Rausch, *J. Am. Chem. Soc.* **103**, 1180 (1981).
248. A. K. Rappe and W. A. Goddard, *J. Am. Chem. Soc.* **104**, 297 (1982).
249. A. R. Middleton and G. Wilkinson, *J. Chem. Soc. Dalton Trans.* **10**, 1888 (1980).
250. N. Krause and D. Seebach, *Chem. Ber.* **120**(11), 1845 (1987).
251. M. D. Schiavelli, J. J. Plunkett, and D. W. Thompson, *J. Org. Chem.* **46**, 807 (1981).
252. T. Yoshida and E. Negishi, *J. Am. Chem. Soc.* **103**, 1276 (1981).
253. U.S. Pat. 3,694,517 (Sept. 26, 1972), W. Schneider (to B. F. Goodrich); Jpn. Kokai Tokkyo Koho 75 88,059 (July 15, 1975) (to Montedison); Ital. Pat. 932,191 (Nov. 15, 1972) (to Montedison).
254. F. Guerin, D. H. McConville, and N. C. Payne, *Organometallics* **15**, 5085 (1996).
255. A. Clearfield and co-workers, *Can. J. Chem.* **53**, 1622 (1975).
256. V. V. Tkachev and L. O. Atomyan, *Zh. Strukt. Khim.* **13**, 287 (1972).
257. I. A. Ronova and N. V. Alekseev, *Zh. Strukt. Khim.* **18**, 212 (1977).

258. E. F. Epstein and I. Bernal, *Inorg. Chim. Acta* **7**, 211 (1973).
259. V. Kocman and co-workers, *J. Chem. Soc. Chem. Commun.* **21**, 1340 (1971).
260. D. F. Hunt, J. W. Russell, and R. L. Torian, *J. Organomet. Chem.* **43**, 175 (1972).
261. A. N. Nesmeyanov and co-workers, *J. Organomet. Chem.* **61**, 225 (1973).
262. A. N. Nesmeyanov and co-workers, *Zh. Strukt. Khim.* **13**, 1033 (1972); **16**, 759 (1975).
263. M. Hillman and A. J. Weiss, *J. Organomet. Chem.* **42**, 123 (1972).
264. A. N. Nesmeyanov and co-workers, *Dokl. Chem.* **163**, 704 (1965).
265. C. Cauletti and co-workers, *J. Electron Spectrosc. Relat. Phenom.* **18**, 61 (1980).
266. A. A. MacDowell and co-workers, *J. Chem. Soc. Chem. Commun.* **9**, 427 (1979).
267. O. S. Roshchupkina and co-workers, *Sov. J. Coord. Chem.* **1**, 1052 (1975).
268. E. Samuel, R. Ferner, and M. Bigorgne, *Inorg. Chem.* **12**, 881 (1973).
269. G. Balducci and co-workers, *J. Mol. Struct.* **64**, 163 (1980).
270. M. Spoliti and co-workers, *J. Mol. Struct.* **65**, 105 (1980).
271. N. N. Vyshinskii and co-workers, *Tr. Khim. Khim. Tekhnol.* 64 (1973); **119**, 123 (1974).
272. G. Condorelli and co-workers, *J. Organomet. Chem.* **87**, 311 (1975).
273. D. W. Clack and K. D. Warren, *Theor. Chim. Acta* **46**, 313 (1977); *Inorg. Chem. Acta* **24**, 35 (1977); **30**, 251 (1978); *J. Organomet. Chem.* **162**, 83 (1978).
274. V. E. L'vovskii, *Soviet J. Coord. Chem.* **4**, 1266 (1978).
275. V. E. L'vovskii and G. B. Erusalimskii, *Soviet J. Coord. Chem.* **2**, 934, 1221 (1976).
276. E. G. Muller, S. F. Watkins, and L. F. Dahl, *J. Organomet. Chem.* **111**, 73 (1976).
277. E. G. Muller, J. L. Petersen, and L. F. Dahl, *J. Organomet. Chem.* **111**, 91 (1976).
278. J. L. Petersen and co-workers, *J. Am. Chem. Soc.* **97**, 6433 (1975).
279. A. M. McPherson, G. D. Stucky, and co-workers, *J. Am. Chem. Soc.* **101**, 3425 (1979).
280. V. E. Lvovsky, E. A. Fushman, and F. S. Dyachkovsky, *J. Mol. Catal.* **10**, 43 (1981).
281. T. D. Grabik and co-workers, *Russ. J. Phys. Chem.* **52**, 894 (1978).
282. V. I. Tel'noi and I. B. Rabinovich, *Conf. Int. Thermodyn. Chim.* **1**, 98 (1975).
283. T. Mukaiyama, *Angew. Chem. Int. Ed. Engl.* **16**, 817 (1977); J. Lange, J. M. Kanabus-Kaminska, and A. Kral, *Synth. Commun.* **10**, 473 (1980); M. T. Reetz, *Angew. Chem. Int. Ed. Engl.* **21**, 96 (1982).
284. R. C. Paul and co-workers, *J. Less Common Met.* **17**, 437 (1969).
285. A. M. Cardoso, R. J. H. Clark, and S. Moorhouse, *J. Chem. Soc. Dalton Trans.* **7**, 1156 (1980).
286. G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.* **76**, 4281 (1954).
287. L. Summers and R. H. Uloth, *J. Am. Chem. Soc.* **76**, 2278 (1954); **77**, 3604 (1955).
288. R. B. King, *Organometallic Syntheses*, Vol. 1, Academic Press, New York, 1965, pp. 75–78.
289. R. D. Gorsich, *J. Am. Chem. Soc.* **82**, 4211 (1960).
290. Rus. Pat. 825,534 (May 7, 1981), Y. A. Sorokin and co-workers (to Scientific Research Institute of Chemistry, Gorko).
291. Brit. Pat. 793,354 (Apr. 16, 1958) (to National Lead Co.).
292. Brit. Pat. 798,001 (July 9, 1958) (to National Lead Co.).
293. J. A. Marsella, K. G. Moloy, and K. G. Caulton, *J. Organomet. Chem.* **201**, 389 (1980).
294. L. E. Manzer, *J. Organomet. Chem.* **110**, 291 (1976).
295. F. H. Kohler and D. Cozek, *Z. Naturforsch. Tell B* **33**, 1274 (1978).
296. D. Nath, R. K. Sharma, and A. N. Bhat, *Inorg. Chim. Acta* **20**, 109 (1976).
297. K. Chandra and co-workers, *J. Indian Chem. Soc.* **58**, 10 (1981).
298. R. K. Tuli and co-workers, *Trans. Met. Chem.* **5**, 49 (1980).
299. K. Chandra and co-workers, *Inorg. Chim. Acta* **37**, 125 (1979).
300. A. K. Holliday and co-workers, *J. Organomet. Chem.* **57**, C45 (1973).

301. A. N. Nesmeyanov and co-workers, *Bull. Acad. Sci. USSR Div. Chem. Sci.* 777 (1967).
302. K. Chandra and co-workers, *Chem. Ind. (London)*, 288 (1980).
303. M. F. Lappert and co-workers, *J. Chem. Soc. Dalton Trans.* 805 (1981).
304. J. E. Bercaw, *J. Am. Chem. Soc.* **96**, 5087 (1974).
305. T. J. Katz, N. Acton, and G. Martin, *J. Am. Chem. Soc.* **95**, 2934 (1973).
306. J. A. Smith and co-workers, *J. Organomet. Chem.* **173**, 175 (1979).
307. J. A. Smith and H. H. Brintzinger, *J. Organomet. Chem.* **218**, 159 (1981).
308. C. E. Carraher, Jr. and S. T. Bajah, *Brit. Polym. J.* **7**(3), 155 (1975).
309. J. Jeffery and co-workers, *J. Chem. Soc. Dalton Trans.* **7**, 1593 (1981).
310. G. K. Barker and M. F. Lappert, *J. Organomet. Chem.* **76**, C45 (1974).
311. B. Wozniak, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* **A3**, 3116 (1971).
312. J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *J. Am. Chem. Soc.* **98**, 6529 (1976).
313. J. X. McDermott and G. M. Whitesides, *J. Am. Chem. Soc.* **96**, 947 (1974).
314. N. J. Foulger and B. J. Wakefield, *J. Organomet. Chem.* **69**, 161 (1974).
315. R. Jimenez and co-workers, *J. Organomet. Chem.* **174**, 281 (1979).
316. M. F. Lappert and C. L. Raston, *J. Chem. Soc. Chem. Commun.* **24**, 1284 (1980).
317. H. Sakurai and H. Umino, *J. Organomet. Chem.* **142**, C49 (1977); Rus. Pat. 816 437 (Feb. 10, 1981) (to Mitsubishi Chemical Industries KK).
318. S. A. Ciddings, *Inorg. Chem.* **3**, 684 (1964).
319. H. Surer, S. Claude, and A. Jacot-Guillarmod, *Helv. Chim. Acta* **61**, 2956 (1978).
320. T. P. Bryukhanova and co-workers, *Tr. Khim. Khim. Tekhnol.* 101 (1974).
321. J. J. Eisch and R. J. Manfre, *Fundam. Res. Homog. Catal.* **3**, 397 (1978).
322. J. J. Eisch, R. J. Manfre, and D. A. Komar, *J. Organomet. Chem.* **159**, C13 (1978).
323. B. B. Snider and M. Karras, *J. Organomet. Chem.* **179**, C37 (1979).
324. D. C. Brown and co-workers, *J. Org. Chem.* **44**, 3457 (1979).
325. H. E. Tweedy and co-workers, *J. Mol. Catal.* **3**, 239 (1977–1978).
326. U.S. Pat. 3,969,429 (July 13, 1976), to G. P. Belov and co-workers.
327. M. Peng and C. H. Brubaker, *Inorg. Chim. Acta* **26**, 231 (1978).
328. M. D. Rausch, W. H. Boon, and E. A. Mintz, *J. Organomet. Chem.* **160**, 81 (1978).
329. M. D. Rausch, W. H. Boon, and H. G. Alt, *J. Organomet. Chem.* **141**, 229 (1977).
330. W. H. Boon and M. D. Rausch, *J. Chem. Soc. Chem. Commun.* **11**, 397 (1977).
331. J. L. Atwood and co-workers, *J. Am. Chem. Soc.* **98**, 1454 (1976).
332. H. Alt and M. D. Rausch, *J. Am. Chem. Soc.* **96**, 5936 (1974).
333. H. G. Alt and M. D. Rausch, *Z. Naturforsch. Teil B* **30**, 813 (1975).
334. R. W. Harrigan, G. S. Hammond, and H. B. Gray, *J. Organomet. Chem.* **81**, 79 (1974).
335. C. H. Bamford, R. J. Puddephatt, and D. M. Slater, *J. Organomet. Chem.* **159**, C31 (1978).
336. H. G. Alt and co-workers, *J. Organomet. Chem.* **107**, 257 (1976).
337. G. A. Razuvaev, V. P. Mar'in, and Yu. A. Andrianov, *J. Organomet. Chem.* **174**, 67 (1979); G. A. Razuvaev and co-workers, *J. Organomet. Chem.* **164**, 41 (1979).
338. J. Mattia and co-workers, *Inorg. Chem.* **17**, 3257 (1978).
339. E. G. Berkovich and co-workers, *Chem. Ber.* **113**, 70 (1980).
340. V. B. Shur and co-workers, *J. Organomet. Chem.* **78**, 127 (1974).
341. M. K. Grigoryan and co-workers, *Bull. Acad. Sci. USSR Div. Chem. Sci.* 1024 (1978).
342. M. D. Rausch and H. B. Gordon, *J. Organomet. Chem.* **74**, 85 (1974).
343. G. J. Erskine and co-workers, *J. Organomet. Chem.* **170**, 51 (1979).
344. G. J. Erskine, D. A. Wilson, and J. D. McCowan, *J. Organomet. Chem.* **114**, 119 (1976).
345. J. A. Waters, V. V. Vickroy, and G. A. Mortimer, *J. Organomet. Chem.* **33**, 41 (1971).

346. C. P. Boekel, J. H. Teuben, and H. J. de Liefde Meijer, *J. Organomet. Chem.* **102**, 161 (1975).
347. C. P. Boekel, J. H. Teuben, and H. J. de Liefde Meijer, *J. Organomet. Chem.* **107**, 317.
348. C. P. Boekel, J. H. Teuben, and H. J. de Liefde Meijer, *J. Organomet. Chem.* **81**, 371 (1974).
349. F. W. Hartner and J. Schwartz, *J. Am. Chem. Soc.* **103**, 4974 (1981).
350. K. C. Ott and R. H. Grubbs, *J. Am. Chem. Soc.* **103**, 5922 (1981); *Chem. Eng. News*, 34 (Apr. 19, 1982).
351. T. Yoshida and E. I. Negishi, *J. Am. Chem. Soc.* **103**, 1276 (1981).
352. Y. Le Page and co-workers, *J. Organomet. Chem.* **193**, 201 (1980).
353. A. Glivicky and J. D. McCowan, *Can. J. Chem.* **51**, 2609 (1973).
354. L. J. Baye, *Synth. React. Inorg. Met. Org. Chem.* **5**, 95 (1975).
355. L. J. Baye, *Synth. React. Inorg. Met. Org. Chem.* **2**, 47 (1972).
356. C. R. Bennett and D. C. Bradley, *J. Chem. Soc. Chem. Commun.* **1**, 29 (1974).
357. R. V. Bynum and co-workers, *Inorg. Chem.* **19**, 2368 (1980).
358. P. L. Maxfield and E. Lima, *Proceedings of the 16th International Conference on Coordination Chemistry*, Dublin, Ireland, 1974, p. R58.
359. A. Jensen and co-workers, *Acta Chem. Scand.* **26**, 2898 (1972).
360. J. L. Burmeister and co-workers, *Inorg. Chem.* **9**, 58 (1970).
361. S. J. Anderson, D. S. Brown, and K. J. Finney, *J. Chem. Soc. Dalton Trans.* **1**, 152 (1979).
362. S. J. Anderson, D. S. Brown, and A. H. Norbury, *J. Chem. Soc. Chem. Commun.* **23**, 996 (1974).
363. J. Besangon and D. Camboli, *Compt. Rend.* **288C**, 121 (1979).
364. A. Chiesi-Villa, A. G. Manfredotti, and C. Guastini, *Acta Cryst.* **B32**, 909 (1976).
365. K. Issleib, H. Kohler, and G. Wille, *Z. Chem.* **13**, 347 (1973).
366. D. Camboli, J. Besancon, and B. Trimaille, *Compt. Rend.* **290C**, 365 (1980).
367. J. Besangon and co-workers, *Compt. Rend.* **287C**, 573 (1978).
368. L. Saunders and L. Spirer, *Polymer* **6**, 635 (1965).
369. R. B. King and R. N. Kapoor, *J. Organomet. Chem.* **15**, 457 (1968).
370. G. A. Razuvaev, V. N. Latyaeva, and L. I. Vyshinskaya, *Dokl. Chem.* **138**, 592 (1961).
371. T. S. Kuntsevich and co-workers, *Kristallografiya* **21**, 80 (1976).
372. V. P. Nistratov and co-workers, *Tr. Khim. Khim. Tekhnol.* 54 (1975).
373. J. C. G. Calado and co-workers, *J. Chem. Soc. Dalton Trans.* 1174 (1981).
374. L. Rosch and co-workers, *J. Organomet. Chem.* **197**, 51 (1980).
375. E. Hengge and W. Zimmermann, *Angew. Chem. Intl. Ed.* **7**, 142 (1968).
376. G. A. Razuvaev and co-workers, *Bull. Acad. Sci. USSR Div. Chem. Sci.* 2310 (1978).
377. G. A. Razuvaev and co-workers, *J. Organomet. Chem.* **87**, 93 (1975).
378. B. Stutte and co-workers, *Chem. Ber.* **111**, 1603 (1978).
379. G. Schmid, V. Batzel, and B. Stutte, *J. Organomet. Chem.* **113**, 67 (1976).
380. H. G. Raubenheimer and E. O. Fischer, *J. Organomet. Chem.* **91**, C23 (1975).
381. E. O. Fischer and S. Fontana, *J. Organomet. Chem.* **40**, 159 (1972).
382. H. Kopf and R. Voigtlander, *Chem. Ber.* **114**, 2731 (1981).
383. K. Issleib, F. Krech, and E. Lapp, *Synth. React. Inorg. Met. Org. Chem.* **7**, 253 (1977).
384. K. Issleib, G. Wille, and F. Krech, *Angew. Chem. Intl. Ed.* **11**, 527 (1972).
385. J. M. McCall and A. Shaver, *J. Organomet. Chem.* **193**, C37 (1980).
386. E. Samuel, *Bull, Soc. Chim. France*, 3548 (1966).
387. J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.* **96**, 2248 (1974).
388. J. C. LeBlanc, C. Moise, and T. Bounthakna, *Compt. Rend.* **278C**, 973 (1974).
389. M. B. Bert and D. Gervais, *J. Organomet. Chem.* **165**, 209 (1979).
390. G. V. Drozdov, A. L. Klebanskii, and V. A. Bartashev, *J. Gen. Chem. USSR* **33**, 2362 (1963).

391. M. A. Chaudhari and F. G. A. Stone, *J. Chem. Soc.* **A1**, 838 (1966); M. A. Chaudhari, P. M. Treichel, and F. G. Stone, *J. Organomet. Chem.* **2**, 206 (1964).
392. K. Andra, *J. Organomet. Chem.* **11**, 567 (1968).
393. J. C. LeBlanc, C. Moise, and J. Tirouflet, *Nouv. J. Chim.* **1**, 211 (1977).
394. T. Marey and co-workers, *Compt. Rend.* **284C**, 967 (1977).
395. J. Besangon, S. Top, and J. Tirouflet, *Compt. Rend.* **281C**, 135 (1975).
396. J. Besangon, F. Hug, and M. Colette, *J. Organomet. Chem.* **96**, 63 (1975).
397. R. Sharan, G. Gupta, and R. N. Kapoor, *Indian J. Chem.* **20A**, 94 (1981).
398. R. Sharan, G. Gupta, and R. N. Kapoor, *J. Less Common Met.* **60**, 171 (1978).
399. A. R. Dias, M. S. Salema, and J. A. M. Simoes, *J. Organomet. Chem.* **222**, 69 (1981).
400. H. Suzuki and T. Takiguchi, *Bull. Chem. Soc. Jpn.* **48**, 2460 (1975).
401. R. S. Arora, M. B. Bhalla, and R. K. Multani, *Indian J. Chem.* **16A**, 169 (1978).
402. R. S. P. Coutts and co-workers, *Austr. J. Chem.* **19**, 1377 (1966).
403. M. Sato and T. Yoshida, *J. Organomet. Chem.* **67**, 395 (1974).
404. H. Kopf and M. Schmid, *Angew. Chem. Intl. Ed. Engl.* **4**, 953 (1965).
405. A. Kutoglu, *Acta Crystallogr.* **B29**, 2891 (1973).
406. A. Kutoglu, *Z. Anorg. Allgem. Chem.* **390**, 195 (1972).
407. D. Sen and U. N. Kantak, *Indian J. Chem.* **13**, 72 (1975).
408. S. K. Sengupta, *Indian J. Chem.* **20A**, 515 (1981).
409. R. S. Arora and co-workers, *J. Chinese Chem. Soc. (Taipei)* **27**, 65 (1980).
410. W. L. Steffen, H. K. Chun, and R. C. Fay, *Inorg. Chem.* **17**, 3498 (1978).
411. K. Chandra and co-workers, *J. Inorg. Nucl. Chem.* **43**, 663 (1981).
412. K. Chandra and co-workers, *J. Inorg. Nucl. Chem.* **43**, 29 (1981).
413. K. Chandra and co-workers, *Trans. Met. Chem.* **5**, 209 (1980).
414. N. K. Kaushik, B. Bhushan, and G. R. Chhatwal, *Z. Naturforsch.* **34b**, 949 (1979).
415. B. Bhushan and co-workers, *J. Inorg. Nucl. Chem.* **41**, 159 (1979).
416. N. K. Kaushik, B. Bhushan, and G. R. Chbatwal, *Trans. Met. Chem.* **3**, 215 (1978).
417. N. K. Kaushik, B. Bhushan, and G. R. Chhatwal, *Synth. React. Inorg. Met. Org. Chem.* **8**, 467 (1978).
418. P. C. Bharara, *J. Organomet. Chem.* **121**, 199 (1976).
419. O. N. Suvorova, V. V. Sharutin, and G. A. Domrachev, *3rd Mater. Vses Semin.* **1977**, 132 (1978).
420. G. Fachinetti and co-workers, *J. Am. Chem. Soc.* **100**, 1921 (1978).
421. G. G. Dvoryantseva and co-workers, *Dokl. Chem.* **161**, 303 (1965).
422. A. N. Nesmeyanov, O. V. Nogina, and V. A. Dubovitskii, *Bull. Acad. Sci. USSR Div. Chem. Sci.* 1395 (1962).
423. A. N. Nesmeyanov, O. V. Nogina, and A. M. Berlin, *Bull. Acad. Sci. USSR Div. Chem. Sci.* 743 (1961).
424. G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.* **76**, 4281 (1954).
425. K. Doppert and R. Sanchez, *J. Organomet. Chem.* **210**, C9 (1980).
426. K. Doppert, *Makromol. Chem. Rapid Commun.* **1**, 519 (1980).
427. K. Doppert, *J. Organomet. Chem.* **178**, C3 (1979).
428. K. Chandra, R. K. Tuli, N. K. Bhatia, and B. S. Garg, *J. Indian Chem. Soc.* **58**, 122 (1981).
429. D. Pacheco and co-workers, *Inorg. Chim. Acta* **18**, L24 (1976).
430. H. Klein and U. Thewalt, *Z. Anorg. Allgem. Chem.* **476**, 62 (1981).
431. P. M. Druce and co-workers, *J. Chem. Soc.* **A3**, 2106 (1969).
432. V. K. Jain and co-workers, *J. Indian Chem. Soc.* **57**, 6 (1980).
433. D. Nath and A. N. Bhat, *Indian J. Chem.* **14**, 281 (1976).
434. C. E. Carraher and J. D. Piersma, *Makromol. Chem.* **152**, 49 (1972).
435. C. E. Carraher and co-workers, *J. Macromol. Sci. Chem.* **A16**, 195 (1981).
436. C. E. Carraher and J. L. Lee, *J. Macromol. Sci. Chem.* **A9**, 191 (1975).

437. C. E. Carraher and J. L. Lee, *Am. Chem. Soc. Div. Org. Coat. Plast. Chem. Pap.* **34**, 478 (1974).
438. C. E. Carraher and R. Frary, *Br. Polym. J.* **6**, 255 (1974).
439. C. E. Carraher and R. A. Frary, *Makromol. Chem.* **175**, 2307 (1974).
440. C. E. Carraher and J. D. Piersma, *J. Macromol. Sci. Chem.* **A7**, 913 (1973).
441. C. E. Carraher and L. S. Wang, *Angew. Makromol. Chem.* **25**, 121 (1972).
442. P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organomet. Chem.* **33**, 181 (1971).
443. U.S. Pat. 3,782,917 (Jan. 1, 1974), J. J. Mrowca (to E. I. du Pont de Nemours & Co., Inc.).
444. U.S. Pat. 3,728,365 (Apr. 17, 1973), J. J. Mrowca (to E. I. du Pont de Nemours & Co., Inc.).
445. G. Fachinetti and C. Floriani, *J. Organomet. Chem.* **71**, C5 (1974).
446. G. Fachinetti and C. Floriani, *J. Chem. Soc. Chem. Commun.* **11**, 654 (1972).
447. R. J. H. Clark, J. A. Stockwell, and J. D. Wilkins, *J. Chem. Soc. Dalton Trans.* **2**, 120 (1976).
448. K. W. Chiu and co-workers, *J. Chem. Soc. Dalton Trans.* **10**, 2088 (1981).
449. H. Yasuda and co-workers, *Bull. Chem. Soc. Jpn.* **53**, 1089 (1980).
450. S. Akutagawa and S. Otsuka, *J. Am. Chem. Soc.* **97**, 6870 (1975).
451. F. Sato and co-workers, *J. Chem. Soc., Chem. Commun.* **21**, 1140 (1981).
452. K. Kaeriyama, *Makromol. Chem.* **175**, 2285 (1974).
453. K. Kaeriyama, *Makromol. Chem.* **153**, 229 (1972).
454. T. Saito, *J. Chem. Soc. Chem. Commun.* **22**, 1422 (1971).
455. J. Tsuji and S. Hashiguchi, *Tetrahedron Lett.* **21**, 2955 (1980).
456. D. F. Williams, *Syst. Aspects Biocompat.* **1**, 169 (1981).
457. U.S. Pat. 4,272,588 (June 9, 1981), B. E. Yoldas, A. M. Filippi, and R. W. Buckman (to Westinghouse Electric Corp.).
458. Brit. Pat. 2,067,540 (July 30, 1981), J. H. Novak and G. L. Smay (to American Glass Research).
459. Jpn. Kokai Tokkyo Koho 81 88,843 (July 18, 1981) (to Matusushita Electric Works).
460. U.S. Pat. 3,094,436 (June 18, 1963), H. Schroder (to Jenaer Glaswerk Schott and Gen.).
461. Jpn. Kokai Tokkyo Koho 81 60,068 (May 23, 1981) (to Tokyo Shibaura Electric, Ltd.).
462. Jpn. Kokai Tokkyo Koho 81 114,904 (Sept. 9, 1981) (to Nippon Telegraph and Telephone).
463. Jpn. Kokai Tokkyo Koho 81 37,173 (Aug. 29, 1981) (to Sharp KK).
464. Jpn. Kokai Tokkyo Koho 81 116,015 (Sept. 11, 1981) (to Suwa Seikosha KK).
465. Jpn. Kokai Tokkyo Koho 81 116,016 (Sept. 11, 1981) (to Suwa Seikosha KK).
466. Jpn. Kokai Tokkyo Koho 81 63,846 (May 30, 1981) (to Suwa Seikosha KK).
467. Jpn. Kokai Tokkyo Koho 81 94,651 (July 31, 1981) (to Tokyo Denshi Kagaku).
468. U.S. Pat. 4,279,654 (July 21, 1981), S. Yajima and co-workers (to Research Institute for Special Inorganic Materials) ; S. Yajima and co-workers, *J. Mater. Sci.* **16**, 1349 (1981).
469. U.S. Pat. 4,246,314 (Jan. 20, 1981), A. Marzocchi, M. G. Roberts, and C. E. Bolen (to Owens Corning Fiberglas Corp.).
470. U.S. Pat. 4,269,756 (May 26, 1981), T. Y. Su (to Union Carbide).
471. Ger. Offen. 3,026,987 (Feb. 12, 1981), R. G. Adams and S. J. Milletari (to J. P. Stevens and Co.).
472. Rus. Pat. 235,907 (Jan. 24, 1969), L. V. Golosova and K. S. Zatsepin.
473. G. Winter, *J. Oil Color Chem. Assoc.* **36**(402), 689 (1953); **34**(367), 30 (1951); A. Hancock and R. Sidlow, *J. Oil Color Chem. Assoc.* **35**(379), 28 (1952).
474. G. Pagliara, *Pitture Vernici* **40**, 279 (1964).
475. Jpn. Kokai Tokkyo Koho 80,11,147 (Mar. 22, 1980) (to Kansai Paint Co.).

476. U.S. Pat. 4,224,213 (June 9, 1978), S. D. Johnson (to Cook Paint & Varnish Co.).
477. Jpn. Kokai Tokkyo Koho 80,152,759 (Nov. 28, 1980) (to Dainippon Toryo Co.).
478. U.S. Pat. 3,524,799 (Aug. 18, 1970), K. H. Dale (to Reynolds Metals Co.).
479. Jpn. Kokai Tokkyo Koho 80,141,573 (Nov. 5, 1980) (to Showa Keikinzoku KK).
480. Rus. Pat. 744,014 (June 2, 1980) (to Enam Chem. EQP Res.).
481. Jpn. Kokai Tokkyo Koho 81,104,973 (Aug. 21, 1981) (to Toray Industries).
482. Brit. Pat. 786,388 (Nov. 20, 1957) (to National Lead Co.).
483. U.S. Pat. 2,888,367 (May 26, 1959), W. L. Greyson (to Hitemp Wires, Inc.).
484. U.S. Pat. 3,862,099 (Jan. 21, 1975), N. S. Marans (to W. R. Grace).
485. Jpn. Kokai Tokkyo Koho 77,10,322 (Jan. 26, 1977), T. Yoshimura and co-workers (to Kaikin Kogyo Co.).
486. Jpn. Kokai Tokkyo Koho 81 30,472 (Mar. 27, 1981) (to Furukawa Electric Co.).
487. A. M. Usmani and co-workers, *Rubber Chem. Technol.* **54**, 1081 (1981).
488. Jpn. Kokai Tokkyo Koho 77 132,082 (Nov. 5, 1977), I. Sugiyama, H. Doi, and Y. Takaoka (to Matsumoto Seiyaku Kogyo Co.).
489. Belg. Pat. 887,145 (July 20, 1981) (to Toray Silicone Co.).
490. Jpn. Pat. 71 22,878 (June 30, 1971) I. Honda (to Kuraray Co.).
491. Eur. Pat. 1,217,118 (June 26, 2002), K. E. Allewaert, P. J. Vander Elst, and A. E. Van Royen (to 3M Innovative Properties Co.).
492. Eur. Pat. 1,493,716 (Jan 5, 2005), K. E. Allewaert, P. J. Vander Elst, and A. E. Van Royen (to 3M Innovative Properties Co.).
493. N. V. Vakrameeva and co-workers, *Kozh. Obuvn. Promst.* **23**, 37, 43 (1981).
494. Brit. Pat. 1,374,263 (Nov. 20, 1974), T. Keating (to Imperial Chemical Industries).
495. U.S. Pat. 4,234,497 (Nov. 18, 1980), M. Honig (to Standard Lubricants).
496. Ger. Offen. 2,004,098 (Aug. 12, 1971), R. Tuma and R. Lebender (to Dynamit Nobel AG).
497. A. G. Okuneva and co-workers, *Plast. Massy*, 10 (1981).
498. U.S. Pat. 4,260,735 (Apr. 7, 1981), J. A. Bander, S. D. Lazarus, and I. C. Twilley (to Allied Corp.).
499. Jpn. Kokai Tokkyo Koho 80 125,120 (Sept. 26, 1980) (to Toray Industries, Inc.).
500. Ger. Offen. 2,751,385 (May 24, 1978), S. P. Elliot (to E. I. du Pont de Nemours & Co., Inc.).
501. *Organic Titanium Compounds as Acrylic Ester Alcoholysis Catalysts*, Titanium Intermediates, Ltd., London, 1967.
502. Jpn. Kokai Tokkyo Koho 79,125,617 (Sept. 29, 1979), T. Onoda, K. Tano, and Y. Hara (to Mitsubishi Chemical Industries).
503. Ger. Offen. 2,922,343 (Dec. 4, 1980), B. Luthingshauser and C. Lindzus (to Dynamit Nobel AG).
504. Jpn. Kokai Tokkyo Koho 74,95,918 (Sept. 11, 1974), K. Kimura and H. Ito (to Toa Gosei Chemical Industry Co.).
505. Eur. Pat. 968,995 (Jan. 1, 2000), K. Nakamura, I. Tsubuka-shi and F. Kawataka (to Mitsubishi Gas and Chemical Co. Inc.).
506. N. Lewis, C. Ribas and A. Wells, *Synlett.* **S1**, 957 (1998).
507. M. D. Curran, T. E. Gedris, and A. E. Stiegman, *Chem.Mater.* **10**, 1604 (1998).
508. Jap. Pat. 2004-277,592 (Oct. 7, 2004), K. Tomoyuki and M. Nobuo (to Teijin Ltd.).
509. U.S. Pat. 5,744,457 (Apr. 28, 1998), S. D. Hilbert and T. G. Davis (to Eastman Chemical Co.).
510. U.S. Pat. 5,866,133 (Mar. 23, 1999), S. D. Hilbert and T. G. Davis (to Eastman Chemical Co.).
511. Jap. Pat. 2004-127,592 (Oct. 7, 2004), K. Tomoyuki and M. Nobuo (to Teijin Ltd.).
512. U.S. Pat. 5,106,944 (Apr. 21, 1992), B. J. Sublett (to Eastman Chemical Co.).

513. Jap. Pat. 3-341,430 (Aug. 8, 1995), H. Heiwa and co-workers (to Mitsubishi Chemical Corp.).
514. U.S. Pat. 5,656,716 (Aug. 12, 1997), W. Schmidt, U. Thiele, W. Griebler, B. Hirthe, and E. Hirschberg (to Zimmer AG and Sachtleben Chemie GmbH.).
515. U.S. Pat. 6,667,238 (Dec. 23, 2003), Y. Fujimori, N. Nukui, Y. Yatsugi, and K. Matsui (to Mitsubishi Chemical Corp.).
516. U.S. Pat. 5,684,116 (Nov. 11, 1997), M. G. Martl and co-workers (to Akzo Nobel N.V.).
517. U.S. Pat. 6,316,584 (Nov. 134, 2001), U. seidel and M. G. Martl (to Akzo Nobel N.V.).
518. Jap. Pat. 98-168,030 (June 23, 1998), O. Masamichi and S. Yasusuki (to Mitsubishi Chemical Corp.).
519. Jap. Pat. 11-269,258 (Oct. 5, 1999), W. Totu (to Mitsubishi Chemical Corp.).
520. L. H. Buxbaum, *Angew.Chem.* **80**, 225 (1968).
521. H. Zimmermann and E. Leibnitz, *Faserforsh. Text. Tech.* **16**, 282 (1965).
522. Eur. Pat. 826,713 (Aug. 13, 1998), D. A. Shiraldi (to Hoechst Celanese Corp.).
523. U.S. Pat. 4,031,165 (June 21, 1977), N. Saiki, Y. Takeuchi and H. Saiki (to Teijin Ltd.).
524. U.S. Pat. 6,166,170 (Dec. 26, 2000), D. E. Putzig (to E.I.DuPont de Nemours and Co.,Inc.).
525. Brit. Pat. 2,314,081 (Dec. 17, 1997), J. Ridland (to Tioxide Specialties Ltd.).
526. World Pat. 03/045550 (June 5, 2003), C. Lindell, J. Ridland, and N. Slack (to Johnson Matthey PLC).
527. World Pat. 04/050239 (June 17, 2004), C. Lindell, N. Slack, and M. Partridge (to Johnson Matthey PLC).
528. Eur. Pat. 1,413,593 (Apr. 28, 2004), T. Yamamoto and co-workers (to Teijin Ltd.).
529. Eur. Pat. 1,090,943 (Apr. 11, 2001), K. C. Cannon, S. R. Seshadri, and R. R. Drikx (to Atofina Chemicals).
530. U.S. Pat. 6,258,925 (July 10, 2001), C. M. Dowling and S. R. Seshadri (to Atofina Chemicals).
531. U.S. Pat 6,500,915 (12/31/ 2002), Y. Fujimura, S. Anno, and N. Nukui (Mitsubishi Chemical Corp.).
532. U.S. Pat. 6,372,879 (Apr. 12, 2002), C. M. Dowling, W. Bin Chen, and S. R. Seshadri (to Atofina Chemicals).
533. Eur. Pat. 634,435 (Jan. 18, 1995), W. H. F. Borman and T. G. Shannon (to General Electric Co.).
534. Jap. Pat. 5-117,379 (May 14, 1993), S. Dhino and T. taniguchi (to Kuraray Co.).
535. B. Fortunato, A. Murari, P. Manaresti, and P. Monari, *Polymer* **35**(18), 4006 (1994).
536. U.S. Pat. 6,632,917 (Oct. 14, 2003), R. V. Kulkarni and L. Dominquesz (to Artiva North America).
537. U.S. Pat. 6,013,746 (Jan. 11, 2000), R. Hagen, E. Shaaf, and H. Zimmermann (to Karl Fischer I GmbH.).
538. U.S. Pat. 6,132,868 (Oct. 17, 2000), L. R. Dean, W. A. Haile, and R. L. McConnell (to Eastman Chemical Co.).
539. U.S. Pat. 6,139,954 (Oct. 31, 2000), L. R. Dean, W. A. Haile, and R. L. McConnell (to Eastman Chemical Co.).
540. Brit. Pat. 2,333,525 (July 28, 1999), J. Ridland (to Tioxide Specialties Ltd.).
541. World Pat. 99/28033 (June 10, 1999), J. Ridland and I. Hepplewhite (to Tioxide Specialties Ltd.).
542. World Pat. 2/42537 (May 30, 2002), A. Bellamy and co-workers (to Imperial Chemical Industries PLC).
543. World Pat. 01/56694 (Aug. 9, 2001), C. Lindall, and J. Ridland (to ACMA Limited).

544. Eur. Pat. 1,031,590 (Aug. 30, 2000), B. Otto, U. Thiele, and X. Guo (to Lurgi Zimmer A.G.).
545. U.S. Pat. 6,358,578 (Mar. 19, 2002), B. Otto, U. Thiele, and J. Schiebish (to Zimmer A.G.).
546. U.S. Pat. 6,417,320 (July 7, 2002), B. Otto, U. Thiele, and X. Guo (to Zimmer A.G.).
547. U.S. Pat. 6,841,505 (Jan. 11, 2005), D. E. Putzig and W. G. Peet (to E.I.DuPont de Nemours and Co.,Inc.).
548. Jap. Pat. 62-141,022 (June 24, 1987), H. Iida and H. Takagama (to Toray Industries).
549. Jap. Pat. 62-225,523 (Oct. 3, 1987), K. Azuma, H. Iida, and H. Takagama (to Toray Industries).
550. F. Pilati and co-workers, *Polymer* **24**(11), 1479 (1983).
551. F. Pilati and co-workers, *Polymer* **26**(11), 1745 (1985).
552. B. Fortunato and co-workers, *Polym. Commun.* **27**(1), 29 (1986).
553. B. Fortunato and co-workers, *Polym. Commun.* **30**(2), 55 (1989).
554. H. L. Traub and co-workers, *Angew. Makromol. Chem.* **230**, 179 (1995).
555. J. Hsu and K. Y. Choi, *J. Appl. Poly. Sci.* **32**(1), 3117 (1986).
556. Y. Yurramendi, M. J. Barandiaran, and J. M. Asua, *J. Macromol. Sci. Chem.* **A24**(11), 1357–1367 (1987).
557. P. Fritzsche, G. Rafler, and K. Tauer, *Akta. Polym. Commun.* **40**(30), 143 (1989).
558. U.S. Pat. 6,075,115 (June 13, 2000), D. E. Putzig and W. G. Peet (to E.I.DuPont de Nemours and Co.Inc.).
559. World Pat. 98/24855 (June 11, 1998), P. Swan, M. Bellas, and T. Bowles (to Eastman Chemical Co.).
560. G. Ratner and co-workers, *Akad. Polym.* **34**, 48–51 (1983).
561. U.S. Pat 4,329,444 (May 11, 1982), W. F. H. Borman (to General Electric Co.).
562. U.S. Pat. 6,657,040 (Dec. 2, 2003), T. Heinz, M. Klatt, and R. Neuhaus (to BASF A.G.).
563. U.S. Pat. 5,015,759 (May 14, 1991), D. J. Lowe (to E. I. DuPont de Nemours and Co., Inc.).
564. Eur. Pat. 46,670 (Mar. 3, 1982), H. K. Hall and A. B. Padias (to Celanese Corp.).
565. U.S. Pat. 6,043,335 (Mar. 28, 2000), T. E. Banach and co-workers (to General Electric Co.).
566. U.S. Pat. 5,516,579 (May 14, 1996), W. You, W. Lin, H. Wang, and J. Wang (to Industrial Technology Research Institute).
567. Jap. Pat. 57-85818 (May 28, 1982), S. Tetsuya and I. Koichi (to Mitsubishi Chemical Industry Ltd.).
568. U.S. Pat. 5,661,214 (Aug. 26, 1997), D. J. Brunelle and J. A. Serth-Guzzo (to General Electric Co).
569. U.S. Pat. 5,668,186 (Sept. 16, 1997), D. J. Brunelle, D. Kailasam, and J. A. Serth-Guzzo (to General Electric Co.).
570. U.S. Pat. 5,710,086 (Jan. 20, 1998), D. J. Brunelle, T. Takekoshi, and J. A. Serth-Guzzo (to General Electric Co.).
571. U.S. Pat. 6,525,164 (Feb. 25, 2003), G. R. Faler (to Cyclics Corp.).
572. U.S. Pat 2003/0195328 (Oct. 16, 2003), Y. Wang and P. D. Phelps (to Cyclics Corp.).
573. U.S. Pat. 6,831,138 (Dec. 14, 2004), Y. Wang (to Cyclics Corp.).
574. Y. Kim, G. K. Jnaneshwara, and J. G. Verkade, *Inorg. Chem.* **42**(5), 1437 (2003).
575. P. Albert, H. Warth, and R. Miilhaupt, *Macromol. Chem. Phys.* **197**, 1633 (1996).
576. U.S. Pat. 4,074,006 (Feb. 14, 1978), E. Loldebuck and B. Gorowitz (to General Electric Co.).
577. U.S. Pat. 4,148,989 (Apr. 10, 1979), G. Tews, H. Wulff, and G. Schade (to Dynamit Nobel A.G.).

578. U.S. Pat. 5,391,643 (Feb. 21, 1995), J. Ridland and B. Jolly (to Tioxide Specialties Ltd.).
579. U.S. Pat. 5,688,894 (Nov. 18, 1997), J. Ridland (to Tioxide Specialties Ltd.).
580. Brit. Pat. 2,304,109 (Mar. 12, 1997), J. Ridland (to Tioxcide Specialties Ltd.).
581. Eur. Pat. 32,587 (July 29, 1981), M. J. Keogh (to Union Carbide Corp.).
582. Jpn. Kokai Tokkyo Koho 79 77,635 (June 21, 1979), M. Yoshiaki and co-workers (to Kansai Paint Co.).
583. U.S. Pat. 5,453,479 (Sept. 26, 1995), W. F. H. Borman and T. G. Shannon (to General Electric Co.).
584. P. Schnurrenberger, M. Zuger, and D. Seebach, *Helv. Chem. Acta* **65**(4), 110, 1197 (1982).
585. U.S. Pat. 5,371,172 (Dec. 6, 1994), E. Takayama, I. Niikura, and T. Hokari (to Showa Highpolymer Co.); U.S. Pat. 4,348,498 (Sept. 7, 1982), H. Kamio, Y. Ogino, and K. Nakamura (to Nippon Mining Co.).
586. Brit. Pat. 994,717 (June 10, 1965) (to Dr. Beck and Co.).
587. U.S. Pats. 4,297,447-4,297,449 (Oct. 27, 1981), C. J. Stark (to General Electric Co.).
588. Ger. Offen. 3,028,114 (Feb. 12, 1981), S. R. Stoelzer and R. E. Wiley (to Acheson Industries, Inc.).
589. Jpn. Kokai Tokkyo Koho 81,88,471 (July 17, 1981) (to Mitsui Toatsu Chem.).
590. Ger. Offen. 3,038,646 (Apr. 23, 1981), K. Kawasumi, H. Watanabe, and J. Seto (to Sony Corp.).
591. Jpn. Kokai Tokkyo Koho 81,75,544 (June 22, 1981) (to Suwa Seikosha KK).
592. Brit. Pat. 922,456 (Apr. 3, 1963), G. E. Westwood (to Berger, Jensen, and Nicholson, Ltd.).
593. U.S. Pat. 3,679,721 (July 25, 1972), D. W. Brook and R. Ward (to British Titan Products Co. Ltd.).
594. U.S. Pat. 3,694,475 (Sept. 26, 1972), D. W. Brook and P. D. Kay (to British Titan Ltd.).
595. U.S. Pat. 4,874,806 (Aug. 17, 1989), P. D. Kay and K. McDonald (to Tioxide Group PLC).
596. U.S. Pat. 5,076,847 (Dec. 31, 1991), P. D. Kay and K. McDonald (to Tioxide Group PLC).
597. U.S. Pat. 4,159,209 (June 26, 1979), P. Womersley (to Manchem., Ltd.).
598. U.S. Pat. 3,013,895 (Dec. 19, 1961), M. S. Agruss (to Miehle-Goss-Dexter, Inc.).
599. U.S. Pat. 3,682,688 (Aug. 8, 1972), C. T. Hughes and D. O. Paulsen (to E. I. du Pont de Nemours & Co., Inc.).
600. Jpn. Kokai Tokkyo Koho 47,29,571 (Aug. 3, 1972) (to Dainippon Ink and Chemicals, Inc.).
601. U.S. Pat. 4,617,408 (Oct. 14, 1986), H. Nestler and D. Barfurth (to Dynamit Nobel AG).
602. U.S. Pat. 4,909,846 (Mar. 20, 1990), D. Barfurth and H. Nestler (to Dynamit Nobel AG).
603. U.S. Pat. 4,931,094 (June 5, 1990), D. Barfurth, C. Lindzus, and H. Nestler (to Tioxide Group PLC).
604. U.S. Pats. 4,659,848 (Apr. 21, 1987) and 4,705,568 (Nov. 10, 1987), P. D. Kay and M. C. Girot (to Tioxide Group PLC).
605. U.S. Pat. 5,286,774 (Feb. 15, 1994), G. McGibbon and J. E. Robinson (to Tioxide Specialties Ltd.).
606. C. Parducci, *Pitture Vernici* **56**(4), 19 (1980); technical bulletin, *Titanium and Zirconium Chelates for the Printing Ink Industry*, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1997.
607. Brit. Pat. 759,570 (Oct. 17, 1956) (to National Lead).

608. U.S. Pat. 4,483,712 (Nov. 20, 1984), P. N. Murphy (to Crown Zellerbach Corp.).
609. Jpn. Koksai Tokkyo Koho 58,134,164 (Aug. 10, 1983) (to Dainippon Ink and Chemicals, Co.).
610. World Pat. 80,2292 (Oct. 30, 1980), M. L. Barstall and B. D. Podd (to National Research and Development).
611. U.S. Pat. 5,821,276 (Oct. 13, 1998), R. H. Duncan (to Tioxide Specialties Ltd.).
612. U.S. Pat. 2,970,126 (Jan. 31, 1961), E. D. Brown Jr. (to General Electric Co.).
613. U.S. Pat. 2,732,320 (Jan. 24, 1956), C. J. Guillissen (to Union Chimique Belge).
614. U.S. Pat. 2,911,324 (Nov. 3, 1959) (to Bradford Dyers Association Ltd.).
615. Brit. Pat. 1,406,336 (Sept. 17, 1975), M. Camp and J. Dumoulin (to Rhone-Poulenc).
616. Eur. Pat. 164,470 (Dec. 18, 1985) (to Dow Corning).
617. U.S. Pat. 3,151,099 (Sept. 29, 1964), P. L. Brown and J. L. Hyde (to Rhone-Poulenc).
618. U.S. Pat. 3,161,614 (Dec. 15, 1964), L. F. Ceyzeriat and G. L. Pagni (to Dow Corning).
619. U.S. Pat. 3,378,520 (Apr. 16, 1968), H. Sattleger and co-workers (to Farbenfabriken Bayer).
620. U.S. Pat. 3,334,067 (Aug. 1, 1967), D. Weyenberg (to Dow Corning).
621. U.S. Pat. 3,856,839 (Dec. 24, 1974), S. D. Smith and S. Hamilton, Jr. (to General Electric Co.).
622. U.S. Pat. 5,530,082 (June 25, 1996), R. Friebe, W. Weber, and K. Sockel (to Bayer AG).
623. U.S. Pat. 5,428,103 (June 27, 1995), R. Friebe, J. Huggins, W. Weber and K. Sockel (to Bayer AG).
624. U.S. Pat. 5,032,660 (July 16, 1991), P. D. Kay and D. A. Brown (to Tioxide Group PLC).
625. U.S. Pat. 6,107,380 (Aug. 22, 2000), E. R. Evans (to General Electric Co.).
626. U.S. Pat. 5,755,866 (May 26, 1998), B. P. Bayly, G. M. Lucas and V. W. Stuart (to General Electric Co.).
627. S. J. Monte, *Ken-React Reference Manual, Titanate, Zirconate and Aluminate Coupling Agents*, Kenrich Petrochemicals Inc., Bayonne, N.J., 1993.
628. U.S. Pat. 4,098,758 (July 4, 1978), S. J. Monte and P. F. Bruins (to Kenrich Petrochemicals Inc.).
629. U.S. Pat. 4,087,402 (May 2, 1978), S. J. Monte and G. Sugarman (to Kenrich Petrochemicals Inc.).
630. U.S. Pat. 4,261,913 (Apr. 14, 1981), S. J. Monte and G. Sugarman (to Kenrich Petrochemicals Inc.).
631. U.S. Pat. 4,277,415 (July 7, 1981), G. Sugarman and S. J. Monte (to Kenrich Petrochemicals Inc.).
632. U.S. Pat. 4,600,789 (July 15, 1986), G. Sugarman and S. J. Monte (to Kenrich Petrochemicals Inc.).
633. U.S. Pat. 5,079,286 (Jan. 7, 1992), H. Hanisch and co-workers (to Hues Troisdorf AG).
634. U. Schubert, *J. Chem. Soc. Dalton Trans.* 3343 (1996).
635. J. Livage, H. Imai, and C. Sanchez, *Prog. Solid St.Chem.* **18**, 259 (1988).
636. R. C. Mehrotra and A. Singh, *Chem. Rev.* **96**(1), 1 (1996).
637. M. M. Yusef, H. Iami, and H. Hirashima, *J. Sol–Gel Sci. Tech.* **28**, 97 (2003).
638. K. C. Song and S. E. Pratsinis, *J. Am. Ceram. Soc.* **84**(11), 92 (2001).
639. K. C. Song and S. E. Pratsinis, *J. Mater. Res.* **15**(11), 2322 (2000).
640. U.S. Pat. 4,543,341 (Sept. 24, 1985), E. A. Barringer, M. B. Fegley Jr., and H. K. Bowen (to Massachusetts Institute of Technology).
641. M. L. H. Edelson and A. M. Glaeser, *J. Am. Ceram. Soc.* **71**(4), 225 (1988).
642. U.S. Pat. 4,732,750 (Mar.22 1988), W. L. Olsen and W. E. Liss (to Allied-Signal Co.).

643. A. Soloviev, H. Jesen, G. Sogaard, and A. V. Kanaev, *J. Mater. Sci. Lett.* **38**, 3315 (2003).
644. U.S. Pat. 5,776,239 (July 7, 1998), S. A. Bruno (to E.I.DuPont de Nemours and Co., Inc.).
645. M. Takagi, T. Maki, M. Mihahara, and K. Mae, *Chem. Eng. J.* **101**, 269 (2004).
646. H. Kominami, Y. Tikada, H. Yamagiwa, and Y. Kera, *J. Mater. Sci. Lett.* **15**, 197–200 (1996).
647. D. Vorkapic and T. Matsoukas, *J. Am. Ceram. Soc.* **81**(11), 2815 (1998).
648. H. Moeckel, M. Giersig, and F. Willig, *J. Mater. Chem.* **9**, 3051 (1999).
649. N. Uekawa and co-workers, *J. Mater. Res.* **18**(4), 797 (2003).
650. W. E. Stallings and H. H. Lamb, *Langmuir* **19**, 2989 (2003).
651. V. Colvin and co-workers, *J. Am. Chem. Soc.* **121**, 1613 (1999).
652. K. Kominam and co-workers, *Cat. Lett.* **46**, 235 (1997).
653. T. Trung, W. Cho, and C. Ha, *Mater. Lett.* **57**, 2746 (2003).
654. S. J. Lee and C. H. Lee, *Mater. Lett.* **56**, 705 (2002).
655. K. Kanie and T. Sugimoto, *Chem. Commun.* 1584 (2004).
656. P. A. Venz, J. L. Woolfrey, J. R. Bartlett, and R. L. Frost, *Ceram. Trans.* 83 (1998).
657. I. N. Martyanov and K. J. Klabunde, *J. Catal.* **225**, 408 (2004).
658. A. F. Torres-Requena and D. R. Acosta-Najarro, *Emerging Fields in Sol-Gel Sci. Tech.*, 322 (2003).
659. Eur. Pat. 997,575 (May 3, 2000), T. Mori (to Kyorasha Co. Ltd.).
660. Eur. Pat. 884,320 (Dec. 16, 1998), T. Kemmitt and co-workers (to Industrial Research Limited).
661. T. J. Boyle and co-workers, *J. Am. Chem. Soc.* **121**, 12104 (1999).
662. U.S. Pat. 5,766,784 (June 16, 1998), S. Basdkaran and J. L. Graff (to Batelle Memorial Institute).
663. S. Lee, J. Drwiega, C. Wu, D. Mazyck, and W. M. Sigmund, *Chem. Mater.* **16**, 1160 (2004).
664. Jap. Pat. 2003-001116 (Jan.7. 2003), K. Satoshi (to Daiken Industries Ltd.).
665. W. Daowd and J. H. Xin, *J. Sol–Gel Sci. Tech.* **29**, 25 (2004).
666. Y. Bessekhouad, D. Roberts, and J. V. Weber, *Int. J. Photoenergy* **5**, 153 (2003).
667. H. Kominami and co-workers, *Cat. Lett.* **91**(1–2), 41 (2003).
668. K. L. Yeung and co-workers, *J. Cat.* **219**, 107 (92003).
669. D. Jiang, H. Zhao, S. Zhang, and R. John, *J. Cat.* **223**, 212 (2004).
670. L. Cao and co-workers, *J. Cat.* **196**, 253 (2000).
671. S. H. Elder and co-workers, *J. Am. Chem. Soc.* **122**, 5138 (2000).
672. C. Burda and co-workers, *Nano Lett.* **0**(0), A-C (2004).
673. A. Xu, Y. Gao, and H. Liu, *J. Cat.* **207**, 151 (2002).
674. B. Malinowska and co-workers, *Int. J. Photoenergy* **5**, 147 (2003).
675. X. Z. Li, H. Liu, L. F. Cheng, and H. J. Tong, *Environ. Sci. Technol.* **37**, 3989 (2003).
676. G. Goutailler and co-workers, *J. Mater. Chem.* **13**, 342 (2003).
677. Jap. Pat. 2003-1116 (Jan. 7, 2003), S. Kishimoto (to Daiken Industries Ltd.).
678. World Pat. 3/022462 (Mar. 20, 2003), J. B. Schutt (to Adsil SC).
679. K. Okuyama and co-workers, *AIChE J.* **32**(12), 2010 (1986).
680. F. C. Mayville, R. E. Partch, and E. Matijevak, *J. Colloid Interface Sci.* **120**(1), 135 (1987).
681. G. Beaucage, J. Hueon-Lee, D. J. Kohls, and S. E. Pratsinis, *Nanopart. Res.* **1**, 379–392 (1999).
682. M. Visca and E. Matijeic, *J. Colloid Interface Sci.* **68**(2), 308 (1978).
683. F. Kirkber and H. Komiyama, *Adv. Ceram. Mater.* **3**(5), 511 (1988).
684. J. D. Casey and S. J. Haggerty, *J. Mater. Sci.* **22**, 4307 (1987).

685. D. M. Schleich and B. Walter, *Nanostructure Mater.* **8**(5), 579 (1997).
686. V. Jokanovic, A. M. Spasic, and D. Uskokovic, *J. Colloid Interface Sci.* **278**, 342 (2004).
687. J. M. Burlitch, *J. Sol–Gel. Sci. Technol.* **6**(3), 235 (1996).
688. C. B. Almquist and P. Biswas, *J. Cat.* **212**, 145 (2002).
689. C. Li, G. Yang, and Z. Wang, *Mater. Lett.* **57**(13-14), 2130 92003).
690. D. Li and Y. Xia, *Nano Lett.* **0**(0), A-F (2004).
691. G. Kitrov, *MRS Bulletin*, Aug., 3–4 (2000).
692. A. Y. Stakheev and co-workers, *Studies Surface Sci. Cat.* **143**, 509 (2002).
693. R. E. Rimen, R. R. landham, and H. K. Bowen, *J. Am. Ceram. Soc.* **72**(5), 821 (1989).
694. W. J. Kim and W. S. Ahn, *Cat. Lett.* **94**(3-4), 187 (2004).
695. A. Corma and co-workers, *J. Cat.* **145**, 151 (1994).
696. U.S. Pat. 6,110,269 (Aug. 29, 2000), A. Sugawara, T. Nishide, T. Seino, and Y. Kai (to Nissan Motor Co., Ltd.).
697. U.S. Pat. 5,200,167 (Apr. 6, 1993), U. Maeda, T. Imagawa, and M. Noriz (to Nippon Soda Co., Ltd.).
698. Jap. Pat. 3-76,819 (Apr. 2, 1991), S. Miyama and co-workers (to Nippon Soda Co. Ltd.).
699. H. S. Yunjg and co-workers, *J. Colloid Interface Sci.* **279**, 479 (2004).
700. M. Visca and E. Matijevic, *J. Colloid Interface Sci.* **68**, 308 (1979).
701. J. R. Bartlett, D. Gazeau, T. Zemb, and J. L. Woolfrey, *Langmuir* **14**(13), 3538 (1998).
702. A. Balboa, R. E. Partch, and E. Matijevic, *Colloids Surfaces* **27**, 123 (1987).
703. Eur. Pat. 1,184,365 (Mar. 6, 2002), D. Y. S. Min and co-workers (to Samsung Electronics).
704. K. Woo, W. I. Lewe, J. S. Lee, and S. O. Kang, *Inorg. Chem.* **42**, 2378 92003).
705. U.S. Pat. 3,301,723 (Jan. 31, 1967), J. D. Crisp (to E. I. du Pont de Nemours & Co., Inc.).
706. U.S. Pat. 3,355,366 (Nov. 28, 1967), W. M. Lyerley (to E. I. du Pont de Nemours & Co., Inc.).
707. U.S. Pat. 3,840,520 (Oct. 8, 1974), R. Nordgren and C. I. Carl (to General Mills Chemicals).
708. U.S. Pat. 4,692,273 (Sept. 8, 1987), K. Lawerence (to Hewlett-Packard).
709. T. Sakaguchi, A. Nakajima, and T. Horikoshi, *Nippon Kagaku Kaishi* 788 (1979).
710. Jpn. Kokai Tokkyo Koho 81 109,266 (Aug. 29, 1981) (to Mitsubishi Pencil Co.).
711. K. J. Schmalzl and P. D. Evans, *Poly. Deg. Stab.* **82**, 409 (2003).
712. World Pat. 02/85589 (Oct. 31, 2002), T. Staffel, M. Schmitt, W. Heilen, and M. Hoschke (to B.K.Giulini Chemie GmbH.).
713. Jpn. Pats. 71 12,085 (Mar. 27, 1971), K. Hamahiro, Y. Yoshioka, and H. Sakurai (to Kuraray Co.); 71 12,089 (Mar. 27, 1971), Y. Yoshioka, S. Kurokawa, and K. Hashita (to Kuraray Co.); 71 405 (Jan. 7, 1971), T. Ashikaga and U. Maeda (to Kuraray Co.).
714. Jpn. Pats. 71 38,410 (Nov. 12, 1971), T. Asikaga and S. Higashimori (to Kuraray Co.); 71 38,411 (Nov. 12, 1971), T. Ashikaga and U. Maeda (to Kuraray Co.).
715. U.S. Pats. 3,941,728-3,941,730 (Mar. 2, 1976), J. C. Solenberger (to E. I. du Pont de Nemours & Co., Inc.).
716. U.S. Pat. 4,113,757 (Sept. 12, 1978), P. D. Kay (to Tioxide Group).
717. Rus. Pat. 380,774 (May 15, 1973), to A. F. Tishchenko and co-workers.
718. Ger. Offen. 2,326,828 (Nov. 29, 1973), M. Camp and J. Dumoulin (to Rhone-Poulenc S.A.).
719. Czech. Pat. 181,452 (Jan. 15, 1980), E. Wurstova.

720. U.S. Pat. 4,288,496 (Sept. 8, 1981), R. E. Reusser and B. E. Jones (to Phillips Petroleum Co.).
721. Jpn. Kokai Tokkyo Koho 78, 24,408 (Mar. 7, 1978), T. Noguchi and co-workers (to Kureha Chemical Industry Co.).
722. Jpn. Kokai Tokkyo Koho 80, 167,211 (to Matsumoto Seiyaku Kogyo Co.).
723. Rus. Pat. 443,859 (Sept. 25, 1974), to T. P. Osipova and A. A. Kas'yanova.
724. Jpn. Kokai Tokkyo Koho 74, 36,998 (Apr. 5, 1974), M. Komeyama, S. Murakami, and H. Ohnishi (to Kuraray Co.).
725. S. D. Voronkevich, L. K. Zgadzai, and M. T. Kuleev, *Plast. Massy* 64 (1973).
726. A. A. Panasevich, S. P. Nichiporenko, and G. M. Nikitina, *Tr. Mezhvuz. Konf. Primen. Plastmass Stroit.* **3**, 174 (1970).
727. Ger. Offen. 2,310,820 (Sept. 13, 1973), A. E. Vassiliades, D. N. Vincent, and M. P. Powell (to Champion Paper Co.).
728. Research Disclosure 20402, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1981.
729. U.S. Pat. 3,888,312 (June 10, 1975), R. L. Tiner and co-workers (to Halliburton Co.).
730. U.S. Pat. 4,749,040 (June 7, 1988), R. M. Hodge (to Dowell Schlumberger Inc.).
731. U.S. Pat. 4,780,223 (Oct. 25, 1988), S. E. Baranet, R. M. Hodge and C. H. Kucera (to Dowell Schlumberger Inc.).
732. U.S. Pat. 4,861,510 (Aug. 29, 1989), R. M. Hodge (to Dowell Schlumberger Inc).
733. U.S. Pat. 4,464,270 (Aug. 7, 1984), K. H. Hollenbeak and C. J. Githens (to Halliburton Services Co.).
734. U.S. Pat. 4,502,967 (Mar. 5, 1985), M. J. Conway (to Halliburton Services Co.).
735. U.S. Pat. 4,657,080 (Apr. 14, 1987), R. M. Hodge (to Dowell Schlumberger).
736. U.S. Pat. 4,462,917 (July 31, 1984), M. J. Conway (to Halliburton Services Inc.).
737. U.S. Pat. 4,470,915 (Sept. 11, 1984), M. J. Conway (to Halliburton Services Inc.).
738. U.S. Pat. 4,609,479 (Sept. 2, 1986), K. C. Schmeltz (to E. I. du Pont de Nemours & Co., Inc.).
739. Eur. Pat. 195,531 (Sept. 24, 1986), D. E. Putzig and K. C. Schmeltz (to E. I. du Pont de Nemours & Co., Inc.).
740. U.S. Pat. 3,860,622 (Jan. 1, 1978), R. C. Wade (to Ventron Corp.).
741. U.S. Pat. 4,514,309 (Apr. 30, 1985), S. K. Wadhwa (to Hughes Tool Co.).
742. U.S. Pat. 6,214,773 (Apr. 10, 2001), P. C. Harris and co-workers (to Halliburton Services Inc.).
743. R. K. Prud'homme, *Polym. Mater. Sci. Eng.* **55**, 798 (1986).
744. J. Kramer and R. K. Prud'homme, *Polym. Mater. Sci. Eng.* **57**, 376 (1988).
745. D. I. Collias and R. J. Prud'homme, *J. Rheol.* **38**(2), 217 (1994).
746. U.S. Pat. 3,784,579 (Jan. 8, 1974), R. E. McGlothlin and co-workers (to Dresser Industries).
747. U.S. Pat. 3,878,111 (Apr. 15, 1975), R. E. McGlothin and T. E. Cox (to Dresser Industries).
748. U.S. Pat. 3,141,503 (July 21, 1964), N. Stein (to Secony Mobil Oil Co.).
749. U.S. Pat. 4,996,336 (Feb. 26, 1991), D. E. Putzig (to E. I. du Pont de Nemours & Co., Inc.).
750. U.S. Pat. 5,393,611 (Feb. 28, 1995), B. Flamme (to Ewald Doerken AG).
751. World Pat. 01/85854 (Nov. 15, 2001), V. Clerici, A. Wilhelmi, and J. Jamashita (to Dow Corning Corp.).
752. U.S. Pat. 5,874,570 (Feb. 23, 1999), S. Tamura and co-workers (to Fuji Electric Co. Ltd.).
753. U.S. Pat. 5,905,009 (May 18, 1999), Y. Nakamura, E. Egota, T. Tsubota, and M. Miyazawa (to Fuji Electric Co. Ltd.).
754. Eur. Pat. 584,698 (Aug. 17, 1993), C. Hsiao and co-workers (to Xerox Corp.).

755. Jap. Pat. 2004-085636 (Mar. 18, 2004), K. Suraga and M/Okaji (to Mitsubishi Paper Mills Ltd.).
756. Jap. Pat. 2000-258,939 (Sept. 22, 2000), H. Arisue and T. Horiuchi (to Mitsubishi Paper Mills Ltd.).
757. Jap. Pat. 08-292,588 (Nov. 5, 1996), Y. Tomouchi and co-workers (to Fuji Electric Co.Ltd.).
758. World Pat. 97/17388 (May 15, 1997), B. A. A. Jung, J. W. Leenslag, H. G. G. Verbeke, and D. A. E. Geukens (to Imperial Chemical Industries).
759. World Pat. 01/07498 (Feb. 1, 2000), C. J. Skinner (to Huntsman ICI Chemicals).
760. World Pat. 01/51536 (July 19, 2001), M. Partridge and B. F. Stengel (to Imperial Chemical Industries).
761. U.S. Pat. 5,902,835 (may 11, 1999), I. K. Meier, M. L. Listemann, and M. J. Kimock (to Air Products and Chemicals, Inc.).
762. World Pat. 03/020783 (Mar. 13, 2003), K. Brecht, W. Grimm, S. Schleiermacher, and M. Schutze (to Bayer AG).
763. World Pat. 03/018662 (Mar. 6, 2003), M. G. Davidson, M. D. G. Lunn, A. L. Johnson, and B. F. Stengel (to Johnson Matthey PLC).
764. World Pat. 2004/044027 (May 27, 2004), B. F. Stengel, D. Jenkins, and S. H. M. Gibson (to Johnson Matthey PLC).
765. World Pat. 98/15585 (Apr. 16, 1998), C. K. Skinner and J. Ridland (to Tioxide Specialties Ltd.).
766. World Pat. 2004/050734 (June 17, 2004), B. F. Stengel, N. Slack, M. G. Partridge, and S. H. M. Gibson (to Johnson Matthey PLC).
767. U.S. Pat. 6,048,943 (Apr. 11, 2000), E. J. Blok, L. G. Wideman, P. H. Sandstrom and M. L. Kralevich Jr. (to Goodyear Tire and Rubber Co.).
768. U.S. Pat. 6, 313,206 (Nov. 6, 2001), E. J. Blok, L. G. Wideman, P. H. Sandstrom, and M. L. Kralevich Jr. (to Goodyear Tire and rubber Co.).
769. T. Maschmeyer and co-workers, *Chem Commun.* 1847 (1997).
770. M. Crocker, R. H. M. Harold, and A. G. Orpen, *Chem. Commun.* 2411 (1997).
771. U.S. Pat. 6,380,406 (Apr. 30, 2002), K. M. Carrull (to Arco Chemical Technology).
772. J. M. Notestein, E. Iglesia, and A. Katz, *J. Am. Chem. Soc.* **126**, 16478 (2004).
773. T.-C. Chai and C.-M. Wei, *Fen Hsi Hua Hsueh* **7**, 327 (1979).
774. V. D. Bakalov, V. V. Dunina, and V. M. Potapov, *Zh. Anal. Khim.* **34**, 2138 (1979).
775. G. D. Brykina and T. A. Belyavskaya, *Vestn. Mosk. Univ. Khim.* **13**, 608 (1972).
776. C. G. Macarovici and E. Motiu, *Stud. Univ. Babes–Bolyai Ser. Chem.* **16**, 39 (1971).
777. R. M. Dranitskaya, A. I. Gavril'chenko, and L. A. Okhitina, *Zh. Anal. Khim.* **25**, 1740 (1970).
778. Y. I. Tur'yan and co-workers, *Zh. Neorg. Khim.* **23**, 2061 (1978).
779. Y. K. Tselinskii and V. K. Gadzhun, *Sov. J. Coord. Chem.* **4**, 1028 (1978).
780. E. I. Stepanovskii, G. M. Fofanov, and G. A. Kitaev, *Zh. Neorg. Khim.* **24**, 941 (1979).
781. F. G. Banica and L. Carlea, *Rev. Chim. (Bucharest)* **30**, 640 (1979).
782. A. Y. Nazarenko and I. V. Pyatnitskii, *Zh. Neorg. Khim.* **23**, 2655 (1978).
783. A. A. Popel, A. N. Glebov, and Y. I. Saltnikov, *Zh. Neorg. Khim.* **24**, 2409 (1979).
784. I. V. Pyatnitskii and R. S. Kharchenko, *Ukr. Khim. Zh.* **33**, 734 (1967).
785. V. M. Savostina, F. I. Lobanov, and V. M. Peshkova, *Zh. Neorg. Khim.* **12**, 2162 (1967).
786. V. K. Zolotokhin, O. M. Gnatishin, and E. I. Senchishin, *Visn. L'uiv. Derzh. Univ. Ser. Khim.* **17**, 40 (1975).
787. I. V. Pyatnitskii and A. Y. Nazarenko, *Zh. Anal. Khim.* **32**, 853 (1977); *Zh. Neorg. Khim.* **22**, 1816 (1977).

788. Y. K. Tselinskii, L. Y. Kvyatokovskaya, and V. K. Gadzhun, *Zh. Fiz. Khim.* **50**, 3002 (1976).
789. R. S. Ramakrishna and D. T. A. Seneratyapa, *J. Inorg. Nucl. Chem.* **39**, 333 (1977).
790. Ger. Offen. 1,811,502 (June 26, 1969), R. H. Stanley, D. W. Brook, and L. L. Lawrence (to British Titan Products Co.).
791. C. G. Macarovici and L. Czegledi, *Reu. Roum. Chim.* **14**, 57 (1969); *Stud. Univ. Babes-Bolyai Ser. Chem.* **22**, 25 (1977).
792. F. I. Lobanov and co-workers, *Zh. Neorg. Khim.* **14**, 1077 (1969); *Vestn. Mosk. Uniu. Khim.* **24**, 121 (1969).
793. Rus. Pat. 67 26,628 (Dec. 16, 1967), I. Sugiyama, K. Takahashi, and N. Takahashi (to Matsumoto Pharmaceutical Industry Co.).

GENERAL REFERENCES

J. H. Clark, *The Chemistry of Titanium and Vanadium*, Elsevier, Amsterdam, The Netherlands, 1968.

R. J. H. Clark, in J. C. Bailar and co-workers, eds., *Comprehensive Inorganic Chemistry*, Vol. 3, Pergamon Press, London, 1973, pp. 355–417.

P. C. Wailes, R. S. P. Coutts, and H. Weigold, *Organometallic Chemistry of Titanium, Zirconium, and Hafnium*, Academic Press, Inc., New York, 1974.

R. J. H. Clark, D. C. Bradley, and P. Thornton, *Chemistry of Titanium, Zirconium, and Hafnium*, Pergamon Press, New York, 1975.

R. J. H. Clark, S. Moorhouse, and J. A. Stockwell, *J. Organometal. Chem. Library* **3**, 223 (1977); literature covered through 1975.

E. Muller, ed., *Houben-Weyl's Methods in Organic Chemistry*, 4th ed., Vol. 13, Part 7, Georg Thieme, Stuttgart, Germany, 1975.

Gmelin, *Handbuch der Anorganischen Chemie*, 8th ed., Springer Verlag, Berlin, 1977.

Annual Surveys

K. S. Mazdiyasni, in K. Niedenzu and H. Zimmer, eds., *Annual Reports in Inorganic and General Synthesis*, Academic Press, Inc., New York, 1972, pp. 73–81; 1973, pp. 137–147.

J. J. Alexander, in K. Niedenzu and H. Zimmer, eds., *Annual Reports in Inorganic and General Synthesis*, Academic Press, New York, 1974, pp. 130–141; 1975, pp. 138–151; 1976, pp. 151–166.

F. Calderazzo, *Organomet. Chem. Rev.* **B4**, 12 (1968); **5**, 547 (1969); **6**, 1001 (1970); **9**, 137 (1972); *J. Organomet. Chem.* **53**, 179 (1973); **89**, 193 (1975); surveys cover the years 1967–1972.

P. C. Wailes, *J. Organomet. Chem.* **79**, 201 (1974); **103**, 475 (1975); **126**, 361 (1977); surveys cover the years 1973–1975.

J. A. Labinger, *J. Organomet. Chem.* **138**, 185 (1977); **167**, 19 (1979); **180**, 187 (1979); **196**, 37 (1980); **227**, 341 (1981); surveys cover the years 1976–1980.

R. C. Fay, *Coord. Chem. Rev.* **37**, 9 (1981); covers the literature on titanium for 1979; review for later years may appear subsequently.

Specialist Periodical Reports of the Chemical Society (London), Organometallic Compounds, contain numerous references on titanium compounds which can be located through the volume indexes.

Titanium Alkoxides, Amides, and Polyalkoxides

D. C. Bradley, in F. G. A. Stone and W. A. Graham, eds., *Inorganic Polymers*, Academic Press, New York, 1962, pp. 410–446.

D. C. Bradley, *Prep. Inorg. React.* **2**, 169 (1965).

D. C. Bradley, *Coord. Chem. Rev.* **2**, 299 (1967).

D. C. Bradley, *Inorg. Macromol. Rev.* **1**, 141 (1970).

Ziegler-Natta Polymerization

G. Henrici-Olivé and S. Olivé, *Chemtech* 746 (1981); a readable overview of this complex topic.

J. Boor, *Ziegler-Natta Catalysts and Polymerization*, Academic Press, New York, 1979.

C. E. Schildknecht and I. Skeist, *Polymerization Processes*, John Wiley & Sons, Inc., New York, 1977.

J. C. W. Chien, *Coordination Polymerization*, Academic Press, New York, 1975.

H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.* **18**, 99 (1980).

Lower Valent Titanium Compounds

R. S. P. Coutts and P. C. Wailes, *Adv. Organometal. Chem.* **9**, 136 (1970).

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