ARON OXETANE

OXT-101 (OXA)

TOAGOSEI CO., LTD.

What's Oxetane ?

ARON OXETANE, 4-membered cyclic ether compounds, are new cationic monomers for UV-curing system developed by TOAGOSEI. With high basisity and ring strain, oxetane compounds show higher ring-opening polymerizability than other cyclic ethers including epoxy compounds.

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

Benefits of Cationic Curing System

In comparison with conventional radical curing systems, cationic system generally have the following benefits.

1. Low Shrinkage → Excellent Adhesion to Substrates and High Gross
2. Low Skin Irritation → High Safety and Easy Handling
3. No Oxygen Inhibition → Fast Curing at even Thin Thickness

Benefits of Oxetane

Additionary, oxetane compunds have the following strong points as photo-cationic monomer, compared with conventional epoxy compounds.

1. Rapid Polymerization → High Molecular Weight and Tough Film Property
2. Cure Improvement by formulating with Epoxy Compounds
   → High Manufacturing Efficiency, Low Initiator Content Needed
3. Not Mutagenic → High Safety
4. Few Generation of -OH → Water and Humidity Resistnace, 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 wide-ranged patent licences. Please contact us before using oxetanes.

OXT-101 (OXA)

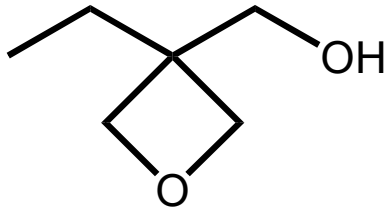
OXT-101 is bifunctional compound having both oxetanyl ring and alcoholic -OH. In cationic systems, appropriate amount of OH function is known to accelerate cure speed by reacting with propagating chain ends (chain transfer). OXT-101 has excellent diluency and cure promoting effects. Films cured with OXT-101 generally show improved thermal and chemical resistance.

Product Name: ARON OXETANE OXT-101(OXA)

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

Abbreviated Name: OXA (Oxetane Alcohol)

Chemical Structure:



Purity:	>98%	Molecular Weight:	116.2
Appearance:	clear liquid	Boiling Point:	105 ℃. / 0.93kPa
Freezing Point:	-37℃	Specific Gravity:	1.024 (20℃)
Viscosity:	22.4 mPa·s (25℃)	Flash Point:	110℃(OPEN CUP)
Skin Irriitation:	0.2(P.I.I.)	LD_{50}:	>2,000mg/kg(oral-rat)
NOEL:	250mg/kg/day	Ames Test:	negative
CAS No.:	3047-32-3	TSCA Inventory:	included
EC No.:	221-254-0(EINECS)	NDSL Inventory:	included

Main Applications: Coatings, Inks, Adhesive

Benefits: high diluency, high curing responce

Test Formulation 1 (OXT-101 / Cycloaliphatic Epoxide)

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

Resin Formulation of OXT-101 / Cycloaliphatic Epoxide

		Fomulation No.			
		1	2	3	4
Formulation	OXT-101(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 Costed 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[9](%)	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)	3,100	9,800	10,700	12,300
	E"max[11](℃)	23	18	95	77
	Tan δ max[11](℃)	68	110	116	94
	Cross-linking Density[11](mol/m^3)	-	8.9 X 10^4	2.5 X 10^5	1.5 X 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 10 cm / conveyer speed 10 m / min. 2 pass, 2) Coated film thickness = 100 – 200 μ m, Substrate:OPP film, Irradiation condition = 80W high press. Mercury lamp / lamp height 10 cm / conveyer speed 10 m / min. 6 pass, 3) 3,4-Epoxycyclohexylmethyl-3',4'-epoxycyclohexyl carboxylate(Dow Chemical UVR-6110), 4) Mixed arylsulfonium hexafluorophosphate salts(Dow Chemical UVI-6990), 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 steam-washing 30 min. at 130℃, 2atm. Press., 10) Tensile speed = 200mm / min. Chuck interval = 100mm., 11) Dynamic modulus measurement: 10 Hz, speed of rising Temp. 4℃ / min., 12) Calculation from specific gravity between the cured item and each of the raw materials.

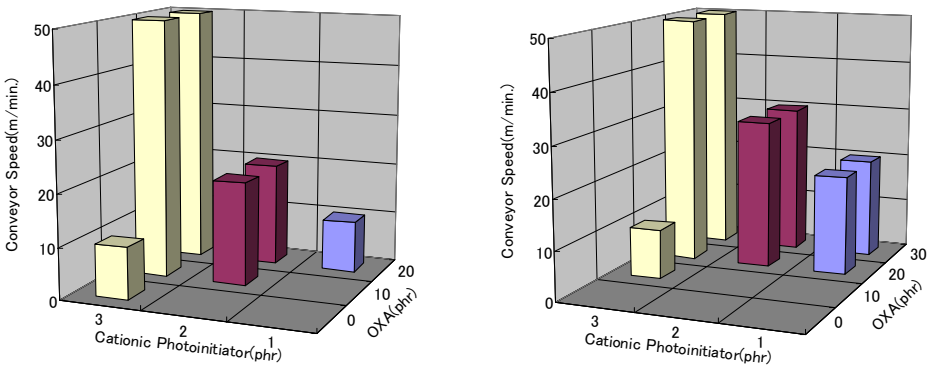
○ OXT-101 shows excellent diluency, which leads to improvement of the cured film by increasing polymeric contents.

○ OXT-101 improves cure responce, which enables cost down reduction by decreasing the amount of expensive photo-initiator.

○ OXT-101 improves chemical resistance of cured film.

○ OXT-101 gives flexible films with high bending strength and excellent processibility.

Estimations of Cure Responce vs. Initiator contents



Coating thickness:10 μ m　　Coating thickness:30 μ m

Substrate: Chroming steel Al plate, Irradiation condition＝80W high pressure mercury lamp / lamp height 10cm
Fomulation: Cycloaliphatic epoxide / OXT-101(OXA) / Cationic Photoinitiator=(100-X) / X / 1, 2 or 3. Cycloaliphatic epoxide: 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexylcarboxylate (DOW Chemical UVR-6110)
Cationic photo-initiator: triallylsulfonium hexafluorine salt mixture (DOW Chemiical UVI-6990)

○ OXT-101 was proved to be a excellent diluent; with 20% addition of OXT-101, a third of initiator is enough for corresponding cure responce to blank formulation. (10 μ m thickness)

○ Improvement of cure responce is enhanced with thickness.

Test Formulation 2 (OXT-101 / 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 OXT-101 / Bisphenol-A Epoxide

		Fomulation No.			
		1	2	3	4
Formulation	OXT-101(phr)		10	25	50
	Bisphenol-A 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)	8,800	1,800	680	180
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	77	67	49
	Tan δ max[9](℃)	87	92	91	58
	Cross-linking Density[9](mol/m^3)	2.8 X 10^5	3.3 X 10^5	2.6 X 10^5	1.8 X 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 10 cm / conveyer speed 10 m / min. 2 pass, 2) Coated film thickness = 100 – 200 μ m, Substrate:OPP film, Irradiation condition = 80W high ppress. Mercury lamp / lamp height 10 cm / conveyer speed 10 m / min. 6 pass, 3) Bisphenol-A diglycidylether(Tohto kasei YD-128), 4) Mixed arylsulfonium hexafluorophosphate salts(Dow Chemical UVI-6990), 5) Rotary Viscometer type E at 25℃, 6) Cross-cut adhesion test, 7) Flexural test, 8) Tensile speed = 200mm / min. Chuck interval = 100mm., 9) Dynamic modulus measurement: 10 Hz, speed of rising Temp. 4℃ / min., 10) Calculation from specific gravity between the cured item and each of the raw materials.

○ OXT-101 is applicable to the formulation with bisphenl-A type epoxide which has usually poor cationic polymerizablity.

○ OXT-101 shows remarkable diluency and improves workability.

○ OXT-101 gives flexible films with high bending strength and excellent processibility.

Solubility of Photo-initiator for OXT-101

Sulfonium Salts

Photo-initiator	Solubility
UVI-6992[1)]	>10wt%
SP-150[2)]	>10wt%
SP-152[2)]	>10wt%

1)Dow Chemical
2)ADEKA

Iodoniumu Salts

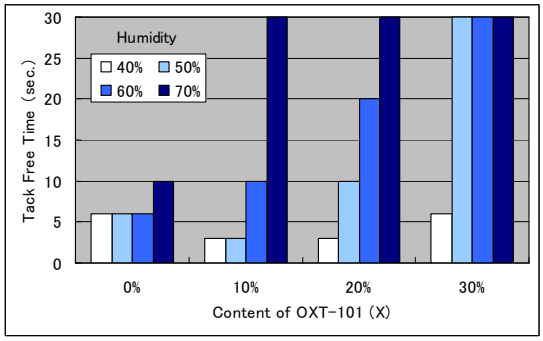
Photo-initiator	Solubility
Irgacure 250[1)]	>10wt%
Rhodosil 2074[2)]	>10wt%
WPI-113[3)]	>10wt%

1)Ciba Speciality Chemicals
2)Rhodia
3)Wako Pure Chemical Industries

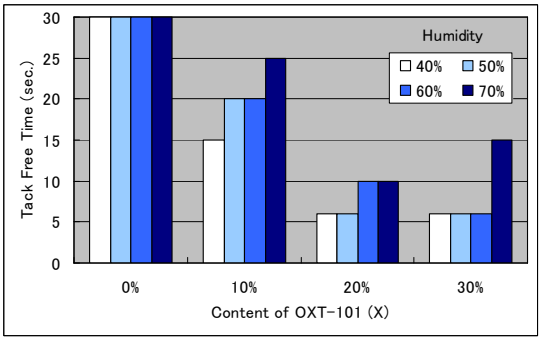
Solubility of OXT-101 for Solvent

Solvent	Solubility	Solvent	Solubility
Acetone	> 50wt%	Methoxy Propylacetate	> 50wt%
2-Propanol	> 50wt%		
Toluene	> 50wt%	Cyclohexane	< 50wt%

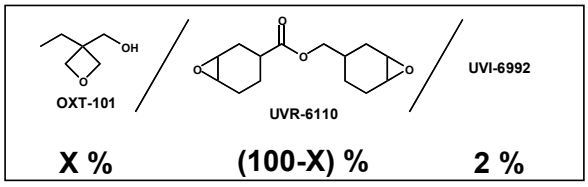
Influence of Humidity



Coating Thickness : ca. 3 μ m



Coating Thickness : ca. 20 μ m



UVR-6110: 3,4-Epoxycyclohexylmethyl-3',4'-epoxycyclohexylcarboxylate (Dow Chemical)
UVI-6992:Triarylsulfonium hexafluorophosphate(Dow Chemical)
Substrate: Steel plate, Irradiation condition = 200W Mercury Xenon lamp, 22.0mW/cm^2

To establish constant humidity conditions, UV irradiator unit(UVF-203S:SAN-EI ELECTRIC) was set in a booth covered with plastic films, which is connected to humidity controller. Controlling the atmosphere in the booth to 40, 50, 60 or 70%RH at 28 to 30℃ by the humidifier, the formulated liquid sample was coated on a steel plate using bar applicator and kept in the booth for 5 min. before UV irradiation.

For Thin Coating

Low Ambient Humidity → Increasing in content of OXT-101, curing rate goes **up**.

High Ambient Humidity → Increasing in content of OXT-101, curing rate goes **down**.

For Thick Coating

Increasing in content of OXT-101, curing rate goes up.

Curing rate is not affected in comparison with thin coating much.

○ At more than 70%RH, curing rate goes down. Therefore, curing at less than 60%RH is recommended.

○ The cured oxetane compounds have a high degree of polymerization.

○ The resultant film perform good properties.

Precautions in Handling

OXT-101 is highly stable and safe diluent for cationic cure formulations. OXT-101 may , however, polymerize by heat, light and contamination with a foreign substance. In handling OXT-101, the following precautions should be taken to avoid accidents.

【Handling】
1. Do not handle OXT-101 near fire or heat sources.
2. Use with adequate ventilation. Avoid breathing vapor.
3. Wear appropriate protective equipment such as protective glove, goggle 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 OXT-101.

【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 fresh 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.
2. Keep container closed to avoid absorbing moisture.

【Waste Disposal method】
1. Send to a licensed reclaimer or to a permitted incinerator.

For more detailed information about OXT-101, please refer to Safety Data Sheet. Feel free to contact the following address for inquiry or request of samples and related documents.

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