技 術 資 料

Technical Information

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Application of ORGATIX as **Catalyst**

Use as catalysts for esterification, urethane formation and silicone curing

Matsumoto Fine Chemical Co.,Ltd.

HEAD OFFICE 5-13-2, Minamiyawata, Ichikawa-shi, Chiba, 272-0023 JAPAN

TEL +81-47-393-6330

FAX +81-47-393-1063

OSAKA OFFICE Kawaramachi SF Bldg. 6F

3-4-15, Kawaramachi, Chuo-ku, Osaka, 541-0048 JAPAN

TEL +81-6-7654-6862

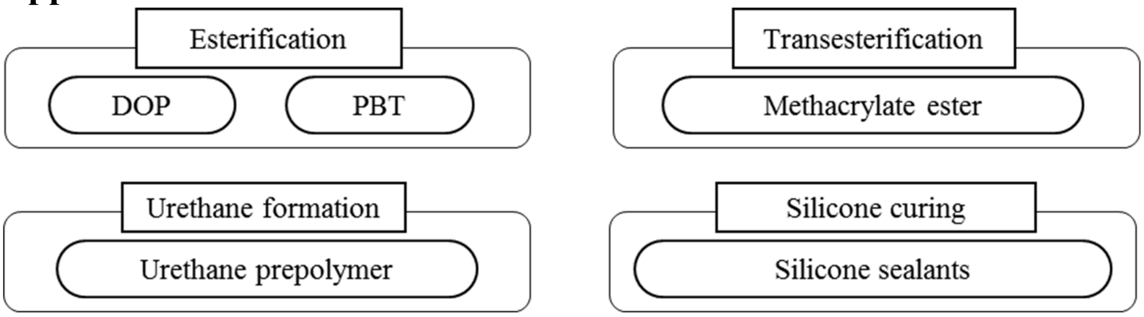
FAX +81-6-7655-2087

ORGATIX is the trade name for organic titanium and organic zirconium compounds developed by Matsumoto Fine Chemical. Titanium/Zirconium compounds are known as effective catalysts for various chemical reactions and have been used as the material for a Ziegler-Natta catalyst used in olefin polymerization. In recent years, they are often used as catalysts for esterification (transesterification), urethane formation and silicone curing while attracting attention as alternatives to organic tin catalysts which have safety concerns.

1. Advantages

- High catalytic activity
- High level of safety
- Catalytic activity will eventually be lost by hydrolysis, reducing the effects of catalysts on finished products.

2. Application

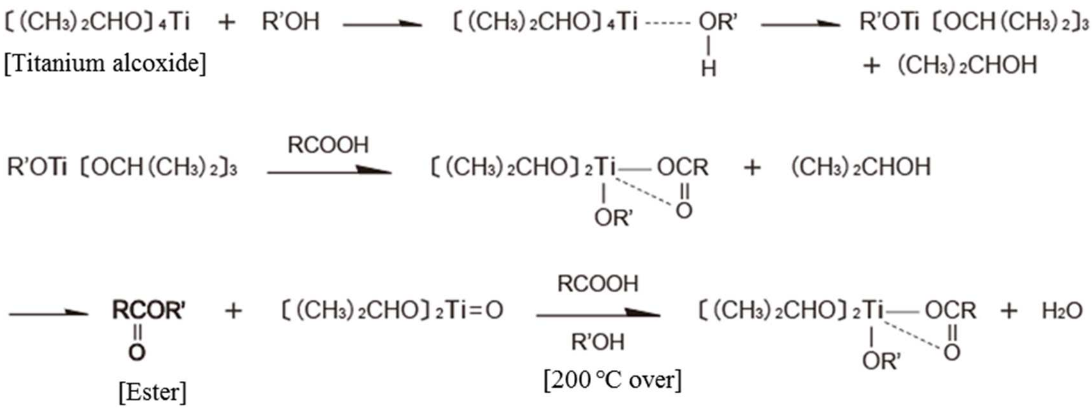


3. Mechanism and examples of reaction

3-1 Esterification catalysts

ORGATIX serves as an excellent catalyst for esterification/transesterification reaction between alcohols and carboxylic acids with less side reactions, allowing for production of high quality ester.

<Fig. 1 Esterification mechanism in the case of using ORGATIX>



As shown in Fig. 1, titanium alkoxide facilitates coordinating alcohols and carboxylic acids to titanium atoms, allowing for esterification. Titanium chelate as well as titanium alkoxide exhibit catalytic activity for esterification. It is important to select the optimum compound to achieve higher yield.

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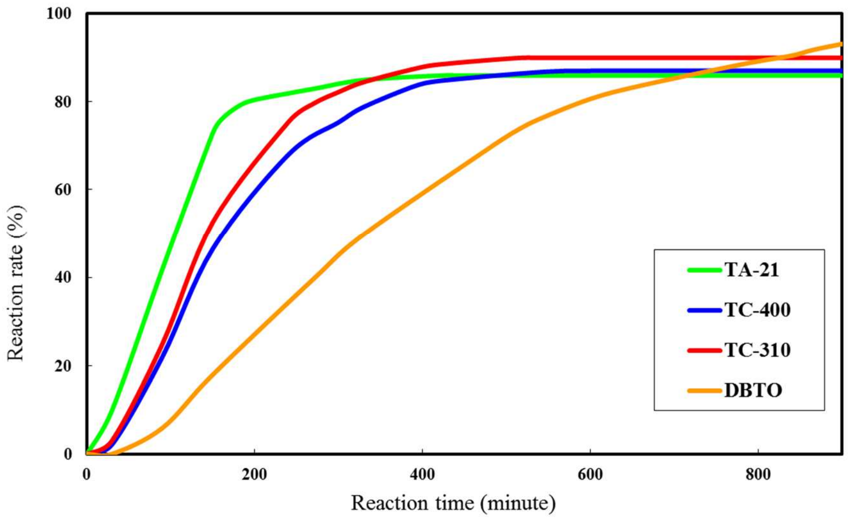
Below are reaction examples conducted by Matsumoto Fine Chemical and synthesis disclosed in a Japanese patent application publication:

Example 1: Esterification between 2-ethylhexanol and isophthalic acid

Charged 2-ethylhexanol and isophthalic acid into a reactor with a Dean-Stark trap with a ratio of OH:COOH at 1.3:1.0 (mole ratio), and charged a catalyst to be 0.1 wt% of content. Then, initiated reaction at 190 °C while performing dehydration. Used three types of compounds including TA-21 (tetrabutoxy titanium), TC-310 (titanium lactate chelate), TC-400 (triethanolamine titanate chelate) as catalysts and dibutyltin oxide (DBTO) for comparison.

<Fig. 2 Performance of catalyst in esterification>



Example 2: Production method of polybutylene terephthalate (PBT) (JP S62-141022)

<Esterification>

Raw materials	Usage
Terephthalic acid	755
1,4-butanediol	696
Titanium triethanol aminate (TC-400)	0.75

<Reaction condition>

Esterification

230 ℃ x 3.5 hours

<Polycondensation>

Raw materials	Usage
Polymer obtained above esterification	100
Titanium triethanol aminate (TC-400)	0.075

Polycondensation

245 ℃ x 3.5 hours

(under 1 mmHg)

Example 3: Production method of Dioctyl phthalate (DOP) (JP 2006-273799)

Raw materials	Usage
Terephthalic acid	100
2-ethylhexanol	196
Titanium tetra-isopropoxide (TA-8)	0.13

<Reaction condition>

4 hours of reaction

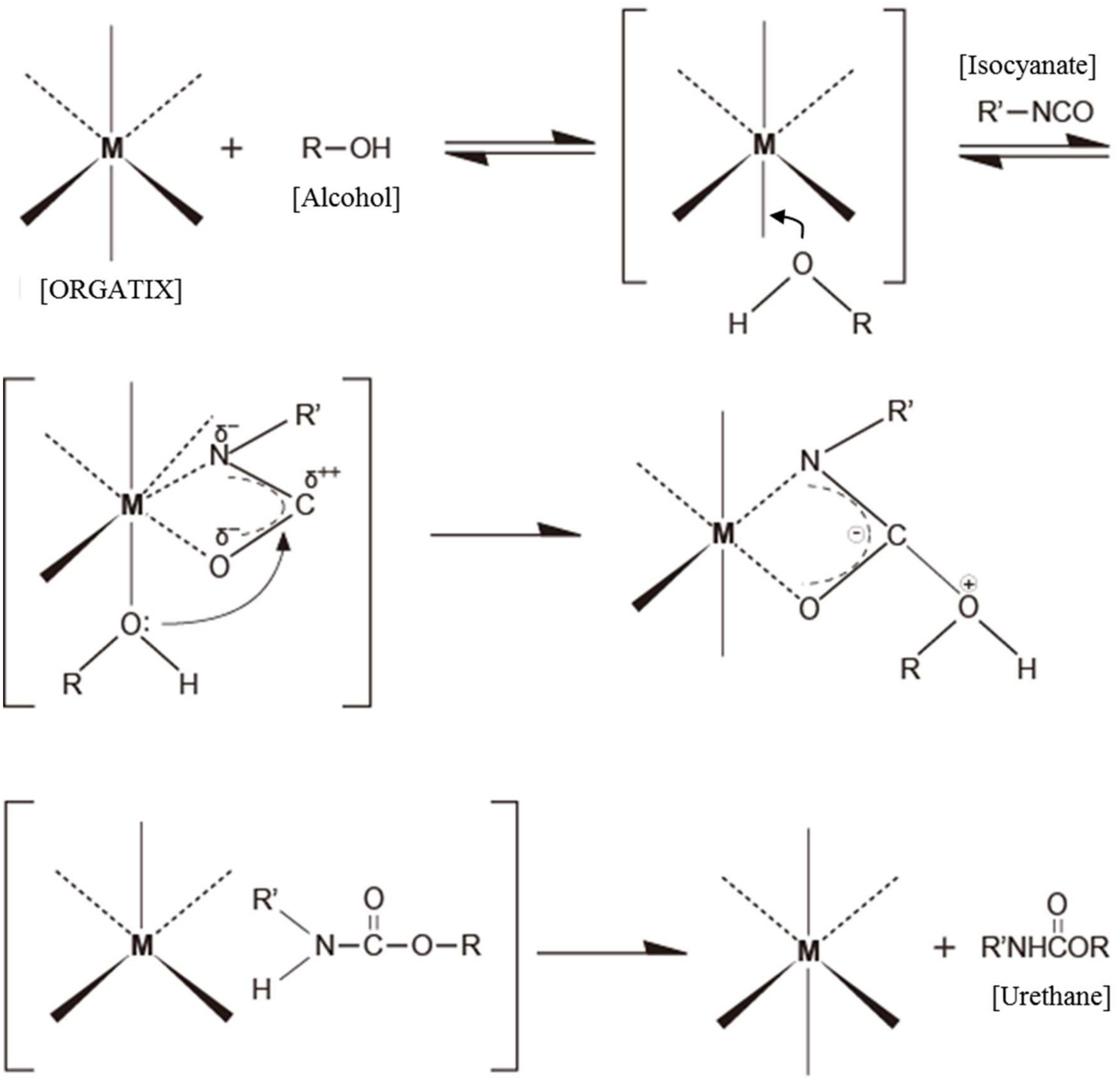
in the oil bath heated to 220 ℃

ORGATIX has a high initial activity and serves as an effective catalyst for synthesizing polybutylene terephthalate (PBT) and dioctyl phthalate (DOP).

3-2 Urethane formation catalysts

ORGATIX has catalytic activity for urethane formation by hydroxyl group and isocyanate group. It has a higher degree of safety as compared with commonly used organic tin catalysts.

<Fig. 3 Mechanism of urethane forming using ORGATIX (J. Robbins's scheme)>



As shown in Figure 3, urethane formation occurs as a hydroxyl group, and then an isocyanate group is coordinated to ORGATIX. In general, however, coordinate bonding between ORGATIX and a hydroxyl group is initiated promptly; hence it is a common practice to add ORGATIX, polyol and isocyanate at the same time.

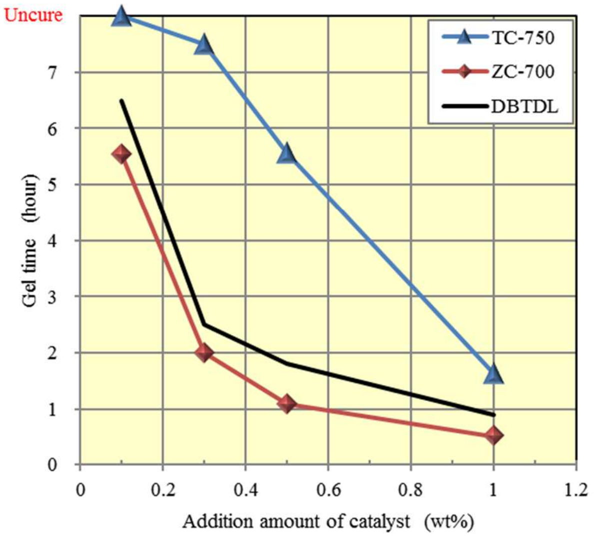
Below are reaction examples conducted by Matsumoto Fine Chemical and synthesis disclosed in a Japanese patent application publication:

<u>Example 1: Urethane formation by acrylic polyol and isocyanate compound</u>

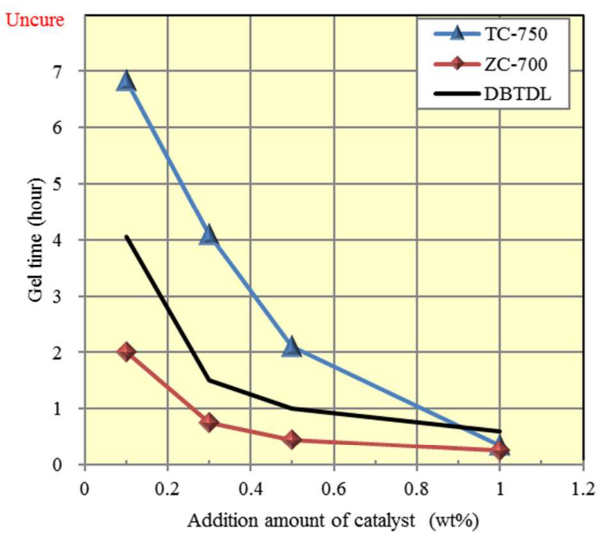
Mixed acrylic polyol (Olester Q164, Mitsui Chemicals) and tolylene diisocyanate or 1,6-diisocyanate hexane with the ratio of OH:NCO at 1:1 (mole ratio) at room temperature, and then, added a catalyst. Let it stand at room temperature and measured gelling time to compare performance of catalysts. Used the three agents below as catalysts individually:

TC-750 (Titanium ethyl acetoacetate), ZC-700 (Zirconium tetra acetylacetonate)、DBTDL (Dibutyl tin dilaurate)

<Fig. 4 Performance of catalyst in reaction between acrylic polyol and isocyanate compound>



Polyol: Acrylic polyol
Isocyanate: Toluene diisocyanate (TDI)
Mixture ratio: OH / NCO = 1 / 1 (mole ratio)
Curing condition: Under room temperature



Polyol: Acrylic polyol
Isocyanate: 1,6-diisocyanate hexane (HDI)
Mixture ratio: OH / NCO = 1 / 1 (mole ratio)
Curing condition: Under room temperature

★ZC-700 (zirconium compound) exhibits equivalent or higher catalytic activity than tin compounds. Titanium compounds also exhibit catalytic activity equivalent to tin compounds as long as the content is approximately 1.0 wt%.

<u>Example 2: Example of manufacturing method of thermoplastic polyurethane (JP 2004-352800)</u>

This is an example of a manufacturing method of thermoplastic polyurethane by use of an extrusion cylinder. In this example, a reactant of polyol and organic titanium compound was used as a catalyst.

<Preparation of catalyst-containing diol>

Raw materials	Usage
Diethyl carbonate	1445.5
3-methyl-1,5-pentanediol	1681.5
Tetra n-butyltitanate (TA-21)	0.18

<Reaction condition>

At first, reacts diethyl carbonate with 3-methyl-1,5-pentanediol in 180 - 190 ℃. After that, adds TA-21 and continues to react under reduced pressure.

<Urethane formation>

Reacts urethane forming in twin-screw extruder.

○ Hopper feed rate

Mixed polyol*1: 72.47g/min

HDI : 27.53g/min

○Temperature inside extruder: 170 - 200 ℃

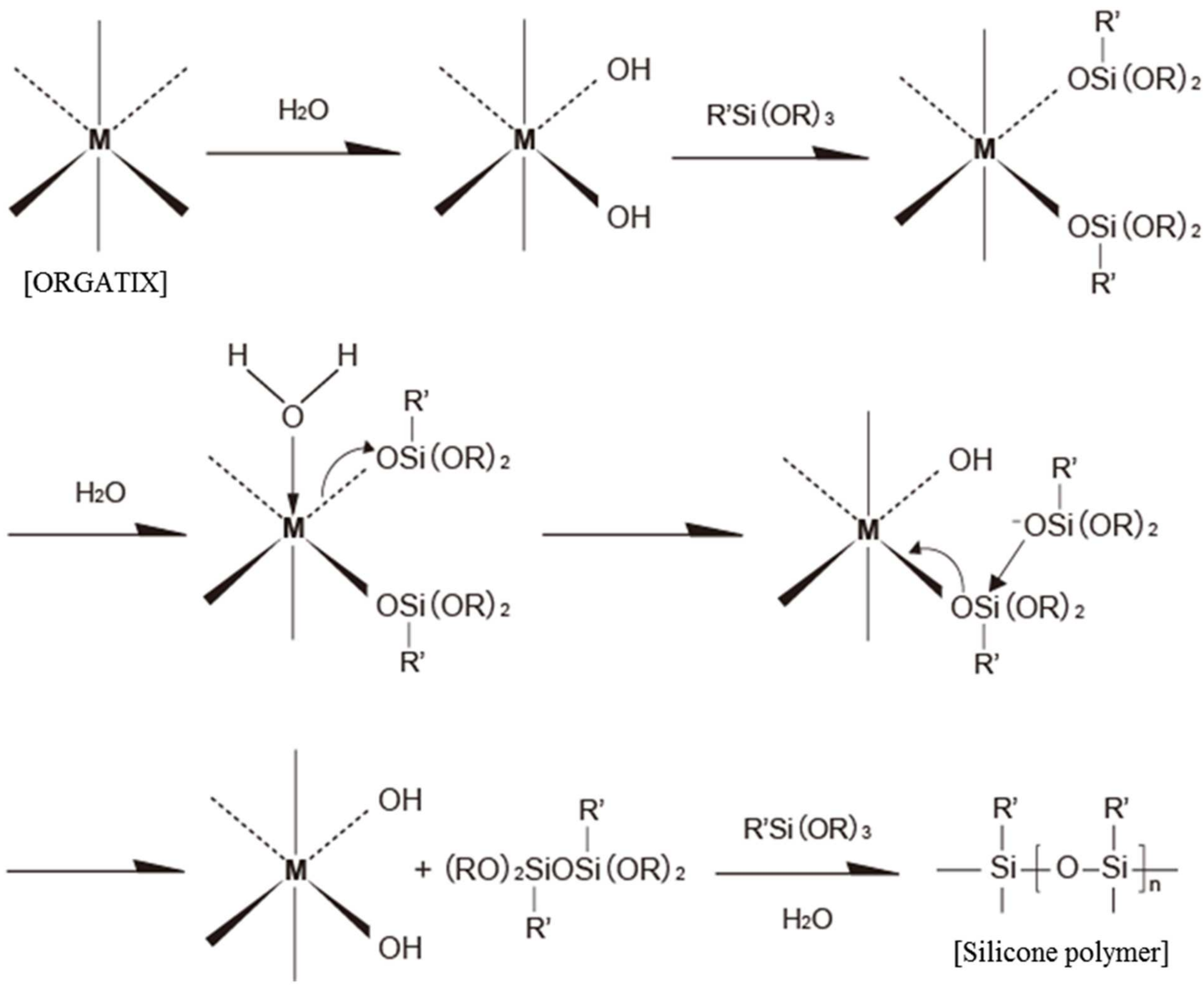
*1: Mixed polyol

Catalyst-containing diol / 1,4-butanediol = 874.1 / 125.9 (weight ratio)

3-3 Catalyst for curing silicone resin

ORGATIX exhibits catalytic activity which enhances condensation reaction of Si-OH and Si-OR. This property is useful as a curing catalyst for silicone sealant. In addition to having an effect as a catalyst, ORGATIX also helps improve adhesion.

<Fig. 5 Reaction mechanism of silicone curing in the case of using ORGATIX>



As shown in Figure 5, ORGATIX acts as a catalyst for Si-OR condensation reactions which require moisture in the air (room temperature vulcanizing: RTV).
As a usage example of ORGATIX as a curing catalyst for RTV silicone, studies which explore catalysts for dealcoholized silicone sealant are underway and some applications, as mentioned below, are available:

Example 1: Usage as a one-component dealcoholized RTV silicone (silica-filled silicone: clear sealant)

Adding titanium alkoxide to RTV silicone with the composition below brings about a low color, cured material.

Raw materials	Usage
Silicone polymer	85 - 90
Fumed silica	7 - 10
Closslinker	4 - 9
Adhesion promotor	0 - 3
Inorganic pigment	1 - 2
Catalyst (Titanium alchoxide)	1

Example 2: Usage as a one-component dealcoholized RTV silicone (calcium carbonate-filled silicone: colored sealant)

Adding ethyl acetoacetate titanate chelate (ORGATIX TC-750) to RTV silicone with certain composition improves preservation stability of RTV silicone as compared with adding titanium alkoxide:

Raw materials	Usage
Silicone polymer	40 - 60
Surface-treated calcium carbonate	35 - 55
Closslinker	2 - 5
Adhesion promotor	1 - 2
Inorganic pigment	1 - 2
Catalyst (ORGATIX TC-750)	1

Considerations for using ORGATIX as a curing catalysts

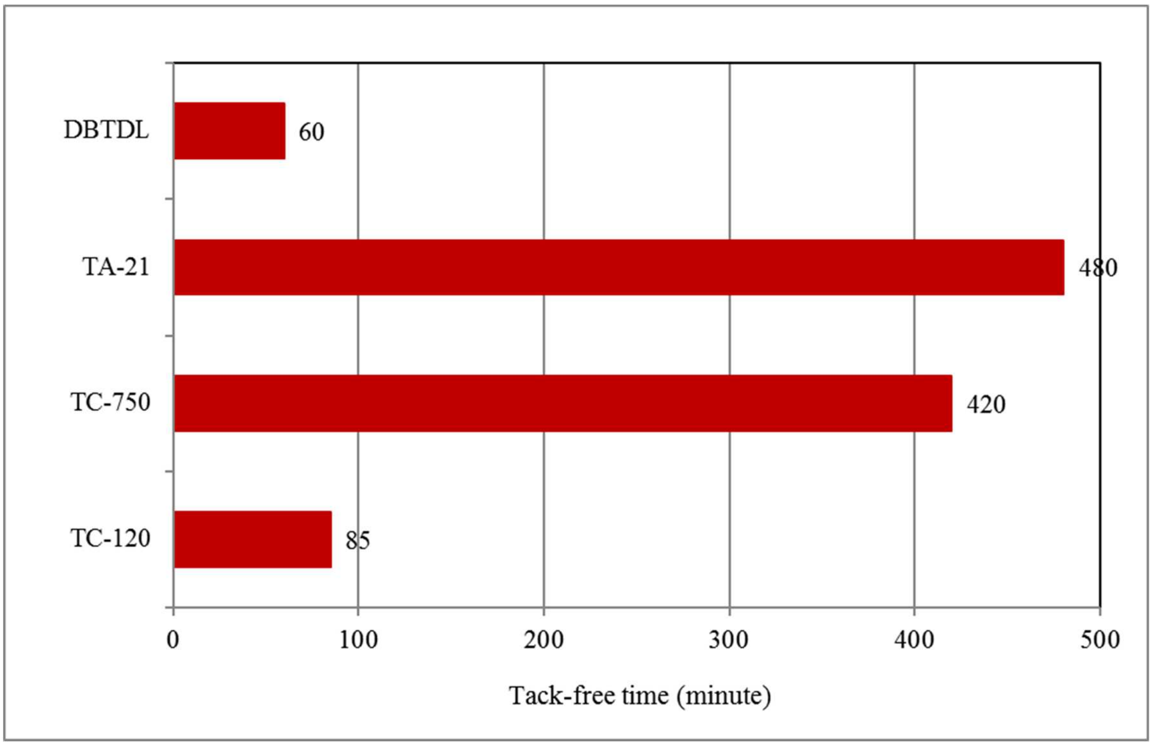
- Adding titanium alkoxide or titanium chelate to silicone polymer may cause a rapid increase in viscosity temporarily. This is caused by pseudo-crosslink between the silicone polymer and titanium compound. After stirring for a while, the viscosity will return to the level it should be at.
- Amino silane cannot be used as an adhesion promotor for general titanium compounds. This is because the titanium compound reacts with an amino group of amino silane, resulting in a decline in catalytic activity. Therefore, it is necessary to select an adhesion agent which has no amino group or a catalyst like one mentioned in Example 3.
- Titanium catalysts can be used in condensation reactions of dealcoholized silicone only. If used for deoximation and acetic acid type silicone, free substances may react with titanium, resulting in strong color development.

Example 3: Combined use with amino silane (adhesion enhancer)

Prepared a catalyst by mixing ORGATIX, γ-aminoethyl aminopropyl trimethoxysilane and vinyltrimethoxysilane at a ratio of 2:1:4 (by weight). Then, mixed the catalyst and dimethylpolysiloxa containing a hydroxyl group at both terminals at a ratio of 7:100 (by weight). Let it stand at room temperature in an open state and measured the time until the surface hardened (tack free time).

Used three types of catalysts including TA-21 (tetrabutoxy titanium), ORGATIX TC-750 (titanium ethyl acetoacetate), and ORGATIX TC-120 and dibutyltin dilaurate (DBTDL) as a control catalyst.

<Fig. 6 Performance of catalyst in silicone curing in the case of combination use with amino silane>



If amino silane is used in combination with general titanium compounds, it initiates coordinate bonding, resulting in a decline in catalytic activity of the titanium compounds and an extremely-long tack free time. However, some types of organic titanium compounds have structures which can resist activity inhibition by amino silane. It is recommended to use ORGATIX TC-120 for RTV silicone formulated with amino silane.

4. Safety of ORGATIX

Organic tin compounds commonly used as catalysts have low LD_{50} and are known as environmentally hazardous substances. ORGATIX, on the other hand, is an environmentally friendly compound with high LD_{50} as shown below. It is decomposed into oxides eventually by the action of hydrolysis.

Product name	Acute toxicity (oral) LD_{50}
ORGATIX TA-8	7,460 μL/kg
ORGATIX TA-21	3,122 mg/kg
ORGATIX TC-310	>2,500 mg/kg
ORGATIX TC-400	>2,500 mg/kg
ORGATIX ZC-150	719 mg/kg
ORGATIX ZC-700	272 mg/kg
Dibutyl tin dilaurate	175 mg/kg
Titanium oxide	60,000mg/kg (TDLo)

5. Removal of catalysts

After esterification or transesterification by use of ORGATIX, it may be necessary to remove deactivated titanium compounds in some cases. In general, this is done by adding water to obtained ester to initiate hydrolysis and then conducting distillation for purification. It can also be removed by adding water and an aid, such as activated carbon and a filtering solution for separation.

6. Instructions for use of ORGATIX

Some products may be corrosive and/or flammable. Please read the Safety Data Sheet of product before use.

Contact Us: Matsumoto Fine Chemical Co., Ltd.
5-13-2, Minamiyawata, Ichikawa-shi
Chiba, 272-0023, Japan
Tel: +81-47-393-6330
Fax: +81-47-393-1063
http://www.m-chem.co.jp/

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