Introduction

DuPont™ TYZOR® organic titanates and zirconates are used as catalysts for chemical manufacture; in augmenting coatings, adhesives, and printing inks; and to improve the properties of coatings in electronics, glass, and metal products. DuPont is the industry leader in pioneering and manufacturing organic titanates and supplies a broad range of products for a variety of industrial applications.

DuPont TYZOR® organic titanates and zirconates offer superior product quality as well as the versatility of a large product line. Compounds ranging from highly reactive tetraalkyl titanates to stable chelates are available. This wide selection enables specification of the titanate or zirconate with the precise reactivity for each application or reaction condition.

TYZOR® organic titanates and zirconates perform four important functions, that are the key to the versatility of TYZOR® organic titanates and zirconates:

1. Catalysis, particularly esterification, transesterification, polyesterification, polycondensation polymerization and olefin polymerization.

2. Polymer cross-linking, which improves viscosity control properties of solutions, paints, and other coatings. The crosslinking property of TYZOR® organic titanates and zirconates can also augment adhesion properties of coatings, paints, inks and other surface materials.

3. Surface modification when applied by itself or in combination with other materials and can control the properties of adhesion, lubricity, or pigment dispersability.

4. A reagent used to create gel-sols, ceramics, heterogeneous catalysts, catalyst support manufacture, piezoelectric materials, and grease additive.

In many of these applications, TYZOR® titanates and zirconates are superior to other chemicals in their ease of use, cost effectiveness, uniqueness of effect, and freedom from undesirable side effects.

Production of TYZOR® products is back integrated to the titanium-bearing ore. Involvement from mine to production to customer guarantees a dependable supply of these DuPont products. With production facilities in both the United States and Europe, DuPont offers its customers worldwide availability and timely delivery.

DuPont emphasizes quality in every phase of the production cycle, which ensures that all TYZOR® products meet the highest specifications and are able to satisfy exacting customer requirements.

TYZOR® organic titanates and zirconates, like other DuPont offerings, are backed up by a worldwide sales and service network. The TYZOR® Technical Service Team has experienced representatives who are trained to help customers with special technical needs or highly specific questions.

The TYZOR® product line from DuPont has much to offer: versatility, availability, quality, service, and dependability. TYZOR® organic titanates and zirconates provide the chemist with versatile tools for product and process innovation.

This booklet contains additional information and specifications on TYZOR® products. Table 1, which follows, shows the major industrial applications of TYZOR organic titanates and zirconates. Table 2 shows major product grade groupings, along with properties and types of applications.

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<td>Titanium dioxide coatings for transistors</td>
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<td>Improved liquid crystal display (LCD) properties</td>
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<td>Films</td>
<td>Surface modif</td>
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<tr>
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<td></td>
<td>Pigment disp</td>
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<td>Printing ink binder cross-linking</td>
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<td>Surface modif</td>
<td>Improved printability of surfaces</td>
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<td>Corrosion-res...</td>
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<td>Oil field</td>
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<td>Pigments</td>
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<td>Pigment dispersion</td>
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<td>Resin cross-linking</td>
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<td></td>
<td>Surface modif</td>
<td>Filler dispersion and improved compatibility of filler</td>
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<td>with polymer matrix, viscosity reduction</td>
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<td>Primers for metals,</td>
<td>Surface modif</td>
<td>Adhesion promotion, Corrosion resistance</td>
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<td>plastics, rubbers</td>
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<td>Textiles</td>
<td>Catalysis</td>
<td>Polyester manufacture</td>
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**TABLE 2**

<table>
<thead>
<tr>
<th>Grades*</th>
<th>Type</th>
<th>Properties</th>
<th>Applications</th>
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</thead>
<tbody>
<tr>
<td>TYZOR® TPT, TnBT, TOT NPT, TPT-20B</td>
<td>Tetraalkyl titanate</td>
<td>Moisture-sensitive 100% active, very reactive</td>
<td>Cross-linking in nonaqueous formulations, Catalysis, Surface modification</td>
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<tr>
<td>TYZOR® AA-Series AA, GBA, GBO, AA-75, AA-65 AA-105</td>
<td>Titanium chelate</td>
<td>75% - 100% active in alcohol Activated at 100 to 250°C (212 to 482°F)</td>
<td>Used in aqueous and nonaqueous formulations, Delayed cross-linking</td>
</tr>
<tr>
<td>TYZOR® DC</td>
<td>Titanium chelate</td>
<td>Not soluble in water 100% active Activated at 100 to 250°C (212 to 482°F)</td>
<td>Used in nonaqueous formulations, Delayed cross-linking</td>
</tr>
<tr>
<td>TYZOR® TE</td>
<td>Titanium chelate</td>
<td>Soluble in water (slow hydrolysis) 80% active in alcohol Activated at 100 to 250°C (212 to 482°F) and a pH from 4 to 10</td>
<td>Used in aqueous and nonaqueous formulations, Delayed cross-linking</td>
</tr>
<tr>
<td>TYZOR® LA</td>
<td>Aqueous titanium chelate</td>
<td>50% active in water Activated at 100 to 250°C (212 to 482°F) and a pH from 5 to 10 Most reactive of aqueous chelates</td>
<td>Used in aqueous formulations, Delayed cross-linking, Esterification, Catalyst</td>
</tr>
<tr>
<td>TYZOR® 131</td>
<td>Aqueous titanium chelate</td>
<td>Miscible with water Activated at 100 to 250°C (212 to 482°F) and a pH from 6 to 10</td>
<td>Used in aqueous formulations, Delayed cross-linking</td>
</tr>
<tr>
<td>TYZOR® NPZ, NBZ</td>
<td>Tetraalkyl zirconate</td>
<td>Moisture-sensitive Contains alcohol solvents</td>
<td>Cross-linking in nonaqueous formulations, Catalysis, Reagent, Surface modification</td>
</tr>
</tbody>
</table>

* Please consult specific product information sheet for additional information and for product listings by country.

**Composition**

DuPont supplies two general classes of organic titanates: tetraalkyl titanates, which can be represented by the general structure Ti(OR)₄, and titanate chelates, represented by

![Molecular structure](image)

In this molecular structure, X represents a functional group containing oxygen or nitrogen, and Y represents a two- or three-carbon chain.

The chelates can be further subdivided into two groups:

- **Nonaqueous**, including products that are supplied either as 100% active materials or as a solution in alcohol—TYZOR® TE, AA-series, DC, and related products.
- **Aqueous**, including products that are supplied as water solutions—TYZOR® LA, 131, 217, and 218.
Tetraalkyl titanates

TYZOR® organic titanates of the alkyl titanate type are

- TYZOR® TPT—tetraisopropyl titanate
  \[ \text{Ti(OC}_3\text{H}_7\text{)}_4 \]
- TYZOR® TnBT—tetra-\textit{n}-butyl titanate
  \[ \text{Ti(OC}_4\text{H}_9\text{)}_4 \]
- TYZOR® TOT—tetrakis(2-ethylhexyl)titanate
  \[ \text{Ti(OCH}_2\text{CHC}_4\text{H}_9}\text{)}_4 \]

Titanate chelates

The compositions of some DuPont titanate chelates are shown below.

TYZOR® AA-series—acetylacetonate titanate chelate

TYZOR® DC—ethyl acetoacetate titanate chelate

TYZOR® TE, triethanolamine titanate chelate, is a mixture of chelates with at least one component that has the following cage structure:

TYZOR® LA—lactic acid titanate chelate, ammonium salt
Reactions

Hydrolysis

Tetraalkyl titanates hydrolyze rapidly when exposed to water, and atmospheric moisture produces condensation products with high molecular weights. In the presence of alcohols, however, the extent of hydrolysis and polymerization can be retarded, which is attributable to the solvation effect of the alcoholic solvents on the alkyl titanate. The hydrolysis proceeds with the intermediate formation of a coordination complex between the ester and water, followed by elimination of an alcohol molecule.

\[ \text{Ti(OR)}_4 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} \cdot \text{Ti(OR)}_4 \rightarrow \text{Ti(OR)}_3\text{OH} + \text{ROH} \]

The monohydroxy ester, however, cannot be isolated and immediately reacts with an additional mole of titanate to form a dimeric product:

\[ \text{Ti(OR)}_3\text{OH} + \text{Ti(OR)}_4 \rightarrow (\text{RO})_3\text{TiOTi(OR)}_3 + \text{ROH} \]

Further hydrolysis of the hexaalkoxy compound proceeds in steps until titanium dioxide or hydrous titanium dioxide is obtained. These reactions may be represented as follows:

\[ 2[(\text{RO})_3\text{Ti–2O} + 2\text{H}_2\text{O} \rightarrow \text{HOTi(OR)}_2\text{OH} + 2 \text{ROH} \]

Reaction with more water, in sequence:

\[ \rightarrow \text{HOTi(OH)}_2\text{OH} \text{ (may be polymeric) } \rightarrow \text{TiO}_2\cdot2\text{H}_2\text{O} + 4\text{ROH} \]

Whether hydrous titanium dioxide of indefinite composition or titanium dioxide itself is obtained as the end product depends on the temperature and rate of water addition at which hydrolysis is conducted. When conducted with care, hydrolysis results in a clear, amorphous film of titanium dioxide.

The hydrolysis rate of the titanate esters depends on the size and complexity of the alkyl groups—as their size increases, the rate of hydrolysis decreases.

The chelated titanates are much less susceptible to hydrolysis than are the tetraalkyl titanates. TYZOR® LA and 131 are so stable that they are sold as aqueous solutions. TYZOR® TE can be diluted with water; however, hydrolysis occurs slowly over time.

A simple test shows the difference between the following two groups:

- Easily-hydrolyzed metal-acid esters
- Chelates that do not hydrolyze or are difficult to hydrolyze

In the test, 5g of the substance to be examined is dissolved in 50 ml anhydrous isopropanol, and water is added in drops from a burette to the stirred solution until precipitation or cloudiness occurs. The average amount of water added in this test is shown in Table 3 for several products.

<table>
<thead>
<tr>
<th>Water added in ml</th>
<th>Product Tested</th>
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<tbody>
<tr>
<td>0.01</td>
<td>n-butyl zirconate</td>
</tr>
<tr>
<td>0.02</td>
<td>n-propyl zirconate</td>
</tr>
<tr>
<td>0.5 - 2</td>
<td>ethyl titanate</td>
</tr>
<tr>
<td>0.5-2</td>
<td>n-propyl titanate</td>
</tr>
<tr>
<td>0.5-2</td>
<td>isopropyl titanate</td>
</tr>
<tr>
<td>0.5-2</td>
<td>isobutyl titanate</td>
</tr>
<tr>
<td>0.5-2</td>
<td>2-ethylhexyl titanate</td>
</tr>
<tr>
<td>1 – 2.5</td>
<td>n-butyl titanate</td>
</tr>
<tr>
<td>1 - 2.5</td>
<td>cresyl titanate monomer</td>
</tr>
<tr>
<td>1 - 2.5</td>
<td>cresyl titanate polymer</td>
</tr>
<tr>
<td>1.5 - 3</td>
<td>n-butyl titanate polymer</td>
</tr>
<tr>
<td>120- 150</td>
<td>triethanolamine titanate</td>
</tr>
<tr>
<td>160- 190</td>
<td>Titanium acetylacteonate</td>
</tr>
<tr>
<td>&gt; 500</td>
<td>triethanolamine zirconate</td>
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</tbody>
</table>

By choosing constituents that form suitable chelates, it is possible to make products that give values situated between the extremes, although this method is rough at best.

The approximation inherent in this method argues that it should only be used to give an indication of the hydrolysis behavior of the substance in question. Conclusions should not be drawn from this method about behavior toward other reactants.

Alcoholysis and ester interchange

The titanate esters undergo alcoholysis rapidly at room temperature in the absence of any catalyst.

\[ \text{Ti(OR)}_4 + 4 \text{R’OH} \rightarrow \text{Ti(OR’)}_4 + 4 \text{ROH} \]

Mixing tetra isopropyl titanate with a stoichiometric quantity of the alcohol and then distilling isopropyl
alcohol usually produces higher esters or mixed esters. This ability to react rapidly and at room temperature with hydroxyl-containing materials has led to numerous industrial applications of alkyl titanates.

Enols derived from aldehydes also react by alcoholysis with the alkyl titanates to give vinyl titanates.²

Alkyl titanates also undergo ester interchange with carboxyl esters:

\[
\text{Ti(OR)₄} + 4 \text{R’COOR”} \rightarrow \text{Ti(OR’”₄} + 4 \text{R’COOR}
\]

The equilibrium reaction can be forced to completion by distilling the lower boiling product or byproduct.³

### Reactions with acids

Alkyl titanates react rapidly with carboxylic acids to form titanium acylates, which exist primarily in their polymeric forms.

\[
\text{Ti(OR)₄} + \text{R’COOH} \rightarrow \text{Ti(OR)₃(OCOR’)} + \text{ROH}
\]

\[
\text{Ti(OR)₄} + 2 \text{R’COOH} \rightarrow \text{Ti(OR)₂(OCOR’₂} + 2 \text{ROH}
\]

The tendency of titanium to increase its coordination number is shown by the association of acylates to form bridged structures.

Bridged structures are commonly formed as follows:

If a mixture of an alkyl titanate and a carboxylic acid is heated in an attempt to force the replacement of more than two alkoxy groups, one of two results is produced: an organic ester and a condensed titanate ester or an alkoxy polytitanyl acylate.⁴

### Reactions with acid anhydrides

Alkyl titanates react rapidly with acid anhydrides. For example

\[
\text{Ti(OR)₄} + (\text{CH₃CO})₂O \rightarrow \text{Ti(OR)₃(OCOCH₃)} + \text{CH₃COOR}
\]

The resulting trialkoxytitanium acylate may then condense further, as indicated above (see Reactions with Acids).

### Reactivities

TYZOR® tetraalkyl titanates are the most reactive titanates available. Their reactivity decreases with increasing molecular weight; TYZOR® TPT reacts faster than TYZOR® TnBT, and TYZOR® TnBT reacts faster than TYZOR® TOT. In situations where moisture is a problem, TYZOR® TE can be used.

In general, titanate chelates are much less reactive than the tetraalkyl titanates. The chelates undergo the same reactions as the tetraalkyl types when the
chelate structure is activated by heat or by adjusting the pH to higher values (greater alkalinity).

The reactivities of the TYZOR® chelates in order of decreasing rate are TYZOR® LA, TE, DC, AA-Series, and 131. Laboratory evaluations should be performed on specific products to determine their reactivity in a given reaction system.

Other Reactions
Additional information on the above reactions and other reactions of organic titanates is given in review articles.5,6

Properties

Thermal stability and pyrolysis
TYZOR® TPT can be distilled, unchanged, at atmospheric pressure. However, all alkyl titanium esters pyrolyze at 350°C (662°F) or higher. The primary decomposition products of tetraisopropyl titanate appear to be propylene, isopropyl alcohol, and titanium dioxide. A clear film of TiO₂ can be deposited if pyrolysis is conducted by impinging an air or nitrogen stream containing a low concentration of tetraisopropyl titanate on a hot surface (500 to 600°C [932 to 1112°F]). Such films are considerably harder than those produced by hydrolysis of alkyl titanates and contain no residual organic matter.7

Individual product sheets are available; these contain the properties of each TYZOR® grade.

Applications

Catalytic applications
Organic titanates are valuable catalysts in a number of chemical reactions. They are particularly useful in esterifications and transesterifications. In this application, the use of organic titanates accomplishes the catalysis with a minimum of undesirable side reactions and results in a high yield of esters with good color and odor. For example, esters can be made from carboxylic acids and secondary alcohols with only a minor amount of olefin formation, in contrast to conventional acid catalysis, which produces substantial amounts of olefins.

Titanates are particularly useful for reactions involving unsaturated reactants and amino alcohols. Similarly, titanates are condensation catalysts in the manufacture of polyesters. Organic titanates are also useful for the catalysis and cross-linking of a wide variety of other resin types, such as polyolefins, polyurethanes, epoxies, phenolics, and silicones. Organic titanates may be used as catalysts for aldol condensations and in Meerwein-Ponndorf-Verley reductions.

Esterification Transesterification
Organic titanates often give faster reaction rates and higher yields than conventional acid catalysts. In the synthesis of n-decyl acrylate by the transesterification of ethyl acrylate with n-decyl
alcohol, using TYZOR® TPT as the catalyst gives results that are superior to those expected when using sulfuric acid and p-toluene-sulfonic acid.

One major advantage of using organic titanates is the quality of the excess alcohol recovered from the reactions. Whereas acid-catalyzed methods often cause extensive degradation of the alcohol during the reaction, titanate catalysis avoids this degradation, allowing recycling of recovered alcohols.

Equally important is the ability of organic titanate catalysis to avoid color buildup in the product and to provide high-purity esters suitable for the most demanding applications.

In reactions where color formation is a persistent problem even with titanates, several methods have been reported to minimize such formation, including the use of phosphorous compounds,8, 9 mixed metal catalysts,10-12 organic amine co-catalysts,13-15 and titanium chelates.16-18

Titanates are also superior catalysts in certain cases in which color is a problem because of the quality of raw materials. Using organic titanates in the manufacture of trimellitate esters, for example, provides improved color in addition to the advantages of higher yield, decreased cycle time, and increased product purity.

**Polysiloxanes**

Organic titanates are valuable as catalysts for the polymerization of many types of siloxanes.19-25 Using these titanates permits more rapid curing at a lower temperature than could otherwise be obtained. In many cases, the titanates not only serve to catalyze the reaction, but they also cross-link the silicone structures. As a result, the cured resins exhibit harder surfaces and improved heat and electrical resistance.

**Olefins polymerization**

Titanium compounds are used extensively to polymerize a variety of olefinic hydrocarbons.26-32

Since the original disclosures of Natta and Ziegler, hundreds of patents embodying various refinements and applications of the catalyst systems have been issued. Titanites are used in some of these applications, generally in combination with other organometallic compounds (e.g., aluminum alkyls).

Advantages claimed for organic titinate catalysts include:

- Production of a polymer with better physical properties than can be obtained from TiCl4-based catalysts
- No danger of acid corrosion of reaction vessels
- Chloride-free polymer
- Solvent-soluble catalyst systems

**Other Catalytic Applications**

Organic titanates have been reported to be useful catalysts for several other classes of resins, including polyformaldehydes,33 polycarbonates,34, 35 and polyurethanes.36, 37

**Cross-Linking**

TYZOR® organic titanates cross-link polymers through the active hydrogens of hydroxyl, amino, amido, carboxyl, and thio groups. These reactions are of great value in producing resins and coatings with improved hardness, solvent resistance, and electrical properties.

Organic titanates undergo alcoholysis as follows:

\[
\text{Ti(OR)}_4 + 4 \text{R'}\text{OH} \rightleftharpoons \text{Ti(OR')}_4 + 4 \text{ROH}
\]

If ROH is more volatile than R’OH, it may be removed by evaporation or distillation, shifting the equilibrium to the right, to convert all the R’OH to Ti(OR’)4. This reaction is sometimes called ester interchange of a titanate, because the alkyl groups in an ester of ortho-titanic acid are interchanged.
Hydroxy cross-linking is a form of alcoholysis. If R'OH is an alcohol with a high molecular weight and includes film-forming substances, such as a natural or synthetic polymer, the same reaction takes place.

The fate of the third and fourth alkoxy groups on the titanate varies. Additional cross-linking through alcoholysis of these groups may be possible, depending on steric considerations and the availability of additional active cross-linking sites.

If the third and fourth alkoxy groups are not cross-linked, they may subsequently hydrolyze to hydroxyl groups when the substance is exposed to moisture. Again, depending on steric considerations, the third and fourth alkoxy (or hydroxyl) groups may condense with similar groups on another titanate molecule to form a polymeric titanate configuration. This mechanism is not confined to hydroxyl groups but is useful for cross-linking through any group offering an available, active hydrogen.

If a substance to be cross-linked has one reactive site, the molecular weight may be doubled or even quadrupled by reaction with a titanate. Two active sites (such as an α,ω-glycol) might tend to form long-chain polymers, although cross-linking through the titanate might occur. Available mid-chain sites (in addition to the alpha, omega-sites) offer the possibility of a complex cross-linking action involving three or more chain sites and two to four titanate sites.

### Surface Modification

The use of titanates for surface modification is based on their ability to hydrolyze to a coating that is very thin, primarily inorganic, and amorphous while having repeating units of –OTiO–.

The properties of this film depend on the type and amount of titanate used, the thickness of the application, and the temperature of the surface. The best performance is obtained when the substrate contains functional groups with active hydrogens.

This hydrolyzed reactive coating of TiO₂ modifies surfaces to give the following unique properties:

- It promotes adhesion of films and coatings to glass, metal, and plastics.
- The coating improves dispersibility of pigments and fillers in aqueous or nonaqueous systems and reduces viscosity.
- It provides scratch-resistance and reflective properties to glass.
- It modifies frictional characteristics.

### Testing for Titanium

Because primed and unprimed surfaces are almost indistinguishable in visual checks, several methods have been developed for identifying the final, primed surface.

One method is to check the wetting properties with solvents if the primed and unprimed surfaces are known to have different wetting properties.

Another method is to analyze for the presence of titanium. Note that spot tests do not indicate the quality of coating regarding either thickness or coverage.

### Spot Tests for Titanium

- **Hydrogen peroxide.** Several drops of 10% sulfuric or hydrochloric acid are placed on the film’s surface and rolled over an area to increase the extent of contact. Then two drops of 30% hydrogen peroxide are added to the treated area. A yellow color indicates titanium.

- **Chromotropic acid** (used as a 5% solution of the sodium salt in water). One to two drops of dilute sulfuric or hydrochloric acid solution are placed on the film’s surface and rolled over an area. A drop of a 5% solution of the sodium salt of chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulfonic acid) is added to the treated area. A reddish-brown color indicates titanium.

- **Disodium 1,2-dihydroxybenzene-3,5-disulfonate.** One drop of 10% hydrochloric acid solution is placed on the film’s surface and spread over an area of about 1 to 2 inches with a glass stirring rod. This area is allowed to dry partially. Then one drop of a 10% solution of disodium 1,2-dihydroxybenzene-3,5-disulfonate is added to the acid-treated area and spread it around with a glass rod. A
yellow ring around the outer edge of the wet area indicates titanium.

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