技　術　資　料

Technical Information

☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆

Application of ORGATIX as

Urethane Formation Catalysts

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

URL:http://www.m-chem.co.jp/

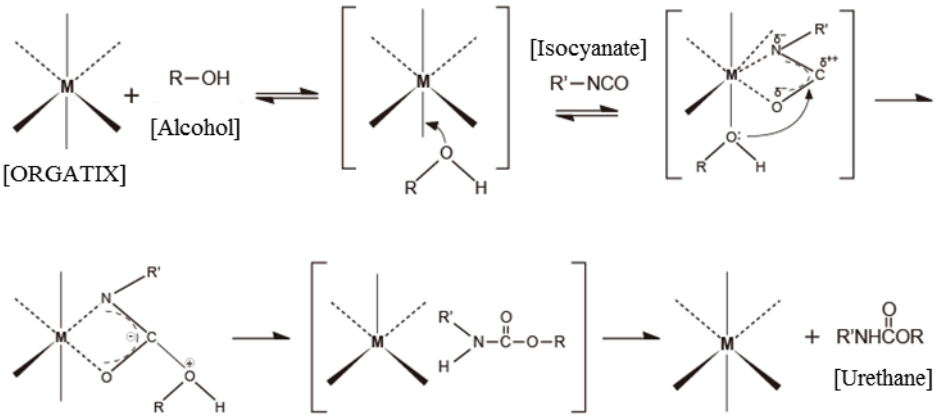
ORGATIX is the trade name for organic metal compounds developed by Matsumoto Fine Chemical.

Titanium/Zirconium compounds are known as effective catalysts for various chemical reactions and have been used as material for a Ziegler-Natta catalyst used in olefin polymerization. In recent years, they are attracting attention particularly from the urethane industry as alternatives to organic tin catalysts which have safety concerns.

1. Reaction mechanism

ORGATIX has a catalytic reaction for urethane formation with hydroxyl group and isocyanate group.

<Figure. Reaction mechanism of ORGATIX for urethane formation (J. Robinson's Scheme) >



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

2. Recommended grade (for air-drying urethane)

Product name		ORGATIX **TA-30**	ORGATIX **TC-750**	ORGATIX **ZC-700**	ORGATIX **ZC-150**
Chemical name		Tetra 2-ethylhexyl titanate	Ethylacetoacetate titanate	Zirconium tetra acetylacetonate	Zirconium tetra acetylacetonate
Apperance		Pale yellow liquid	Pale yellow to orange red liquid	Pale yellow liquid	White to slightly yellow powder
Content		more than 99%	95%	20%	more than 99%
Solvent		–	IPA: less than 5%	Toluene: 49% Methanol: 12% Acetylacetone: 19%	–
Inventory	Japan	Registered	Registered	Registered	Registered
	USA				
	Korea				
	China				
	REACH(EU)	N/A	N/A	N/A	N/A
Package size		15kg	15kg	9kg	10kg
Feature		High activity	General-use	High activity Liquid	Powder Toluene free

Revised date: June 1st, 2017

<Table. Recommended grade for combination of polyol and isocyanate>

Organic titanium/zirconium compounds have different reaction activities depending on the types of polyol and isocyanate. Below are typical combinations of compounds and their recommended grade.

	Toluene diisocyanate (TDI)	1,6-Hexamethylene diisocyanate (HDI)	4,4'-diphenylmethane diisocyanate (MDI)
Polyether Polyol	○ ***TA-30*** ○ ***TC-750***	○ ***TC-750*** △ ***TA-30***	◎ ***TA-30*** ○ ***TC-750***
Polyester polyol	◎ ***ZC-700*** ○ ***TC-750***	○ ***TC-750*** △ ***TA-30***	ON DEMAND (*)
Acrylic Polyol	◎ ***ZC-700***	◎ ***ZC-700***	ON DEMAND (*)

◎: Excellent, ○: Better, △: Good

(*) We will conduct a test and an evaluation of compounds upon request.

<Table. Appearance of cured urethane by ORGATIX>

Organic titanium/zirconium compounds tend to involve color development in the course of urethane formation. In particular, a mix of titanium compound and an aromatic compound will cause strong yellowing.

	ORGATIX TA-30	ORGATIX TC-750	ORGATIX ZC-700
Polyester polyol + TDI			
Polyester polyol + HDI			

*Organic zirconium compounds (ZC-700, etc.) are effective in preventing the color development.

Revised date: June 1st, 2017

3. An example of experiments conducted by Matsumoto Fine Chemical and synthesis disclosed in a Japanese patent application publication

◆Evaluation method

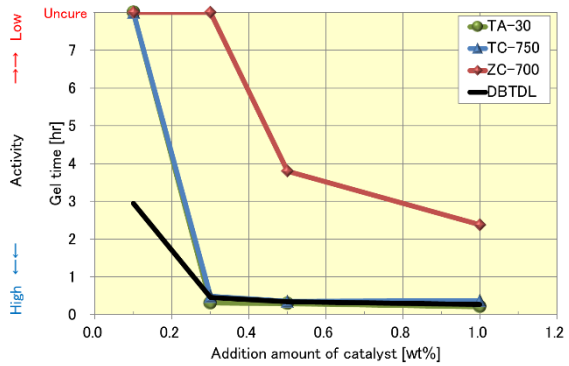
After mixing polyol and isocyanate with the ratio of OH : NCO at 1 : 1 (mole ratio) at room temperature, a catalyst is added. Measured gelling time when let to stand at room temperature to compare performance of catalysts. Used the compounds below as catalysts.

Product name	Chemical name
TA-30	Tetra 2-ethylhexyl titanate
TC-750	Ethyl acetoacetate titanate
ZC-700	Zirconium tetra acetylacetonate
DBTDL	Dibutyl tin dilaurate

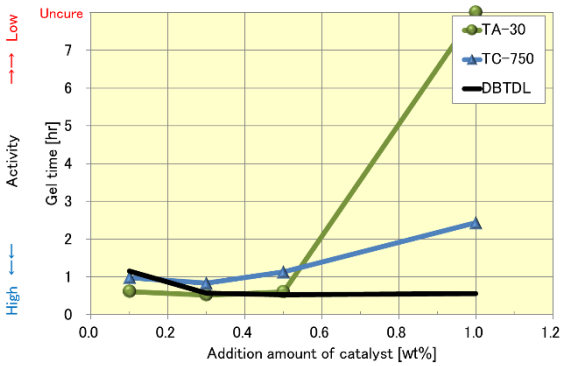
◆Example I

Base resin・・・Polyether polyol (EXCENOL 1020 from AGC)

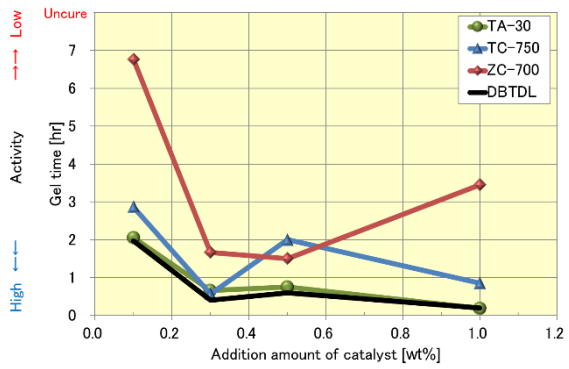
① Curing agent： TDI



②Curing agent：HDI



③ Curing agent：MDI

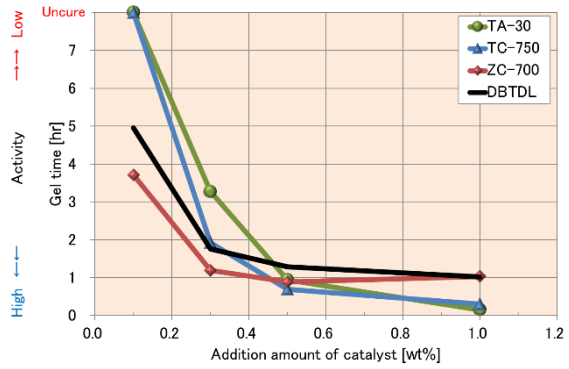


Revised date: June 1st, 2017

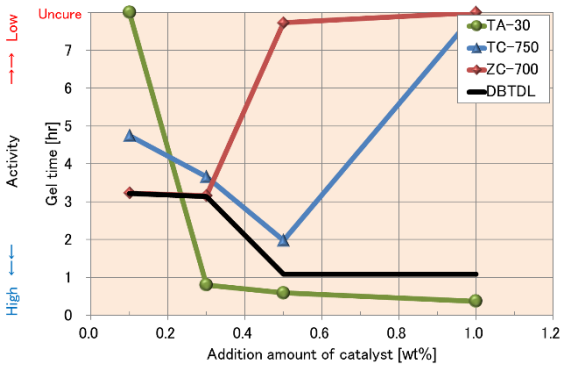
◆Example II

Base resin: Polyester polyol (OD-X-2376 from DIC)

① Curing agent： TDI



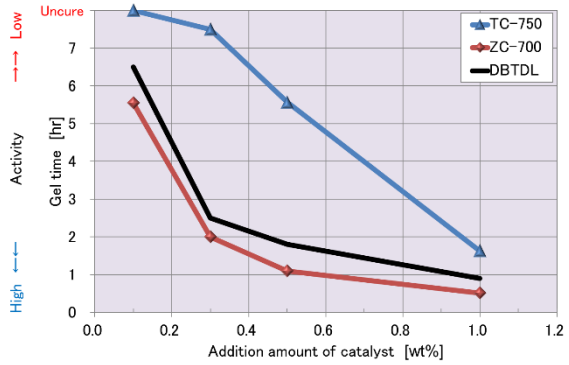
②Curing agent：HDI



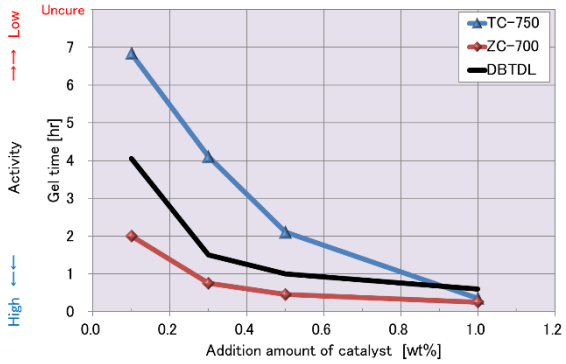
◆Example III

Base resin: Acrylic polyol (Olester Q164 from Mitsui Chemical)

① Curing agent： TDI



②Curing agent：HDI



◆Example of manufacturing method of thermoplastic polyurethane (JP 2004-352800)

This is an example of a manufacturing method of thermoplastic polyurethane by use of an extrusion cylinder.

<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)

Revised date: June 1st, 2017

4. Introduction of research and development results

4-1. Catalyst for blocked isocyanate: Sample no. X-1301

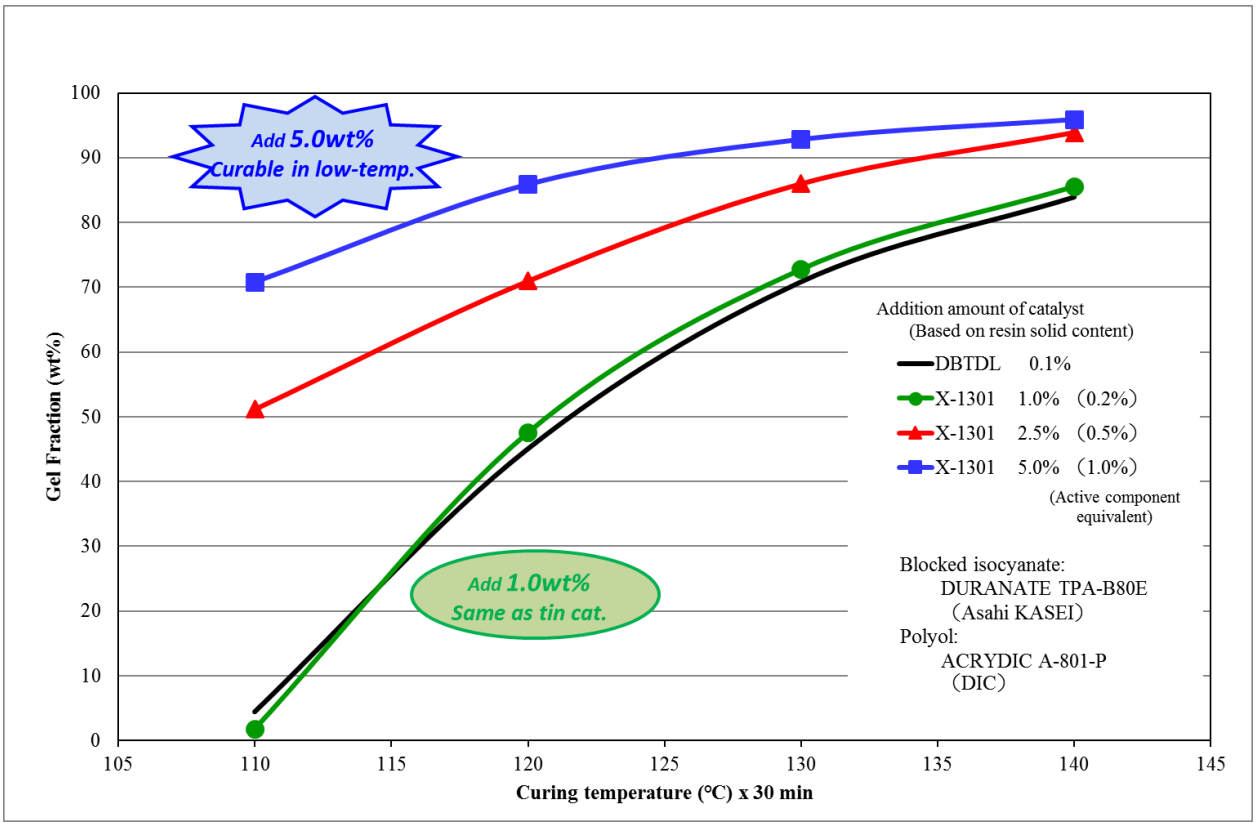
We have newly developed a prototype "Sample no. X-1301," a urethane-forming catalyst for blocked isocyanate. X-1301 is a liquid catalyst containing zinc compound and offers the following advantages:

- Easy-to-handle liquid catalyst
- Cured at low temperatures with controlled additive amount
- No use of organic tin catalysts such as dibutyltin dilaurate (DBTDL) which raises safety concerns
- Less coloration as compared with organic titanium catalysts which cause strong yellowing

4-2. Outline

Prototype name	Sample No. X-1301			
Main component	Zinc compound	Inventory	MITI (Japan)	✓
			TSCA (USA)	✓
Appearance	Pale yellow liquid		ECL (Korea)	✓
Metal content	4.7%		IECSC (China)	✓
Component	Zinc compound : 19%		Taiwan	✓
	MEK : 43%		REACH(EU)	N/A
	Methanol : 29%	Pacage size & MOQ	1kg CAN	5kg / order
	Acetylacetone : 9%		16kg CAN	64kg / order

4-3. Addition amount of catalyst vs Gel fraction



Recommended addition amount of catalyst: 1.0 wt% - 5.0 wt%　(based on the resin weight)

Revised date: June 1st, 2017

5. Safety of ORGATIX

Organic tin compounds commonly used as catalysts are subject to various laws and regulations and known as environmentally hazardous substances. ORGATIX, on the other hand, is not subject to most laws and regulations. As shown in below table, it has high LD_{50} as compared with organic tin compounds.
ORGATIX eventually decomposes into oxides by hydrolysis and thus causes less burden on the environment.

Product name	Acute toxic (Oral) LD_{50}
ORGATIX TA-21	3,122 mg/kg
ORGATIX TA-30	2,000 mg/kg
ORGATIX TC-750	3,980 mg/kg
ORGATIX ZC-150	719 mg/kg
ORGATIX ZC-700	272 mg/kg
DBTDL (Ref.)	175 mg/kg
Titanium oxide (Ref.)	60,000 mg/kg (TDLo)

6. Instructions for use of ORGATIX

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

This material was issued with the purpose of providing information based on the data available at the present time. No warranty is made as to the information given.

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/

Revised date: June 1st, 2017