TOAGOSEI

ARON OXETANE

OXT-101

TOAGOSEI CO., LTD.

OXT technical report

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What is Oxetane

Oxetanes, 4-membered cyclic ethers, are new cationic monomers for UV-cure system developed by Toagosei Co.,Ltd. With high basisity and ring strain, oxetane compounds have the highest ring-opening polymerizability among various cyclic ethers including epoxy compounds.

Although oxetane was recognized as an excellent cationic monomer, few industrial applications had been developed. We paid attention to the potential of oxetane as a new UV-cure monomer and have established industrial manufacturing recently. With its beneficial performances as a photo-curable monomer, we believe oxetane helps cationic system broaden its application field.

Benefits of Cationic System

Comparison to conventional radical cure systems, cationic systems have the following benefits.

①Low Shrinkage → Excellent Adhesion to Substrates, High Gloss

②Low Skin Irritation → High Safety and Processibility

③No Oxygen Inhibition → Fast Cure even on Thin Film

Benefits of Oxetane

Additionally, oxetane compounds have the following strong points as photo-cationic monomers, compared to conventional epoxy compounds.

①Rapid Polymerization → High Molecular Weight and Tough Film Properties

②Cure Improvement by formulating with Epoxy Compounds

→ High Manufacturing Efficiency, Low Initiator Content needed

③Not Mutagenic → High Safety

④ No Generation of -OH → Water and Humidity Resistance, Excellent Electric Properties

⑤ High Stability under High Temperature or Basic Condition → Long Shelf Life

We have been pursuing R&D of Oxetanes for many years and hold a wide-range of patent licenses. Please contact us before using oxetanes.

OXT technical report OXA

OXT-101 (OXA)

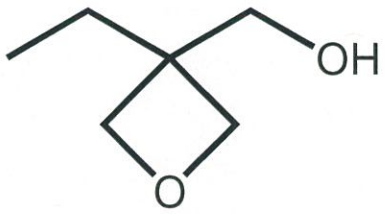
OXA is bifunctional compound having both oxetanyl ring and alcoholic -OH. In cationic systems, appropriate amount of OH function is known to accelerate cure speed by reacting with propagating chain ends (chain transfer). OXA has excellent diluency and cure promoting effects. Films cured with OXA generally show improved thermal and chemical resistance.

Product Name: ARON OXETANE OXT-101(EOXA)

Chemical Name: 3-Ethyl-3-hydroxymethyl-oxetane

Abbreviated Name: OXA (Oxetane Alcohol)

Chemical Structure:



Purity:	>98%	Molecular Weight:	116.2
Appearance:	clear liquid	Boiling Temperature:	105 ℃/7 mmHg
Melting Temperature:	-37℃	Specific gravity:	1.024 (20℃)
Viscosity:	22.4 mPa•s (25℃)	Flash Point:	112℃(OPEN CUP)
Primary Irritation Index(PII):	0.2	LD_{50}:	>2,000mg/kg
NOEL	250mg/kg/day	Ames Test:	negative
CAS No：	3047-32-3	TSCA Inventory:	included
EINECS No.:	221-254-0	NDSL Inventory:	included

Main Application: **Coatings, Ink**

Benefits: **high diluency, high cure response**

Test Formulation 1 (OXA/Cycloaliphatic Epoxide)

Formulations with cycloaliphatic epoxide, available as photo-cationic monomer, were investigated and the cured film properties were estimated.

Resin Formulation of OXA/Cycloaliphatic Epoxide

	No.	1	2	3	4
Formulation	OXA (phr)		10	25	50
	Cycloaliphatic Epoxide[3] (phr)	100	90	75	50
	Cationic Photoinitiator[4] (phr)	3	3	3	3
	[epoxy]/[OH]		7.6	2.5	0.85
	Viscosity[5] (mPa.s)	336	182	96	47
For Thin coated film[1]	Acetone Extractability[6] (%)	14.7	7.3	8.2	16.0
	Pencil Strength	3H-4H	3H-4H	3H	2H
	Adhesion[7]	100/100	100/100	100/100	100/100
	Flexural Test[8] 10mm ϕ	-	-	+	+
	2mm ϕ	-	-	-	+
	After Retort Treatment[9]				
	Pencil Strength	4H	4H	3H	2H
	Adhesion[7]	100/100	100/100	100/100	100/100
	Flexural Test[8] 10mm ϕ	-	-	+	+
	2mm ϕ	-	-	-	+
For Thick coated film[2]	Acetone Extractability[6] (%)	42.5	23.3	2.2	0.7
	Tensile Strength[10] (kg/cm^2)	84	98	214	185
	Elongation at Break[10] (%)	13.0	1.0	2.0	1.5
	Tensile Modulus[10] (kg/cm^2)	3100	9800	10700	12300
	E''_{max}[11] (℃)	22.9	17.5	95.1	77
	$\tan\delta_{max}$[11] (℃)	68.2	109.7	116.0	94.4
	Cross-linking Density[11] ($mol./m^3$)	-	8.9×10^4	2.5×10^5	1.5×10^5
	Specific Gravity	1.23	1.22	1.20	1.17
	Shrinking with Curing[12] (%)	4.4	4.8	5.1	6.4

1)Coated film thickness = About 10 μ m, Substrate: Chroming steel Al plate
Irradiation condition = 80W high press. mercury lamp / lamp height 10cm / conveyer speed 10m/min. 2 pass
2)Coated film thickness = 100 - 200 μ m, Substrate: OPP film
Irradiation condition = 80W high press. mercury lamp / lamp height 10cm / conveyer speed 10m/min. 6 pass
3)3,4-Epoxycyclohexylmethyl-3,4-Epoxycyclohexylcarboxylate
(UCC UVR-6110, Daicel chemical Celloxide 2021P)
4)Triallylsulfonium - Hexafluorine salt mixture (UCC UVI-6990, Daicel UCB Uracure 1591)
5)Rotary Viscometer type E at 25 ℃
6)Dipped in Acetone for one day and dried. Calculation with loss of weight.
7)Cross-cut adhesion test
8)Flexural test
9)Tested one day after steat-washing 30min.at 130℃ ,2 atm.press.
10)Tensile speed = 200m/min. Chuck interval = 100mm
11)Dynamic modulus measurement: 10Hz,speed of rising Temp. 4℃/min.
12)Calculation from specific gravity between the cured item and each of the raw materials.

○ OXA shows excellent diluency, which leads to improvement of the cured film by increasing polymeric contents.

○ OXA improves cure response, which enables a reduction in cost by decreasing the amount of expensive photo-initiator.

○ OXA improves chemical resistance of cured film.

○ OXA gives flexible films with high bonding strength and excellent processibility.

Estimations of Cure Response vs. Initiator contents

○ OXA was proven to be an excellent dilutant; with 20% addition of OXA, a third of initiator is enough for corresponding cure response to blank formulation. (10 μ thickness)

○ Improvement of cure response is enhanced with thickness.

Amount of Initiator vs. Surface Cure Rate(m/min.)

Thickness	Initiator	OXA/Cycloaliphatic Epoxide			
(μm)	(phr)	0/100	10/90	20/80	30/70
10	1	-	-	10	
10	2	-	20	20	
10	3	10	>50	>50	
30	1	-	-	20	10
30	2	-	-	30	30
30	3	-	10	>50	>50

1)thickness/substrate=ca.10 μ m/chroming steel Al plate, Irradiation condition:=80W high pressure mercury lamp/lamp height 10cm

2)cycloaliphatic epoxide: 2,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (UCC UVR-6110, Daicel chemical Celloxide 2021P)

3)cationic photo-initiator: triallylsulfonium hexafluorine salt mixture (UCC UVI-6990, Daicel UVB Uvacure 1591)

○ *Test Formulation 2 (OXA/bisphenol-A Epoxide)*

Formulations with bisphenl-A type epoxide, most commonly used as thermosetting resin, were investigated and the cured film properties were estimated.

Resin Formulation of OXA/bisphenol-A Epoxide

	No.	1	2	3	4
Formulation	OXA (phr)		10	25	50
	bisphenol-A Epoxide[3] (phr)	100	90	75	50
	Cationic Photoinitiator[4] (phr)	3	3	3	3
	Viscosity[5] (mPa.s)	8755	1830	682	184
For Thin coated film[1]	Pencil Strength	2H	3H	2H	2H
	Adhesion[6]	100/100	100/100	100/100	100/100
	Flexural Test[7] 10mm ϕ	-	+	+	+
	2mm ϕ	-	+	+	+
For Thick coated film[2]	Tensile Strength[8] (kg/cm^2)	361	353	303	125
	Elongation at Break[8] (%)	2.0	2.0	2.0	1.0
	Tensile Modulus[8] (kg/cm^2)	24,000	18,000	15,000	13,000
	E''_{max}[9] (℃)	71.2	76.5	67.1	49.1
	tan δ max[9] (℃)	86.6	92.0	90.6	57.8
	Cross-linking Density[9] ($mol./m^3$)	2.8×10^5	3.3×10^5	2.6×10^5	1.8×10^5
	Specific Gravity	1.22	1.18	1.14	1.14
	Shrinking with Curing[10] (%)	3.9	1.9	0.9	3.4

1)Coated film thickness = About 10 μ m, Substrate: Chroming steel Al plate
Irradiation condition = 80W high press. mercury lamp / lamp height 10cm / conveyer speed 10m/min. 2 pass
2)Coated film thickness = 100 - 200 μ m, Substrate: OPP film
Irradiation condition = 80W high press. mercury lamp / lamp height 10cm / conveyer speed 10m/min. 6 pass
3)bisphenol-A digricydylether Tototasei Y-128
4)Triallylsulfonium - Hexafluorine salt mixture (UCC UVI-6990, Daicel UCB Uracure 1591)
5)Rotary Viscometer type E at 25 ℃
6)Cross-cut adhesion test
7)Flexural test
8)Tensile speed = 200m/min. Chuck interval = 100mm
9)Dynamic modulus measurement: 10Hz,speed of rising Temp. 4℃/min.
10)Calculation from specific gravity between the cured item and each of the raw materials.

○ OXA is applicable to the formulation with bisphenl-A type epoxide which has usually poor cationic polymerizablity.

○ OXA shows remarkable diluency and improves workability.

○ OXA gives flexible films with high bonding strength and excellent processibility.

Precautions in Handling

OXA is highly stable and safe diluent for cationic cure formulations. OXA may, however, polymerize by heat, light and contamination with a foreign substance. In handling OXA, the following precautions should be taken to avoid accidents.

【Handling】

1. Do not handle OXA near fire or heat sources.
2. Use with adequate ventilation. Avoid breathing vapor.
3. Wear appropriate protective equipment such as protective gloves, goggles, and safety glasses. Avoid direct contact with eyes, skin, mucous membranes and clothing.
4. In case of spilling, wipe up with towel and dispose by incineration or absorb on inert mineral filler and collect in a closed container.
5. Wash hands sufficiently after handling OXA.

【First Aid Measures】

1. In case of skin contact, immediately wash with lots of soap and water. Remove contaminated clothing and shoes. Get immediate medical attention if irritates persists after washing.
2. In case of eye contact, immediately flush eyes with lots of running water for at least 15 minutes. Get immediate medical attention.
3. If inhaled, remove to flesh air. If not breathing, give artificial respiration and get medical attention immediately.
4. If swallowed, get immediate medical attention. Do not give anything to an unconscious or convulsing person.

【Storage】

1. Store in a cool dark place in original package.
4. Keep container closed to avoid absorbing moisture.

【Waste Disposal method】

Send to a licensed reclaimer or to a permitted incinerator.

For more detailed information about OXA, please refer to Material Safety Data Sheet. Feel free to contact the following address for inquiry or request of samples and related documents.

TOAGOSEI CO.,LTD.

1-14-1,Nishi-Shinbashi,Minato-ku,Tokyo,JAPAN

TEL:03-3597-7332 FAX:03-3597-7380